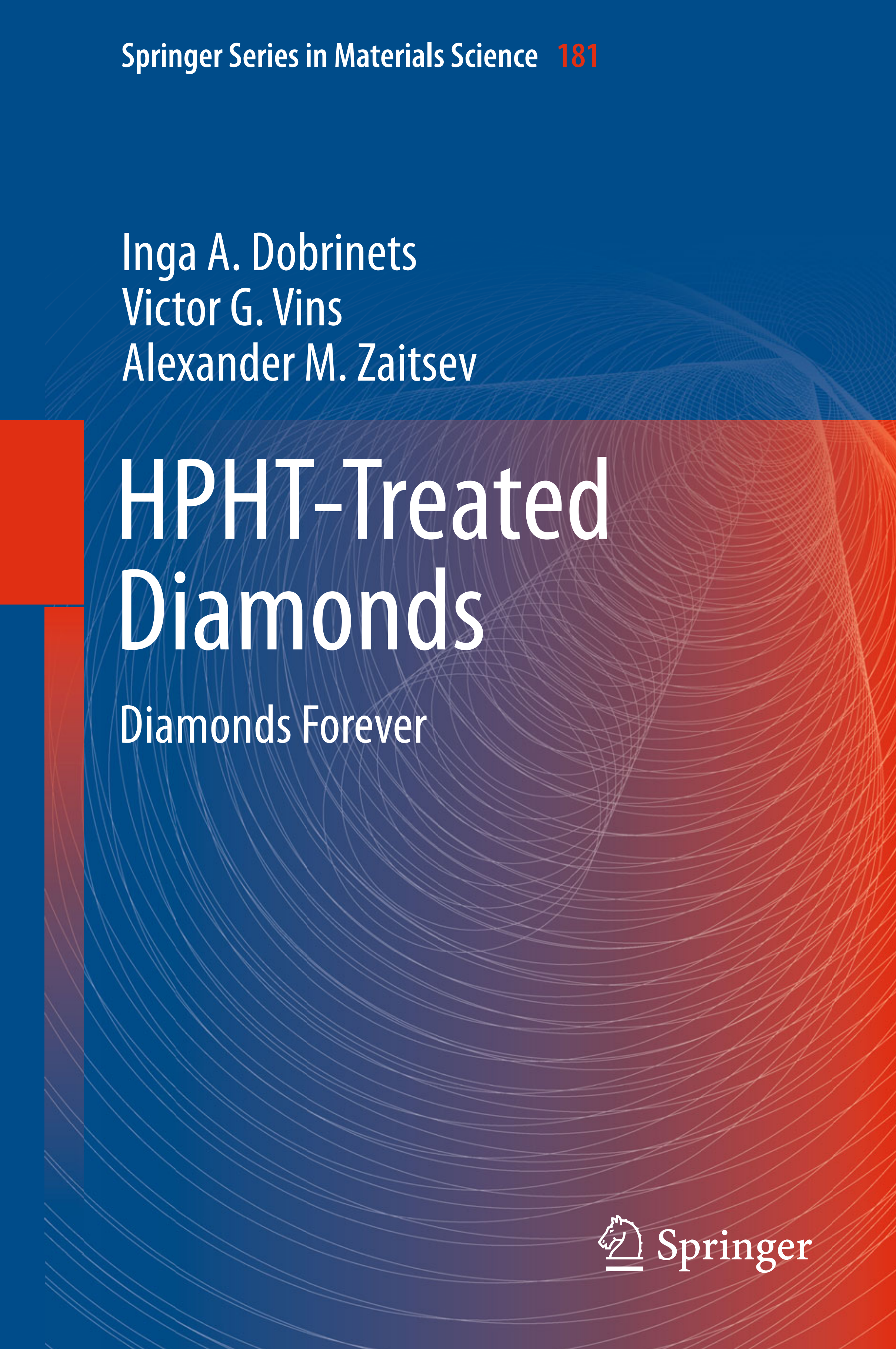

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Inga A. Dobrinets
Victor G. Vins
Alexander M. Zaitsev

HPHT-Treated Diamonds

Diamonds Forever

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Inga A. Dobrinets · Victor G. Vins
Alexander M. Zaitsev

HPHT-Treated Diamonds

Diamonds Forever

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Inga A. Dobrinets
RUBION
Ruhr-Universität Bochum
Bochum
Germany

Alexander M. Zaitsev
Engineering Science and Physics
College of Staten Island
Staten Island, NY
USA

Victor G. Vins
VinsDiam, Ltd.
Novosibirsk
Russia

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To our curious and inspiring children
Valeria, Vitaly, Kirill and Marina

Preface

This book is an attempt to put together and critically analyze the available data on diamonds processed by the methods involving high pressure, high temperature annealing—so-called "HPHT treatment." The commercial aim of HPHT treatment is to change/improve the body color of diamond and hence to increase its price as a gemstone. As any treatment, HPHT treatment must be disclosed by the seller. However, the treatment history of many gem diamonds remains undisclosed and this poses a great danger for potential buyers. At present, the recognition of HPHT-treated diamonds is not a simple task and, as such, it cannot be accomplished by most jewelers selling or buying diamonds. The confident recognition can be done only in the gem labs equipped with specialized and expensive microscopes and spectrometers. The reason for the complexity of recognition of HPHT-treated diamonds is that HPHT treatment mimics very much the process of natural heating of diamonds in earth. Hence the HPHT-treated diamonds may seem very natural. Yet, some specific features of HPHT-treated diamonds and their untreated counterparts do differ and these differences are used for the detection of treatment. In most cases, these differences relate to the internal impurity-defect structure of diamond and they can be recognized only by specialists with solid backgrounds in research. By now, the diamond research community has accumulated a considerable amount of data on the processes of HPHT treatment and the physical and gemological properties of HPHT-treated diamonds. However, this information is scattered over numerous publications, many of which are not readily available. Also, some data published by different authors are controversial. Thus in order to come to a right decision, a critical analysis is required. Keeping all this information together at hand is a challenge for most gemologists and especially for those entering the field. The aim of this book is to help to meet this challenge. Another aim of this book is to give a deeper insight into the HPHT treatment of diamond from the points of view of a scientist, a gemologist, a treatment technologist, and a businessman dealing with HPHT-treated diamonds and to provide the most consistent criteria for practical recognition of HPHT-treated diamonds. Analyzing the data presented in early publications, we have made attempts to interpret it using the new knowledge gained in recent years. This retrospective approach has contributed much to the state of our understanding of HPHT treatment of diamonds.

Although we tried to give the most comprehensive analysis of the existing information, this book is not a manual for quick identification of HPHT-treated diamonds. Rather it is a review showing that the challenge of recognition of HPHT-treated diamonds is much more serious than we may think. In some cases, fortunately rare ones, we have to admit that the present level of our knowledge is not sufficient for the identification of HPHT treatment. However, we hope that this book will benefit those dealing with treated diamonds and help them avoid mistakes when reporting HPHT treatment.

Bochum, Germany	Inga A. Dobrinets
Novosibirsk, Russia	Victor G. Vins
New York, USA	Alexander M. Zaitsev

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Glossary

ABC diamonds	Diamonds exhibiting simultaneous presence of A-, B-, and C defects in IR absorption spectra
APHT	Atmospheric pressure high temperature. APHT annealing is a high temperature heating in an inert gas atmosphere at temperatures exceeding 1,700 °C. It is used as an inexpensive alternative to HPHT treatment
“Blue transmitter”	Diamond exhibiting strong blue luminescence of N3 center, when viewed under bright daylight. This blue luminescence may be referred to as the “blue transmission” effect
Center	See optical center
CL	Cathodoluminescence. CL is a luminescence excited by energetic electrons, e.g., in electron microscopes
Color center	Optical center active in absorption in the visible spectral range
CVD diamonds	Diamonds grown by chemical vapor deposition method. Usually, CVD diamonds are grown in methane-containing microwave plasma
Defect	Any imperfection of regular diamond crystal lattice. For instance, carbon atoms located in irregular crystal lattice sites, or vacant lattice sites are intrinsic defects. Impurity atoms are impurity defects. Most defects in diamond are complexes comprising intrinsic and impurity defect components
Fluorescence	Fast luminescence with lifetime shorter than 1 ms. Practically, fluorescence is observed while diamond is under external excitation, e.g., under UV illumination. Fluorescence stops immediately after the excitation is switched off

FSI	Full spectrum illumination. Two methods of illumination of diamond with light, when measuring its absorption spectrum, are full spectrum illumination and monochromatic illumination. In monochromatic illumination regime, only absorption features of optical centers are present in the spectrum. This regime is used for accurate measurements of "pure" absorption spectra. In full spectrum illumination regime, both absorption and luminescence features of optical centers are present in the same spectrum. FSI regime is an inexpensive alternative for the measurements of absorption spectra with simultaneous detection of the optical centers with strong luminescence. For instance, FSI absorption technique is used for rapid and accurate characterization of diamonds exhibiting "transmission" effects (see "blue, green and red transmitters")
FWHM	Full width at half magnitude, a measure of the width of a spectral line in optical spectrum
Ga	Gigaannum, a unit of time. 1 Ga = 1,000,000,000 years
"Green transmitter"	Diamond exhibiting strong green luminescence of H3 center when viewed under bright daylight. This green luminescence may be referred to as the "green transmission" effect
GPa	Gigapascal, a unit of pressure. 1GPa = 10,000 bar
HPHT	High pressure high temperature
HPHT diamond (HPHT-grown diamond)	Diamond grown in laboratory using HPHT method. Like natural diamonds, the HPHT-grown diamonds can be additionally subjected to HPHT treatment in order to modify their color. HPHT diamonds grow at temperatures in the range 1,200–1,400 °C, whereas their HPHT treatment is performed at temperatures over 2,000 °C
FTIR	Fourier transform infrared spectroscopy. FTIR is IR spectroscopy which uses Fourier transformation method for recording spectra. FTIR spectroscopy is one of the most reliable methods used for recognition of diamond and non-diamond materials
IR	Infrared, usually infrared spectral range
IR absorption spectroscopy	Absorption spectroscopy in the spectral range from 750 to about 100,000 nm (100–13,000 cm^{-1})
LHeT	Liquid helium temperature
LNT	Liquid nitrogen temperature

LPHT	Low pressure high temperature. LPHT annealing is a high temperature heating in vacuum at temperatures over 1,700 °C. It is used as an inexpensive alternative to HPHT treatment
Luminescence	Emission of light by an object (e.g. by diamond) under external excitation (e.g. under illumination with UV or laser light). Two major types of luminescence are fluorescence and phosphorescence
LWUV	Long wave ultraviolet. It is a term used in gemology for UV light produced by mercury lamp in a spectral range from about 300 to 400 nm with the maximum intensity at a wavelength of 365 nm
Ma	Megaannum, a unit of time. 1 Ma = 1,000,000 years
Multi-process treatment	Treatment of diamond using combination of different processes. If details are not specified, the multi-process treatment involves consecutive application of: (i) HPHT annealing (ii) irradiation with electron of energy of 1–3 MeV (iii) annealing at temperatures 600–1,000 °C at ambient pressure
NIR	Near infrared. A part of IR spectral range from 750 to about 2,000 nm. In near infrared, optical centers of diamond can be still active in luminescence. However, the luminescence efficiency of diamond at wavelengths over 1,000 nm is negligible. At wavelengths over 2,000 nm, diamond does not produce detectable luminescence
Optical center	Spectral feature in optical spectrum. Optical center is a combination of narrow lines and broad bands. Each optical center originates from defects of a certain type and therefore its spectral structure is unique. Optical centers are signatures of corresponding defects. Optical centers are used for optical detection of defects, their identification, and the measurements of their concentration. One of the most characteristic features of an optical center in UV, Vis and near IR spectral range is ZPL, the wavelength of which is frequently used for labeling this center and the corresponding defects
Phosphorescence	Slow luminescence with lifetime longer than 1 ms. In practice, phosphorescence is observed as afterglow of diamond after the exciting UV light is switched off

PL	Photoluminescence. PL is a luminescence excited by light (e.g. UV or laser light). PL is the most common type of luminescence techniques used for characterization of diamonds and the most sensitive method used for detection of optically active defects. Modern PL instruments are capable of detecting defects with concentrations well below 1 ppb
ppb	Part per billion. For diamond, 1 ppb = 1.76×10^{14} cm^{-3}
ppm	Part per million. For diamond, 1 ppm = 1.76×10^{17} cm^{-3}
R	The diamond Raman line (usually on PL graphs)
Raman spectroscopy	An optical spectroscopy used for detection of vibrations (e.g. phonons) of diamond crystal lattice. Raman spectroscopy is used as the ultimate method of recognition of diamond and non-diamond materials
"Red transmitter"	Diamond exhibiting strong red luminescence of the NV-center when viewed under bright incandescent light. This strong red luminescence may be referred to as the "red transmission" effect
RT	Room temperature
SWUV	Short wave ultraviolet. SWUV is a term used in gemology for UV light with a wavelength about 250 nm produced by mercury lamp
TL	Thermoluminescence. Thermoluminescence is a luminescence emitted by crystal (e.g. diamond) during its slow heating performed after the crystal has been illuminated with intense light (e.g. with mercury lamp)
UV	Ultraviolet
UV spectroscopy	Luminescence or absorption spectroscopy in a spectral range from 200 to 400 nm
Vibronic	Assisted by atom vibrations (e.g. phonons). Vibronic side band (phonon side band) of an optical center is a broad structured band spreading from ZPL towards shorter wavelengths in absorption spectra and from ZPL towards longer wavelengths in luminescence spectra. Vibronic side band is a unique feature of an optical center and, alone with ZPL, is used for its identification

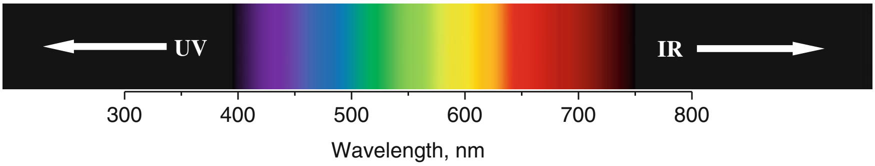

Fig. 1 Wavelength range of the visible spectral range and the wavelengths of different colors

Vis	Visible, visible spectral range. Colors of the visible spectrum and corresponding wavelengths are shown above (Fig. 1)
ZPL	Zero-phonon line. ZPL is the narrowest spectral feature of an optical center. Wavelength of ZPL is a characteristic parameter commonly used for quick identification of optical centers and correspondingly for spectroscopic identification of defects in diamond

Chapter 1
Introduction

Perfect colorless natural diamonds and diamonds of clear fancy colors are rare and expensive. Structurally imperfect diamonds and the diamonds of dull color, e.g. those of brown or gray colors, or tinted with yellow, constitute a vast majority of natural diamonds and are priced much lower. People have been always searching for methods of "improvement" of these low-priced natural diamonds in order to make them more valuable. Reduction of brown coloration of natural diamonds and making them colorless is one of the most desirable "improvements".

Color of a diamond is determined by its internal impurity-defect structure. Advances in understanding this structure and development of technologies enabling to control it by means of high-temperature-assisted atomic transformations were the starting points of HPHT treatment—annealing at high temperature under high pressure. Along with the understanding of the physics of the annealing of diamond crystal, the development of economically efficient high pressure, high temperature equipment has been an important issue of practical implementation of HPHT treatment. The new type of this equipment, the split-sphere press-less system (BARS apparatus), originally developed in Novosibirsk, USSR (Ran and Malinovskii 1975; Malinovskii et al. 1981, 1989) was one of the technical achievements stimulated proliferation of commercial HPHT treatment.

Commercial (and non-disclosed) production of HPHT-color-enhanced diamonds can be traced back to 1996 (Fryer 1997; Van Bockstael 1997; Buerki et al. 1999; McClure and Smith 2000; Reinitz and Moses 1997; Overton and Shigley 2008). In those days the gem trade could not expect such diamonds on the market. Suspicion was raised by the sudden and unusual appearance of many diamonds of intense green-yellow color, revealing noticeable green luminescence when viewed in daylight (so called "green transmitters"). Along with the "green transmission" effect, those stones showed intense absorption of H2 center—a very rare feature in spectra of natural diamonds. At that time, the high-pressure, high-temperature processing of diamond was just a research subject of a few laboratories studying physics and mineralogy of diamond. HPHT annealing technique was not used on a large scale and it had not been acknowledged as a commercial method of diamond

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treatment (Anthony et al. 2000; Shigley et al. 1993). As such, HPHT treatment was generally unknown for jewelry and gemological community.

The formal announcement of HPHT treatment of gem diamonds for commercial purposes was done by General Electric and Lazar Kaplan International in 1999 (Rapnet 1999). The gemological community was not prepared to meet this challenge. The feeling of unpreparedness was greatly stimulated by the statement made by General Electric that HPHT-treated diamonds were indistinguishable from their natural untreated counterparts (Chalain et al. 1999). The General Electric developers presented HPHT treatment as an “attempt to recreate the natural geological processes and to allow the diamond to reach its optimal colorless potential” (Woodburn 1999). Indeed, HPHT treatment followed the process of natural annealing of diamonds in earth in many aspects. As a result, the HPHT-processed diamonds seemed very natural leaving little clue as to how to distinguish them from the untreated ones. In 2000, William Boyajian, President of GIA, wrote: “This [HPHT treatment] is arguably one of the most serious challenges the diamond industry has ever faced” (Boyajian 2000).

The diamond trade and gemologists rejected the consideration of HPHT annealing as a “natural” improvement of diamonds. The HPHT annealing was classified as treatment and many concerns and questions were raised about its recognition (Schmetzer 1999). All major gemological labs and some university labs started intense studies aimed at finding specific features of HPHT-treated diamonds. The gemologists reconsidered the criteria of characterization of diamonds and revised their reports issued before on some “unusual” natural diamonds. By 2002 it had become clear that HPHT processing had existed for many years in Russia (Van Royen and Palyanov 2002) and that activity was the origin of HPHT-treated diamonds on the gem market.

Initially HPHT treatment was designed as a technology of “improvement” of the color grade of brown low-nitrogen diamonds by removing their brown coloration. Very soon, however, it was recognized that HPHT treatment was a powerful technique to change the color of almost any diamond. It was found that the absorption spectra of HPHT-treated diamonds, and therefore their color, strongly depended on the starting impurity-defect composition. Furthermore, this composition, and consequently the result of HPHT treatment, could be considerably altered when other processes influencing the impurity-defect structure of diamond were involved. As a result, the multi-process treatment was developed. The most popular multi-process treatment was the treatment involving consecutive application of HPHT annealing, electron irradiation and conventional annealing at atmospheric pressure. This multi-process treatment could induce practically any color in diamond (Overton and Shigley 2008; Perret 2006; Kitawaki 2007).

By the time of announcement of HPHT treatment, the number of the treated stones released to the gem market was relatively small. In 2000, James Shigley, a leading gemologist of GIA, noted in his review (Shigley 2000) that “HPHT-treated diamonds are a rare event to encounter with in gem market”. However, the amount of HPHT color-treated diamonds grew and very soon the threat of the HPHT treatment to the integrity of the gem diamond market became real.

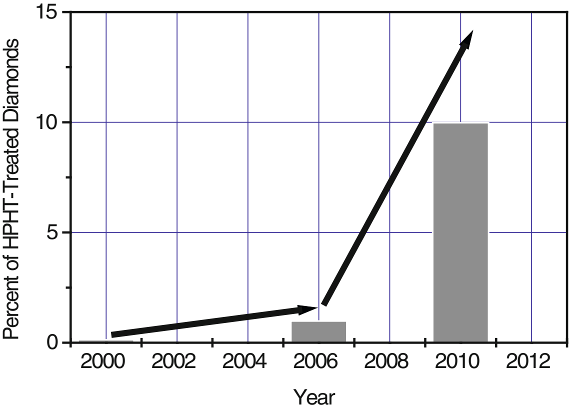

Fig. 1.1 HPHT treatment and the trade in the undisclosed HPHT-treated diamonds are growing businesses: Year 2000—“HPHT-treated diamonds are a rare event to encounter with in gem market” (Shigley 2000). Years 2006–2007—one to two of 100 diamonds submitted to EGL USA for the “origin of color” test and selected for advanced testing. 2010–up to 10 of 100 colored diamonds submitted to EGL USA for the “origin of color” test and selected for advanced testing

It became clear that the establishment of reliable criteria of recognition of HPHT-treated diamonds was vital for diamond trade. Today, the HPHT-treated colorless diamonds and diamonds of highly priced “fancy colors” are produced on a commercial scale and are no longer a rarity. Percentage of large HPHT-treated diamonds of both types Ia and IIa is constantly growing (Wang and Moses 2011), indicating considerable advances in HPHT treatment technology. Modern HPHT setups are capable of simultaneously processing several stones of a few carats each, or individual stones of a size of a few tens of carats. Percentage of the color-treated diamonds, including HPHT-treated once, may attain as much as 5 % of the stones routinely submitted to a gemological laboratory for certificate and selected for advanced test of “origin of color” (Dobrinets and Zaitsev 2010) (Fig. 1.1).

HPHT treatment of light brown type IIa diamonds is of special importance in the business. These diamonds are the starting material for production of colorless gems of high color grades. The proportion of the colorless type IIa stones in the market steadily increases both in size and in color grade. Whereas it was almost impossible to encounter a perfect 15 ct HPHT-treated diamond in 2003, now it is not the case. Modern high-pressure, high-temperature apparatus allows to process diamonds of any reasonable size resulting in polished gems of highest quality the weight of which may exceed 30 carats (Shigley 2005; Darley 2011; Wang and Moses 2011). Recently The Gemological Institute of America reported that a significant number of large HPHT-treated diamonds of high clarity were submitted for grading. The weight of those diamonds ranged from 3 to nearly 20 ct and their color grade varied from “D” to “J”. It is remarkable, that most of those diamonds were submitted for grading without proper disclosure (Wang and Moses 2011; Southern Jewelry News, 02 February 2011, http://southernjewelrynews.com).

Today, the virginity of almost all type IIa diamonds has to be carefully tested with reliable means of identification of HPHT treatment. Without such testing, no one can be confident about the natural origin of color of a type IIa diamond, if it is bought from third parties (Fisher 2008).

By now, extensive research on HPHT-treated diamonds has been performed and a rather clear picture of both the physical principles of HPHT process and the resulting product has been formed. It proves to be a very complex picture involving numerous visual, structural and spectroscopic features, many of which can be identified and measured only using sophisticated microscopic-imaging techniques and top spectroscopic instruments. In many cases, reliable identification and reporting of HPHT-treated diamonds requires complex comparative analysis of their many structural and optical parameters and the comparison of the obtained data with that published in numerous articles, conference proceedings, lab reports and books.

In the book below, the complexity of HPHT treatment, as it seen from the points of view of a gemologist grading diamonds, a technologist doing HPHT treatment, and a physicist studying the properties of diamond materials, is shown is many details. The conclusions made in this book are based on the analysis of the data taken from hundreds of publications and the original data obtained from the measurements of several thousand diamonds treated by HPHT annealing and by multi-process treatment.

Chapter 2
Diamonds Used for HPHT Treatment

Type, color and clarity are three major parameters, which determine suitability of diamond for HPHT treatment. Color is of primary commercial importance. Initial color is the reference point for the evaluation of improvement of the diamond's appearance, increase in its price, and effectiveness of the HPHT treatment procedure.

Clarity is the parameter, which sets the limits of the suitability of diamond for commercial HPHT treatment. Since HPHT annealing is frequently performed at pressures and temperatures close to or within the range of stability of graphite, the inclusions may considerably stimulate graphitization of the surrounded diamond lattice. Moreover, inclusions weaken locally diamond crystal thus resulting in development of cracks. The formation of cracks is especially effective when the pressure applied to the diamond during processing is not uniform. Thus, HPHT treatment may reduce the clarity grade of diamond but rarely increases it. If a diamond has low initial clarity, the HPHT processing may reduce its clarity grade to a level, which would make the treatment unprofitable.

Diamond type is a technological rather than commercial parameter. However, type of the diamond intended for HPHT treatment is a key factor for the technologist when he chooses the treatment conditions with the aim of achievement of desirable final color.

2.1 Types of Diamond

Notion of the diamond type is a corner stone in the understanding of the physics behind HPHT treatment. The types differentiate diamonds with different content of nitrogen and boron—two major impurities, which determine the optical and electrical properties of diamond. For HPHT treatment, the presence of nitrogen and transformation of the nitrogen-related defects are of particular importance. The standard method of recognition of diamond types is IR absorption spectroscopy. Each diamond type has its specific IR absorption spectrum. Boron is

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optically active when present in the diamond lattice in the simplest form of single substitutional atoms. It reveals characteristic absorption spectrum in the Vis and IR spectral regions. The optical activity of nitrogen is much more versatile. Nitrogen is optically active when present in form of different point and extended defects of different atomic composition. These nitrogen-related defects induce hundreds of optical centers throughout UV, Vis and IR spectral ranges (Zaitsev 2002). There are four major types of diamond: Ia, Ib, IIa and IIb.

2.1.1 Type I Diamonds

Type I diamonds are the nitrogen-containing ones. They are the most abundant diamonds in nature. Formally, a diamond is of type I when the concentration of nitrogen in it is above the sensitivity limit of conventional IR absorption spectroscopy, what is about 1 ppm. Practically, nitrogen content in natural type I diamonds exceeds 10 ppm and may be as high as 3,000 ppm. Type I diamonds with nitrogen content below 10 ppm are frequently referred to as low-nitrogen type I diamonds.

Subdivisions of type I are type Ia and type Ib. Type Ia diamonds are those containing nitrogen in aggregated forms, when the majority of nitrogen is present in complexes of two and more nitrogen atoms. The major aggregates of nitrogen are A-, B- and B'-defect (Platelets). Type Ib diamonds contain nitrogen predominantly in form of single substitutional nitrogen atoms (C defects) and only minor amount of nitrogen is aggregated. Single substitutional nitrogen atoms are omnipresent impurity in diamond. It is a very rare event that the presence of C defects in a natural diamond could not be detected (Sobolev et al. 1986; Fisher 2012). The highest concentration of single substitutional nitrogen, which can be found in natural type Ib diamonds, may reach a value of 500 ppm. Atomic models of C-, A-, and B defects are shown in Fig. 2.1.

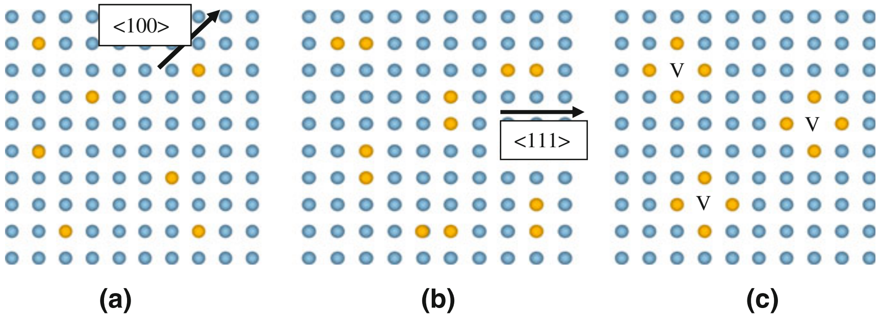


Fig. 2.1 Atomic models of the basic nitrogen defects: **a** single substitutional atoms (C defects), **b** pairs of the nearest substitutional nitrogen atoms (A defects), **c** complexes of four nearest substitutional nitrogen atoms surrounding vacancy (B defects). *Blue* and *yellow circles* denote carbon and nitrogen atoms respectively

Atomic structure of A defects is established quite well. It is a pair of neighboring nitrogen atoms in substitutional positions (nitrogen molecule N_2 imbedded into diamond lattice, Fig. 2.1b). The atomic model of B defects is still debated, though the most acknowledged version is a tetrahedron of four neighboring substitutional nitrogen atoms surrounding a vacancy (Fig. 2.1c). The atomic model of the B' defects is even more obscure. The commonly used model of B'-defect is a macroscopic planar segregation of interstitial carbon atoms along cubic (100) crystallographic planes decorated with some nitrogen (Fig. 5). Because of the planar structure, the B'-defects are usually referred to as "Platelets". Typically, Platelets have rectangular shape and their size is in the range of a few tens of nanometers. However, Platelets can be as large as tens of micrometers and then they can be observed in cathodoluminesence (Collins and Woods 1982) and electron microscope (Kiflawi et al. 1998).

There is no any reliably established atomic model of Platelets so far. We use a working model which suggests that the Platelet is a planar aggregation of interstitial carbon atoms around B defect (Fig. 2.2). We assume that B defects serve for intrinsic interstitials as condensation centers. Hence the size of Platelets and the nitrogen content within them depends on the thermodynamic parameters (temperature, pressure), time and concentration of B defects. In theory, one Platelet contains only one B defect. Thus, the larger the Platelet the smaller relative concentration of nitrogen in the Platelet. In diamonds with high concentration of B defects, many small Platelets form and, consequently, relative concentration of nitrogen in them may be rather high (over 10 %) (Goss et al. 2003 and references therein). With time, as the Platelets grow, the relative nitrogen concentration goes down. In diamonds with low concentration of B defects, the Platelets may rich great size still containing only few B defects. Thus, the relative concentration of nitrogen in such Platelets may be close to zero.

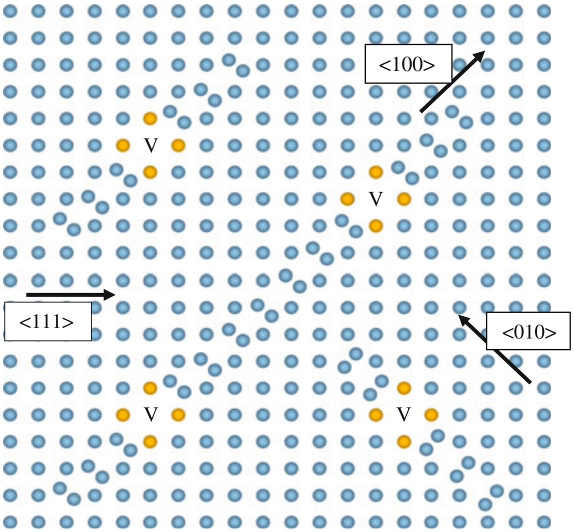


Fig. 2.2 Working atomic model of the B'-defect (the Platelet) used in this book: B defects decorated by carbon interstitials. Two (100) nearest planes of 3-coordinated interstitial carbon atoms surround B defect. B defects serve as centers of condensation for interstitial carbon atoms. In diamonds with high concentration of B defects, one platelet may include several B defects over its area. *Blue* and *yellow circles* denote carbon and nitrogen atoms respectively

An important issue concerning the process of formation of Platelets is the source of interstitials. Our model of Platelets suggests that the amount of interstitials required to from Platelets is greater than that of B defects. Thus, the release of interstitials during the aggregation of A defects into the B defects is not the only source. The further feasible processes, in which high concentration of interstitials can be generated and which always occur in natural diamonds while in earth, are the plastic deformation and the motion of dislocations.

Additional labeling of type Ia diamonds with letters A, B, C and B' is used to indicate the dominating form of nitrogen defects. For instance, type IaA diamonds contain nitrogen predominantly in the form of A defects. Type IaABb diamonds are these containing comparable concentrations of A-, B- and C defects. Symbols $<$ and $>$ may be used to show the prevailing defects. For instance, type IaA $>$ b describes a diamond with dominating concentration of A defects and a measurable concentration of C defects. For instance, this type is a common result of HPHT treatment applied to originally type Ib diamonds. Some natural diamonds are of this type too. Type IaB $>$ A $>$ b describes a diamond with dominating concentration of B defects, which also contains some A defects and measurable traces of C defects. This type is very common for nitrogen-containing HPHT-treated diamonds, whereas it is very rare for natural untreated diamonds.

Total nitrogen content in natural type Ia diamonds may be very high—up to 10,000 ppm (Sobolev et al. 1986). High-nitrogen diamonds have most nitrogen in the aggregated forms (A-, B- and B'-defects). Concentration of C defects in natural diamonds usually does not exceed 50 ppm and rarely goes above 100 ppm. However, there are reports on natural brown-yellow diamonds containing C defects in concentrations over 500 ppm (Hainschwang et al. 2006a; Vins et al. 2008).

In some natural diamonds, only one form of nitrogen defects can be seen in IR absorption spectra and, on this basis, these diamonds are ascribed to "pure" types IaA, IaB, or Ib. However, even in these diamonds of pure type, trace concentrations of all other nitrogen defects can be detected by more sensitive EPR and/or PL methods. There is no natural diamond, in which all forms of nitrogen defects could not be detected (Sobolev et al. 1986).

The A-, B- and B'-defects do not absorb light in the visible spectral range. Therefore, type Ia diamonds are colorless. In contrast, C defects strongly absorb in the green and blue spectral ranges and, because of this, type Ib diamonds are orangey-yellow in color.

2.1.2 Type II Diamonds

Type II diamonds are those containing no measurable amount of nitrogen. Practically, to be of type II, a diamond has to contain less than 1 ppm nitrogen. Further division of type II into types IIa and type IIb is used to distinguish between diamonds, which do not contain boron (type IIa) and those, which contain boron impurity (type IIb). Boron concentration in natural type IIb diamonds is usually low and it rarely exceeds 1 ppm. Type IIb diamonds are also the most low-nitrogen natural diamonds with typical nitrogen concentration in the range of 0.01 ppm. Type IIb diamonds show characteristic boron-related broad-range optical absorption starting in IR and spreading through the red towards green spectral range. This absorption makes type IIb diamonds blue.

Type IIa diamonds are nominally impurity-free ones, however, they may contain small but still detectable amount of major nitrogen A-, B- and C defects, as well as their derivatives. These are, for instance, N3, H3 and NV defects (see below), which can be detected using sensitive PL spectroscopy. Their concentration, however, is too low to produce optical absorption in Vis spectral range and to affect the colorless appearance of type IIa diamonds.

2.1.3 Natural Occurrence of Diamond Types

The vast majority of natural diamonds are plastically deformed nitrogen-rich brown diamonds of type Ia. These diamonds contain nitrogen in different forms and belong to the most common mixed type IaABB'. About 98 % of all natural diamonds are of type IaABB'. Of these, about 90 % are high-nitrogen diamonds containing greater than 1,000 ppm nitrogen. Diamonds of pure types are very rare in nature. Natural occurrence of pure type IaA diamonds is less than 0.05 % (Bokiy et al. 1986). No more than 0.2 % of natural diamonds are those of pure type IaB. Type Ia+Ib diamonds with dominating concentration of C defects are also rare and they amount to about 0.8 % of all natural stones. Natural diamonds, which can be ascribed to type Ib are very rare comprising not more than 0.1 % of all natural diamonds. Although being classified as type Ib diamonds, all natural diamonds of this type commonly contain at least A defects in measurable concentrations (Schmetzer 1999a; Collins 2001). In contrast, natural diamonds with measurable content of C defects rarely contain B defects. However, mixed type IaABB' diamonds may contain small amount of C defects. Especially low C defect content is in natural diamonds with dominating B and B' defects.

The A-, B- and C defects are rarely present together in low-nitrogen diamonds of brown to yellow color and in low-nitrogen chameleon diamonds (Hainschwang et al. 2005a). The presence of nitrogen in all aggregated forms is explained by naturally occurring decomposition of B defects by moving dislocations during plastic deformation the diamonds experience in earth (Nadolinny et al. 2009). The diamonds, containing simultaneously A-, B- and C defects in concentrations measurable in IR absorption, are termed as ABC diamonds (Fig. 2.3).

Low-nitrogen diamonds are rare in nature. Type IIa diamonds amount to less than 2 % of all recovered diamonds in major diamond deposits. The relative number of low-nitrogen and type IIa diamonds increases with size. Many large cut diamonds are of type IIa including the biggest and the most famous: Golden Jubilee (545.7 carats), Cullinan I (530.2 carats), Cullinan II (317.4 carats), Centenary (273.8 carats), De Beers Millennium Star (203 carats).

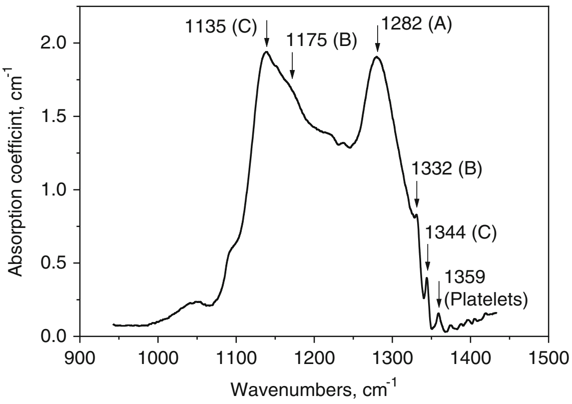


Fig. 2.3 IR absorption spectrum of a natural untreated ABC diamond of fancy *deep brown yellow color*. The spectrum shows the presence of all major nitrogen defects: C, A, B and B'. The spectral position (1,359 cm^{-1}) and the spectral width (7 cm^{-1}) of the platelets peak fit well into area of untreated diamonds (see Fig. 6.77). A developed Amber center present in the spectrum confirmed the untreated nature of the stone (not shown)

Type IIb diamonds are extremely rare, comprising less than 0.001 % of all natural diamonds.

2.1.4 Recognition of Diamond Types

A standard way to determine type of a diamond is to measure its IR absorption spectrum. All nitrogen and boron defects defining the diamond type are optically active and their content can be accurately measured via intensity of the corresponding absorptions. Usually IR absorption spectroscopy in the spectral range from 400 to 1,400 cm^{-1} is used to measure the nitrogen concentration of 1 ppm and above. For concentrations below 1 ppm, Vis and UV absorption spectroscopy is employed. A more detailed description of the optical absorptions (optical centers) related to the nitrogen- and boron-containing defects is given below in Chap. 5.

If a natural diamond is colorless, its type can be also recognized by examining it in microscope in polarized light. Most type IIa diamonds possess high dislocation density and show in polarized light characteristic birefringence strain patterns ("tatami" pattern) extending through the whole volume of diamond (Fig. 2.4). In contrast, type Ia diamonds have less dislocations and exhibit banded birefringence strain patterns usually spreading along one dominating direction (Berman 1965; Chalain 2003). However, the nitrogen content influencing the birefringence pattern of diamond is rather high (over 20 ppm). Because of this, the birefringence pattern method is not suitable for differentiation between type IIa and low-nitrogen type Ia diamonds.

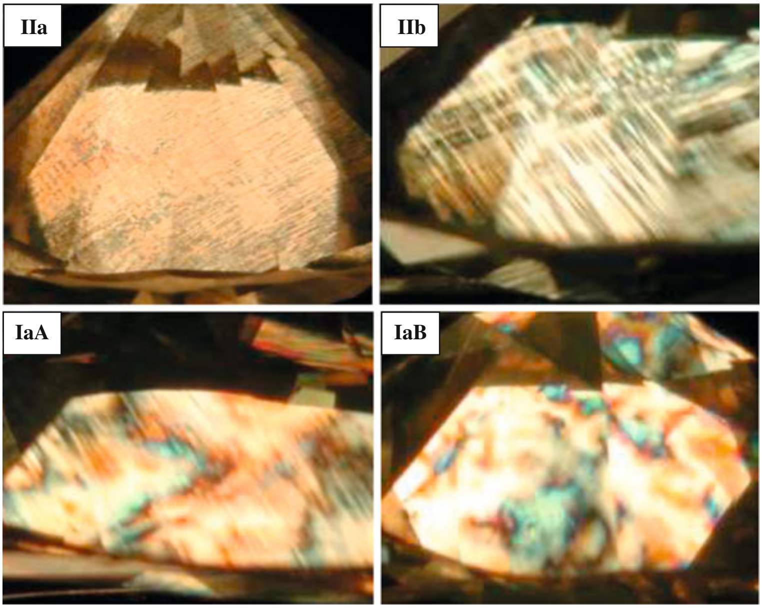


Fig. 2.4 Examples of birefringence patterns of diamonds of different types. Anomalous double refraction pattern called "tatami" is characteristic of natural type II diamonds. "Tatami" is not obvious in type I diamonds (courtesy of D. Simic)

Nitrogen A- and C defects and boron are electrically active in diamond. A- and C defects are both donors and may deliver free electrons in diamond lattice via ionization (Collins et al. 2000). Yet, the ionization energies of A- and C defects are too high (4 and 1.7 eV respectively) to allow them to release free electrons at room temperature. Thus, the nitrogen-containing diamonds of type I are highly insulating at room and even at elevated temperatures. Substitutional boron atoms are acceptors in the diamond lattice and, when ionized, deliver free holes. The ionization energy of boron is 0.38 eV, what is much less than the ionization energy of the nitrogen defects. An appreciable number of boron acceptors are ionized at room temperature and this provides a measurable electrical conductance. This electrical conductance is a unique feature of type IIb diamonds.

The described classification is a physical classification of diamond as a material and it is applicable to diamonds of any nature and origin. It is equally used for classification of natural, synthetic (both HPHT-grown and CVD-grown), untreated and treated diamonds. A scheme of diamond types and their characteristic colors is presented below in Fig. 2.5.

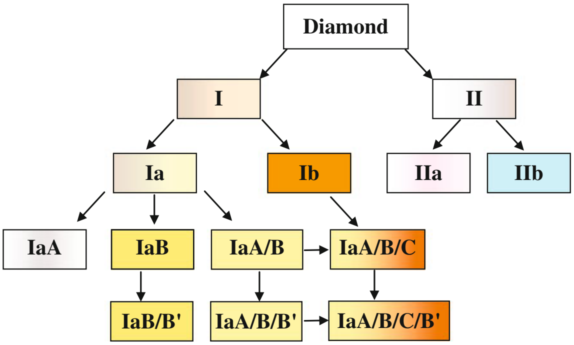


Fig. 2.5 Types of diamond and their characteristic colors

2.2 Colors of Natural Diamonds

The color of any colored diamond results from the presence of defects. Impurity-free, structurally-perfect diamonds are colorless. However, not all defects induce color, but only those optically active in the visible spectral range. For instance, the nitrogen-related A- and B defects are active only in IR and UV spectral ranges and therefore they do not affect the colorless appearance of type Ia diamonds. However, in most natural diamonds, the A- and B defects produce optically active derivatives, like H3, H4 and N3 defects, and then type Ia diamonds acquire yellowish color.

Two major types of optically active defects rendering natural diamond non-colorless are nitrogen-containing defects and aggregation of vacancies. The nitrogen-containing defects are formed of nitrogen captured from the environment during the diamond grow. The vacancies and their aggregates are formed in cause of plastic deformation the diamonds experience in earth. It is a rare event that in nature diamond grows in nitrogen free environment. Also it is a rare event that diamond is surrounded by uniform stable medium during its billion year history in earth. Hence vast majority of natural diamonds contain nitrogen and are plastically deformed. The most common color of these diamonds is unpleasant brown with a tint of yellow. Rare nitrogen-containing but non-deformed diamonds change their hue from colorless to yellow as the nitrogen concentration grows. Very rare nitrogen-free, non-deformed diamonds are perfectly colorless and, because of this, the most valuable gems.

The most common optical centers affecting the color grade of natural diamonds are the Brown absorption continuum (responsible for brown color), the N3 and N2 centers (responsible for yellow color) and the C defect absorption continuum (responsible for orangey-yellow color). Typical UV–Vis absorption spectra of natural diamonds are shown below in Fig. 2.6.

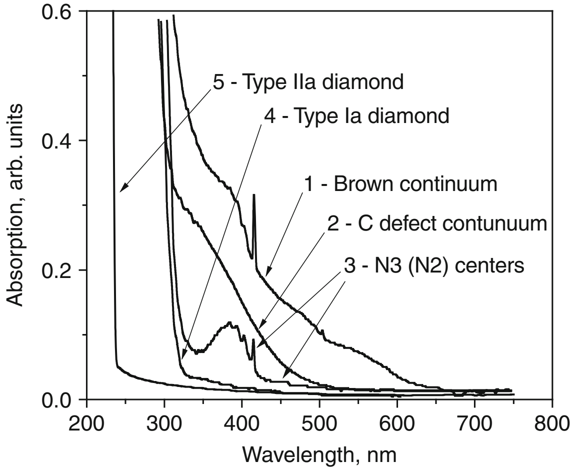


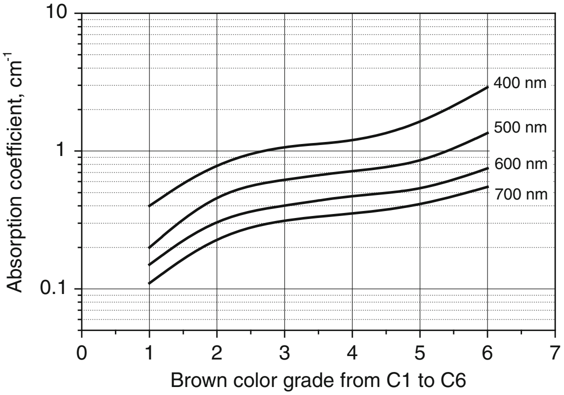
Fig. 2.6 Absorption spectra of diamonds of typical natural colors. *Curve 1* represents *brown color* type IaA/B diamonds. The brown absorption continuum is the major absorption feature responsible for brown coloration. *Curve 2* represents *yellow* type Ib and type Ia+Ib diamonds. The C defect absorption continuum is the major absorption feature determining color. The C defect absorption continuum differs from the brown absorption continuum by much lower absorption in the *yellow* and *red* spectral ranges. *Curve 3* represents type Ia diamonds of *cape yellow color*. The main absorption center of these diamonds is the N3 (N2) center band absorbing in the *blue* and *green* spectral ranges. *Curve 4* represents *non-colored* type Ia diamonds. Traces of the N3 (N2) center band in the spectral range from 350 to 480 nm make most of these diamonds *near-colorless* [based on the data from (De Weerdt and Collins 2007)]. *Curve 5* represents *colorless* type IIa diamonds

2.2.1 Brown

Brown is the common color of natural diamonds. Brownish tinge can be recognized in 98 % of all as-mined diamonds. An increased attention to the diamonds of brown color in the last decade is stimulated by the possibility of “improving” their color and converting them into diamonds of bright fancy colors using HPHT treatment. Brown diamonds can be of any type and they are mined from many deposits all over the world. However, the brown color is especially characteristic of natural type IIa diamonds. It has been shown that the presence of nitrogen in A and B aggregates stiffens the diamond lattice against distortion by natural plastic deformation (Nailer et al. 2007). Thus, low-nitrogen diamonds experience stronger plastic deformation than their nitrogen-rich counterparts when under equal mechanical stress.

Brown color of majority of brown diamonds is caused by the absorption continuum, which starts in the near IR spectral range and gradually increases towards shorter wavelengths—so-called the Brown Absorption Continuum (Fig. 2.6). The Brown Absorption Continuum of many brown diamonds has some secondary features like H3 center seen as a band with a maximum at 480 nm and the Pink

Fig. 2.7 Absorption intensity at different wavelengths (as indicated) within Vis spectral range for the brown diamonds, the absorption spectra of which dominate by the Brown Absorption Continuum



Band with a maximum at 550 nm. These features may result in yellow, green and pink modifying colors.

According to the DTC color scale, the intensity of brown color of diamond is characterized by six grades from C1 (the least intense) through C6 (the darkest brown). The brown color is determined visually using master stones of corresponding colors. It can be also evaluated from the measurements of the absorption intensity of the Brown absorption continuum (Fig. 2.7). The brown color scale is not uniform in terms of absorption intensity. The absorption strength of the Brown Absorption Continuum increases only slightly for the grade change from C3 to C4, whereas the absorption increase is considerable when the grade changes from C1 to C3 and from C5 to C6.

Another grade scale of color of brown diamonds uses four categories: Br1 through Br4. An approximate correspondence between the DTC scale and the Br scale is: Br1–C1, Br2–C2 to C3, Br3–C4 to C5, Br4–C6. The Br scale is more uniform as compared with the DTC scale. The Br scale is more convenient for the characterization of rough brown diamonds selected as starting material for HPHT treatment.

Brown diamonds can be grouped into two major categories, which reflect two different types of color distribution: (1) the distribution in form of brown striations (brown graining) and (2) non-graining distribution, which may be either uniform, or in form of irregular patches, or showing some zoning (Fritsch et al. 2005; Massi et al. 2005). The brown graining follows {111} slip planes (Fig. 2.8) and may penetrate though the whole diamond body. These diamonds exhibit strong traces of plastic deformation on the surface like etched pits and grooves. Plastically deformed diamonds, as the most populated category of brown diamonds, can be termed as regular brown diamonds. Diamonds of this category are the most common starting material for commercial HPHT treatment.

Although the brown graining is localized in the deformed areas, the deformation itself is not the primary reason of brown coloration. Because of this, not all plastically deformed diamonds are brown. Artificially induced plastic deformation during non-hydrostatic HPHT treatment at a temperature of 1,600 °C and

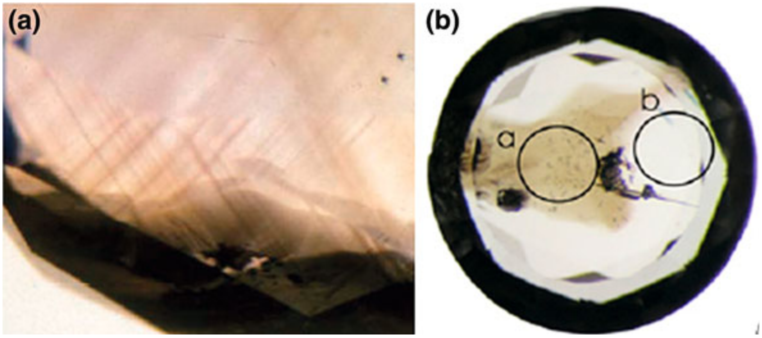


Fig. 2.8 **a** Brown graining in a natural regular brown diamond (Kitawaki 2007). **b** A natural diamond exhibiting *brown coloration* due to high content of CO_2 molecules (Hainschwang et al. 2008) (with permission of the Diamond and Related Materials journal)

a pressure of 6 GPa does not result in brown color (Kanda et al. 2005). Thus, the plastically deformed areas are just the places where the optical centers responsible for the brown coloration are generated. These defects can be vacancy clusters, defects responsible for the Amber Center and dislocations (Fritsch et al. 2005; Hounsome et al. 2006, 2007; Vins et al. 2008). Although all these defects can contribute to the brown graining, the vacancy clusters seem to be the most effective ones (Bangert et al. 2009).

Production of vacancies by plastic deformation and their accumulation into vacancy clusters may begin at a temperature of 1,200 °C, when diamond loses its rigidity and dislocations start to form. Thus, it is assumed that the generation of brown color in natural diamonds may occur in earth at rather low temperatures and the defect structure of such diamonds may reveal characteristic features of low temperature heating. For instance, it can be a trace concentration of single non-aggregated vacancies, which survived the natural heating and which can be detected as a weak GR1 center (see Chap. 5). HPHT treatment removes single vacancies and destroys the GR1 center completely. Consequently, traces of the GR1 center in natural diamonds with brown coloration is an indicator of their pristine state.

In plastically deformed brown type Ia diamonds, no correlation between brown color and nitrogen content has been found (Chapman 2010). However, there is some correlation between internal strain in type Ia diamonds and their brown coloration, the brown color being associated with lower strain fields (Van Royen 2006; Chapman 2010).

Brown color can be artificially induced in diamonds, when they are heated at high pressure at non-hydrostatic conditions resulting in internal strain (Howell 2009). However, the strain alone does not result in brown color. Instead, the brown coloration in the deformed diamonds is distributed rather uniformly throughout the bulk and it does not follow the slip bands or any other crystallographic features. It might be that the concentration of the defects responsible for the brown coloration in the slip planes is a slow kinetic process occurring after the internal strain has been induced.

Along with the plastically deformed brown diamonds colored by the deformation-induced graining, there are brown diamonds, color of which is caused by micro-inclusions and defects generated by non-deformational mechanisms. These diamonds can be termed as irregular brown diamonds. The defects contributing to brown color of irregular brown diamonds have been identified as C defects in type Ib diamond, micro-inclusions of non-diamond phases, imbedded CO_2 molecules, hydrogen-related defects, some unknown intrinsic defects in type IIa and IaB diamonds (Ewels et al. 2001; Fritsch et al. 2005; Hainschwang et al. 2008; Barnes et al. 2006). Prominent non-graining brown diamonds are CO_2-rich ones (Hainschwang et al. 2008). These diamonds can be recognized by shapeless brown areas (Fig. 2.8b). The nature of the optical centers responsible for brown color of CO_2-rich diamonds has not been established yet. However, it is known that these centers are much more stable than the vacancy clusters in plastically deformed brown diamonds. Due to this high stability, the brown color of CO_2-rich diamonds stands HPHT treatment even when performed at very high temperatures. Because of this, the CO_2-rich brown diamonds are not used for commercial HPHT color enhancement.

2.2.2 *Yellow*

Two major reasons for yellow color in natural diamonds are the absorption of the N3 and N2 optical centers and the continuous absorption in the visible spectral range due to C defects. The N3 and N2 absorptions cause the color of so-called “cape-yellow” diamonds, which are the most common naturally-colored gem diamonds of pleasant colors (Johnson and Moe 2005) (Fig. 2.9). The cape-yellow diamonds are of type Ia with nitrogen content of at least 200 ppm. A considerable portion of nitrogen in these diamonds is in the form of B defects. The vast majority of light yellow natural diamonds are colored this way. Some cape-yellow diamonds have high content of hydrogen, which provides an additional weak absorption in the yellow to green spectral range. Because of this absorption, the color of the hydrogen-rich yellow diamonds may have an unwanted gray modifier.

The N3 and N2 centers are very temperature stable and therefore cape-yellow color component of natural diamonds cannot be removed or reduced by HPHT treatment. Instead, in some cape-yellow diamonds, HPHT treatment may enhance absorption of the N3 and N2 centers resulting in a deeper yellow color. Whereas the N3/N2 absorptions are in general not affected much by HPHT treatment, the hydrogen-related grayish color can be reduced or even removed by HPHT treatment. Thus, HPHT-treated cape-yellow diamonds are also something to encounter with in the gem diamond market.

The absorption in the Vis spectral range due to C defects causes orangey-yellow or “canary-yellow” color, which can be easily distinguished from the cape-yellow

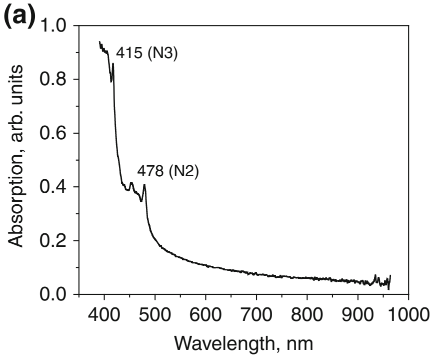


Fig. 2.9 **a** Absorption spectrum of a typical natural *cape-yellow* diamond. Enhanced absorption starting in the *green* spectral range and rapidly increasing towards *blue* and UV spectral range is the cause of the *yellow* coloration. **b** Absorption spectrum of a type Ib diamond exhibiting the absorption continuum due to C defects. C defects absorb light in the *yellow* and *green* spectral ranges stronger than N2 centers in *cape-yellow* diamonds. Due to this difference, type Ib diamonds have an *orange* modifier in their color when compared with the *cape-yellow* diamonds

color. The absorption spectra of cape-yellow and canary-yellow diamonds are also very different (compare Fig. 2.9a, b). The C defects are very effective in absorption. Just a trace concentration of C defects may affect color grade of natural diamond. A concentration of C defects of 0.1 ppm reduces the color grade of diamond to a level of J. A few ppm C defects is sufficient to cause a fancy yellow color (Collins 2001; Kitawaki 2007). Deep yellow color, characteristic of rare natural type Ib diamonds and most synthetic diamonds, is caused by C defect concentration of 20 ppm and above (Claus 2005). Very deep yellow color of synthetic diamonds is due to high content of C defects in the concentration range of 200 ppm (Collins 2003). Extremely high content of C defects (above 1,000 ppm) causes very deep yellow/brown color (Collins 2001). Although the increase in the intensity of yellow color follows the C defect concentration, it is difficult to accurately link defect concentration to color grade for different diamonds due to the effect of size, shape and cut (Fisher 2012).

Very rarely, natural diamonds with strong absorptions in H3 and H4 centers (see below Chap. 5) acquire orange-yellow color, which may resemble the color of type Ib diamonds (Fig. 2.10a). Some natural yellow diamonds with rather pronounced orange modifier owe their color to a broad absorption band with maximum intensity at a wavelength of 480 nm accompanied by an absorption continuum steadily increasing towards shorter wavelengths (Collins 2001) (Fig. 2.10b). Although the spectral position of the absorption maximum of the 480 nm band coincides with that of the H3/H4 centers, the 480 nm band is a different optical center and it should not be confused with the H3 and H4 centers (Collins 2003).

C defects have moderate temperature stability. Thus, the canary-yellow color induced by C defects is easily affected by HPHT treatment. HPHT treatment, when

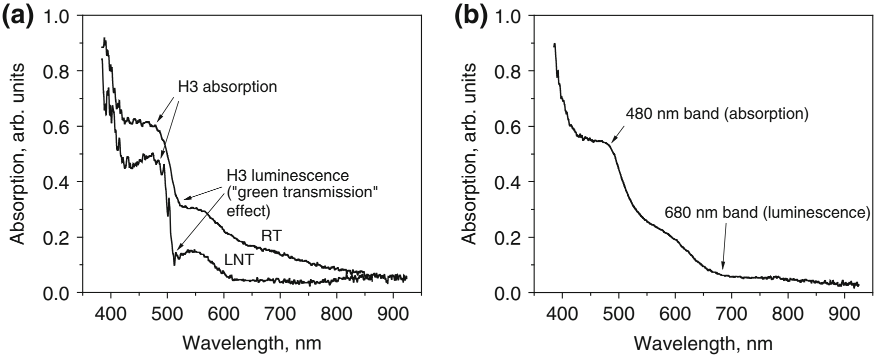


Fig. 2.10 **a** FSI absorption spectra of a natural *orangey-yellow* type IaAB diamond showing naturally present H3 center. The H3 absorption band, when recorded at room temperature, resembles the 480 nm band. Yet the measurement at liquid nitrogen temperature reveals fine structure of the H3 band, what makes it distinguishable from the 480 nm band. In this diamond, the H3 center also exhibits noticeable "green transmission" effect which makes the diamond to look *greener*. **b** FSI absorption spectrum of an *orangey-brownish-yellow* natural diamond with absorption in the 480 nm band recorded at liquid nitrogen temperature. The 480 nm band exhibits no fine spectral structure. Orange tint of the color of this diamond is enhanced by the luminescence band at 680 nm, which is the emission replica of the 480 nm absorption band. This effect is analogous to the "green transmission" effect of the H3 center

performed at temperatures below 2,000 °C, reduces concentration of C defects and may convert intense canary-yellow color of type Ib diamonds into light yellow, or even make these diamonds near colorless type IaA. However, HPHT treatment performed at high temperature (2,200 °C and above), reversibly produces C defects in type Ia diamonds and may strengthen the yellow color component.

2.2.3 Blue to Violet

Natural boron-containing type IIb diamonds are blue or more typically blue-gray. When viewed in polarized light, natural IIb stones, like other type II diamonds, have characteristic tatami-structure due to low-nitrogen content. Some natural blue diamonds owe their color to high concentration of hydrogen, which absorb in red and yellow-green spectral ranges. Rarely, high-hydrogen diamonds reveal a strong broad-band absorption starting at 600 nm and spreading towards IR spectral range. This absorption may add a greenish tint to the blue and violet color (Darley and King 2007) (Fig. 2.11).

Blue and violet colors cannot be produced by HPHT treatment. However, HPHT treatment can considerably improve the boron-induced blue color of bluish-gray or gray type IIb diamonds via reduction or removal of the gray component.

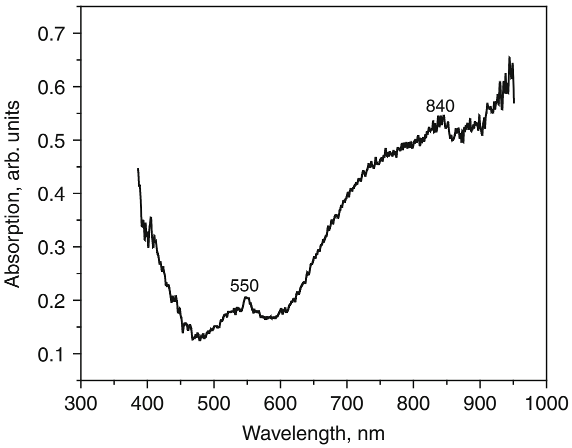


Fig. 2.11 Absorption spectrum of a high-nitrogen, high-hydrogen type IaAB diamond of fancy *violet gray color*. The *violet* modifier of the color is caused by the transparency windows at a wavelength of 470 nm. The absorption feature at 550 nm, which also adds to the *blue-violet* coloration, is probably due to hydrogen

The bluish color can be also stimulated by natural irradiation, which produces the GR1 center. Electron-irradiated pale-blue diamonds called “ice-blue diamonds” are quite popular in the gem market (Kitawaki 2007).

2.2.4 Green

Many diamonds from some deposits (e.g. from Congo and Canada) have homogeneous surface coloration in blue and green colors because of natural alpha- and/or beta-irradiation. This type of coloration of natural rough diamonds was described in (Orlov 1973). The main reason of the radiation-induced green color is the absorption of GR1 center (Fig. 2.12a). Light green coloration may be observed through the whole diamond body (body distribution of vacancies producing the GR1 center) indicating the action of deeply penetrating beta- and gamma-radiation (Yelisseyev et al. 2004). Alternatively, green coloration can be concentrated close to the surface as a result of dominating irradiation with alpha-particles, which penetrate into diamond to a depth of a few microns only.

Natural untreated green diamonds have very light color because of weak GR1 absorption. These diamonds often exhibit green to brown irradiation spots (radiohalos, Fig. 2.12b) on naturals (e.g. on unpolished parts of girdle of cut diamonds) (Kitawaki 2007; Hargett 1991). This feature makes the naturally irradiated green diamonds distinguishable from the green diamonds processed by the radiation treatment. However, it is important to understand that the radiohalos are not the ultimate proof of the natural body color of green diamonds. Instead, the diamonds with natural radiohalos can be irradiated with high energy electrons with the aim of improvement of their body color and then the radiohalos can be conveniently used as a “solid” proof that these diamonds are “naturally” irradiated. Moreover, radiohalos can be produced on the diamond surface artificially applying irradiation

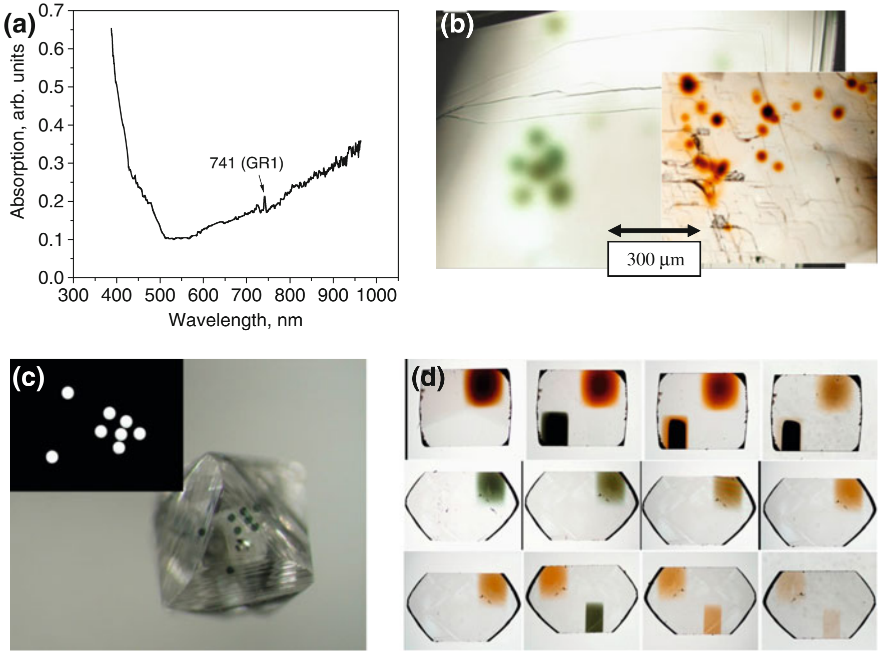


Fig. 2.12 **a** Absorption spectrum of a very *light green* type IaB natural diamond showing weak GR1 center and rather developed H3 center. The *green color* of this diamond is distributed through the whole diamond body. Low intensity of the GR1 center (absorption coefficient is about 0.08 cm^{-1}) suggests its natural origin. **b** Well-shaped, *circular green* and *brown* natural radiohalos on surface of an octahedron from Guaniamo, Venezuela (Nasdala et al. 2012). **c** A little natural diamond octahedron ion-irradiated through a mask (shown in the insert) demonstrating a way of making artificial radiohalos (courtesy of L. Nasdala). **d** *Ion-irradiated spots* on surface of natural diamond plates. These *spots* have been irradiated with different ions, at different energies, with different doses and annealed at different temperatures. Depending on the parameters of the irradiation and annealing, the color of the irradiated areas can be *green*, *orange*, *brown* and *black* (Nasdala et al. 2012)

with light ions (e.g. He or C ions) through a stencil mask (e.g. perforated foil) (Nasdala 2012) (Fig. 2.12c). The color of the artificial radiohalos can be made quite identical to those of natural ones (Fig. 2.12d).

Some natural diamonds exhibit green color when viewed under daylight illumination. This light-induced green color is the result of intense luminescence of H3 optical center excited by blue and UV components of the daylight. Such diamonds are known as “green transmitters”. In perfect low-nitrogen diamonds with little content of A defects, the H3 defects are very effective in green luminescence under daylight excitation. Thus, even being present in small concentrations, the H3 defects may considerably contribute to green color via the characteristic green emission in the spectral range 500–550 nm (Fig. 2.13). The green color of “green transmitters” considerably weakens or completely disappears when diamond is viewed in incandescent light.

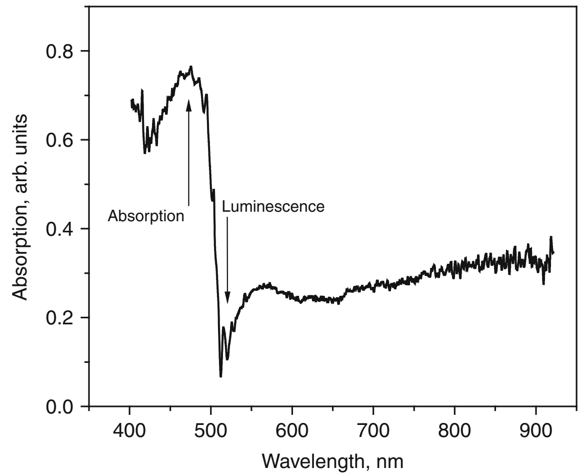


Fig. 2.13 FSI absorption spectrum of a natural low-nitrogen type IaAB diamond of fancy *yellowish green color* measured at liquid nitrogen temperature. The dominating *green color* of this diamond results from the H3 center luminescence seen in the absorption spectrum as a "reverse" structured band in the spectral range 500–550 nm. The fine structure of this band corresponds to the vibronic features of the H3 center in luminescence

Some natural yellow-green (yellowish-green) diamonds owe their color to nickel-related optical centers (Wang and Moses 2007). Color of these diamonds resembles the color of synthetic diamonds grown at elevated temperatures in the presence of Ni impurity (Vins 2002). Thus, one may assume that the natural Ni-rich diamonds of greenish color also grew in earth at elevated temperatures exceeding 1,450 °C. Therefore, these stones may exhibit some features characteristic of HPHT-treated diamonds processed at low temperatures of 1,600–1,700 °C.

Green color of natural diamonds induced both by H3 and Ni-related centers can be considerably modified, enhanced or reduced by HPHT treatment. The most characteristic example of this change is the HPHT-induced green transmitters. Whereas the "green transmission" effect is a rare feature of pristine natural diamonds, it is a very common result of HPHT treatment performed at temperatures below 2,000 °C. HPHT-induced "green transmission" effect is particularly pronounced in diamonds with low content of A defects.

2.2.5 *Pink and Red*

Natural diamonds are rarely pink and very rarely purple. It is believed that, like color of most brown diamonds, pink/purple coloration is the result of plastic deformation too. Pink coloration of natural diamonds does not depend on the presence of nitrogen impurity, and these diamonds can be of types I and II (King et al. 2002; Fisher et al. 2009).

Pink coloration, like brown graining, is also restricted to thin bands parallel to octahedral slip planes (pink graining). However, pink color is distributed rather homogenously within these bands. Nitrogen-containing pink-purple diamonds are

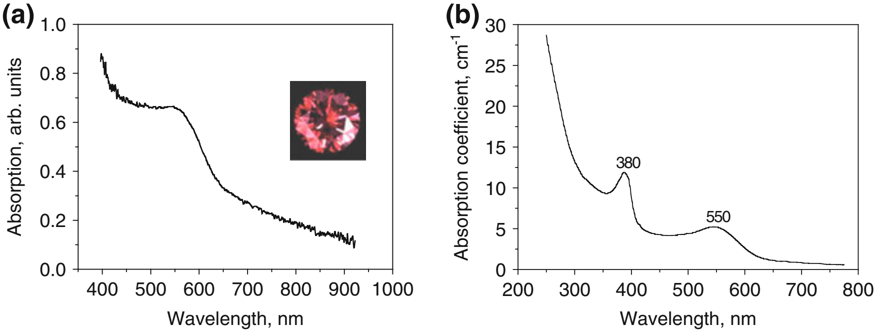


Fig. 2.14 **a** Absorption spectrum of an Argyle low-nitrogen type IaB pink diamond exhibiting a pronounced Pink Band. In this diamond, the Pink Band superimposes with the brown absorption continuum of a moderate strength—a typical absorption spectrum of natural pink diamonds. Insert shows photo of a diamond of this type [re-plotted from Chapman et al. (1996)]. **b** UV/Vis/NIR absorption spectrum showing the dominant absorption bands at 390 and 550 nm typical for natural pink diamonds [re-plotted from (Fisher et al. 2009)]. Two major transparency windows at wavelengths from 400 to 500 nm (*blue color*) and above 600 nm (*red color*) produce *pink color* of this diamond

frequently of dominant type IaA (Titkov et al. 2008). This observation implies that pink-purple diamonds had been brought from the earth interior to the surface at early stages of their formation and the processes of the nitrogen aggregation in these diamonds had not been completed. Such an immature defect structure of many pink/purple natural diamonds poses additional difficulties in detection of HPHT treatment. Indeed, presence of traces of C defects, which are otherwise a strong evidence of HPHT treatment, is not a rare event for untreated type IaA pink/purple diamonds. Therefore, the detection of C defects in these diamonds cannot be considered as a proof of HPHT treatment.

The primary reason of pink color of plastically deformed natural diamonds is a broad absorption band with maximum at about 550 nm—so-called “Pink Band” (Fig. 2.14a). Pink color may be also highlighted by the presence of an absorption band with maximum at 390 nm (Fig. 2.14b). A diamond, the absorption spectrum of which has these two bands of comparable strength, has particularly pleasant pink color. The 390 and 550 nm bands can occur in both type I and type IIa diamonds. However, their strength is usually weaker in nitrogen-free diamonds.

Naturally occurring NV centers (575 and 638 nm centers, see below) may also contribute to red color of untreated natural diamonds. Although it is an extremely rare event that a natural diamond has the 575 nm center strong enough to affect its color (Fritsch 1998; Scarratt 1987), such diamonds are documented in literature. Visible absorption spectra of these diamonds may contain 638 nm (NV$^-$ center), H3 and H4 absorptions (Wang et al. 2003).

2.2.6 Gray

Gray color of diamonds is the result of uniform absorption throughout the whole visible spectral range. Since perfectly uniform absorption in a wide spectral range occurs rarely, gray color of natural diamonds is usually accompanied by faint tints of yellow, green, blue or pink. It is believed that the two major sources of gray color are graphitic micro-inclusions and hydrogen (Vins and Kononov 2003). The graphitic inclusions work as light scattering centers causing Rayleigh scattering, rather than light absorbing centers. Because of this scattering, gray diamonds may have translucent appearance. The size of the graphitic micro-inclusions varies and may reach a few micrometers. The big graphitic inclusions can be seen in microscope and identified by their characteristic hexagonal shape. The most probable explanation of the uniform formation of graphite nano-crystals through the body of gray diamonds is that these diamonds grew at the temperature–pressure parameters close to the diamond-graphite phase transition. A less probable mechanism could be the direct incorporation of graphitic inclusions during the diamond growth.

The hydrogen-related defects work like regular absorbing optical color centers. All natural diamonds contain considerable amount of hydrogen, some of which is present in form of optically active defects. In nature, diamonds always grow in the presence of hydrocarbons (mainly methane and the products of its dissociation), carbon oxides, nitrogen hydrides, hydrogen and other gasses (Digonsky and Digonsky 1992). It is also believed that the crystallization of diamond from graphite occurs directly during dissociation of hydrocarbons into carbon and hydrogen irrespective of the growth medium: gaseous, silicate solutions, or metal melts. During the crystallization of carbon, hydrogen may form CH radicals on diamond surface and on the lateral edges of the graphite crystals. It is known that during heating with increasing temperature, hydrocarbons polymerize and experience complex transformations until final graphite phase is formed. During these transformations, hydrogen content reduces. Upon completion of the conversion of hydrocarbons into graphite, hydrogen can localize only on the lateral edges of the graphite crystals. Hence the amount of the remaining hydrogen is determined by the concentration of the graphite crystals and their size: the smaller the graphite crystals the greater amount of hydrogen.

Gray diamonds grew at the conditions of high oversaturation, when the diamond growth medium rapidly cooled down during its travel to the earth surface. Analysis of the impurity-defect structure of gray diamonds suggests that these diamonds experienced rapid annealing, the last period of which was at the conditions close to the graphite-diamond phase equilibrium. Low growth temperature of gray diamonds resulted in the preferential formation of "low-temperature" nitrogen defects: C- and A defects. Thus, natural nitrogen-containing diamonds of gray color are usually of type IaA. The intensity of A center in spectra of these diamonds can be as high as 65 cm^{-1}. Yet some type IaA gray diamonds may exhibit the presence of traces of C defects. In addition to A- and C defect absorptions, all gray diamonds, irrespective of their type, reveal in their spectra strong hydrogen-related centers, the most intense being the 3,107 and 1,405 cm^{-1} ones.

In type IIb diamonds, gray color may be accompanied by additional brown coloration. Combined effect of the absorption continuum due to boron and the brown absorption continuum due to vacancy clusters may essentially result in gray color. Majority of natural type IIb diamonds have grayish tint because of this effect.

2.3 Color of Diamonds Used for HPHT Treatment

There are four main color-based categories of diamond used for commercial HPHT treatment. The HPHT-induced color changes are very different for diamonds of different categories. The first category comprises type IIa brown diamonds. These diamonds, and especially those of high clarity and light brown color, are suitable for the production of the most perfect high color stones. Brown type IIa diamonds are also used for production of light pink stones, the pink color of which is identical to that of untreated natural pink diamonds. The diamonds of this category are the most valuable starting material for HPHT treatment.

The second category comprises type IaB brown diamonds. The primary aim of HPHT treatment of these diamonds is the production of near colorless stones and, in rare cases, low grade colorless stones. Since HPHT treatment always produces in nitrogen-containing diamonds at least traces of the optical centers active in the visible spectral range, brown type IaB diamonds cannot be converted into colorless stones of high color grade. Another aim of treatment of brown (as well as near-colorless and low color grade) type IaB diamonds is production of pink stones. In this case, the diamonds are subjected to multi-process treatment resulting in the formation of NV^- center of moderate intensity. HPHT annealing of type IaB diamonds does not produce much C defects even at high temperatures. Hence the resulting color of the treated diamonds is not affected by the C defect absorption continuum. The most beautiful pink color is achieved when two major absorption centers N3 and NV^- have comparable intensities. Visible transmission spectrum of these diamonds has two windows at wavelengths around 480 nm (blue) and above 640 nm (red). The combination of these two colors makes diamonds pink.

The third and the most populated category is high clarity type IaAB brown diamonds. Inclusion-free brown diamonds of type Ia are starting material for making beautiful high clarity diamonds of fancy yellow and green-yellow colors. Appearance of some HPHT-treated type Ia diamonds can be very attractive by far exceeding that of any natural untreated stone of this hue. Another aim of treatment of brown type IaAB diamonds is the production of red stones (Imperial Red diamonds). For this purpose, multi-process treatment is applied. The treated red diamonds owe their color to the very strong NV^- center, the absorption of which forms pronounced transmission window in the red spectral range. High-nitrogen diamonds treated in this way may also reveal strong C defect absorption continuum, which adds to diamond color an orange modifier. In order to achieve a pleasant red color, the diamonds should not contain much nitrogen. High concentration of nitrogen results in too intense optical centers and too deep red color, which could be even modified with unwanted brown tint.

Low clarity type Ia diamonds of any unattractive colors (mostly brown and gray) are the diamonds of the fourth category. The aim of HPHT treatment of these diamonds is the color improvement and obtaining saturated fancy colors, which could hide the included interior.

The four diamond categories mentioned above comprise the diamonds, which are most frequently used for HPHT treatment. However, any natural diamond, regardless its type, color and clarity, can be treated by HPHT annealing with the aim of increasing its commercial value. Even colorless diamonds of the highest color and clarity can be subjected to HPHT treatment with the aim to add them rare fancy colors.

Chapter 3
Parameters of HPHT Treatment

In its essence, HPHT treatment is a high temperature annealing. Thus, its main parameters are the annealing temperature, the chemical composition of the medium (atmosphere) in which annealing is performed, the pressure the diamonds experience in the medium during annealing, and the duration of the annealing. During HPHT treatment, pressure and temperature are set so that the treated diamonds are brought into the thermodynamic range, where the atomic diffusion is fast enough to provide considerable atomic transformations of optically active defects in a reasonably short time ranging from few seconds to few hours (Anthony et al. 1995). For most defects, these transformations occur more effectively, when diamond is in plastic state. The pressure–temperature range of the threshold, beyond which diamond loses its rigidness and becomes ductile, is in the range of 5–7 GPa and 900–1,200 °C respectively [e.g., Bulanova (1995)]. DeVries showed that at pressures of 4–6 GPa diamond could be plastically deformed at temperatures starting from 900 °C (DeVries 1975). Figure 3.1 compares the pressure–temperature dependence of the plastic-rigid transition of diamond with the pressure–temperature parameters used for commercial HPHT treatment. It is seen that HPHT treatment is always performed in the area of plasticity of diamond.

Since at normal pressure diamond is a metastable carbon phase, it is important to compare the pressure-temperature parameters of HPHT treatment with those of the graphite-diamond phase transition. Figure 3.1 shows that HPHT treatment is performed at pressures and temperatures about the graphite-diamond phase transition line. Yet, in order to reduce pressure and to simplify the process, HPHT treatment is frequently performed within the range of stability of graphite. In these cases, the treatment time is kept rather short (a few minutes) in order to avoid extensive graphitization. When working in the range of stability of graphite, it is also important to use perfect starting material with the least content of non-diamond inclusions and voidites. The structural imperfections cause internal stress and weaken the diamond lattice thus promoting the conversion of diamond into graphite.

A small deviation from the diamond-graphite phase equilibrium line does not play significant role in the transformation of the nitrogen defects and does not

I. A. Dobrinets et al., *HPHT-Treated Diamonds*, Springer Series
in Materials Science 181, DOI: 10.1007/978-3-642-37490-6_3,

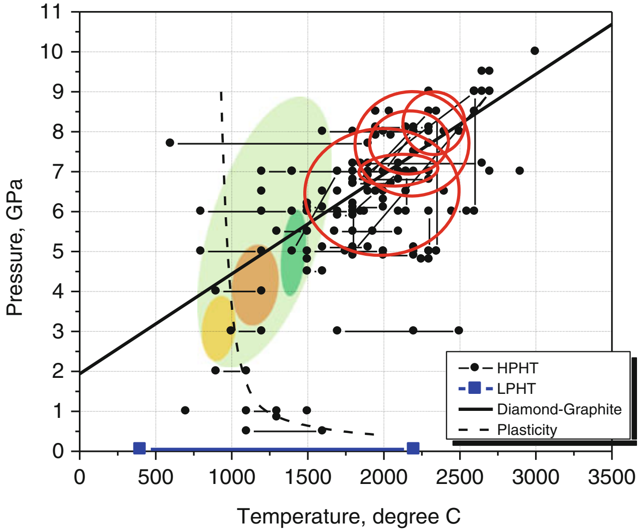


Fig. 3.1 Pressure-Temperature diagram of graphite-diamond phase transition compared with the published experimental data on HPHT annealing (*black circles*). The diamond-graphite equilibrium line (Simon-Berman line) is shown by *black solid line* and the pressure–temperature threshold of the diamond plastic yield is shown by dashed curve (Kennedy and Kennedy 1976; Anthony et al. 1994). Parameters of annealing at low pressure (in vacuum or at ambient pressure) are shown with *squares* and *line*. The colored areas show the pressure–temperature ranges of possible natural HPHT annealing (*light green*), commercial HPHT treatment of different companies (*red ovals*), natural growth and natural high temperature annealing (*green*), natural plastic deformation (*brown*), and natural low temperature annealing (*yellow*). It is seen that the pressure–temperature areas of HPHT treatment and natural HPHT annealing differ considerably

influence much the process of graphitization during short time HPHT treatment. However, it may be a crucial for kinetics of growth and dissolving of the Platelets.

3.1 Temperature

Temperature is the most important parameter of HPHT treatment. Increase in temperature exponentially accelerates the atomic diffusion and initiates the defect transformation processes with high activation energies. For each 100 °C in temperature increase, the mobility of nitrogen in diamond increases almost by an order of magnitude (Evans et al. 1975; Bonzel et al. 1978; Koga et al. 2003). Although one tries to perform HPHT treatment at maximum possible temperatures, it is difficult and expensive to run a controlled HPHT process at temperatures above 2,500 °C. Therefore, usually the temperature range for the commercial HPHT treatment is 1,800–2,300 °C. However, much broader temperature range from 1,500 °C and as high as 3,000 °C under stabilizing pressure of 10 GPa is possible for HPHT treatment. For instance, low temperature HPHT annealing may be performed in combination with electron irradiation.

The temperature range used for heat treatment of diamonds may be split into the following intervals, each being characterized by major defect transformations influencing the diamond color.

Very low temperatures spread from 600 to 1,500 °C. Annealing of diamond at very low temperatures does not require stabilizing pressure and it can be performed in vacuum or inert gas atmosphere for a long time. These temperatures are too low for the direct transformations of the major nitrogen defects. However, at temperatures close to 1,500 °C, the vacancy clusters may start to dissociate. The released vacancies may form the H3 defects in type Ia brown diamonds and make them green.

Very low temperatures are not used for HPHT treatment alone. Though, these temperatures are used to achieve the color changes in irradiated diamonds. The irradiation-induced vacancies become mobile at temperatures over 500 °C, they form complexes with all major nitrogen defects and stimulate the nitrogen aggregation. These processes may cause considerable color changes in diamond. Annealing at very low temperatures is a common step of multi-process treatments, e.g., the treatment used for the production of Imperial Red diamonds.

The range of very low temperatures comprises the temperatures of growth and post-growth annealing of diamonds in nature. At these temperatures, the motion of interstitials and vacancies is activated, the aggregation of vacancies occurs and natural diamonds acquire brown color. Very low temperatures are used for the treatments where the formation of vacancy-related defects is required: e.g., partial annealing of irradiated diamonds, or creation of NV centers in irradiated diamonds.

Low temperatures cover the range from 1,600 to 1,900 °C. These temperatures are high enough to cause rapid graphitization of some natural diamond. Hence the safe annealing at low temperatures must be performed under stabilizing pressure. Low temperature annealing, like very low temperature annealing, is rarely used for sole HPHT treatment for it does not change rapidly the color of most natural diamonds. However, HPHT annealing at low temperatures may cause considerable color changes, when it is applied to irradiated diamonds. Besides, low temperature HPHT treatment performed for a few hours may be sufficient for complete removal of brown hew in light brown diamonds. Temperature–pressure parameters of low temperature HPHT treatment are very close to those of the natural annealing in earth. Hence its recognition poses the most severe problems.

Moderate annealing temperatures cover the range from 1,900 to 2,100 °C. At these temperatures, most defects, responsible for brown color of natural regular brown diamonds, anneal out and major nitrogen-vacancy defects are formed. The aggregation and dissociation processes of major nitrogen defects become noticeable at these temperatures too. HPHT annealing at moderate temperatures is used as an inexpensive and reliable treatment of light brown diamonds. Annealing at moderate temperatures is frequently used to achieve pink color in type IIa brown diamonds.

The annealing performed at temperatures from 2,100 to 2,300 °C is a ***high temperature annealing***. At these temperatures, brown color of most brown natural diamonds is removed in several minutes. At high temperatures, the processes of aggregation and dissociation of nitrogen defects occur most effectively. Yet, high temperatures generate an appreciable concentration of C defects in type Ia diamonds and this peculiarity makes high temperature HPHT treatment fairly easily recognizable.

The temperatures over 2,300 °C are ***very high temperatures***. Commercial HPHT treatment is rarely performed at these temperatures. At very high temperatures most nitrogen defects aggregate. The rate of aggregation depends on pressure and the initial nitrogen content. At the pressures above the graphite-diamond phase transition, the aggregation dominates and nitrogen-containing diamonds are converted into type IaB. At pressures below the graphite-diamond phase transition, the dissociation processes may dominate and the treated diamonds have type Ia(B > A).

When discussing temperature as a parameter of HPHT treatment, it is important to keep in mind that accurate measurement of temperature in high pressure cell still remains an unmet challenge. Temperature can be fairly well measured directly using thermocouples up to 1,700 °C. Higher temperatures are measured only indirectly using calibrations against electrical power used for heating of high pressure cell. These calibrations strongly depend on many technical parameters of the high pressure apparatuses and they can differ considerably. At very high temperatures above 2,500 °C, the error of the temperature measurement may exceed 100 °C. This error is one of the main reasons of discrepancy between the results reported by different authors.

3.2 Pressure

Along with temperature, pressure is the second most important parameter of HPHT treatment. High pressure helps to reach the area of plasticity. Plastic flow may considerably stimulate the defect transformations and generation of the defects, which otherwise cannot be formed at high temperature alone. Yet, pressure does not influence the defect transformation as much as temperature: a 1 GPa change in pressure leads to a change in diffusion coefficients of carbon and nitrogen of only about 30 % (Koga et al. 2003). Our experiments on high temperature annealing performed at low pressure revealed that natural diamonds can withstand a few minutes heating in vacuum at a temperature of 2,100 °C. Although severe outer graphitization may occur during such a heating, the interior of inclusion-free diamonds remains perfect. In hydrogen atmosphere, diamond can withstand short-time annealing at temperatures as high as 2,200 °C. At such a high temperature, the annealing time is kept a few seconds only (Fleischer and Williams 1994). Although the temperature range of the low pressure annealing may be the same as that used for HPHT treatment, its result is different. Indeed, at low pressure, even at a temperature of 2,200 °C, diamond still remains in the rigid state, whereas it is already in the range of plasticity at a temperature as low as 1,000 °C, if the heating is performed at a pressure of 5 GPa (Fig. 3.1).

In addition to rendering diamond plastic, the external pressure also increases the phase stability of diamond. At normal conditions, diamond lattice is in a compressed state (sp^3 C–C covalent bond is shorter in diamond lattice than it is in equilibrium state). Because of this stress, diamond is metastable. This internal compression can be considered as the internal pressure, the magnitude of which is comparable with the diamond-graphite phase equilibrium line on the pressure–temperature diagram (Fig. 3.1).

The presence of impurity atoms with atomic radii greater than that of carbon (e.g., nitrogen) increases the lattice parameter and reduces the internal pressure. The reduction of the internal pressure is greater in diamonds with nitrogen complexes and therefore the nitrogen aggregation is a favorable process of the nitrogen defect transformations. Application of external pressure brings diamond lattice to equilibrium and promotes the nitrogen aggregation. For this reason, the external pressure suppresses the dissociation of nitrogen complexes. Correspondingly, the pressure reduction during HPHT treatment shifts the aggregation-dissociation processes towards dissociation.

An example of the influence of pressure on the nitrogen defect transformations in diamond is the dissociation of nitrogen complexes into isolated atoms. It was found that heating at 2,300 °C at a pressure of 8.5 GPa for 15 min causes decomposition of 10 % of A-aggregates of nitrogen, whereas the heating at the same temperature but under a lower pressure of 5–6 GPa and even shorter time increases the decomposition rate to 50 % (De Weerdt and Collins 2003).

The influence of pressure on the aggregation of carbon interstitials is similar to that of nitrogen: high pressure, in the range of stability of diamond, stimulates the aggregation, whereas low pressure, in the range of stability of graphite, promotes dissociation. Figure 3.2 shows that the annealing of the Platelets peak in type IaB natural diamond during HPHT treatment strongly depends on pressure. It is very slow at temperatures and pressures in range of diamond stability and it increases drastically when diamond is annealed under lower pressure in the range of stability of graphite.

Opposite effect is expected for small radius impurity atoms and vacancies. For these defects, external pressure should promote the dissociation. Indeed, the dissociation of vacancy clusters in diamonds goes faster under higher pressure. Hence, the reduction of brown color is more effective for HPHT treatments performed at elevated pressure. For instance, annealing of a brown diamond at temperatures in the range from 1,800 to 2,100 °C at normal pressure reduces its color only moderately. In contrast, HPHT annealing of a diamond of the same initial color at the same temperatures may remove brown color almost completely.

An important factor of pressure is its uniformity or hydrostaticity. During HPHT treatment, the pressure applied to diamond should be as hydrostatic as possible. Non-hydrostatic pressure may break diamond, or it may cause plastic deformation, which in turn may induce unwanted defects affecting the final color

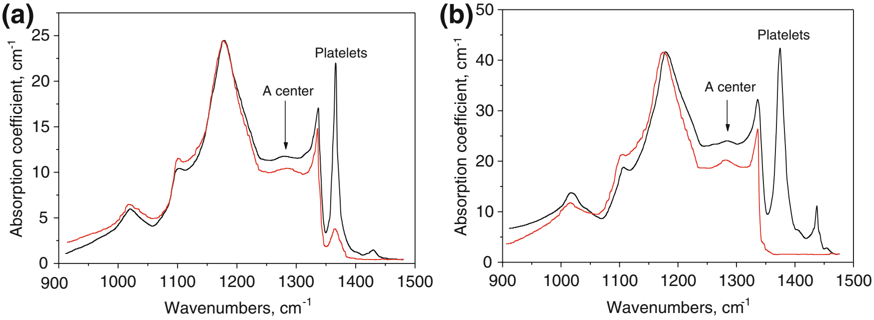


Fig. 3.2 IR spectra of regular IaB diamonds before (*black curves*) and after (*red curves*) HPHT treatment at a temperature of 2,600–2,650 °C for 9 h in the temperature–pressure range of diamond stability (**a**) and for 4 min in the temperature–pressure range of graphite stability (**b**) [the data from (Evans et al. 1995)]. The rate of formation of the A center is comparable in both cases

of diamond. The minimization of the pressure non-uniformity is achieved by appropriate design of the high pressure cell, where diamond is annealed. However, even in the ideal cell, the non-uniform stress inside the diamond during annealing may be considerable. The reason is the unpredictable distribution of the initial internal stress, which is present in any natural diamond and which is impossible to control. In order to reduce the influence of the initial internal stress, the diamonds are pre-shaped before HPHT treatment. The aim of the pre-shaping is the removal of the areas of possible non-uniformity: the surface caverns, inclusions, cracks (see Sect. 8.2).

3.3 Time

The third important parameter of HPHT treatment is duration of annealing. It may vary from a few seconds (pulse HPHT treatment) to a few minutes (as it is in most cases of commercial treatment) and even several hours. The physical principles of the short-time HPHT treatment is similar to those of the pulse annealing used in electronic industry for processing of ion-implanted semiconductors. The pulse HPHT treatment is an inexpensive procedure and therefore favorable. A characteristic feature of the pulse heating is a very non-equilibrium defect structure leading to a distinctively unnatural combination of defects. Because of this, the short-time HPHT treatments can be relatively easily recognized by comparing the concentrations of the defects with different temperature stability and kinetics rate. For instance, pulse HPHT treatment is too short to allow nitrogen to diffuse and aggregate. Thus, the resulting set of the nitrogen defects may reveal increased content of the simplest forms like NV defects.

The rate of the defect transformations and the time required to reach the equilibrium defect concentration strongly depend on the type of the defects and the annealing temperature. Single vacancies are very mobile defects and, once the activation temperature is achieved (e.g., at 900 °C), they anneal out in a matter of seconds. Because of this fast kinetics, the isolated vacancies (GR1 center) are never observed in HPHT-treated diamonds. In contrast, the diffusion of impurities in diamond lattice is a much slower process and the transformation of the impurity-related defects may take few hours at temperatures of HPHT treatment. For instance, the dissociation of A defects and the increase in the concentration of C defects during HPHT annealing increases almost linearly with time for short-time treatment and it may take up to 1 h until the equilibrium concentration of the C defects is achieved (Claus 2005). At lower temperatures, like the ones natural diamonds experience in earth, the establishment of equilibrium may take billions years.

The duration of HPHT annealing required to achieve the new equilibrium concentrations of defects also depends on the initial defect content. De Weerdt and Collins showed that in diamonds with initial concentration of A defects 7 and 15 ppm, 3 and 10 min HPHT treatments at a temperature of 2,300 °C increase the amount of the C defect concentration to 0.04 and 0.06 ppm in the lower nitrogen diamond, and 0.04–0.12 ppm in the higher nitrogen diamond (De Weerdt and Collins 2003). This result suggests that 10 min annealing is sufficient to reach the defect equilibrium in diamond with low impurity content and it requires much longer time when the impurity concentration in diamond is high.

A further example of the influence of the annealing time on the defect composition in HPHT-treated diamonds is given in (De Weerdt and Collins 2007). It has been shown that short-time HPHT treatment of type Ia brown diamonds makes them green, whereas the prolonged one makes the diamonds yellow. This color change suggests that the formation of H3 defects in brown diamonds occurs much faster than the dissociation of A defects into C defects. Hence, at the initial stages of HPHT treatment, the H3 center is the dominating color center and its high absorption intensity makes diamond green. During long-time HPHT annealing, the vacancy clusters anneal out and the source of vacancies depletes. As a result, the formation of new H3 defects stops and the H3 defect concentration starts to decrease due to the dissociation of the H3 defects into C defects. If the annealing time is long enough, the C defect concentration becomes high enough to provide dominating yellow color.

Short-time HPHT treatment may also result in a high concentration of defects with low-temperature stability and slow annealing kinetics. The NV defects are an example. The NV defects are unstable at temperatures of HPHT treatment. Yet they always reveal their presence in HPHT-treated diamonds as the NV^0 and NV^- centers in PL and absorption spectra.

Duration of HPHT treatment is also an important parameter in term of graphitization. Commercial HPHT treatment is frequently performed at temperatures in the range of stability of graphite. Thus, the treatment time has to be kept short enough in order to prevent excessive graphitization. The time of safe annealing decreases drastically with the temperature increase. For instance, HPHT treatment at a temperature of 1,900 °C can last for many hours without a trace of graphitization. If the temperature is increased to 2,500 °C, diamond may be completely graphitized in a minute.

General picture of evolution of concentration of the basic defects determining the final color of initially brown type Ia diamonds after short and prolonged HPHT treatment is shown in Fig. 3.3. Short-time HPHT annealing at low temperatures does not change initial brown color considerably. Yet, prolonged low temperature treatment makes diamonds brownish-green. When brown type Ia diamonds are HPHT annealed at moderate temperatures, in a short time they become brownish green. For longer treatment times, the diamonds acquire yellowish-green color. If the annealing temperature is raised to 2,300 °C, short-time annealing makes diamonds yellow-green. Prolonged annealing at high temperatures makes initially brown diamonds greenish-yellow and yellow.

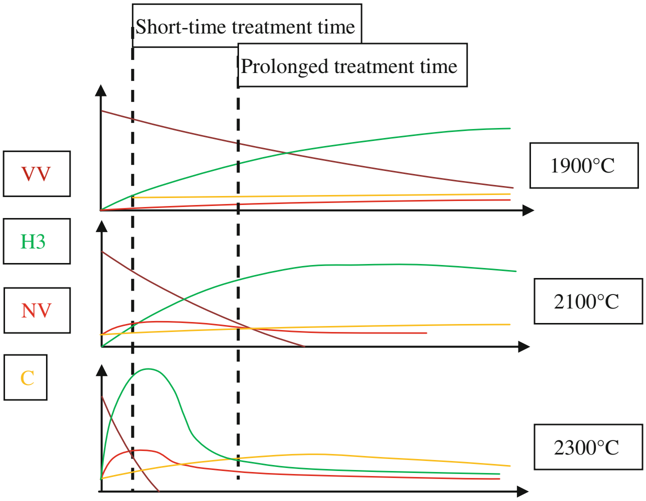


Fig. 3.3 Schematic presentation of the change of concentration of vacancy clusters (VV), H3, NV and C defects in brown type Ia diamonds versus time of HPHT treatment performed at different (as indicated) temperatures [based on the data from (De Weerdt et al. 2004)]. At low annealing temperatures, slow dissociation of the vacancy clusters and slow increase in concentration of H3 defects occurs. Formation of C- and NV defects is negligible. At moderate temperatures, the dissociation of vacancy clusters and the reduction of brown color go much faster. A considerable concentration of H3 defects appears. Dissociation of A- and H3 defects results in the growing concentration of C- and NV defects. When the vacancy clusters anneal out, the concentration of H3 defects stabilizes and the concentration of NV defects reduces. The concentration of C defects steadily grows with time. At high temperatures, complete dissolving of vacancy clusters occurs in a short time. High concentration of H3 defects and enhanced concentration of NV defects are created during the destruction of the vacancy clusters. Once the vacancy clusters have disappeared, the H3 and NV defects anneal out rapidly contributing to the increase in the concentration of C defects

3.4 Comparing HPHT Treatment and Natural HPHT Annealing

Every natural diamond experienced natural HPHT annealing during its growth in the earth interior and during its post-growth history when traveling to the earth surface. This fact is the background for the diamond "treaters" trying to justify HPHT treatment as a "natural" process and, as such, undistinguishable from the natural annealing. Yet, the studies of HPHT-treated diamonds show that the resulting defect structure produced by HPHT treatment does differ from that of untreated natural diamonds. Understanding these differences is the key for the recognition of HPHT-treated diamonds.

The defect structure of natural diamonds differs from that of the HPHT-treated counterparts because of the difference in the parameters of HPHT treatment and natural annealing. Although this difference is quantitative rather than qualitative, its impact on the resulting defect structure of diamond is considerable. HPHT treatment is ***always*** performed for time incomparably shorter than that of the natural annealing. HPHT treatment is ***almost always*** performed at temperatures considerably higher than those, diamonds experience in nature. Commercial HPHT treatments are frequently performed at pressures corresponding to the phase stability of graphite—an unlikely condition for diamonds in nature. Thus, HPHT-treated and natural untreated diamonds have different defect compositions, which reflect very different equilibrium defect concentrations characteristic for low and high temperatures. For instance, HPHT-treated diamonds always have unproportionally high content of temperature stable defects.

Natural diamonds have been exposed to geological temperature and pressure for a long time up to 3.5 billion years. Majority of natural diamonds were formed in subcontinental lithosphere at depths of 180–200 km, where temperature and pressure could vary from 900 to 1,400 °C and 4–7 GPa respectively. For instance, type I diamonds from the kimberlite pipe "Mir", grew at temperatures of 1,400–1,450 °C under pressure of 4–6 GPa (Vins and Kononov 2003).

After the period of growth, most natural diamonds passed through the "hot" periods of post-growth annealing, during which temperature could reach 1,700 °C (Kiflawi and Bruley 2000; Howell 2009). Some diamonds from South Africa and Brazil show evidence of the residence in the lower mantle at depths up to 700 km, what suggests a pressure over 8 GPa and a temperature over 1,700 °C (Meyer and Seal 1998; Kirkley et al. 1991; Ito and Katsura 1989; Harris et al. 1997; Luth 2012), 1,800 °C being the maximum.

This natural HPHT annealing occurred for very long time and resulted in the aggregation of nitrogen impurity and conversion of nitrogen containing diamonds into type Ia. At temperatures of 1,700 °C, the aggregation of nitrogen approaches completion when B- and N3 defects dominate and C defects are almost undetectable (Kiflawi and Bruley 2000, Collins et al. 2005). Yet, since nitrogen aggregation at geological temperatures is an extremely slow process, the intermediate nitrogen aggregates like A- and H3 defects are readily present too.

One expects that the diamonds with appreciable concentration of A defects were not exposed to high geological temperatures and the diamonds with dominating concentration of A defects (type IaA diamonds) were extracted from the earth exterior at early stages of their history.

It is remarkable that natural diamonds of "pure" type IaA always contain minor content of C defects, the concentration of which is usually in a certain ratio with the concentration of A defects. This concentration ratio is rather constant for diamonds mined from one and the same pipe. In (Sobolev. et al. 1986), the content of C defects in type I diamonds recovered from three different pipes is compared. The most probable C defect concentrations are 0.1, 0.4, and 0.8 ppm respectively. In diamonds of pure Ia type from Yakutian deposits, the relative concentrations of C-, A- and B defects follow the ratios $N_C/N_A = 0.002–0.005$ and $N_B/N_A = 0.85–2.3$. This definite amount of C defects is the result of the annealing at the particular temperature–pressure conditions, which were specific for a given pipe. This fact suggests that in natural diamonds the nitrogen defects are in equilibrium concentrations characteristic of temperatures below 1,700 °C and these diamonds have never experienced short-time heating at high temperature.

In contrast to the natural HPHT annealing, HPHT treatment is performed at much higher temperatures and much shorter times. High temperature considerably increases the equilibrium concentration of dispersed nitrogen. During HPHT treatment, and especially during high temperature treatment, the nitrogen aggregation cannot go above 96 % thus always resulting in reverse dissociation of nitrogen aggregates (Kiflawi and Bruley 2000; Collins et al. 2000). Hence, after HPHT treatment, vast majority of type Ia diamonds reveal reverse decomposition of the nitrogen aggregates into C defects and formation of the defect composition, which is highly non-equilibrium for low temperatures.

Generation of C defects, which are donors in diamond lattice, charges negatively many other defects. As a result, HPHT-treated type Ia diamonds reveal "unnatural" presence in optical spectra strong optical centers due to negatively charged defects. For instance, unproportionally high intensity of NV^- and H2 centers is a common feature of absorption and PL spectra of HPHT-treated type Ia diamonds (Newton 2006).

Although the defect composition is different for treated and untreated diamonds, it cannot be considered as the ultimate proof of treatment or otherwise its absence. Indeed, some natural diamonds may exhibit very non-equilibrium defect compositions typical of HPHT-treated diamonds. For instance, these are the diamonds, which experienced natural heating at the conditions of the stability of graphite. These diamonds have unproportionally low concentration of Platelets, although they clearly exhibit the nitrogen defect composition characteristic of the last stage of the nitrogen aggregation. Of course, the destruction of Platelets is not necessarily stipulated by high temperatures. In plastically deformed diamonds, the Platelets can be destroyed by moving dislocations at relatively low temperatures. However, in diamonds with no sign of plastic deformation, one has to assume that it is the temperature what caused the collapse of Platelets (Lang et al. 2007).

Distinguishing between natural HPHT annealing and HPHT treatment of natural diamonds with traces of brown color can be particular challenging. Reduction of brown coloration does not require high temperatures and therefore is supposed to be a common natural process. An example of such a "natural HPHT treatment" is studied in (Nailer et al. 2007). It has been found that bicolor Argyle diamonds, which comprise colorless zones and zones of brown color, have considerably less nitrogen in the brown zones than in the colorless ones (2–5 times less). The colorless zones tend to be predominantly of type IaB, whereas the brown zones are predominantly of type IaA. There is also a tendency that the colorless zones have smaller amount of Platelets than the brown zones. A conclusion has been made that nitrogen stiffens diamond lattice and does not allow it to be easily deformed. It might be also that the colorless zones are those which experienced a high temperature natural HPHT annealing, what resulted in the removal of brown color and reduction of concentration of A defects and Platelets.

Chapter 4
HPHT-Induced Transformations

The aim of HPHT treatment is to improve color of natural diamonds with unattractive colors. To do so, the impurity-defect structure of diamond must be modified so that the unwanted color centers are removed and the desirable ones are induced. Although the physical principle of HPHT treatment is fairly simple (it is high temperature atomic diffusion and/or atomic re-arrangement within defects), the variety of the atomic rearrangement pathways makes the HPHT-induced transformations a very complex process. Yet there are two major processes, which control the formation of the impurity-defect structure of diamond during HPHT treatment. They are the aggregation of simple nitrogen defects into multi-atom complexes and the dissociation of complex nitrogen aggregates into more simple complexes and isolated nitrogen atoms. Understanding these processes is the key for both an HPHT technologist trying to achieve the best color for a particular diamond and a gemologist working on recognition of HPHT-treated diamonds.

The HPHT-induced nitrogen defect transformations involve many different defects. It is a complex process, which strongly depends on the parameters of treatment and the initial impurity-defects content and the structural perfection of diamond. Due to this complexity the results of HPHT treatment may considerably vary even for identically treated diamonds.

4.1 Nitrogen Aggregation

In diamond, the aggregation of nitrogen atoms into multi-atom complexes is a natural process. Diamond crystal lattice, even perfect one, is not in equilibrium. It is internally compressed and, because of this internal compressive stress, diamond is a metastable phase at low external pressure. In order to bring diamond to equilibrium, an external pressure equalizing the diamond's internal pressure must be applied. At room temperature it is about 2 GPa (Fig. 3.1). With temperature, the internal pressure grows and makes diamond increasingly metastable. Presence of nitrogen expands the diamond crystal lattice and reduces the internal stress. This

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reduction is greater when nitrogen form multi-atom complexes. For instance, the presence of A defects at a concentration of 1,500 ppm increases the lattice constant of diamond by 0.000028 nm (Kurdumov et al. 1994; Lisoivan and Sobolev 1974). Hence the aggregation of nitrogen is a thermodynamically favorable process and it occurs at any temperature.

Like for any thermodynamic process, the nitrogen aggregation cannot go to full completion. An equilibrium amount of dispersed nitrogen is always present. The equilibrium concentration of dispersed nitrogen increases with temperature, yet at any temperature, it remains much smaller than that of the nitrogen aggregates. Therefore, for most natural diamonds, the main tendency in the transformation of the nitrogen defects during HPHT treatment is aggregation (Kiflawi and Lawson 1999).

During growth, diamonds capture nitrogen impurity in form of individual atoms. As a result, the as-grown nitrogen-containing diamonds, both natural and synthetic, are of type Ib. When as-grown diamonds are further exposed to high temperature annealing, the isolated nitrogen atoms migrate and form energetically more favorable multi-atom defects (Evans and Qi 1982; Goss et al. 2003; Vins et al. 2006). The nitrogen aggregation is a multistep process involving migration of isolated nitrogen atoms (C defects), pairs of nitrogen atoms (A defects) and multiatom complexes like B defects. The diffusivity of nitrogen decreases with the level of aggregation. The C defects are the most mobile, whereas the B defects are the least mobile (Koga et al. 2003).

Formation of two-atom aggregates is the first step of the aggregation process. It involves the aggregation of C defects and their derivatives (e.g., NV defects) into A defects and their derivatives (e.g., H3 defects). Although the nitrogen aggregation occurs at any temperature, in diamonds with moderate nitrogen content, the measurable change in the concentration of dispersed and aggregated nitrogen occurs only at temperatures over 1,700 °C. Heating at temperatures below 1,700 °C does not result in obvious nitrogen aggregation even in type Ib natural diamond heated for a long time. No change of yellow color of these diamonds occurs too (Howell 2009). Yet in high-nitrogen type Ib diamonds with nitrogen concentration of 500 ppm, the aggregation of dispersed nitrogen atoms into A defects becomes noticeable at a temperature of 1,700 °C. In diamonds with even higher nitrogen content, well above 500 ppm, the aggregation of the dispersed nitrogen can be detected at a temperature as low as 1,500 °C, the process being especially noticeable at low pressures (Kiflawi et al. 1997). In high-nitrogen diamonds, the aggregation of C defects into A defects can almost rich its equilibrium after a few hour annealing at temperatures 1,800–1,900 °C (Shiryaev et al. 2001; Claus 2005; Chrenko et al. 1977; Evans and Qi 1982; Klyuev et al. 1982).

The activation energy of the aggregation of C defects into A defects in natural diamonds ranges from 4.8 to 6.2 eV depending on the total nitrogen content and the presence of other defects and especially vacancy-related ones. In synthetic diamonds, which may contain considerable concentration of transition metal atoms, the activation energy of the C- to A-defect aggregation may vary from 2.6

to 21 eV. Along with the formation of A defects, their derivatives, e.g., the H3 defects, form too.

With the temperature increase, further aggregation of nitrogen into three- and four-atom complexes (N3 defects, B defects and their derivatives) begins. On average, the temperature threshold of this second stage of aggregation is about 2,200 °C (Vins et al. 2008). However, like for the aggregation of dispersed nitrogen into A defects, the formation of multi-atom complexes strongly depends on the nitrogen concentration. In high-nitrogen type Ia diamonds, noticeable aggregation of A defects into B defects occurs at temperatures about 2,100 °C (Vins and Yelisseyev 2008). The activation energy of formation of B defects is about 6.3–7 eV (Goss et al. 2003; Evans 1992; Kiflawi et al. 1997; Vins et al. 2008). This value, which is higher than that of the formation of A defects, explains why high temperatures are required for the aggregation into B defects. Simultaneously with B defects, the N3 defects form too. The N3 defects are an intermediate form of the aggregated nitrogen bridging transition between A- and B-defects. B defects are the most temperature stable nitrogen defects in diamond and therefore they complete the aggregation process. Hence type IaB diamonds are the nitrogen-containing diamonds with the most equilibrium impurity-defect structure.

The process of nitrogen aggregation is a slow kinetic process. It means that the resulting concentrations of different nitrogen defects in diamonds after HPHT annealing strongly depend on the annealing time. For example, in a type Ib diamond, after HPHT treatment at temperatures of 2,300–2,400 °C under pressure 9.5 GPa (temperature–pressure parameters sufficient for the completion of the second stage of aggregation) for 1 h, 95 % of C defects are converted into A defects but only small amount of N3 defects forms. A longer annealing (for 2 h at a temperature of 2,500 °C and a pressure of 9.5 GPa) of this diamond resulted in aggregation of 50 % of nitrogen into B defects, the Platelets and N3 defects (Bunsnl and Grusmn 1985, and references therein). An example of nitrogen aggregation at very high temperatures is shown in Fig. 4.1.

The Platelets participate in the process of nitrogen aggregation via their relation to B defects. The Platelets are not very stable defects and they start to dissociate at temperatures below 1,800 °C. However, during HPHT annealing at much higher temperatures, the Platelets may considerably increase their concentration. This seeming discrepancy implies that the actual concentration of the Platelets is determined by two opposing processes: their formation and dissociation. At high temperatures, large Platelets "evaporate" releasing carbon interstitials and reducing in size. The A defects aggregate into the B defects and release carbon interstitials too. The increased number of B defects and carbon interstitials result in formation of a higher concentration of smaller and less stable Platelets. The reduction of size of Platelets is a common result of short-time HPHT treatments, during which the aggregation of A defects into B defects is far from completion. As the HPHT annealing time increases, almost all nitrogen aggregates into B defects, the source of carbon interstitials depletes, the formation of new Platelets stops and the Platelets start "evaporate". During this evaporation, a process of Ostwald ripening occurs: large Platelets grow incorporating small once.

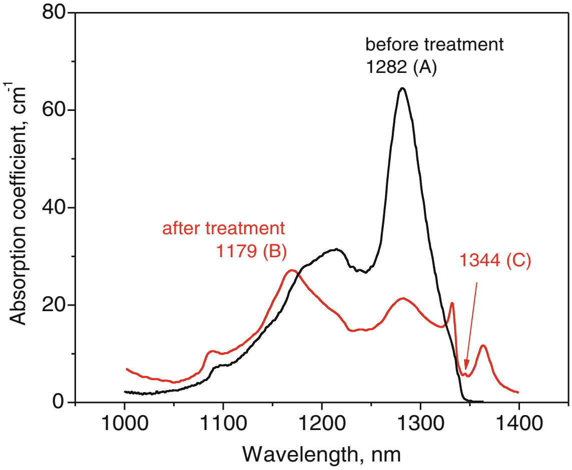


Fig. 4.1 FTIR absorption spectra of an originally type IaA diamond with high concentration of nitrogen (1,100 ppm) recorded before (*black curve*) and after (*red curve*) HPHT treatment performed at a temperature of 2,650 °C for 9 h. Only a minor absorption feature due to C defects (peak at 1,344 cm^{-1}) has been generated by the treatment [re-plotted from Kiflawi and Bruley (2000)]. The diamond type has been converted from IaA into IaABB' with dominating B and B' defects. Approximately equal concentrations of A defects before treatment and B defects after treatment indicate that all B defects were formed of A defects. Very broad Platelets peak is a characteristic feature of HPHT treatment

At very high temperatures exceeding 2,500 °C, large Platelets become unstable, they collapse into dislocation loops and the released nitrogen gathers into nitrogen voidites. At extremely high temperatures, the nitrogen voidites may dissolve into dispersed nitrogen.

Concentration of A defects is a decisive factor in the evolution of Platelets during HPHT annealing. Aggregation of A defects is the source of carbon interstitials and the mechanism of formation of new B defects, which in turn become centers of precipitation of the carbon interstitials. In a way, one may say that the Platelets grow from the A defects. However, in order to outperform the process of the Platelet dissociation and to increase the number of Platelets, the concentration of A defects must exceed 400 ppm. At lower concentrations of A defects, the formation of B defects and the growth of Platelets go slower than the dissociation of the Platelets.

High temperature aggregation of nitrogen is a complex process including all forms of nitrogen defects. The scheme in Fig. 4.2 illustrates the main pathways of this process.

Increase in pressure stabilizes the diamond lattice making it less metastable. This stabilization reduces the rate of nitrogen aggregation. Although the aggregation is the dominating tendency in diamond at any reasonable pressures, it is less pronounced at the pressures above the diamond-graphite phase transition line.

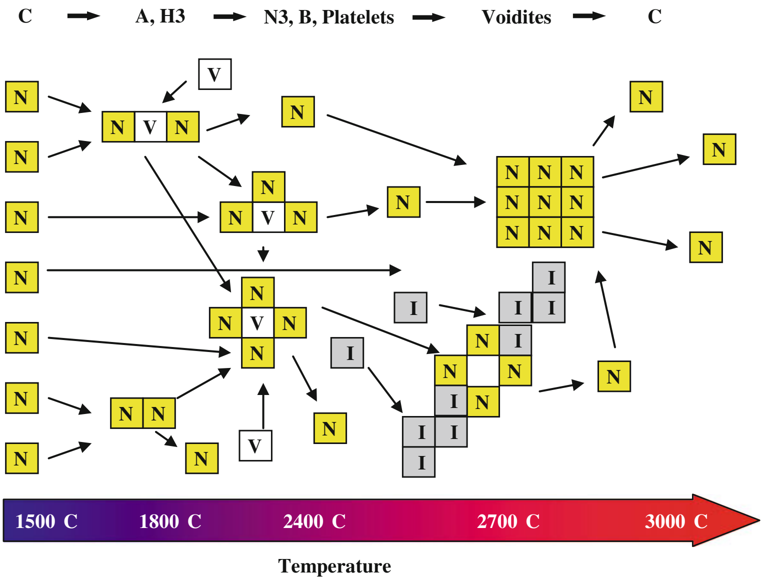


Fig. 4.2 Schematic presentation of the process of aggregation of nitrogen in diamond during HPHT treatment. With the temperature increase, single nitrogen atoms form two-atom complexes (A- and H3-defects), then three- and four-atom complexes (N3 and B defects). Along with the nitrogen aggregation, the formation of multi-atom carbon aggregates—the Platelets occurs. At very high temperatures, the aggregation ends up with the segregation of nitrogen into voidities—nano-bubles of solid nitrogen. At any aggregation stage, a small portion of nitrogen is released in form of isolated atoms (C defects), which are seen in FTIR absorption spectra as a weak line at 1,344 cm^{-1}—an evidence of HPHT treatment

Defect-Stimulated Nitrogen Aggregation

Aggregation of nitrogen defects in diamond can be considerably stimulated by the presence of other impurities and intrinsic defects. The mechanism of this stimulation is the formation of nitrogen-containing mobile complexes, which may aggregate at low temperatures.

Vacancies are the most active catalyst of the nitrogen aggregation. The common mechanisms of the generation of vacancies in natural diamonds are the irradiation with energetic particles, the motion of dislocations and the dissociation of vacancy clusters. Nitrogen is a strong getter of vacancies. Thus, the generation of vacancies in type I diamonds always results in formation of nitrogen-vacancy defects. The nitrogen-vacancy defects are more mobile than the defects composed of nitrogen atoms only and, as such, they have less stable atomic structure than the main nitrogen C-, A- and B-defects. Because of this instability, the nitrogen-vacancy defects involve nitrogen into the aggregation process at relatively low temperatures.

The phenomenon of the vacancy-stimulated nitrogen aggregation was described in (Collins 1980; Allen et al. 1981) and claimed as a technological process of diamond treatment in (Evans and Allen 1981). Considerable acceleration of the aggregation of C defects into A defects in electron-irradiated diamonds may start at a temperature as low as 1,350 °C, which does not require the application of stabilizing pressure. Annealing at 1,600 °C may result in aggregation of a considerable fraction of dispersed nitrogen into complexes (Collins et al. 2000, 2005). Even formation of the Platelets from dispersed nitrogen can be initiated in electron-irradiated diamonds at temperatures as low as 1,600 °C (Evans and Allen 1981). The efficiency of the vacancy-stimilated aggregation of nitrogen considerably increases when the regime of heating is performed in steps with prolonged heating at temperatures allowing preferential formation of the most simple and mobile NV defects. For instance, a long-time annealing of irradiated type Ib diamonds at 800 °C noticeably increases the aggregation of dispersed nitrogen into A- and H3-defects during subsequent heating at a temperature of 1,500 °C. Without the prior pre-heating, similar aggregation could be achieved only at temperatures of 1,600 °C and above (Collins 2001; Mita et al. 1990). High energy electron irradiation, even at a relatively low dose of 10^{17} cm^{-2}, may considerably enhance the aggregation of dispersed nitrogen into A defects. The activation energy of the nitrogen aggregation in the irradiated diamonds has been found be of 3 eV (Kim et al. 2011). The preparatory irradiation strongly increases the aggregation rate of C defects into A defects and allows considerable reduction of temperature, pressure and time of HPHT annealing. This lowers the cost of the HPHT treatment and makes it more commercially attractive (Schmetzer 1999a).

In regular brown type I diamonds, the A defects start to aggregate in B defects during HPHT treatment at temperatures of 2,000 °C. In brown type Ib diamonds, almost complete transformation of nitrogen into A- and B-defects can be achieved at this temperature (Hainschwang et al. 2005). In brown type IaA diamonds, the rate of aggregation of A defects into B defects and Platelets grows with the increase in the intensity of brown coloration (Vins and Yelisseyev 2008). In contrast, in CO_2 and pseudo-CO_2 brown diamonds, which do not have measurable amount of vacancy clusters, the aggregation of nitrogen defects occurs at temperatures characteristic of colorless diamonds. In contrast to brown diamonds, in colorless diamonds, the complete transformation of A defects into B defects is expected at temperatures above 2,600 °C (Kiflawi and Bruley 2000).

The nitrogen aggregation in brown diamonds is also stimulated by the presence of dislocations. Several mechanisms are involved in the dislocation-induced acceleration of the aggregation process (Shiryaev et al. 2007). These are the generation of vacancies by non-conservative dislocation motion, the creation of strain fields promoting mutual approach of nitrogen atoms, and the diffusion of nitrogen atoms along the dislocation lines ("pipe diffusion"). Generation of dislocations is a common process during HPHT treatment. A probable reason is some non-hydrostaticity which always takes place when applying pressure to diamond in HPHT cell. Experiments of Howell (2009) support this idea. Indeed, comparative studies of type Ib diamonds HPHT-treated at hydrostatic conditions and under uniaxial pressure (highly non-hydrostatic) showed that the non-hydrostatically treated diamond acquired uniform brown color and the conversion of 40 % of dispersed nitrogen into A defects was achieved.

Especially effective aggregation of nitrogen in type Ib diamonds can be achieved by multi-cycle HPHT treatment. It is believed that during every HPHT annealing cycle, the applied pressure may have considerable non-hydrostatic component in the periods of pressurizing and depressurizing. This results in the accumulation of high concentration of dislocations and vacancies which facilitate diffusion of nitrogen (Shiryaev et al. 2001).

Along with vacancies, nickel and cobalt impurities may also stimulate the nitrogen aggregation. The aggregation of C defects into A defects in nickel-containing synthetic type Ib diamonds is an example. It was found (Vins 2004), that the nitrogen aggregation increases with the increase in concentration of nickel (relative concentration of nickel was measured via the absorption intensity of the 658.5 nm center). The activation energy of the aggregation process in the nickel-containing diamonds dropped from 6 to 2.8 eV with the increase in the absorption intensity of the 658.5 nm center from 0.1 to 1.5 cm^{-1} (Fig. 4.3). Report on the nickel-stimulated aggregation of C defects into A defects can be also found in (Kim et al. 2011).

The nickel-stimulated aggregation of C defects into A defects is illustrated in Fig. 4.9, where the color transformations in a synthetic diamond after HPHT treatment are shown. Due to enhanced concentration of nickel in the central part, this diamond has much weaker yellow color in its center than at the periphery (Konovalova et al. 2011; Kaziutchits 2008; Kaziutchits et al. 2011). Nickel catalyzes the aggregation of C defects even at the temperature of diamond growth, which was about 1,500 °C for this diamond.

The catalyzing action of nickel could be of the same nature as that of vacancies. Ni atoms readily form nickel-nitrogen complexes, many of which are more mobile than the nitrogen-only defects. The stimulating action of nickel on the nitrogen transformations is well known for synthetic HPHT-grown diamonds. Same mechanism may also work in nickel-containing natural diamonds subjected to HPHT treatment. The enhanced sensitivity of the nickel-rich natural diamonds to

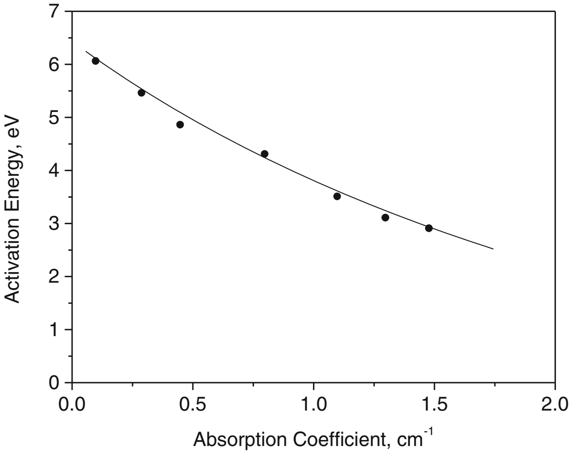


Fig. 4.3 Reduction of the activation energy of aggregation of C defects into A defects in synthetic diamonds with increasing absorption intensity of the nickel-containing center 658.5 nm. In high-nickel diamonds, the activation energy of the nitrogen aggregation may reduce by a factor of three

HPHT treatment must be taken into account when interpreting the composition of optical centers in these diamonds with the aim of recognition of possible HPHT treatment.

Cobalt, compared to nickel, has less influence on the aggregation of nitrogen. The activation energy of the nitrogen aggregation in cobalt-containing synthetic diamonds is slightly reduced to 4 eV. Nevertheless, the presence of cobalt lowers the temperature of nitrogen aggregation. Similar effect is expected for natural diamonds too. However, natural diamonds, containing cobalt in high concentrations have not been studied yet.

4.2 Dissociation of Nitrogen Complexes

The equilibrium concentration of aggregated nitrogen in diamond is high at any temperature. Correspondingly it is low for dispersed nitrogen. Therefore, when a type Ib diamond is heated at high temperature, the nitrogen aggregation is the dominating process in it. Since natural diamonds were annealed in nature at relatively low temperatures, the nitrogen aggregation could not been completed even in billion years. Thus, the tendency towards the aggregation during HPHT treatment prevails in almost all type Ia diamonds. The evidence of this aggregation is the increasing concentration of B defects after HPHT treatment (Buerki et al. 1999). However, high temperatures cause reverse process of dissociation. As a result, all HPHT-treated type Ia diamonds always contain elevated concentration of C defects (Collins et al. 2000). The amount of the dissociated nitrogen increases with the annealing temperature and may vary from 0.001 to 1 % depending on temperature, pressure and the total nitrogen content (Strong et al. 1977, 1977a; Van Royen and Palyanov 2002).

At very low temperatures (below 1,400 °C), the equilibrium concentration of dispersed nitrogen is negligible. At temperatures of 2,000 °C and above, the equilibrium concentration of C defects increases drastically (Brozel et al. 1978; Claus 2005; Vins et al. 2008). Due to this, even short-time HPHT treatment performed at a temperature of 2,000 °C results in formation of a measurable concentration of C defects. However, for temperatures below 2,100 °C, the amount of the dissociated A- and B-defects remains too insignificant to be detected as a reduction in the intensity of IR absorption of the A- and B-centers (Vins et al. 2008). Yet, IR absorption of the C-center can be clearly seen.

Temperature stability of different nitrogen complexes is different and it depends on pressure and the presence of other defects. The nitrogen-vacancy complexes (H4 and H3 defects) are the most unstable ones. The H4 center is destroyed at early stages of HPHT annealing. Kinetic of the dissociation of H4 defects is fast and therefore the H4 center completely disappears even after short-time HPHT treatment at temperatures as low as 1,600 °C. The temperature stability of the H3 center is greater and its dissociation kinetics is slower than that of the H4 defects. The reduction in concentration of H3 defects may be already seen after HPHT

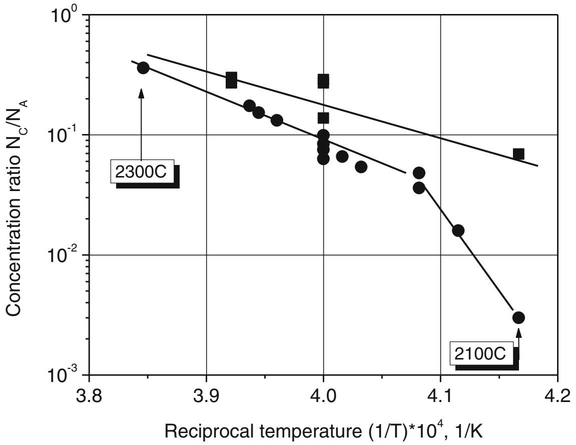


Fig. 4.4 Intensity of C-center relative to the intensity of A-center in natural type IaA colorless (*circles*) and light brown (*squares*) diamonds after HPHT treatment at different temperatures. In colorless diamonds, the presence of C defects is detected after treatments performed at temperatures of at least 2,100 °C, whereas in brown diamonds, HPHT treatment at a temperature of 2,100 °C generates considerable concentration of C defects

treatment at temperatures of 1,700–1,800 °C. However, at these low temperatures, the amount of the dissociated H3 defects still remains too low to produce a measurable concentration of C defects. For instance, in type Ia diamonds after treatment at a temperature of 1,800 °C, the concentration of C defects is below the detection limit of IR absorption spectroscopy and it is not sufficient for the conversion of neutral H3 defects into negatively charged H2 defects (Collins 2001). With temperature increase to 2,000 °C, the concentration of C defects becomes high enough to negatively charge a considerable amount of other defects. Thus, after HPHT treatment at temperatures of 2,000 °C and above, the diamonds with H3 defects also reveal the H2 center in their absorption spectra.

The presence of A defects considerably influences the temperature of dissociation: the higher the A defect content the lower the transformation temperature (De Weerdt and Collins 2003; Brozel et al. 1978; De Weerdt et al. 2004). This effect, however, to some extent may relate to higher concentration of C defects produced in high-nitrogen diamonds and hence their detection at the early stages of dissociation. Although the dissociation of nitrogen complexes occurs at any temperature and at any A defect concentration, the critical temperature of the nitrogen dissociation in colorless type IaAB natural diamonds without noticeable plastic deformation can be set at 2,100 °C (Fig. 4.4). After HPHT treatment at temperatures below 2,100 °C, type IaAB natural diamonds do not show in IR absorption spectra the presence of the C-center.

At high temperatures, the portion of the A defects split into C defects increases and, for the low-nitrogen diamonds treated at a temperatures of 2,500 °C, it may reach 50 %. In high-nitrogen diamonds this portion is less since a considerable amount of A defects aggregates into B defects. Yet, the absolute concentration of C defects increases with the increase in the initial concentration of A defects. In our experiments, the maximum strength of the C-center induced by HPHT treatment was about 2.2 cm^{-1} (measured in the peak 1,344 cm^{-1}), what corresponds to a C defect concentration over 50 ppm.

Slow kinetics of decomposition allows the H3 defects to survive after HPHT treatment performed at high temperature but for a short time. The presence of the H3 center can be seen in absorption spectra of many type I diamonds even after HPHT treatment at a temperature of 2,300 °C (De Weerdt et al. 2004). In PL spectra of any HPHT-treated diamond, the H3 center is always present. It should be kept in mind that the decomposition of H3 defects always goes along with the opposite process of aggregation, during which the A defects, and eventually the H3 defects, form from the dispersed nitrogen. This opposing process may considerably slow down the destruction of the H3 center and even may result in its reverse increase for some time. However, the reduction of the H3 center intensity and the growth of the C defect concentration after HPHT treatment in most type Ia diamonds indicate that the process of decomposition usually prevails.

In diamonds without traces of plastic deformation, the activation energy of dissociation of A defects is rather high amounting 6–7 eV. Hence the equilibrium concentration of the dispersed nitrogen remains much lower than that of the A defects even after high temperature HPHT treatment performed for a long time (Kiflawi and Bruley 2000). For instance, in diamonds with 7 ppm concentration of A defects, the equilibrium concentration of C defects is about 0.22 ppm at a temperature of 2,300 °C. In diamonds with an A defect concentration of 15 ppm, the equilibrium concentration of C defects increases to 0.33 ppm for the same temperature. When the total nitrogen content exceeds 100 ppm, even a few minutes annealing at 2,300 °C produces enough C defects to be detected in IR absorption spectra (De Weerdt and Collins 2008). In order to attain high concentration of C defects, the total nitrogen content must be really high. For instance, the fabrication of Imperial Red diamonds of intense red color requires a few ppm concentration of C defects. This high concentration of C defects can be achieved in type Ia natural diamond if they contain over 800 ppm of nitrogen (Vins 2007).

Dissociation of A defects considerably depends on pressure: pressure suppresses the dissociation. HPHT annealing at a temperature of 2,300 °C under a pressure of 8.5 GPa for 15 min results to a dissociation of 10 % of A defects, whereas the annealing at the same temperature but under a pressure of 5–6 GPa destroys 50 % of A defects even after 7.5 min annealing (De Weerdt and Collins 2003).

B defects are the most stable nitrogen aggregates [e.g., Bunsnl and Grusmn (1985)]. Their dissociation in structurally perfect diamond requires temperatures of at least 2,500 °C. A measurable dissociation of B defects may require even higher temperatures and long annealing times (Brozel et al. 1978; Evans and Qi 1982). There are no reliable reports on the quantitative data on the dissociation of B defects measured as the reduction in the intensity of the B-center in non-brown diamonds. Even after heating at a temperature of 2,700 °C for several hours, the

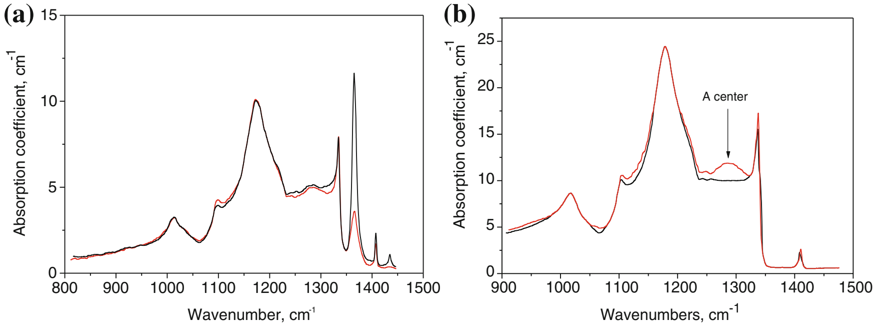


Fig. 4.5 **a** IR absorption spectra of a type IaBB' colorless diamond before (*black curve*) and after (*red curve*) HPHT annealing at a temperature of 2,300 °C under a pressure of 7 GPa for 10 min. The Platelets peak is considerably reduced but not annealed out completely. Traces of the A-center can be seen in the spectrum after annealing. **b** Irregular type IaB diamond before (*black curve*) and after (*red curve*) HPHT treatment for 5 h at a temperature of 2,700 °C under pressure of 9 GPa (diamond-stable conditions) [re-plotted from Evans et al. (1995)]. The formation of A defects is clearly seen. However, the intensity of B-center is not reduced measurably

dissociation of B defects in pure type IaB diamonds was assumed only because of the appearance of small concentrations of C- and A-defects (Vins et al. 2008; Evans et al. 1995) (Fig. 4.5). No generation of the 1,344 cm^{-1} peak due to formation of C defects in those diamonds was reported.

Dissociation of the Platelets is a more complex process as compared with that of the nitrogen-only aggregates. The Platelets are favorable defects in diamond lattice at low temperatures. However, due to low temperature stability, the Platelets collapse during HPHT treatment. Dissociation of platelets can be noticeable at temperatures as low as 1,800 °C, that is at the temperatures, when no degradation of A- and B-defects occurs (Vins et al. 2008). Therefore, in most type Ia diamonds, HPHT treatment decreases intensity of the Platelets absorption.

The evolution of the Platelets during HPHT treatment strongly depends of the presence of A defects and the pressure at which HPHT annealing is performed (Vins et al. 2008; Evans et al. 1995; Goss et al. 2003). High content of A defects considerably slows down the destruction of the Platelets. If the A defect concentration exceeds 400 ppm, the formation of new platelets may prevail over their destruction and then the intensity of the Platelets peak increases after short-time HPHT treatment.

The annealing of Platelets is very sensitive to the value of pressure applied during HPHT treatment. When the pressure is in the range of stability of diamond, the Platelets decompose slowly. Once the pressure drops to the range of stability of graphite, the annealing rate of Platelets increases by orders of magnitude. Such a sharp pressure threshold has not been reported for any other defects in diamond. The decomposition of the Platelets results in formation of the dislocation loops, dispersed nitrogen atoms and small octahedral voidities filled with compressed nitrogen (Evans et al. 1995; Goss et al. 2003). A little increase in the concentration of B defects may be also observed with the dissociation of the Platelets.

Defect-Stimulated Dissociation

Like for the aggregation process, the dissociation of the nitrogen complexes can be enhanced by other defects, e.g., vacancies. Because of the vacancy stimulation, the dissociation of A defects into C defects occurs faster in initially brown diamonds (Vins et al. 2008). In diamonds with intense brown color, vacancies reduce the activation energy of dissociation of A defects to a value of 3.7 eV. The temperature threshold of the nitrogen dissociation in these diamonds decreases to 2,000 °C.

The vacancy-stimulated dissociation of the nitrogen aggregates and formation of C defects in irradiated diamonds was demonstrated in (Woods and Collins 1986; Collins 2001). In type Ia diamonds, the decomposition of A- and B-defects was shown at temperatures as low as 1,400 °C. In order to achieve the transformation at such a low temperature, the diamonds were irradiated and pre-heated at lower temperatures prior to the final annealing at 1,400 °C. In that experiment, the irradiation and pre-heating produced the H3 and H4 defects, which were the vacancy-containing derivatives of the A- and B-defects and which had much lesser temperature stability than A- and B-defects. The generation of C defects in this case was manifested by intense absorption of the H2 center (negatively charged H3 defects) and the NV^- center (negatively charged NV defects). The formation of the H3 and H4 defects in irradiated type Ia diamonds may occur at very low temperatures starting from 500 °C (Zaitsev 2000; Collins 2001).

The defect-stimulated decomposition of the nitrogen complexes is especially pronounced in diamonds, containing predominantly highly aggregated nitrogen. Brown type IaB diamonds exhibit the following changes after HPHT treatment (Vins and Yelisseyev 2008). After processing at 1,800 °C, brown color is reduced and the H3 defects are formed, no change in the intensity of the N3 center is detected. Further heating at a temperature of 1,900 °C causes the increase in the intensity of both the H3 and N3 centers and the generation of C defects. The appearance of the isolated nitrogen atoms can be detected as the rising absorption of the C defect absorption continuum with simultaneous formation of the H2 center. A decrease of the intensity of the Platelets peak is observed too. At temperatures of 2,100 °C and above, the C defects are formed intensively and their concentration may attain 10 ppm. The diamonds acquire bright yellowish-green color and their spectra exhibit strong C defect absorption continuum and the H2 center. The C defects are formed at the expense of the initially present B defects, concentration of which reduces by 10–15 %. At a temperature of 2,200 °C, absorption of the H2 center reduces indicating that the process of destruction of the H3/H2 defects prevails over the process of their production. After HPHT treatment at temperatures up to 2,300 °C, brown type IaB diamonds always acquire yellow–green tint in color and they never get a colorless appearance.

Formation of small concentration of A defects is also observed in type IaB diamonds after HPHT treatment at high temperatures. The most probable mechanism of this effect is the reverse aggregation of the generated C defects. These processes of dissociation-aggregation suggest that the A defects are an intermediate form of nitrogen aggregates, which appear in the process of nitrogen aggregation only.

The vacancy-stimulated splitting of A defects into C defects via formation of H3 defects in brown diamonds during HPHT annealing may considerably increase concentration of dispersed nitrogen (Fig. 4.4). For instance, a pale brown diamond with a 50 ppm concentration of A defects can reveal up to 20 ppm of C defects after 10 min HPHT treatment at a temperature of 2,300 °C. However, the dissociation process prevails as long as the vacancy clusters deliver single vacancies. Once the brown color has gone, the further annealing at the same temperature reversely aggregate the C defects into A defects. Hence the relative concentrations of the A- and C-defects may vary considerably depending on temperature, pressure and time of HPHT treatment, as well as on the intensity of the initial brown color of the treated diamond.

The generation of C defects in brown type Ia diamonds during HPHT treatment is an intense process. It is unlikely to obtain the concentration of C defects below 1 ppm in brown diamonds with the initial content of A defects over 7 ppm. Correspondingly, in brown diamonds with the A defect content of 15 ppm, a few ppm of C defects is expected after HPHT treatment. In general, after HPHT treatment of any type Ia diamond, the concentration of C defects cannot be below 0.1 ppm (Claus 2005).

The vacancy-stimulated decomposition of A defects into C defects is especially pronounced after treatment at moderate temperatures (Fig. 4.4). In brown diamonds, decomposition rate of A defects at a temperature of 2,100 °C may exceed that in colorless diamonds by more than an order of magnitude. However, with the temperature increase, this difference decreases and almost vanishes at temperatures over 2,300 °C. Due to high reactivity of A defects and vacancies, in brown type Ia diamonds with considerable presence of A defects, HPHT treatment always reduces their concentration and forms C- and B-defects. That is, in brown diamonds, the processes of destruction of the A defects always prevail over the processes of their creation.

Although B defects are the most stable nitrogen defects in diamond, they may dissociate in brown diamonds even at temperatures below 2,000 °C. The released vacancies convert B defects into H4 defects, which in turn dissociate into H3 and C defects. B defects can be also split by moving dislocations, which are present in high concentration in brown diamonds. During HPHT treatment at temperatures 2,000–2,100 °C, the movement of dislocations destroys B defects and transforms them into simpler N3-, A-, H3- and C-defects (Vins et al. 2006; Vins and Yelisseyev 2008a). The mechanism of such a “mechanical” destruction of B defects by moving dislocations was discussed in (Nadolinny et al. 2004). It was also shown that the thermal decomposition of B defects is a negligibly weak process. The dislocation-enhanced dissociation of B defects increases the concentration of

C defects, which, however, does not exceed the equilibrium value and remains relatively low even at high temperatures.

Simultaneous generation of N3 and C defects in type IaB diamonds is very unnatural process and the most distinguishing feature of HPHT treatment of these diamonds. This effect can be observed after treatment at temperatures as low as 2,100 °C, when the creation of the A defects is still below the detection limit. Thus, type IaB diamonds, which exhibit a considerable presence of C- and N3-defects, but no A defects, are very likely HPHT-treated ones.

The generation of enhanced concentration of C defects in type Ia diamonds and the conversion of diamond type from Ia to the mixed type ABC are typical results of HPHT treatment at moderate and high temperatures. Although ABC diamonds can be found in nature, most of these diamonds in gem market are HPHT-treated.

4.3 Ultimate HPHT Treatment

With the temperature increase, all nitrogen-containing defects aggregate into the most stable defects, which are the B defects. Thus one might believe that using HPHT treatment at high enough temperature and pressure (in the range of stability of diamond) and long enough time, any natural diamond could be converted into type IaB irrespective of its initial nitrogen composition. The vacancy clusters, which are less stable defects than B defects, would be annealed out completely by this treatment too. Without the presence of vacancies, the B defects have very high temperature stability and they cannot be destructed even at very high temperatures. Following these considerations, one may come to an idea of an "ultimate" HPHT treatment capable of conversion of any natural regular brown diamond into colorless type IaB.

In order to prove this idea, we have performed a 10 min HPHT annealing of a type IaAB plastically deformed brown diamond at a temperature of 3,000 °C under a pressure of 10 GPa. The result is a near colorless diamond. Yet, the diamond is not true colorless because of the presence of traces of non-aggregated nitrogen. It is not clear, what is the reason of these remaining color centers: an equilibrium concentration of non-aggregated nitrogen, or the destruction of B defects. Since the activation energy of the thermal dissociation of B defects remains unknown, the equilibrium concentration of C defects in type I diamonds subjected to "ultimate" HPHT treatment cannot be predicted. However, even in case of extreme thermal stability of B defects, one mechanism of destruction of B defects in natural diamonds during HPHT treatment is always present. It is the non-uniform internal stress. Most natural diamonds are non-uniform in terms of crystal lattice perfection and distribution of impurities. This non-uniformity results in the formation of mechanically "weak" and "strong" areas over the diamond bulk. Because of these areas, the external pressure, even perfectly hydrostatic from outside, distributes through the diamond bulk non-uniformly. At high temperatures, when diamond is brought into the range of plasticity, the non-uniform internal stress will cause generation of dislocations. The moving dislocations inevitably break B defects into smaller nitrogen complexes including C defects. Hence it is expected that in a natural type I diamond, it is impossible to completely remove C defects and, consequently, yellow color by HPHT annealing. Moreover, we believe that in majority of natural brown diamonds, which are internally stressed diamonds, the residual concentration of C defects after "ultimate" HPHT treatment would be high enough to give these diamonds at least light yellow color.

Will the ultimately treated type IaB diamonds pose a problem with their recognition? We believe that they will not. A specific feature of these diamonds is the lack of the hydrogen 3,107 cm^{-1} center for it is always destroyed by high temperature HPHT annealing. The absence of the 3,107 cm^{-1} center is a very rare occasion for natural untreated diamonds of types IaB and IaBB' (Vins et al. 2008; Vins and Yelisseyev 2010). According to the results of our measurements performed on more than 1,000 natural type IaB diamonds, the probability to find one without 3,107 cm^{-1} center is below 0.5 %.

4.4 Multi-Process Treatment

HPHT treatment of diamonds is frequently performed in combination with other technological processes, which may include irradiation with energetic particles (electrons, neutrons, gamma-rays and ions) and conventional low temperature annealing (e.g., Vins 2004a, 2007). Although any type of irradiation can be used for treatment, the irradiation with electrons of energy from 1 to 3 MeV is the most common one. The electrons of this energy propagate in diamond to a depth of a few millimeters, what is deep enough to cause the generation of radiation defects through the body of a 1 carat cut diamond.

An example of the first commercial application of the multi-process treatment is the decoloration of type Ib yellow diamonds via aggregation of C defects into A defects. The usual procedure of this treatment starts from the electron irradiation with a dose of 10^{18} cm^{-2}. The electron irradiation generates vacancies, which interact with C defects and considerably reduce temperature and time of their aggregation into A- and B-defects. The irradiation dose 10^{18} cm^{-2} is sufficient to create vacancy-related defects in a concentration of 100 ppm and to convert all C defects into NV defects practically in any natural type Ib diamond. Subsequent HPHT annealing combines NV defects into A- and B-defects. It is interesting that the irradiation performed prior to HPHT annealing also produces Platelets in type Ib diamond (Evans and Allen 1979). In some cases, the multi-process treatment procedure includes an additional long time annealing at a temperature of 800 °C, which is also performed prior to HPHT annealing. This low temperature annealing helps to convert the nitrogen defects into nitrogen-vacancy complexes and promotes the removal of yellow color.

Production of Imperial Red diamonds is another example of the multi-process treatment involving HPHT annealing. The aim of this treatment is the generation of red color in type Ia diamonds, which have low clarity grade or unpleasant initial color. This is achieved by creation of high concentration of NV defects, which strongly absorb yellow and green light and make diamond preferentially transparent in the red spectral range. The first step of the treatment is a high temperature HPHT annealing, during which the nitrogen complexes dissociate into C defects. The following electron irradiation creates vacancies, which, like C defects, are randomly distributed over the diamond bulk. The last step of the treatment is the annealing at a temperature of 800–1,000 °C, during which the vacancies diffuse to the C defects and form the NV defects.

Multi-process treatment involving irradiation, conventional annealing and HPHT annealing can be performed in different combinations and at various temperature–pressure-time parameters. It is a very effective treatment capable of generation of many different color centers. Using multi-process treatment one can produce diamonds of almost any color.

4.5 Color Transformations

Change of color is the essence of commercial HPHT treatment of diamond. Although the HPHT treated diamonds can be found in every color including colorless, yellow, green, pink and blue (Fig. 4.6), commonly HPHT treatment is used for removal of unpleasant colors, like brown and gray, and making these diamonds colorless. Examples of the color change of brown natural diamonds after HPHT treatment at temperatures from 1,900 to 2,250 °C are given in (Vagarali et al. 2003).

HPHT-induced color change is a complex process involving transformation, diffusion and interaction of many intrinsic and impurity defects. It strongly depends on the initial diamond color and the parameters of HPHT annealing. Different color changes of type IIa and Ia colorless and brown diamonds are described in (Anthony et al. 2001; Vins et al. 2008). Since the temperature of HPHT annealing is much higher than the temperature the diamond is subjected to during the process of making diamond jewelry, the HPHT-induced color is permanent in terms of standard jewelry manufacturing, wear and repair (Overton and Shigley 2008). Thus, the HPHT-treated diamonds are subject to conventional color grading used for natural untreated diamonds.

Complete decoloration of diamond can be achievable only in type IIa diamonds. 80 % of type IIa brown diamonds are converted by HPHT treatment to

Fig. 4.6 Colorless, *yellow* and *pink* diamonds HPHT-treated by Suncrest Diamonds, USA (Simic and Zaitsev 2012)

colorless. In 20 % of cases, they acquire pink or light yellow color (Vins et al. 2008). A very small percentage of type II diamonds reveal after HPHT treatment blue body color (Hall and Moses 2000; Wang and Gelb 2005). A considerable portion of HPHT-treated type IIa colorless diamonds have color grade D to G. These diamonds usually have high structural perfection and the clarity grade of IF to VS2.

After HPHT treatment, high color grades can be obtained only with very low-nitrogen type IIa diamonds. Even small amount of nitrogen, and especially of A defects, prevent from complete decoloration. No commercial color improvement is possible for diamonds with A defect content over 10 ppm (Claus 2005). When the stones are not preselected for IIa type, the resulting color for the majority of them is yellow or yellow/green with a strong "green transmission" effect and strong green fluorescence under UV illumination (Templeman 2000).

Besides decoloration, HPHT treatment is also used for the conversion of unpleasant colors in more appealing yellow, green, orange and red colors and their combinations. This color change can be achieved in type I diamonds with the nitrogen content over 15 ppm. HPHT treatment results in formation of many different nitrogen-containing color centers, the major being the H3 and H2 centers (see below). The dominance of these centers makes most initially brown type Ia diamonds of bright yellow–green color.

The third area of application of HPHT treatment is the color enhancement of low clarity type I diamonds. The aim of this treatment is the generation of deep body color, which can conceal the highly included interior. In order to avoid the excessive internal graphitization, HPHT treatment of included diamonds is not performed at high temperatures. Preparatory irradiation is frequently used for HPHT treatment of highly included diamonds in order to facilitate the generation of optical centers and to reduce the temperature and time of HPHT annealing. The resulting color of HPHT-treated highly included diamonds may contain brown, orange, green and yellow modifiers. Red color can be present too. Table 4.1 shows the basic HPHT-induced color transformations for initially brown/gray diamonds of different types.

Understanding the color transformations is crucial for recognition of HPHT-treated diamonds. If the origin of color of a diamond is questioned, the first question to answer is whether this color can be produced by HPHT treatment and, if yes, whether the impurity-defect composition of this diamond allows generation of this particular color during HPHT annealing. Frequently, the correct answers to

Table 4.1 Basic colors induced in natural diamonds by HPHT treatment

Diamond Type	IIa	IIb	Ia	Ia
Initial color	Brown	Brown/gray	Brown	Colorless
Final color	Colorless Pink/violet Light yellow	Blue	Yellow/green	Yellow

The resulting color of a particular diamond is usually a combination of several hues these two questions is sufficient for confident reporting HPHT treatment, or otherwise its absence.

A well known example of such a “color test“ is the reporting of the non-treated nature of colorless type Ia diamonds. HPHT treatment always results in decomposition of nitrogen aggregates and production of C defects, which, even in small concentrations, add yellow color. If the original color of a type Ia diamond is brown, the removal of this color is always accompanied by production of H3 center, which add yellowish-green color. Therefore, it is impossible to obtain a colorless stone from a nitrogen-containing diamond by any combination of treatments if HPHT annealing is involved. For instance, it is impossible to improve the color grade to colorless or near-colorless diamonds with A defect concentration over 7 ppm (Claus 2005). Thus, the origin of color of a high color type Ia diamond is always reported as “natural” and the certification of these diamonds does not require the “origin of color” test.

Natural diamonds often exhibit colors that correlate to their diamond type. For instance, it is unlikely, that type Ia colorless, brown, light pink and violet diamonds are color-treated. Color-treated type Ia diamonds are usually yellow, green, orange, red or greenish-blue. Untreated type Ib diamonds are almost always brown, yellow or orange, whereas HPH-treated type Ib diamonds can be yellow in and off-color stones. Brownish and grayish type IIa diamonds are very likely untreated. However, colorless type IIa diamonds and those with light pink or blue modifies are probably HPHT-treated (Breeding and Shigley 2009).

Although HPHT-treated natural diamond can have almost any color, two most probable colors, an average natural diamond acquires after an average HPHT treatment, are brown and yellow–green. Absorption spectroscopy studied on 150 HPHT-treated natural diamonds (no pre-selection) revealed two major groups: (1) brown diamonds, which essentially retain their color after treatment, and (2) yellow–green diamonds. The first group of diamonds is characterized by strong H2 and 638 nm (NV^-) centers, whereas the spectra of the second group are dominated by the H2 center (Serov and Viktorov 2007). This observation suggests that, firstly, the presence of brown hue in color of HPHT-treated diamonds is quite common and, secondly, the brown color of most natural brown diamonds is too strong to be removed completely by an average HPHT treatment.

4.5.1 Removal of Brown Color and Decoloration

Removal of brown color of natural low-nitrogen regular brown diamonds was the original intention of commercial HPHT treatment and it remains its main aim at present (Fig. 4.7). Typical reduction of intensity of the Brown Absorption Continuum by HPHT treatment is shown in Fig. 4.7c. It is believed that the reduction of brown color occurs mainly because of dissociation of vacancy clusters. Large clusters comprising 40–60 vacancies have been found as those primarily responsible for brown color. Size of vacancy clusters determines their temperature

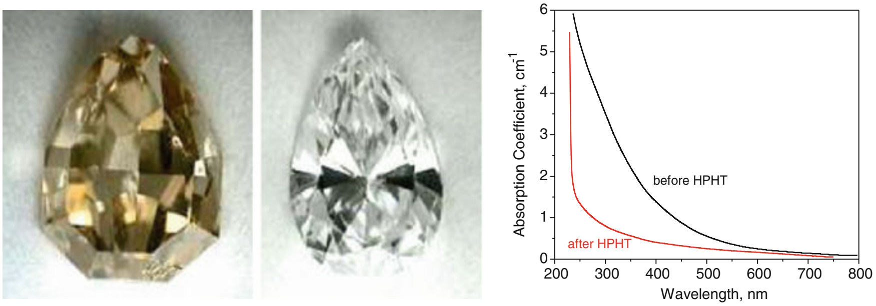


Fig. 4.7 Type IIa natural *brown diamond* before (**a**), and after (**b**) HPHT treatment [http://www.sundancediamonds.com/files/The-Sundance-Process.pdf] (courtesy of Suncrest Diamonds). **c** Absorption spectra of a natural brown type IIa diamond before and after HPHT treatment. Intensity of the Brown Absorption Continuum is strongly reduced by the treatment [re-plotted from Fisher and Spits (2000)]

stability. Small vacancy clusters are more stable and anneal slower than the larger ones (Maeki et al. 2009; Fisher et al. 2009; Bangert et al. 2009).

For the vacancy clusters of a disk shape, the calculations show that the temperature required for their dissociation is of 2,200 °C, which is in a good agreement with the experimental data (Willems et al. 2006; Hounsome et al. 2007). The removal rate of the Brown Absorption Continuum strongly depends on the initial impurity-defect structure of the treated diamond and on temperature of HPHT treatment. Practically, there are two distinctive temperature ranges of treatment of natural brown diamonds: (1) moderate temperatures (1,800–2,100 °C), at which the vacancy clusters dissociate, brown color reduces, and the released free vacancies are captured by nitrogen defects; (2) high temperatures (2,100–2,300 °C), at which the transformation of nitrogen-vacancy defects occurs (Vins and Yelisseyev 2008; Van Royen and Palyanov 2002). Although a slow decoloration of brown diamonds may be observed at temperatures below 1,800 °C (slight decoloration can be observed even after long-time annealing at a temperature of 1,500 °C), fast removal of brown color requires heating at temperatures of at least 2,100 °C. If the annealing temperature is increased to 2,300 °C, brown color of most regular brown diamonds disappears in a few minutes (e.g., Claus 2005). Although brown color gradually reduces with the temperature increase and finally disappears at 2,300 °C, the onset of the fast removal of brown color occurs at a temperature of 2,100 °C (Maeki et al. 2009; Fisher et al. 2009). It is interesting that the reduction of brown color of CVD-grown diamond can be noticeable after HPHT treatment at a temperature of 1,600 °C for 5 min (Crepin et al. 2012).

The activation energy of the removal of brown color in natural type IIa diamonds is rather high amounting 8.0 ± 0.3 eV (Fisher et al. 2009).

There are natural brown diamonds, the remnants of brown color in which can be detected even after high temperature HPHT treatment. Such a high stability of brown color implies participation of very temperature stable defects other than vacancy clusters. Yet, whatever the stability of the Brown Absorption Continuum is, at least partial removal of brown color of regular brown diamond is always achieved after any HPHT treatment. Thus, when establishing the origin of color of diamonds with brown color, one must be aware that brown diamonds can also benefit from HPHT treatment.

HPHT treatment performed at very high temperatures tends to discolor any diamond. High temperature destroys most color centers and promotes their aggregation into optically inactive clusters. For instance, all nitrogen-related optically active defects C-, H3-, H4-, N3- and NV-aggregate during HPHT annealing into optically inactive B defects and Platelets (Vins and Yelisseyev 2008).

Type IIa diamonds

Colorless diamonds of high color grade can be obtained after HPHT treatment of only type IIa diamonds with negligible nitrogen content (Collins 2003; Kitawaki 2007; Moses et al. 1999; Woodburn 1999; Johnson et al. 1999; Collins et al. 2000). Less than 1 % of all natural gem diamonds are suitable for making colorless stones of color grade from D to G. These diamonds are high purity type IIa stones of brown/gray color with the total nitrogen content below 0.1 ppm. The nitrogen content above this limit may result in generation of C defects at a concentration of 0.05 ppm, which would reduce the diamond color to near-colorless (Anthony and Casey 1999; Moses et al. 1999) (Fig. 4.12). Brown diamonds of high purity and structural perfection are very rare and therefore majority of HPHT-treated type IIa diamonds with color grade from D to G and clarity grade from IF to VVS do not exceed weight of 2 carats.

In general, the lower intensity of the initial brown color the better decoloration can be achieved by HPHT treatment. Intense brown color results in generation of too many mobile single vacancies and formation of high concentration of extended defects and non-diamond carbon nano-inclusions, which reduce the overall transparency of diamond and lower its color grade. For instance, light to medium brown type IIa diamonds of N to O color grades can be converted into diamonds of colors D to F (Smith et al. 2000). More intense brown coloration results in a color grade of H and lower.

Type IaB Brown Diamonds

Along with type IIa brown diamonds, brown diamonds of pure type IaB are also very desirable starting material for production of near-colorless diamonds (Haenni 2001). B defects are the most temperature stable nitrogen complexes in diamond and they do not noticeably decompose at temperatures up to 2,300 °C. At this temperature, most defects responsible for the Brown absorption continuum anneal out and brown color in type IaB diamonds can be effectively removed without considerable generation of unwanted yellow color. Typically, it takes a few minute heating at temperatures of 2,200–2,300 °C for the conversion of brown type IaB diamonds into near colorless.

However successful is the reduction of brown color of type IaB diamond, the near-colorless grades can be achieved only in stones with moderate nitrogen content. For instance, HPHT treatment of type IaB brown diamonds with B defect concentration from 5 to 50 ppm transforms them into stones of color grade from G to O. Since high temperature HPHT treatment does decompose at least a little portion of B defects in any natural diamond, the temperature of HPHT treatment is a crucial parameter of the process of decoloration of type IaB brown diamonds. Too high temperatures result in a noticeable decomposition of B defects into C defects and generation of yellow color (Van Royen et al. 2006).

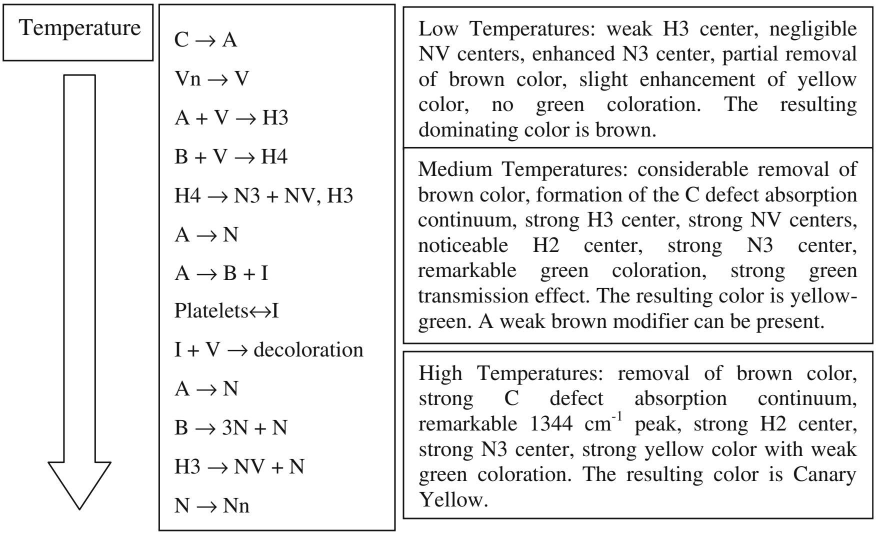
In diamonds with considerable structural non-homogeneity, the decomposition of B defects may start even at temperatures of 2,000 °C. Since the reasonable reduction of brown color requires higher temperatures (Schmetzer 2010), HPHT treatment of diamonds with highly non-uniform distribution of internal stress and nitrogen impurity cannot result in complete decoloration, even if these diamonds had initial light brown color and the treatment is performed at relatively low temperatures. Our experiments performed on large number of diamonds show that the final color of all HPHT-treated type IaB diamond have detectable yellow/green color modifier (Vins et al. 2008; Vins and Yelisseyev 2010).

Type IaAB Brown Diamonds

HPHT treatment of brown type IaAB diamonds also reduces their brown color. These diamonds, however, do not become colorless or near-colorless, but acquire green-yellow color. The activation energy of annealing of brown color is less in type Ia diamonds than in nitrogen-free type IIa diamond, what suggests the stimulating role of nitrogen in the defect transformation processes at high temperatures (Vins 2004). This stimulating action, however, is negligible at low temperatures. Collins and colleagues (Collins et al. 2005) found that the annealing of brown type Ia diamonds at a temperature of 1,700 °C did not change noticeably their color. Some reduction of brown color simultaneously with generation of yellow–green color (creation of H3 and H2 center) was observed after annealing at 1,800 °C (Collins 2001; Vins et al. 2008). In light brown type Ia diamonds, brown color practically disappears after HPHT treatment at a temperature 2,000 °C and the resulting color is determined only by the H3 center (Vins et al. 2008).

Dark brown color is not characteristic of HPHT-treated type Ia diamonds. Instead these diamonds tend to colors with yellow to green to orange hues. The diamonds with intense dominating brown color are with high probability virgin and have not been HPHT-treated. It is remarkable that type Ia HPHT-treated diamonds with brown modifying color frequently have colored graining (e.g., Hainschwang et al. 2006a).

Color change and dominant reactions of major defects in HPHT-treated brown type Ia diamonds versus treatment temperature is given below in Fig. 4.8. Relative concentrations of the resulting defects and, consequently, the resulting color strongly depend on the initial concentration of vacancy clusters, dislocations, nitrogen defects as well as on the treatment time.



Low Temperatures: weak H3 center, negligible NV centers, enhanced N3 center, partial removal of brown color, slight enhancement of yellow color, no green coloration. The resulting dominating color is brown.

Medium Temperatures: considerable removal of brown color, formation of the C defect absorption continuum, strong H3 center, strong NV centers, noticeable H2 center, strong N3 center, remarkable green coloration, strong green transmission effect. The resulting color is yellow-green. A weak brown modifier can be present.

High Temperatures: removal of brown color, strong C defect absorption continuum, remarkable 1344 cm^{-1} peak, strong H2 center, strong N3 center, strong yellow color with weak green coloration. The resulting color is Canary Yellow.

Fig. 4.8 Sequence of the main defects transformations causing the color change of type Ia diamonds after HPHT treatment [based on De Weerdt et al. (2004)]

Irregular Brown Diamonds

Considerable reduction and removal of brown color after HPHT treatment occurs only in regular brown diamonds. Brown color of irregular diamonds (CO_2 and pseudo-CO_2 diamonds) is not affected noticeably by HPHT treatment and many irregular brown diamonds do not change their color at all (Hainschwang et al. 2008, 2005; Reinitz et al. 2000; Chapman 2010). HPHT treatment of these diamonds at temperatures of 2,000–2,100 °C may cause only minor color changes. For instance, irregular diamonds retain their brown color and may acquire additional yellow modifying color. Light-brown irregular type IaB diamonds, which show no presence of Platelets, after HPHT treatment performed at a temperature of 2,200 °C, may even intensify their brown color because of the generation of C defects (De Weerdt and Collins 2007).

HPHT treatment of CO_2 and pseudo-CO_2 diamonds is almost impossible to recognize even using spectroscopic methods (too little changes if any). The only feature, which could be used for the recognition, is the 480 nm absorption band (Collins and Mohammed 1982). Intense 480 nm band and its corresponding replica in luminescence may be considered as indicators of possible HPHT treatment. The defects responsible for the 480 nm absorption band are very active in luminescence causing intense yellow fluorescence of irregular brown diamonds under UV illumination. Sometimes, HPHT treatment of these diamonds can be recognized by their slightly more yellowish color (Hainschwang et al. 2008).

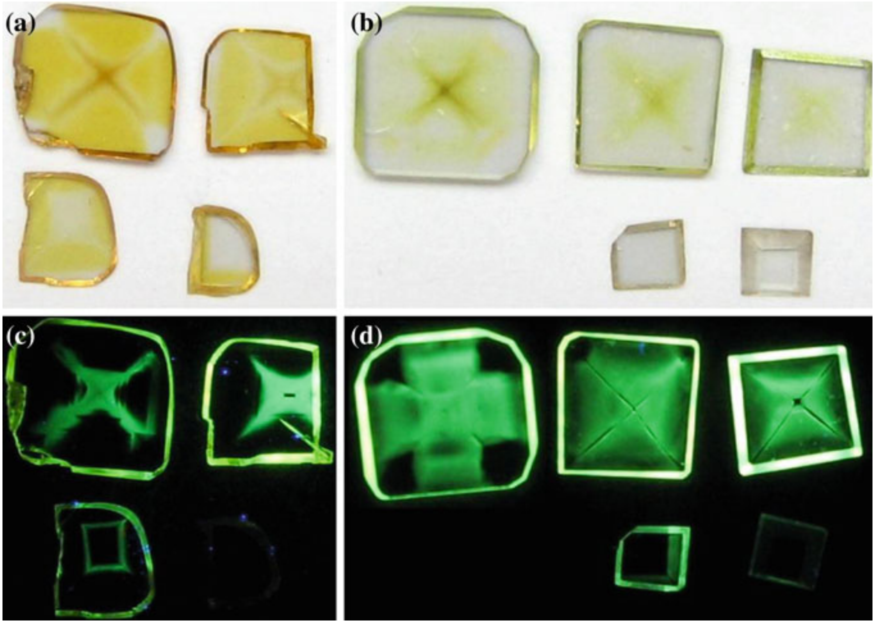


Fig. 4.9 Plates cut of a synthetic type Ib *yellow diamond* before (**a**) and after (**b**) HPHT treatment for 8 h at a temperature of 1,900 °C under a pressure of 6 GPa. *Yellow color* caused by C defects is almost completely removed. However, the central cross-like area with an enhanced content of nickel impurity retains its *yellow–brown color* (Kaziutchits 2008). It is interesting that the *yellow color* induced by C defects is weaker in the nickel-rich central area, suggesting that the aggregation of C defects into A defects in this area occurred during growth at relatively low temperatures. The fluorescence imaging (excitation at a wavelength of 337 nm) of these plates before (**c**) and after (**d**) HPHT treatment is shown. Strong *green* fluorescence expanding over the crystal after HPHT treatment is due to generation of the S3 and S2 nickel-related centers (Kaziutchits et al. 2012)

Decoloration of Yellow Diamonds

Considerable decoloration of type Ib yellow diamonds can be achieved by HPHT treatment performed at temperatures of 1,800 °C and above. The mechanism of reduction of yellow color in these diamonds is the aggregation of C defects into A defects (Fig. 4.9) (Kaziutchits et al. 2012). For instance, synthetic diamonds of saturated yellow color become light yellow after 4 h HPHT annealing at a temperature of 1,700 °C and light green after treatment at a temperature of 1,930 °C (in both cases at a pressure of 5.5 GPa, in the range of stability of graphite) (Yelisseyev et al. 2003).

Considerable reduction of intense yellow color of type Ib diamonds after HPHT treatment is described in (Strong et al. 1977, 1977a; Van Royen and Palyanov 2002). After heating at a temperature of 1,900 °C, an aggregation to 80 % of C defects into A defects can be achieved in high-nitrogen diamonds. In synthetic diamonds, after a long time HPHT annealing, this percentage is even greater

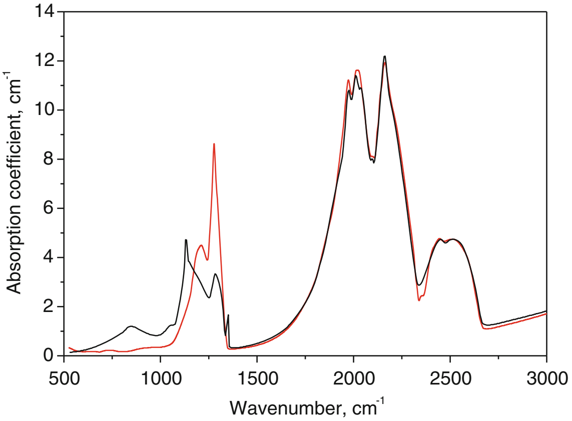


Fig. 4.10 IR absorption spectra of a synthetic diamond before (*black curve*) and after (*red curve*) HPHT treatment performed for 20 h at a temperature of 1,900 °C and a pressure of 6.5 GPa. Almost complete aggregation of C defects into A defects is achieved. Before treatment, the C-center dominates the spectrum. After treatment, C defects cannot be detected by IR spectroscopy [re-plotted from Mudryi et al. (2004)]

(Mudryi et al. 2004) (Fig. 4.10). In this case, the decoloration is strongly stimulated by the presence of nickel. However, the aggregation of nitrogen at high temperatures never reaches its completion. For instance, in decolorized HPHT-treated diamonds with 15 ppm of A defects, a few ppm of C defects is always present and these C defects make these diamonds light yellow (Claus 2005). Because of the residual content of C defects, no commercial color improvement is possible in diamonds with the initial A defect concentration above 7 ppm (Claus 2005).

In type Ib diamonds, commercial HPHT treatment performed with the aim of reduction of yellow color, does not produce N3 center. The absence of the N3 center is a distinctive feature of these diamonds and it can be used for the recognition of HPHT-treated diamonds of Ib character (Collins 2003).

Considerable reduction of yellow color of diamonds with Ib component can be achieved by combination of electron irradiation and HPHT annealing at low temperatures. For instance, irradiation with 2 MeV electrons at a dose of 10^{18} cm^{-2} followed by HPHT annealing at a temperature above 1,600 °C and pressure in the range of stability of diamond removes yellow color. A 1 h HPHT annealing at a temperature over 2,000 °C shifts the absorption edge from 460 to 290 nm and makes initially yellow diamonds actually colorless (Evans and Allen 1981).

In type Ib diamonds, a light brown color may be induced after HPHT treatment as a transient color. The reason of this color transformation is the reduction of the C defect absorption continuum and generation of intense H3 and H2 centers. Combination of these three absorptions produces an absorption continuum over the whole visible spectral range monotonously rising towards shorter wavelengths.

However, further high temperature HPHT treatment of these diamonds makes them almost colorless.

HPHT treatment can remove only the yellow color caused by the C defect absorption continuum that is the canary-yellow color. The cape yellow color caused by the absorption of N3 and N2 centers cannot be eliminated by HPHT annealing or any known multi-process treatment. The N3 defects are very stable and they stand any HPHT annealing. The action of HPHT treatment can be even opposite. In type Ia cape yellow diamonds, HPHT annealing at very high temperature may increase N3 center absorption and intensify the color of these diamonds.

Decoloration of Brown CVD diamond

HPHT treatment is an effective method of improvement of the color quality of CVD diamonds. For instance, it is used to remove brown color of thick CVD diamond films and to make them more attractive as a gem material (Chadwick 2008; Hemley et al. 2009). Large pieces of single crystal CVD diamond grown for the use in jewelry are brown and the removal of the brown color is an important step in the production of CVD gem diamonds. Brown CVD diamonds have specific defect structure and HPHT treatment of CVD diamond may result in colors different from those obtained after HPHT treatment of natural diamonds. Decoloration and/or generation of pink to green colors with orange and gray modifiers are common color transformations in originally brown nitrogen-doped CVD diamonds (Twitchen et al. 2003).

Decoloration of brown CVD diamond starts at very low temperature of 1,200 °C, which does not require application of stabilizing pressure. Annealing at 1,500 °C at ambient pressure for several hours results in a significant increase in transmission in the visible spectral range and makes CVD brown diamond much lighter in color (Twitchen et al. 2003). Full decoloration of low-nitrogen brown to black CVD diamonds can be achieved after HPHT treatment performed at temperatures 1,900 °C and above. A transient light blue color can be observed in these diamonds before they become colorless (Charles et al. 2004). Decoloration of opaque CVD diamonds can be achieved by HPHT treatment at temperatures 1,500–2,200 °C and pressures 4–5 GPa. After heating for several hours at a temperature of 2,400 °C, dark brown CVD diamond can be made near-colorless (Frushour and Li 2002; Twitchen et al. 2003; Anthony et al. 1994, 1996).

Considerable color improvement of CVD diamond can be also achieved by APHT and especially LPHT treatment, which can conveniently performed in the same CVD reactor, which is used for the diamond growth (Fig. 4.11).

4.5.2 Fancy Colors

Final color of an HPHT-treated diamond depends on its initial impurity-defect content and can be of almost any hue. However, the basic color components of

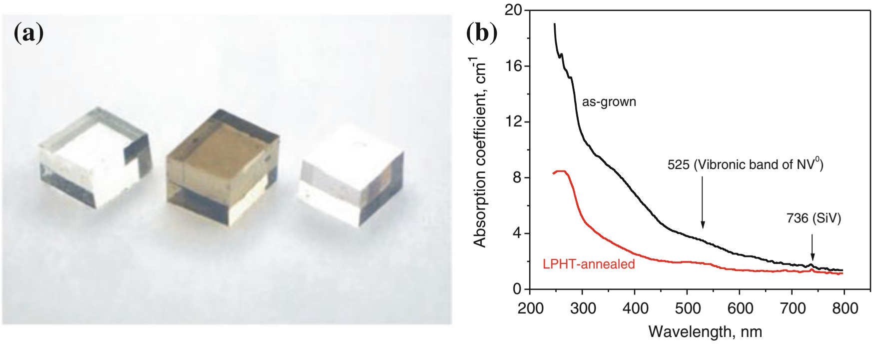


Fig. 4.11 **a** Examples of LPHT annealing of single *crystal brown* CVD diamonds: the middle piece is as-grown diamond; *left* and *right* are diamonds annealed at 1,900 °C for 2 min and 1,800 °C for 3 min respectively. **b** Absorption spectra of a CVD diamond measured at room temperature before annealing (*black curve*) and after LPTH annealing at a temperature of 1,800 °C for 2 min (*red curve*) [re-plotted from Meng Yu-Fei et al. (2008)]. Traces of the SiV center and NV^0 center are seen (permission of the National Academy of Science of USA)

colored HPHT-treated diamonds are yellow, green, pink, red and blue. Of these the most common are green/yellow. Pink and blue HPHT-treated diamonds are much rarer. The ratio of yellow/green colors versus pink and blue roughly follows the ratio of type Ia versus type IIa for natural diamonds. Today, a diamond of any of these colors is subject to the "origin-of-color" test.

Yellow

Saturated yellow color is a common color of treated type Ia diamonds. Yellow color can be induced in different ways including (1) irradiation followed by annealing at a temperatures from 800 to 1,000 °C, (2) low temperature (below 1,900 °C) HPHT treatment of initially brown diamonds, and (3) HTHT treatment of pale cape yellow diamonds (Collins 2001, 2003; Kitawaki 2007). In the latter case, light color of cape yellow diamonds can be increased to vivid yellow (Darley 2011).

HPHT treatment of colorless type Ia diamonds is commercially reasonable when they have low clarity grade. Then the induced fancy color can make these diamonds more attractive. Near-colorless type Ia diamonds are treated with the aim of enhancement their pre-existing yellow color (Collins 2003).

The mechanism of the conversion of color of colorless, near colorless (without brown color component) and light cape yellow type Ia diamonds in yellow during HPHT treatment is the dissociation of A defects and formation of C defects (Vins et al. 2008; Darley 2011). The strength of the canary-yellow coloration added to initially cape yellow diamonds increases with temperature and time of HPHT treatment (Collins 2003; De Weerdt et al. 2004). Reduction of the color grade with the increase in concentration of C defects is shown in Fig. 4.12. If HPHT treatment is performed at relatively low temperatures, neither new color centers nor enhancement of already existing color centers, like the N3 center, occurs simultaneously with the transformation A defects into C defects (Vins et al. 2008).

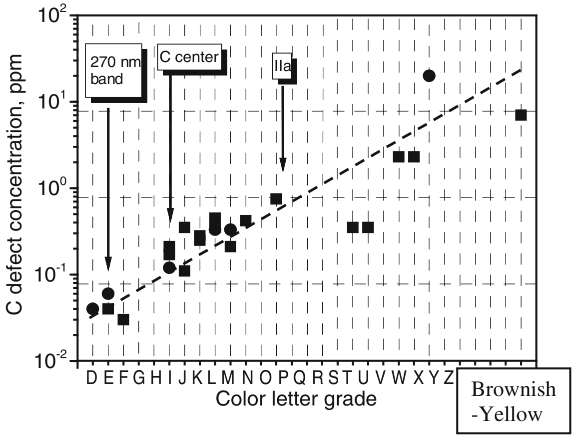


Fig. 4.12 Change in color of initially colorless diamonds with the increase in C defect concentration in HPHT-treated diamonds (*squares*). *Circles* represent untreated natural type IIa and Ib diamonds. *Arrows* show the detection thresholds of C defects via the measurements of the 270 nm absorption band and the C-center absorption. *Label IIa* shows the level of the most intense yellow color, which can be produced in type IIa diamonds by HPHT treatment

Any variations of type Ia non-brown diamonds are suitable for making canary-yellow diamonds (Overton and Shigley 2008; De Weerdt and Collins 2007). Diamonds of type IaA produce pure yellow color (e.g., Vins and Yelisseyev 2008). Near colorless or pale yellow type IaA<B diamonds are converted into stones with more saturated yellow color similar to that of natural canary-yellow diamonds, provided HPHT treatment is performed at temperatures below 1,950 °C. High-nitrogen type IaAB diamonds heavy irradiated with electrons or neutrons and then HPHT annealed at 2,300 °C acquire yellow/orange color due to generation of high concentration of C defects (Collins et al. 2005). Although the yellow color of HPHT-treated diamonds resembles that of the natural ones, the treated diamonds do not show yellow fluorescence under LWUV excitation, which is a characteristic feature of natural canary-yellow diamonds (Collins 2001; Tretiakova 2009).

Generation of yellow color in initially colorless type Ia diamonds starts at a temperature of 1,800 °C (Colinns 2001) and continues with the temperature increase: the higher the temperature the more intense the canary-yellow color. However, the generation of C defects remains low until the temperature reaches 2,000 °C. Thus the diamonds treated at low temperatures normally acquire light yellow color (Brozel et al. 1978; Collins et al. 2000; Hainschwang 2002]. At higher temperatures, yellow color becomes more saturated and its generation proceeds increasingly fast. For instance, colorless type Ia diamonds with the nitrogen content above 100 ppm are converted into yellow after treatment at a temperature 2,300 °C for 3 min (De Weerdt and Collins 2008).

If HPHT treatment is performed at very high temperatures, any natural type Ia diamond irrespective of its initial color acquires yellow color. The reason is the destruction of H3 defects and the complete annealing of the vacancy clusters—two main defects responsible for green and brown color modifiers. H3 defects are readily generated in brown type Ia diamonds during HPHT annealing at lower temperatures. Neither H3 defects nor vacancy clusters survive heating at 2,300 °C and the C defects remain the major color centers in diamonds treated at very high temperature (e.g., De Weerdt and Collins 2007).

Change in color of type Ia yellow diamond after HPHT treatment is reported in (Okano et al. 2006). Treatment makes yellow color more pronounced. If the initial color of type Ia diamonds is colorless or near-colorless (non-brown), the yellow color induced by HPHT treatment may have apparent green color modifier. In this case, the generation of the H3 center responsible for the green color may occur due to poor hydrostatic condition of HPHT treatment, when considerable shear stress produces vacancies and thus H3 defects.

The generation of yellow color with some reduction of brown color is observed after annealing of type Ia brown diamonds at a temperature of 1,800 °C (Collins 2001; Kim and Choi 2005). This yellow coloration is caused by the absorption of H3 defects, which, after such an annealing are mainly in neutral charge state (H3 center). Small amount of the generated C defects also adds to yellow color. With the increase in the treatment temperature and time, the yellow color increases until C defect concentration becomes high enough to negatively charge H3 defects and produce the H2 center. With the appearance of the H2 center, diamonds absorb more in the red and orange spectral ranges and additional green color modifier appears (Wang and Hall 2007; Tretiakova 2009). Combination of yellow and green colors is the most probable color of HPHT-treated type Ia initially brown diamonds. The resulting color is determined by the superposition of the absorptions of H3, H2 and C defect absorption continuum (e.g., Vins et al. 2008).

Pure yellow colors can be reached only after treatment of colorless or near-colorless type Ia diamonds. Green color modifier is generated in initially brown type Ia diamonds only and only in combination with yellow color. Therefore, there are no HPHT-treated diamonds of light green color. However, if the green color component is very intense, it may hide weaker yellow and brown components and then the diamonds look dark green. Deep green color is common for HPHT-treated high-nitrogen type Ia diamonds. Type IaA diamonds of initial gray color can be also converted into yellow by HPHT treatment at temperatures from 1,800 to 2,100 °C (Vins and Kononov 2003).

If HPHT annealing is performed for a short time, the remnants of brown color can be present and the resulting color is brownish yellow–green (e.g., Reinitz et al. 2000). Yellow diamonds produced from brown stones by low temperature HPHT treatment also retain brown modifier in their color. A distinguishing feature of spectra of such diamonds is a broad band at a wavelength of 560 nm (Collins 2001).

In rare cases, one can encounter with HPHT-treated type IIa diamonds of light yellow color. These diamonds are actually low-nitrogen type Ia diamonds formally ascribed to type IIa. The nitrogen content in these diamonds is sufficient to generate C defects in concentrations producing visible yellow color (up to a grade P) (Fig. 4.12). For instance, the generation of a straw-yellow color is reported in some type IIa diamonds after HPHT treatment at a temperature of 2,300 °C and a pressure of 7 GPa (Vins et al. 2008). Although the C defects could not be detected in IR absorption spectra of those diamonds, the 270 nm band in UV absorption spectra manifested the presence of the dispersed nitrogen.

Low color type IIa diamonds of yellow hue are extremely rare in nature. Actually, these diamonds are almost non-existing very low-nitrogen type Ib diamonds. Low-nitrogen type Ia diamonds formally ascribed to type IIa are more probable. In these diamonds, the concentration of C defects is beyond the IR optical absorption detection limit and it cannot influence the diamond color. The only way to induce yellow color in these diamonds is the decomposition of A defects during HPHT treatment. Thus, type IIa yellow diamonds of a color grade H and lower are very probably HPHT-treated (Smith et al. 2000).

Decomposition of A defects is the reason of formation of C defects in type Ia diamonds after HPHT treatment. In diamonds with A defect content of 15 ppm, the equilibrium concentration of C defects after high temperature HPHT heating is about 0.3 ppm, which causes yellow color of intensity M to N. For a concentration of A defects of 7 ppm, the equilibrium concentration of C defects is less amounting about 0.2 ppm (Claus 2005). In order to reach the equilibrium, a prolonged processing for 1 h and longer is required. Since commercial treatment is rarely long-time processing, most HPHT-treated diamonds are those treated for a few minutes only. In 3 and 10 min of heating at a temperature 2,300 °C, the amount of C defects in diamond with 15 ppm of A defects increases to 0.04 and 0.12 ppm respectively. This generates yellow color of grades E and J correspondingly. Same treatment of diamonds with 7 ppm of A defects increases the C defect concentration to 0.042 and 0.06 ppm, what decreases the color grade of these diamonds by 1–2 grades.

The presence of vacancies strongly stimulates the creation of C defects. The concentration of C defects after HPHT treatment in diamonds with vacancy clusters is usually considerably higher than that achieved in diamonds without signs of plastic deformation. Thus in brown diamonds with the A defect content of 7 ppm, a few ppm C defects can be generated by HPHT treatment. Practically, in such diamonds after any HPHT treatment, the C defect concentration cannot be below 0.12 ppm (Claus 2005). Therefore, high color diamonds with weak IR absorption of Ia type and well transparent in short-wavelength spectral range can be reported as non-treated with confidence (e.g., Smith et al. 2000).

HPHT-treated diamonds of common yellow to green color frequently show brown to yellow graining, which is a strong indicator of treatment (Reinitz et al. 2000; Collins 2001; Kitawaki 2007). Collins reported (Collins et al. 2000) that the brown striations become less visible after HPHT treatment at low temperatures of 1,700–1,800 °C and change their color to yellow (Fig. 4.13). It was found that this color change occurs because of generation of H3 centers (Fisher 2008).

The conversion of the brown graining into yellow after HPHT treatment shows that the H3 defects responsible for the yellow coloration are formed preferentially within the areas saturated with vacancy clusters. This suggests that during low temperature HPHT annealing, the generated single vacancies do not migrate over

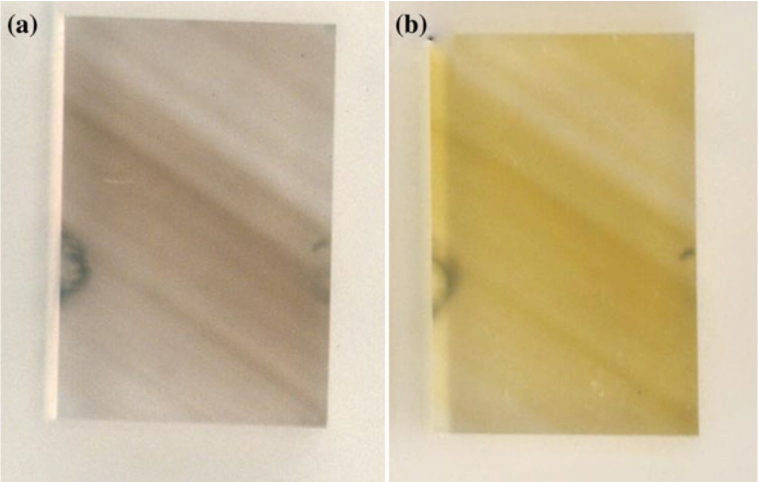


Fig. 4.13 Type Ia diamond **a** before, and **b** after HPHT treatment. *Yellow color* is due to H3 center absorption. HPHT-generated *yellow color* coincides in position with the original *brown color* (Fisher 2008) (courtesy of D. Fisher)

the whole diamond bulk. However, after HPHT treatment at a temperature of 2,000 °C, in regular brown type Ia diamonds, the grainy distribution of color may be practically eliminated and the distribution of color becomes rather homogenous over the diamond body (Hainschwang et al. 2005). The reason of this uniform yellow coloration is the dissociation of A defects into C defects. The distribution of nitrogen does not follow the fine pattern of brown graining and usually it is much more uniform through the diamond bulk than the distribution of plastic deformation. Thus, the formation of C defects and the distribution of the C defect related yellow color are rather uniform.

HPHT annealing of type Ia brown diamonds changes their color in the following sequence: yellow–green/yellow→yellow–green→green–yellowish-green. Brown color disappears gradually. These color transformations start at a temperature of 1,800 °C, when the H3 center begins to form.

Green

Generally, type Ia brown diamonds change their color to yellowish-green after HPHT treatment at moderate temperatures. The dominating H3- and H2-centers are responsible for this color (Overton and Shigley 2008; De Weerdt and Collins 2007). These diamonds are known as "apple green" diamonds (Kitawaki 2007). High-nitrogen diamonds with very intense H3- and H2-centers acquire dark green color. However, pure green color is not a common color produced by HPHT treatment and usually green color of the treated diamonds has a yellow modifier.

If the intensity of H2 center is low, the treated type Ia diamonds tend to have yellow color with a green hue resulting from the H3 center luminescence ("green transmission" effect). Yellow color of the HPHT-treated "green transmitters" has usually saturated intensity and sometimes reveals brownish-orange modifying body color. They look, however, greenish-yellow under daylight illumination and may also show greenish-yellow phosphorescence (Buerki et al. 1999). Because of the H3 center luminescence, the green component of color of HPHT-treated yellowish-green diamonds is stronger when they are viewed in daylight (Anthony et al. 2000). The contribution of the H2 center absorption to the body color of HPHT-treated "green transmitters" is usually little. Bright "green transmitters" have small content of A defects and, consequently, little amount of C defects generated by HPHT treatment. In low C defect diamonds, most H3 defects are in neutral charge state producing optical H3 center. Frequently, "green transmitters" are diamonds of type IaAB with dominating concentration of B defects. High-nitrogen type Ia diamonds with strong H3 absorption and weak "green transmission" effect have a darker green color than typical HPHT-treated diamonds (Wang and Hall 2007). Unfortunately, the above considerations pertain both HPHT-treated and natural "green transmitters" and cannot be used for recognition of treatment.

In order to produce green coloration, type Ia brown diamonds must be processed at relatively high temperature at which the generation of C defects becomes appreciable. Thus, type IaAB brown diamonds become green if heated at 2,000 °C and above (Collins 2001; Kim and Choi 2005; Collins et al. 2005). The generation of C defects is essential for they act as donors in diamond lattice and increase the relative intensity of the H2-center. Absorption of the H2-center reduces the transparency of diamond in the red and yellow spectral range and makes transmission in the green range preferential.

Many HPHT-treated yellowish-green diamonds reveal well-defined octahedral color zoning, which produces strong luminescence under intense illumination (Henn and Milisenda 1999; Anthony et al. 2000). This feature in combination with spectroscopic data is used to establish the origin of color of green diamonds.

An interesting feature of yellowish-green HPHT-treated diamonds is the change of their color during heating. When heated to about 600 °C, color of these diamonds changes from yellowish-green to pure "emerald" green. Upon cooling to RT, the green appearance persists for 10–15 min before it returns to original yellowish-green (Anthony et al. 2000). This effect is most probably due to change in relative intensity of the H3 and H2 centers as well as due to the increase in intensity of the C defect absorption continuum. Such a behavior is not typical for natural green diamonds and it can be used for identification of the origin of color.

HPHT treatment is not the only way to produce green color in a diamond. Brilliant green color can be induced in type Ia diamonds with strong Ib component by electron irradiation followed by subsequent annealing at a temperature above 1,500 °C. Such a treatment suppresses absorption of the NV centers and creates dominating H2 center. In order to achieve a distinctive green color, the annealing must be performed for at least 10 h. The prolonged heating is required for considerable reduction of intensity of NV and H3 centers and removal of the yellow color component (Shuichi and Kazuwo 1990).

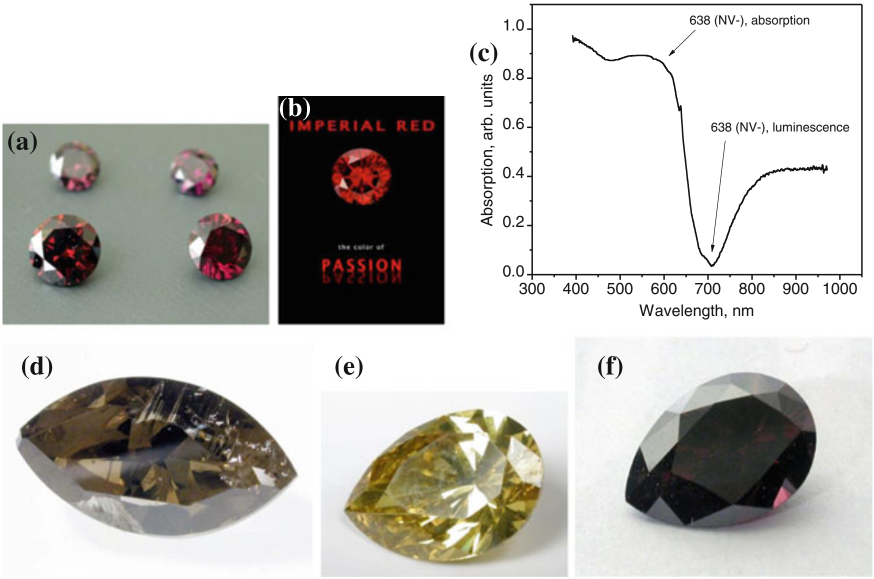


Fig. 4.14 **a** Imperial *Red diamonds* of the size range 0.6–1.5 ct. *Red color* of these type Ia diamonds was induced by HPHT annealing followed by electron irradiation and subsequent heating (courtesy of S. Z. Smirnov). **b** “Imperial Red diamonds” is a trade mark of HPHT-treated *red diamonds* introduced to the market by Lucent Diamonds (www.lucentdiamods.com). **c** FSI absorption spectrum of a typical HPHT-treated diamond of deep *red color*. The spectrum is dominated by intense 638 nm (NV^-) center, which is observed in regimes of absorption (wavelength from 470 to 638 nm) and luminescence (wavelength from 638 to 850 nm). It is this particular combination of the absorption and luminescence, which makes diamond look intense *red*. Because of the high luminescence intensity of the NV^- center (the effect of “red transmitter”), the diamond looks especially bright red, when viewed in daylight. Reduced absorption intensity in the spectral range from 450 to 500 nm may add a *pink* modifying tint to the main *red color*. **d–f** Color transformations in an initially deep brown diamond during the process of making Imperial *Red* diamond: **d** initial pre-shaped stone of *brown color*, **e** after HPHT annealing and final cut this stone had *greenish-yellow color*, **f** after irradiation and conventional annealing the stone acquired deep *pink-red color*

In diamonds, which contain nitrogen in concentrations low enough to be graded as type IIa, HPHT treatment may produce the nitrogen-related centers with intensities high enough to modify the diamond color. e. g., a fancy intense green-yellow type IIa diamond has been reported as HPHT-treated based on this assumption and on the fact that it is a “green transmitter” (Wang et al. 2003).

Red

Red/purple color is the rarest color of natural diamonds. In contrast, artificial red color can be easily achieved by multi-process treatment. The intensity and spectral purity of the HPHT-induced red color can be well controlled by selection of appropriate diamonds and by varying parameters of treatment. Often, the artificial red color is more attractive than the natural one (Fig. 4.14).

The main reason of the induced red color is the absorption and luminescence of intense 638 nm (NV^-) center (Fig. 4.14).

The NV^--center can be directly created by HPHT treatment in brown type Ib diamonds, or in type Ia diamonds with considerable Ib component. In these cases, the formation of the NV^--center occurs immediately during HPHT annealing, when vacancy clusters dissolve and the released single vacancies combine with C defects. In order to generate an intense red color, HPHT annealing has to be performed rapidly. Rapid annealing prevents the reverse destruction of the NV defects. The defect structure of the red diamonds treated this way is in a very non-equilibrium state and it can be easily recognized by comparing relative intensities of different nitrogen-related optical centers, which normally are not observed simultaneously in natural untreated diamonds.

More commonly, red color is induced in regular type IaAB (preferentially type IaA>B) diamonds by a multi-process treatment of the sequence: HPHT annealing, irradiation, conventional low temperature annealing. During this treatment, the three major defect transformations leading to the creation of the NV defects occur separately: (1) generation of C defects, (2) generation of vacancies and (3) aggregation of the vacancies and the C defects. This allows to perform the treatment very controllably and reproducibly. The first step—the HPHT annealing (usually at high temperatures)—is performed in order to decompose the nitrogen aggregates (mainly A defects) and to create high concentration of C defects. The second step—the irradiation (usually with electrons of energy in the range from 1 to 3 MeV)—is performed in order to create isolated vacancies. The third step—the low temperature annealing (in vacuum or inert atmosphere at a temperature in the range from 700 to 1,200 °C)—is performed to combine the C defects with the vacancies into NV defects. Since diamonds treated this way contain a lot of C defects, most NV defects are charged negatively and produce the NV^- optical center.

In order to achieve high concentration of C defects, HPHT treatment is performed at a temperature over 2,100 °C. Vins (2007) reports that in non-brown Ia diamonds, at temperatures above 2,150 °C, up to 20 % of A defects dissociate and form C defects, whereas no appreciable concentration of C defects forms in these diamonds at temperatures below 2,150 °C. In order to convert most C defects into NV defects, high concentration of vacancies is required. For this high dose electron irradiation is applied. The electron energy is not a crucial factor, though energy of at least 2 MeV is recommended. 2 MeV electrons penetrate into diamond to a depth of a few millimeters and uniformly irradiate few carat stones. On the other hand, 2 MeV energy is low enough to ensure the creation of point defects (mostly isolated vacancies) only. Electron doses as high as 10^{19} cm^{-2} can be applied. Such a heavy irradiation makes the as-irradiated diamonds opaque black. After annealing at a temperature of 1,100 °C for 24 h, these diamonds gain intense purple-red color.

In order to increase the rate of dissociation of A defects, a preparatory high dose electron irradiation is performed prior to HPHT annealing. In the pre-irradiated type Ia diamonds, HPHT annealing first converts A defects into H3 defects, and then splits the H3 defects into C defects. The temperature stability of H3 defects is less than that of A defects and therefore they deliver more C defects. The preparatory electron irradiation is recommended for diamonds with moderate nitrogen content, in which the direct generation of high concentration C defects by HPHT annealing is problematic (Vins 2007). For very high-nitrogen diamonds, HPHT annealing step may not be required at all. Just heavy electron irradiation and subsequent annealing at a temperature of 1,100 °C may suffice for obtaining red color in these diamonds (Vins 2007).

The NV^- center is the primary but not the only cause of the Imperial Red color. The other optical centers generated in type Ia diamonds by multi-process treatment are H3, H4, H2, NV^0 and 595 nm centers. Simultaneous absorption of these centers may result in very attractive and unique colors of pink/red hue never met in nature (Vins 2007). This color may range from purple/red to orange/red.

In type Ia diamonds, HPHT treatment cannot dissociate all nitrogen aggregates, even when a heavy preparatory irradiation is applied. In most cases, the concentration of A- and B-defects after HPHT annealing remains greater than that of C defects. Nevertheless, the irradiation and annealing performed after HPHT treatment usually make these diamonds purple/red. At first glance it is a strange behavior for one could expect the formation of the dominating H3 and H4 centers and, consequently, greenish-yellow color. Yet, very high efficiency of C defects in capturing vacancies, which is an order of magnitude greater than that of A- and B-defects explains this seeming contradiction. Thus, the formation of NV defects prevails over the formation of H3 defects even when the concentration of C defects is considerably lower than that of A- and B-defects (Vins et al. 2008).

Absorption of the NV^- center splits the visible transparency range of diamond into two windows at wavelengths longer than 650 nm (red) and shorter than 450 nm (blue). Because of this, diamonds with the dominating NV^- center absorption have pink color (combination of red and blue colors). The presence of the H3 and H4 centers as well as the N3 center, which absorb green–blue light, may essentially suppress the blue transmission window produced by of NV^- center and makes the color pure red. There are rare natural pink diamonds, which owe their color to the NV^- and NV^0 center absorption. However, in contrast to the HPHT-treated red diamonds, these natural red diamonds are of type IIa and their color is pale. The color of these diamonds is not affected by the H3 and N3 center absorptions. In turn, HPHT-treated red diamonds are much darker and higher in saturation (Wang et al. 2005). Besides, the red color of treated diamonds frequently has remnants of brown hue. This brown color component is a distinctive feature of the artificially colored red diamonds.

In contrast to the natural purple diamonds, the coloration of which is characteristically grainy, the purple color of HPHT-treated diamonds is distributed either evenly through the bulk, or it is located in growth zones (Titkov et al. 2008; Wang et al. 2005). In Imperial Red diamonds, the color may be distributed very unevenly within irregular zones formed during growth. These color zones have sharp clear boundaries. They are similar to the luminescence zones observed in DiamondView

Fig. 4.15 **a** Characteristic color zoning in HPHT-treated Imperial *Red* diamonds. The HPHT-induced *red* zoning follows octahedral crystal planes oriented in different directions. This behavior contrasts with the natural *pink-to-red* graining, which usually extends in one direction only (Wang et al. 2005). **b** "Naturally" looking *pink* graining in a diamond treated by multi-process treatment. The color stripes are oriented along one direction (Erel 2009). **c** Color zoning in some Imperial *Red* diamonds exhibits alternating *red* and *yellow colors* (courtesy of S. Z. Smirnov)

imaging. The red zoning reveals growth sectors with different dominating defects, which give rise to sharp-bordered red, orange, green and blue luminescence. The geometry of this color graining mostly follows (111) octahedral growth planes (Wang et al. 2005) (Fig. 4.15a). The color zoning in treated red diamonds reflects the distribution of nitrogen and, hence, follows the growth zones. In contrast, the color graining in natural red diamonds is caused by plastic deformation and follows the crystallographic slip planes. The shape of this zoning, which is different from that seen in natural color pink and red diamonds, is an important feature used for recognition of the treated red diamonds.

The distribution of red-pink color in some diamonds treated by the three-step process exhibits pink graining similar to that observed in natural pink diamonds with strong evidence of plastic deformation (Erel 2009) (Fig. 4.15b). These diamonds may look very "natural". However, the examination of the impurity content of this graining shows that the graining is not caused by the deformation itself (like it is in natural diamonds), but by non-uniform distribution of nitrogen in zones with different level of deformation—an effect reported in (Nailer et al. 2007). Different aggregation state of nitrogen in different zones of the graining is observed in the fluorescence patterns, which show stronger green luminescence of the H3 center in the light stripes and the orange NV center luminescence in the red stripes. In spite of the "natural" look of the HPHT-induced red graining, it can be distinguished from the natural pink graining via very different absorption/luminescence spectra: strong to very strong 638 nm center (NV^-) in treated stones and dominating Pink Band and the 576 nm center in natural red/pink diamonds. Besides, natural red/pink diamonds usually do not have high nitrogen concentration, whereas the treated counterparts are mostly high-nitrogen diamonds.

Spectrally pure red/purple color can be induced in initially colorless or near colorless type Ia diamonds. Brown type Ia diamonds are not desirable starting material for only 2–3 % of them change their color to red without brownish modifier (Vins 2004a). The reason of this brown color is the generation of too many intense color centers absorbing over the whole visible spectral range.

Color Grading of Imperial Red Diamonds

One of the problems with grading red diamonds is the correct description of their color. The color scale, which is commonly used for pink, brownish-pink and reddish-brown diamonds, is not well standardized because of the lack of natural red master diamonds. An attempt to develop a color grading system for red diamonds is described in (King et al. 2002). The red color has been termed as "pink" on the basis of the GIA diamond color grading system, which includes three parameters: hue, tone and saturation (King et al. 1994). According to this system, red color can be described by three hues. "Cooler" hue is termed as purplish pink and it can actually describe purplish red color. "Warmer" hue is described as orangey pink and it can actually describe orangey red color. "Red" hue with no color modifiers is described as pink. In spite of the convenience of this method, some of the actual colors cannot be determined correctly. For example, hues of low saturation, which should be described as brown or brownish, can be perceived as "warmer" hues and erroneously described as orangey (King et al. 2002).

One of the primary issues of grading of diamond color is the establishment of the corresponding reference for the purpose of comparison. Color of diamond is traditionally graded by comparing it with the color of master stones. This method works well when the optical properties of the master stones are similar to those of the graded diamonds. This similarity suggests the same set of the optical centers determining the transmission spectrum. The "master stone" method works very well for cape yellow diamonds, the color of which is determined only by the absorption of the N3/N2 optical centers. Natural cape yellow diamonds are inexpensive and the master stone sets for yellow color are readily available. In contrast, natural red diamonds are extremely expensive. Hence the red master diamonds are not used for practical grading.

The problem with the grading of colors other than yellow becomes even more pronounced in the case of synthetic and color-enhanced diamonds. Application of the same color grading approach to these diamonds results in a dramatic increase in their price. Moreover, the grading of man-made/processed diamonds using characteristics of natural diamonds is wrong in itself for it imposes an idea of their "identity".

Currently, the Imperial Red diamonds are graded by comparing their color with the master stones from GIA Gem Set. Although the material, the red master stones are made of, is not optically identical to red diamond, it is the only available option. Color grading of Imperial Red diamonds is based on the Munsell color system. The relevant hues are orange, orangey-red, red and purplish-red. The term "pink" is not used because it has no distinct color description. Low-saturated or light red, orange or purplish hues are often perceived as pink.

The "green and red transmission" effects may substantially influence the color appearance of Imperial Red diamonds. The red luminescence adds redness to the primary color, whereas the green luminescence adds warm hues to the primary color and makes diamonds look more yellowish and/or orangey (Fig. 4.16a).

Imperial Red diamonds have color appearance ranging from purplish red to orangey red. The two hues have been classified depending on tone and saturation

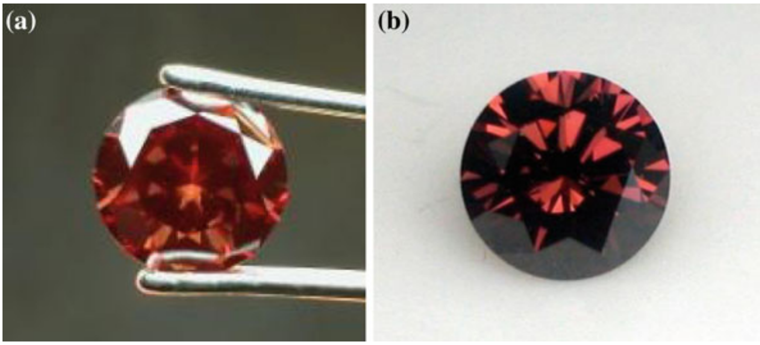


Fig. 4.16 **a** *Imperial Red diamonds* become orangey when illuminated by incandescent light (due to strong luminescence excited by visible light). **b** Fancy Excellent *Imperial Red diamond* (courtesy of S. Z. Smirnov)

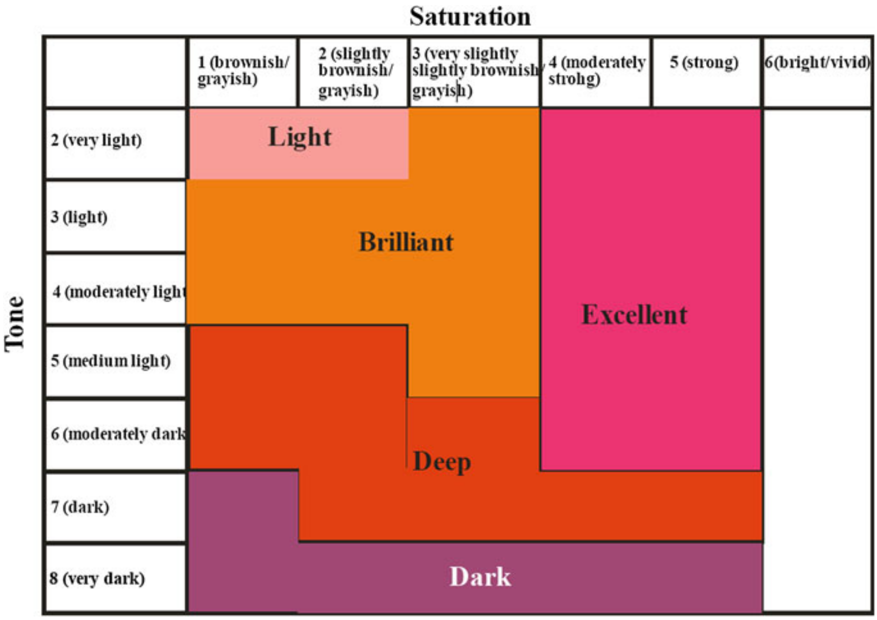


Fig. 4.17 The color system used for color grading of Imperial Red diamonds

(Vins et al. 2005). Figure 4.17 shows the color categories of Imperial Red diamonds. The diamonds in light-to-medium tones and moderately strong-to-strong saturations appear more attractive and are ascribed to the category *Excellent* (Fig. 4.16b). Brownish-red diamonds in medium-light-to-light tones are placed into the category *Brilliant*. The diamonds in moderately dark-to-very dark tones are determined as *Deep* and *Dark*. Weaker saturations refer to lighter grades and stronger saturations—to darker grades.

Radioactivity

During the enhancement process, Imperial Red diamonds are irradiated with high energy electrons. The question, which could be asked, whether these diamonds have residual radioactivity. We examined several largest Imperial Red stones using standard radiometer/dosimeter ANRI-01-02-SOSNA used for the measurements of radioactive contamination of soil, food and household objects. This device detects all types of radiation including gamma- and beta-radiation. All tested diamonds showed the intensity of gamma-radiation from 8 to 13 microroentgen/h, which could not be distinguished from the intensity of the environmental irradiation of 10 microroentgen/h. The total intensity of gamma- and beta-radiation had the same value. Thus, Imperial Red diamonds have been shown to possess no residual radioactivity.

Pink

Occasionally, HPHT treatment changes brown color of some type IIa diamonds to pink (Collins 2003; Kitawaki 2007). Pink diamonds represent a very small fraction of HPHT-treated diamonds on the market because of rarity of the appropriate starting type IIa material (Hall and Moses 2000). These specific diamonds are brown type IIa diamonds, the absorption spectrum of which is dominated by the Brown absorption continuum and two absorption bands at 550 (the Pink Band) and 390 nm (the Violet Band). Although the intensities of these bands do not correlate, the Pink Band is always accompanied by the 390 nm band and it is their combination, what provides the characteristic color of pink type IIa diamonds (Fisher 2009). The conversion of brown diamonds to pink during HPHT treatment occurs due to reduction of the Brown absorption continuum and stimulation of the 390 and 550 nm bands (Burns et al. 2000a).

Traces of the Pink Band can be found in almost every brown type IIa diamond. However, in order to produce reasonable pink color by HPHT treatment, the absorption strength of the Pink Band must be at least 0.5 cm^{-1}. The Pink Band of this intensity is clearly seen over the background of the Brown absorption continuum in untreated brown diamonds and it is an indicator of the suitability of diamond for treatment. Generally the intensity of the Pink Band is not reduced by the optimal HPHT treatment and the development of pink color occurs via weakening of the Brown absorption continuum (Vins and Yelisseyev 2010).

In order to achieve pink color in initially brown type IIa diamonds, they must be annealed at a specific temperature, which in most cases ranges from 2,000 to 2,100 °C. This temperature may be higher for diamonds of darker brown color. Schmetzer (2010) reports that medium brown diamonds acquire pink color when annealed at a temperature of 2,300 °C under a pressure of 8 GPa for 18 min, whereas initially light brown stones are converted into colorless by the same treatment.

Figure 4.18 shows that fast weakening of the Brown absorption continuum and strengthening of the Pink Band occur in a narrow temperature range of 1,900–2,200 °C. It might well happen that the vacancies released from the dissolved vacancy clusters are captured by some unknown defects/impurities and

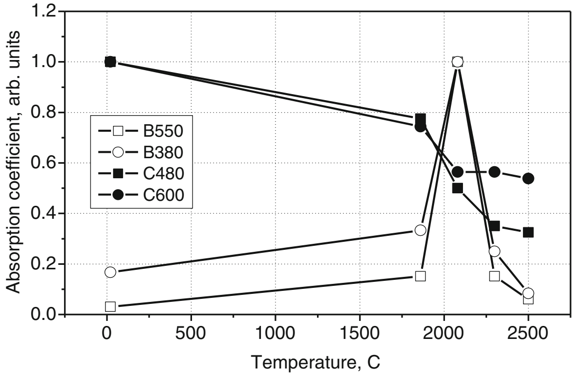


Fig. 4.18 Change in relative intensities of the brown absorption continuum (at wavelengths 490 and 600 nm), the *Pink Band* (at wavelength 550 nm) and the *Violet Band* (at wavelength 390 nm) in type IIa diamond versus temperature of HPHT treatment. Sharp increase in the intensity of the *Pink* and *Violet Bands* occurs at about 2,100 °C, when the brown absorption continuum experiences the maximum annealing rate [re-plotted from Fisher et al. (2009)]

form the defects responsible for the Pink Band. It could be that these defects are strongly distorted NV centers formed in the brown lamellae. Indeed, the absorption range of the Pink Band coincides with that of the NV^--center and both defects have similar temperature stability.

The defects responsible for the Pink Band are more temperature stable than most vacancy clusters producing the Brown absorption continuum. Therefore, the brown diamonds with the Pink Band in their absorption spectra can be converted to brownish pink or pink by appropriate HPHT treatment. The application of pressure during annealing is essential for the stability of the Pink Band. Our experiments show that high temperature annealing in vacuum may noticeably reduce intensity of the Pink Band.

HPHT treatment is successfully used for conversion of brown CVD diamonds into pink. The treatment parameters vary with the quality of the as-grown CVD diamond and the desired final color. Since CVD diamonds grow fast and they do not experience long-term annealing during growth, their brown color is not that stable as the brown color of natural diamonds. In many cases, considerable reduction of brown color of CVD diamonds is achieved by annealing at temperatures 1,400–1,700 °C, which do not require application of stabilizing pressure. Examples of production of pink CVD diamonds are given in (Twitchen et al. 2003). For instance, type IIa brown CVD diamonds (concentration of nitrogen 0.4–0.5 ppm) were converted to light pink brown, or light orangey pink after HPHT annealing at a temperature of 1,700 °C under pressure 6.5 GPa. Low-nitrogen brown CVD diamond with 3.8 ppm nitrogen was converted to pink after annealing at a temperature of 1,600 °C under pressure of 6.5 GPa (Kiflawi and Bruley 2000).

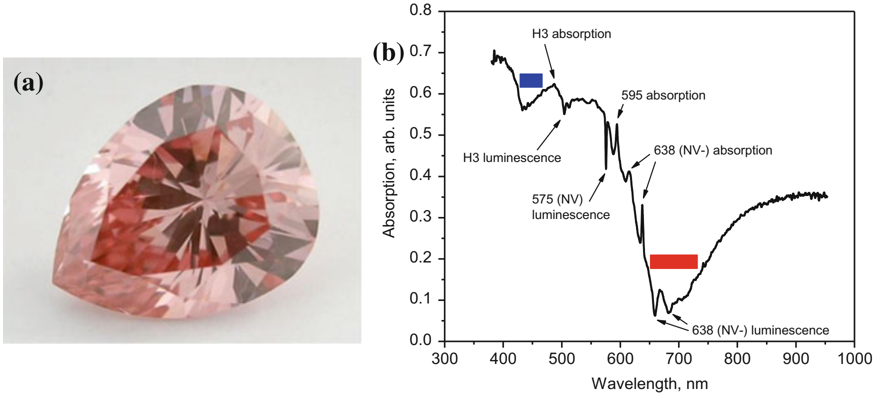


Fig. 4.19 **a** A low-nitrogen diamond (IaB with a few ppm B defects) treated by HPHT annealing followed by electron irradiation and low temperature annealing. **b** In FSI absorption spectrum of this diamond, strong 638 nm (NV^-) and N3 centers produce characteristic features of the "transmission" effect (negative absorption). The 575 nm (NV^0) center is seen in the regime of luminescence. The "red transmission" of the NV^- center and "blue transmission" of the N3 center considerably add to *pink color* of this diamond, when it is viewed in bright daylight. *Red* and *blue bars* show the "blue and red transmission" bands resulting in *pink color*

Pink color in diamond can be achieved by generation of optical centers other that Pink Band. Rarely high-nitrogen natural Ib diamonds had pink-brown color because of strong C defect absorption continuum and a broad absorption band at 610 nm. Breeding (2005) reports, that these diamonds may exhibit irregular color zoning and show no fluorescence when excited with standard UV lamp. However, these diamonds may exhibited weak green fluorescence with narrow brighter boundaries when observed in DiamondView.

Pink color can be induced in brown type IaB diamonds after multi-process treatment. In this case the required absorption is achieved by generation of the nitrogen-related optical centers and first of all the NV^- and N3 centers (Fig. 4.19). Low-nitrogen type IaB diamonds are the most suitable for the following reasons. Firstly, these diamonds have intense N3 center. Secondly, they do not produce too strong NV^- center, which otherwise would make diamond intense red. Thirdly, the dissociation of B defects with the formation of A defects in low-nitrogen diamonds is negligible and, consequently, the "red transmission" of the NV^- center and the "blue transmission" of the N3 center are pronounced.

Orange

Some HPHT-treated diamonds have distinctive orange color. The main reason of this coloration is intense absorption of H3 and/or H4 centers. Strong H3 center is a very common feature of HPHT treated type Ia diamonds, whereas strong H4 center is observed rarely in type IaB diamonds processed at low temperatures for short time and in type Ia diamonds after multi-process treatment. Majority of these stones have moderate nitrogen content and the H3 center is strong both in absorption and luminescence producing the "green transmission" effect. The influence of "green transmission" on the color of HPHT-treated orange diamonds is clearly seen when they are viewed alternatively under illuminations with different spectral content. Color of these diamonds may change from brown greenish-yellow under daylight to orangey-brown under incandescent light. These diamonds may be distinguished spectroscopically by strong H3, NV^0, NV^-, H1a, H1b and 595 nm centers (Reinitz 2007). It is possible that some of the treated orange diamonds have been irradiated and annealed after HPHT treatment. That is a multi-process treatment, similar to that used for the fabrication of Imperial Red diamonds, is employed. In this case, one may say that the orange color is a failed Imperial Red.

HPHT-treated orange diamonds are easily distinguished from their natural counterparts, which owe their orange color to a broad absorption band with maximum at 480 nm. Although the absorption spectrum of the 480 nm band well coincides with that of strongly broadened H3/H4 centers, these three centers do not relate to each other (Collins 2003; Kitawaki 2007). The defects responsible for the 480 nm band are tentatively ascribed to oxygen. The 480 nm band has not been yet reproduced in diamond artificially. Thus, the orange color induced by the 480 nm band can be reported as natural. However, since the 480 nm band is a temperature stable spectral feature, enhancement of the natural orange color can be achieved by HPHT treatment when the brown color component is removed.

HPHT-treated reddish-orange diamonds with NV defects should not be confused with rare natural type Ib diamonds of fancy reddish-orange color. The latter may have C defect content of 30 ppm and about 10 ppm A defects, which cause continuous absorption starting from about 600 nm and rising towards shorter wavelengths (Wang 2008).

Blue

Rarely, HPHT treatment results in blue color of originally gray and brownish gray type IIb diamonds. The nature of the HPHT-induced blue color is the same as for the natural one—the absorption continuum produced by boron acceptors. HPHT treatment does not induce the boron absorption, rather it reduces the concentration of the compensating defects and eliminates the absorption of the Brown absorption continuum, which, together with the boron absorption continuum produces uniform absorption over the whole visible range and, consequently, gray color. Thus, the absorption responsible for blue color is preexisting in natural gray diamonds (Okano et al. 2006; Kitawaki 2007; Overton and Shigley 2008). This behavior is similar to that of conversion of brown type IIa diamonds into pink. Yet the regimes of HPHT treatment for production of blue and pink colors may be very different. Boron is extremely stable defect in diamond and the blue color center stands annealing at any temperature. Therefore, the enhancement of blue color may be performed at very high temperatures capable of removal of all unwanted color centers. In contrast, the Pink Band is not a very stable feature and its optimal enhancement requires precise annealing at a certain temperature, which may not exceed 2,200 °C. Because of this peculiarity, well treated blue diamonds does not have brown modifying color, whereas HPHT-treated pink diamonds frequently exhibit remnants of brown tint in their color.

Another mechanism of induction of blue color in type IIb diamonds by HPHT treatment is the increase of concentration of uncompensated boron acceptors by placing the boron atoms in regular crystal lattice sites (Burns et al. 2000). Substitutional boron atoms are very stable defects in diamond lattice. No color change in IIb synthetic diamonds after HPHT treatment at 2,100 °C was reported in (Chepurov et al. 2008). No transformations of boron impurity in diamond were seen even after HPHT treatment at a temperature of 2,650 °C. Thus, the boron-induced blue color of natural type IIb diamonds cannot be affected by conventional HPHT treatment. Aggregation of boron atoms similar to that known for nitrogen is expected at extremely high temperatures only (Kupriyanov et al. 2008). Such temperatures, however, are not used for commercial treatment of diamonds.

The natural diamonds suitable for production of HPHT-treated blue color stones are rare. Thus, an HPHT-treated blue type IIb diamond is a rare event to encounter with (Hall and Moses 2000). A standard method of recognition of HPHT-treated diamonds is the examination of color of their phosphorescence. Red phosphorescence is characteristic of untreated diamonds, whereas blue phosphorescence is typical for HPHT-treated diamonds.

Natural diamonds of violet coloration may resemble blue ones. Nevertheless, the origin of blue and violet color is different. Violet color is caused mostly by high hydrogen content (Kitawaki 2007). This color cannot be induced by HPHT treatment and the violet color of natural diamonds can be safely reported as natural. Yet, like in the case with the boron-related blue color, HPHT treatment may intensify violet color too.

Gray

The studies of HPHT annealing of gray graphite-containing natural diamonds were reported in (Vins 2001). The mechanism of the defect transformation and the color change was proposed in (Vins and Kononov 2003). Gray color results from numerous micro-inclusions of graphite, which were formed during co-crystallization of diamond and graphite in the presence of hydrocarbons. The hydrogen atoms, released during the crystallization, form CH-radicals on the surface of diamond and on the lateral facets of graphite micro-crystallites. During HPHT annealing, when temperature reaches 1,900 °C, C–H bonds break and the released hydrogen atoms diffuse and form hydrogen-related optical centers. Because of the removal of hydrogen, the graphitic micro-inclusions lose their stability and convert into diamond via polymorphic re-crystallization. As a result, gray color disappears and the treated diamonds become more transparent.

HPHT treatment at moderate temperatures converts low-nitrogen gray diamonds into colorless/near-colorless. However, if the treatment temperature is 2,100 °C and above, or if the nitrogen content is high, the treated diamonds acquire yellow color (Vins and Kononov 2003). The origin of this yellow color is quite obvious. Since natural gray diamonds are preferentially of type IaA, HPHT annealing results in dissociation of A defects and formation of C defects. The

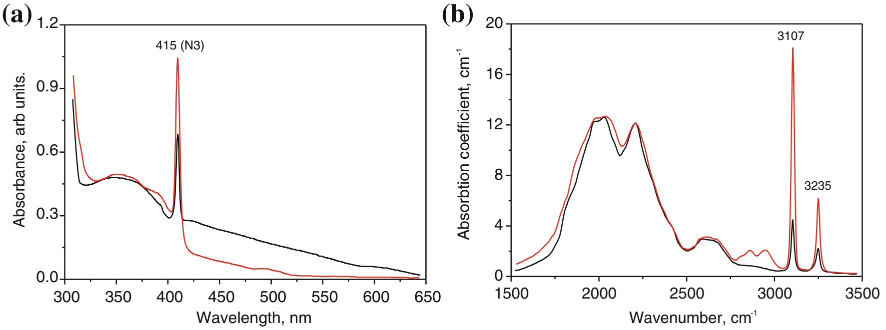


Fig. 4.20 Exemplary Vis (**a**), and IR (**b**) absorption spectra of initially gray type IaA diamonds before (*black curves*) and after (*red curves*) HPHT treatment at temperatures in the range 1,800–2100 °C under pressure 6–7 GPa. Treatment removes the absorption continuum in the visible spectral range and stimulates the C Defect absorption continuum, the N3 center and the hydrogen-related centers, the most intense being the 3,107 cm^{-1} line. *Gray color* of these diamonds is converted into *straw-yellow* [re-plotted from Vins and Kononov (2003)]

increase in concentration of C defects is seen as the strengthening of the C defect absorption continuum and deepening of yellow color.

Initially gray diamonds, converted by HPHT treatment into colorless or near colorless, do not reveal qualitative changes in absorption. However, IR spectra demonstrate a strong (over an order of magnitude) increase in the intensity of the hydrogen-related centers at 3,235, 3,107, 2,786 and 1,405 cm^{-1}. The 3,107 cm^{-1} center may reach strength of 30 cm^{-1}. A considerable increase in intensity of the N3 center and the C defect absorption continuum is observed too (Fig. 4.20). Since in natural type IaA diamonds intensity of the 3,107 cm^{-1} center almost never exceeds 5 cm^{-1}, very high intensity of this center (over 10 cm^{-1}) in type IaA near-colorless diamonds, which may show graphitic micro-inclusions, is a strong indicator of HPHT treatment of initially gray diamonds.

A specific feature of HPHT-treated initially gray type IaA diamonds is he formation of numerous narrow absorption lines in the spectral range of the A-, B- and C-centers. These lines may completely mask the nitrogen-related absorption.

Black

There are few reports on HPHT treatments aimed at obtaining diamonds of black color. It is believed that HPHT treatment may be more efficient in producing black color than annealing in vacuum. The mechanism of induction of black color is the internal graphitization. It seems that the point defects present in natural diamond do not affect their graphitization, whereas the extended defects play the main role (Hall and Moses 2001a).

“Light” black color, which is induced by graphite micro-inclusions, looks like dark gray. It is a very temperature-stable color and it cannot be easily reduced by HPHT annealing. In fact, the graphite-related gray color can be considerably enhanced by HPHT annealing performed at pressures in the range of stability of graphite. This makes the gray diamonds almost black. In contrast, dark gray coloration of non-graphitic origin and especially one induced by hydrogen-related defects may be removed by HPHT treatment.

4.6 Typical Defect Transformations During Commercial HPHT Treatment

Every natural diamond is unique in terms of its impurity-defect structure. Hence, the defect transformations during HPHT treatment and, consequently, the resulting impurity-defect structure and color, are unique for every diamond too. Although any natural diamond can be HPHT-treated, most diamonds used for commercial HPHT treatment belong to certain groups. The diamonds of each group have similar composition of impurities and intrinsic defects and they exhibit similar impurity-defect structure and color after HPHT treatment. These groups are defined as following.

4.6.1 Initially Brown Type IIa Diamonds

The aim of HPHT treatment of brown type IIa diamond is conversion them into colorless and pink. The percentage of type IIa diamonds in nature is very low. Accordingly, relative amount of colorless and pink type IIa diamonds is low too. However, since the recognition of HPHT treatment is most difficult for type IIa diamond and, because only type IIa diamonds can result in high colors after HPHT treatment, the brown type IIa diamonds are the most desirable and sought after starting material. We estimate that at present, at least 10 % of all cut high color high clarity type IIa diamonds are HPHT-treated. This amounts, however, is a negligible fraction of all cut diamonds in the market.

About 80 % of type IIa initially brown diamonds are converted by HPHT treatment into colorless. About 10 % acquire pink color and the rest 10 % become light yellow. To get pink color, the initially brown type IIa diamonds must exhibit intensity of the Pink Band absorption at least 0.5 cm^{-1} over the Brown absorption continuum background (Fig. 4.21b). If the Pink Band intensity is below 0.5 cm^{-1}, the diamond is converted into colorless (Fig. 4.21a). The yellow color is the result of formation of C defects, which can be detected in UV absorption (the 270 nm band) (Fig. 4.21c). Since in most type IIa diamonds brown color disappears completely after a short-time treatment at a temperature of 2,300 °C, these diamonds are rarely treated at higher temperatures. Therefore, the resulting impurity-defect structure of HPHT-treated type IIa diamonds is highly non-equilibrium and comprise defects formed of vacancies and impurity atoms at temperatures typically from 2,000 to 2,300 °C.

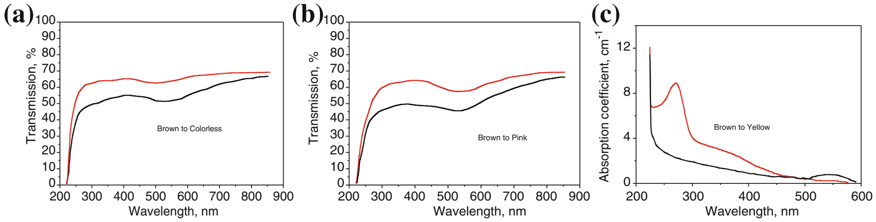


Fig. 4.21 Change in transmission/absorption spectra of initially brown type IIa diamonds after HPHT treatment at a temperature of 2,200 °C and a pressure of 7 GPa. **a** A low-nitrogen type IIa diamond with weak *Pink Band* is converted into colorless. **b** A low-nitrogen type IIa diamond with a *strong Brown* absorption continuum and a strong *Pink Band* is converted into *pink*. There is a tendency: the stronger the intensity of the initial brown absorption continuum the greater probability to obtain *pink color* after HPHT treatment. **c** A type IIa brown diamond with elevated nitrogen content is converted into a *yellow* one after HPHT treatment. The C defect absorption continuum and the 270 nm band dominate the spectrum

4.6.2 Initially Colorless Type IaAB Diamonds

Most colorless type Ia diamonds used for HPHT treatment are highly included. The aim of the treatment is to induce an intense fancy color, which could conceal the included interior. Hence, HPHT-treated type IaAB diamonds frequently have low clarity grade. Since HPHT treatment of type IaAB diamonds always induce in them yellow-green color, any colorless type IaAB diamond have definitely never been treated by HPHT annealing.

HPHT treatment of included type IaAB diamonds is rarely performed at temperatures over 2,300 °C. Very high temperature leads to too intense yellow color. Besides, high annealing temperature increases the risk of massive internal graphitization of included diamond and/or its fracture. The resulting color of initially colorless type Ia HPHT-treated diamonds is yellow because of the increased concentration of C defects. This yellow color resembles canary-yellow color of type Ib diamonds.

A feature of IR spectra of these diamonds is abnormal intensity of the Platelets peak, which is very weak in diamonds containing less than 400 ppm A defects, and very high in diamonds containing more than 400 ppm A defects. HPHT treatment does not change noticeably intensities of other optical defects (e.g., the N3 center) in these diamonds (Fig. 4.22).

Initially colorless type Ia diamonds are the starting material for the production of Imperial Red diamonds. The main distinguishing feature of Imperial Red diamonds is the NV^- center, which is very strong both in luminescence and absorption and has unproportionally low intensity of ZPL (e.g., Fig. 4.19b).

High temperature HPHT treatment of initially colorless type Ia diamonds converts them into very rare in nature ABC-diamonds. Therefore, type IaABb diamonds are very likely HPHT-treated.

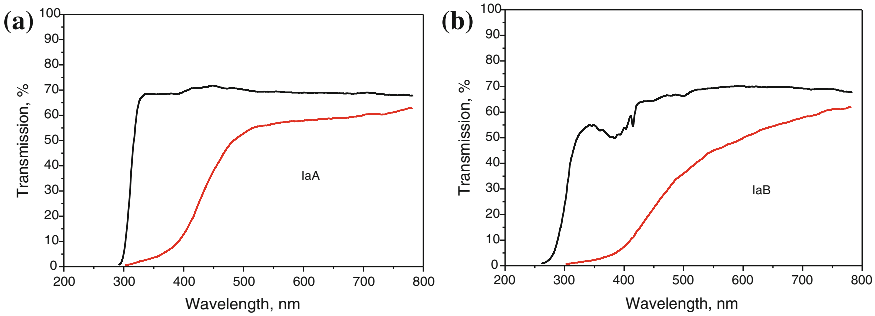


Fig. 4.22 Changes in transmission spectra of initially colorless type Ia diamonds after HPHT treatment: **a** type IaA>B, **b** type IaB>A. Both diamonds show no detectable H3 center. Strong C defect absorption continuum appears in spectra of both diamonds after treatment due to dissociation of A defects into C defects. The features of the N3 center are completely obscured by the C defect absorption continuum

4.6.3 Initially Brown Type Ia Diamonds

Initially brown type Ia diamonds are treated by HPHT annealing with the aim of conversion of their unattractive color into bright yellow-green. These diamonds can be treated in a broad temperature range from 1,800 to 2,500 °C. Considerable reduction of brown color and generation of dominating greenish-yellow color may occur at temperatures as low as 1,800 °C. The characteristic distinguishing feature of initially brown type Ia diamonds treated at low temperature is unusually strong H3 center in absorption and a very bright green fluorescence (Fig. 4.23). As the treatment temperature increases, the diamonds acquire more green color because of the increase in the absorption of the H2 center. After annealing at 2,200 °C, the dominating absorption features are the C defect absorption continuum and the H2 center and the resulting color acquires an orange modifier. Higher temperatures destroy the H3 and H2 centers and the remaining strong C defect absorption continuum makes diamond canary-yellow. The final result of the high temperature HPHT treatment of initially brown type Ia diamonds is ABC diamonds of intense yellow color—a very unusual combination for natural diamonds.

Initially brown type Ia diamonds are also used for the production of Imperial Red diamonds using multi-process treatment. In this case, however, the final color is affected by the absorption of the H3 and H2 centers. This additional absorption decreases transparency of diamond and the red color may lose its purity and brightness.

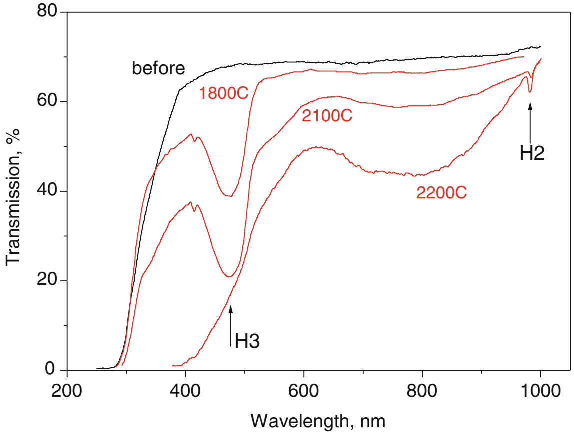


Fig. 4.23 Characteristic changes in transmission spectra of initially brown type Ia diamond treated at temperatures 1,800 °C, 2,100 °C and 2,200 °C. The dominating H3 and H2 centers produce broad absorption bands with maxima at wavelength 480 and 800 nm respectively. ZPL of the H2 center (a line at 986 nm) is pronounced after treatment at a temperature of 2,200 °C

4.6.4 Initially Brown Low-Nitrogen Type IaB Diamonds

HPHT treatment of initially brown type IaB diamonds is performed with the aim of production of near colorless diamonds and diamonds of pink color. In order to obtain near colorless stones, the starting IaB brown diamonds must contain nitrogen in concentration below 70 ppm. HPHT treatment at moderate temperatures considerably reduces brown color but does not produce much C and H3 defects, which otherwise would add excessive yellow color. Too much nitrogen and/or too high temperature of treatment (above 2,100 °C) generate intense C and H3 centers and the resulting color is greenish-yellow. In fact, high temperature annealing results in similar greenish-yellow color for almost any type Ia diamond irrespective of the aggregation state (compare Figs. 4.23 and 4.24).

Specific feature of high temperature HPHT treatment of initially brown type IaB diamonds is the increase in intensity of the N3 center. Absorption of the N3 center together with that of the C defect absorption continuum produces a yellow color which is different from that commonly produced in most HPHT-treated type IaAB diamonds. Intensity of this color depends on the total nitrogen content, but it is never too low not to be seen visually. In general, there is no HPHT treatment which could convert brown type IaB diamond into near-colorless if its nitrogen content exceeds 50 ppm.

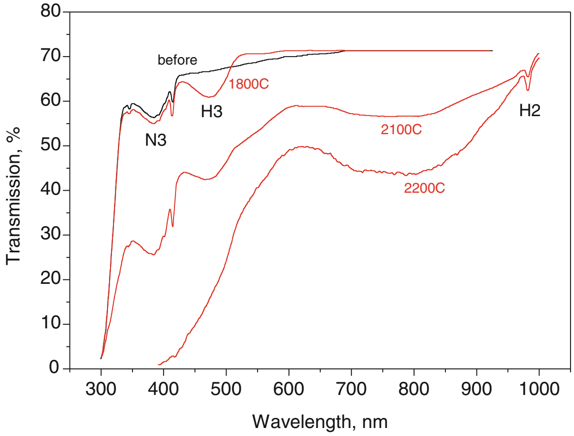


Fig. 4.24 Characteristic changes in transmission spectra of initially brown type IaB diamond treated at temperatures 1,800 °C, 2,100 °C and 2,200 °C. Formation of intense C defect absorption continuum and the H2 center (negatively charged H3 defects) occurs at temperatures above 2,100 °C. If the nitrogen content is low, treatment at temperatures below 2,100 °C reduces brown absorption continuum but does not produce intense optical centers in the visible spectral range. Thus, these treated diamonds look near-colorless

In order to convert initially brown type IaB diamonds into pink, multi-process treatment, similar to that used for production of red diamonds, is performed. The pink color is achieved by the superposition of the absorptions of initially present and strengthened N3 center and the induced NV^{-} center. Together these centers produce two transparency windows at wavelengths of 430 nm (blue) and 670 nm (red), what makes the diamond look pink.

Chapter 5
Structural Features of HPHT-Treated Diamonds

HPHT treatment, as a process performed under high pressure, is prone to inducing in diamond plastic deformation and mechanical damage. Since most natural diamonds are internally non-homogenous, the application of external pressure (even perfectly hydrostatic) may cause a considerable non-uniform stress through the diamond bulk. This stress, together with high temperature, produces macroscopic structural defects and areas of residual plastic deformation, which can be seen in optical microscope.

In HPHT-treated diamonds, the primary macroscopic flaws are surface graining, fractures, disk-shaped fractures surrounding non-diamond inclusions, grain lines, pinpoint inclusions, clouds, graphitization. Twinning lines are observed in many HPHT-treated diamonds too. However, they may not be readily seen in HPHT-treated diamonds of dark color. Pinpoint inclusions and clouds are seen as tiny dark or light crystal inclusions.

Since the ranges of pressure-temperature-time parameters of HPHT treatment and natural HPHT annealing are very different, the induced macro-defects and the characteristics of internal stress in HPHT-treated diamonds may differ from those observed in natural untreated stones. Understanding these differences is important for recognition of HPHT treatment.

HPHT-treated diamonds may display many visual features of treatment: graphitized inclusions, internal cleavages, damaged surfaces, enhanced birefringence. However, all these imperfections may be found in natural non-treated diamonds too. Hence, the presence of macrodefects alone cannot provide a solid support for reporting of HPHT treatment. In this regard, the structural features can be taken into account as "supporting" only. The most important of these features are discussed below.

5.1 Fractures and Cracks

During HPHT annealing, diamond, even when heated in the pressure-temperature range of plasticity, may experience cleavage. This HPHT-induced mechanical damage can be recognized in many ways. First of all, the HPHT-induced cleavage

I. A. Dobrinets et al., *HPHT-Treated Diamonds*, Springer Series in Materials Science 181, DOI: 10.1007/978-3-642-37490-6_5,

frequently follows the shape of the treated diamond. As a result, small cracks, radial fractures and other defects can be found around the girdle forming so-called "beard" (Buerki et al. 1999; Hainschwang 2001). The "bearded" girdles are especially pronounced in not thoroughly repolished HPHT-treated diamonds (Reinitz and Moses 1997). However, good repolishing easily removes this evidence of treatment (Chalain et al. 1999).

Another type of the HPHT-induced mechanical damage, which follows the diamond shape, is small half-moon cracks starting at the surface and propagating to a little depth. These cracks are especially indicative of HPHT treatment when located on the opposite sides of diamond.

Originally fractured diamonds can well withstand HPHT treatment without further extensive damage (Smith et al. 2000). However, the originally present fractures and cracks may change their appearance and these visual changes are a good indicator of treatment. High temperature may alter the internal structure of fractures and cracks, making them textured or "frosted" (Fig. 5.1a). This texture is the result of partial dissolution/etching of the crack surfaces. The cleavages, that reach the diamond surface, exhibit etching along their full extent (Wang et al. 2005).

Original fractures and cracks may be extended in size during HPHT treatment. This extension is seen as "fresh" bright outer fringes (Smith et al. 2000). The "old" cracks surrounded by "fresh" fringes are rarely observed in untreated diamonds and can be considered as a strong evidence of HPHT treatment. Originally bright and reflective natural fractures may get coarse ("frosted") texture and acquire bright transparent extension (fringes) after HPHT treatment. Very little or no graphitization may appear within these cracks.

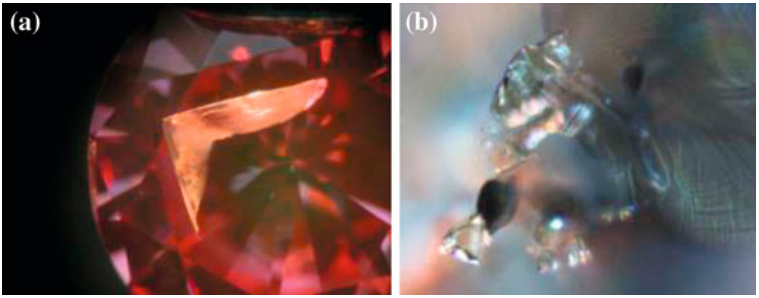


Fig. 5.1 **a** This crack observed in an HPHT-treated imperial *red diamond* has frosted appearance. This type of macroscopic defects is characteristic of imperial *red diamonds*. In some cracks, graphitization is present. Due to their frosty surface, these cracks do not reflect light, but scatter/disperse it and, as a result, are not easy to recognize (courtesy of S. Z. Smirnov). **b** The cracks accompanying the graphitic inclusion in this untreated diamond are clean and transparent

5.2 Inclusions

Cleavages, cracks, inclusions of non-diamond phases and other macro-defects are the places most vulnerable for the HPHT-induced graphitization. Pressure-temperature conditions used for commercial HPHT treatment are frequently set in the range of stability of graphite, what considerably stimulates the development of graphitization. HPHT-treated included diamonds frequently exhibit graphitization along internal fractures, surface-reaching cleavages and on the non-repolished facets (Fig. 5.2). A strong evidence of heating at high temperature is black inclusions surrounded by halo of outward radiating cracks, or graphitized fractures around the girdle (Kim and Choi 2005; Reinitz et al. 2000).

Natural diamonds were exposed to temperature-pressure condition well in the range of stability of diamond phase. As a result, natural diamonds do not show excessive graphitization in the bulk, or on the surface. The natural graphitization, which may appear at inclusions and cracks, does not show signs of exposure to high temperature. In contrast, many HPHT-treated diamonds exhibit traces of the graphitization characteristic of spontaneous conversion of diamond into graphite.

It was shown that type IIb synthetic diamonds exhibited extensive graphitization of the surface after heating at temperatures above 2,100 °C under stabilizing pressure 7 GPa, which leads then to the bulk graphitization. If the pressure applied during HPHT treatment is not sufficient for the stabilization of the diamond lattice, the complete graphitization of diamond at a temperature of 2,300 °C may occur in a matter of a minute (Chepurov et al. 2008). Graphitization is a particularly characteristic feature of very high temperature HPHT treatment. Kupriyanov and colleagues (Kupriyanov et al. 2008) reported that the annealing at a temperature of 2,650 °C for 1 h results in a considerable graphitization within fractures and on diamond surface.

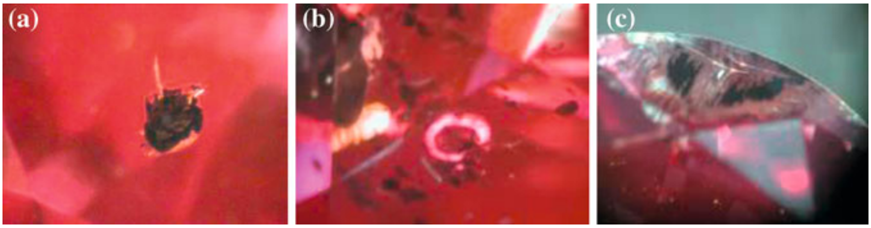


Fig. 5.2 Typical macroscopic defects observed in HPHT-treated diamonds. **a** This black inclusion is observed in an Imperial Red diamond. It is associated with the graphitized diamond-inclusion interface, which was formed during HPHT annealing. Several transparent micro-cracks were formed around the inclusion—a very characteristic feature of HPHT treatment. In most treated diamonds of dark colors, these inclusions are barely visible. Sometimes, the graphitized inclusions emerge on the diamond surface after repolishing and, when their interior crumbles out, leave characteristic caverns. **b** Disk-shaped fractures frequently surround black crystalline inclusions in HPHT-treated diamonds. **c** Sometimes the surface of fractures is stained by graphite, which forms during HPHT annealing (courtesy of S. Z. Smirnov)

Formation of non-diamond and graphitic phases may start in the damaged ("weak") places of the diamond crystal lattice at a temperature as low as 1,500 °C. This graphitization may develop even at stabilizing pressure above 7.7 GPa, which is high enough to keep perfect diamond into the range of its phase stability (Balzaretti and da Jornada 2003). Thus the internal graphitization on irregularities of crystal lattice may occur in diamonds even during low temperature HPHT treatment performed at high stabilizing pressure (Okano et al. 2006).

A coarsely textured graphitization may surround natural inclusions and spread along associated stress fractures. Graphitization is also seen along internal stress fractures, which are surrounded by narrow, highly reflective fringe (Wang et al. 2005).

Black graphitic inclusions are rather common in untreated type IIb blue diamonds. Though, they are less common for untreated yellow diamonds. These inclusions can be surrounded by a crack in a form of halo. In untreated diamonds, the surrounding halos may be thin and shiny, whereas in HPHT treated diamonds, they look sugary, frosty and textured (Gelb and Hall 2002). This "atoll"-like structure with sugary halo is a typical feature of HPHT treated diamonds. Formation of the cracks around inclusions is the result of development of high mechanical stress during heating and cooling of diamond because of the different coefficients of thermal expansion of diamond and non-diamond phases (Chalain 1999). Thus, the presence of inclusions with sharp edges and without any damaged periphery may be considered as a good evidence of untreated diamonds.

In some cases, the graphitization, as a recognition feature of HPHT-treated diamonds, may be misleading for some natural included diamonds may also reveal graphitized inclusions quite identical to those observed in treated stones. Wang reports (Wang et al. 2005) that the graphitization in structurally "weak" sites like interfaces between inclusions and host diamond may be found in many untreated diamonds, which show the evidence of plastic deformation (brown-pink diamonds) (Fig. 5.3). Similarly, tension fractures and graphitization around mineral inclusions frequently look alike in pristine and HPHT-treated diamonds. Thus, the microscopic examination of the graphitic features alone may not provide entirely persuasive evidence of treatment (Tretiakova 2009).

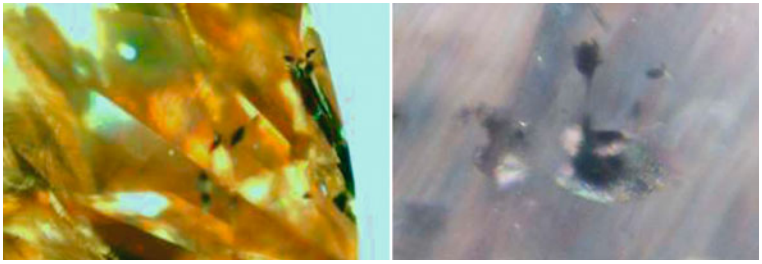


Fig. 5.3 Microscopic images of natural pink-brown diamonds showing natural graphitic inclusions. Some inclusions are surrounded by fringes, which look similar to those observed in HPHT-treated diamonds

Although the graphitization is a characteristic feature of HPHT treatment, it does not show up in many treated diamonds and especially in those of high initial structural perfection. When HPHT-treated diamonds do contain graphitized inclusions, one must take into account that majority of them were present in the diamonds before treatment and HPHT annealing might have only minor influence upon them. Thus the characterization based on the examination of inclusions has very limited capability (Smith et al. 2000; Overton and Shigley 2008). However, careful examination of the internal structure of the inclusions remains an important method of recognition of HPHT treatment for diamonds of "natural" resulting colors. It is of particular importance for type IIa colorless diamonds, the recognition of HPHT treatment of which is sometimes a real challenge even for the labs equipped with good spectrometers.

In spite of the seeming similarity of the natural and HPHT-induced graphitization, one may expect that some graphitic features do differ. Indeed, the graphitization of diamonds in nature occurs at relatively low temperatures for very long time, whereas during HPHT treatment, it is generated at high temperature for very short time. Unfortunately there are no systematic reports on these differences and no clear criteria of the recognition of the HPHT-induced graphitization can be established so far.

Along with graphitic inclusions, HPHT-treated diamonds may reveal some specific inclusions, the structure of which does not relate to direct graphitization. HPHT treatment is usually performed too fast and the pressure applied around diamond has a considerable non-hydrostatic component. Because of this, HPHT treatment, even when performed at pressures and temperatures of plasticity of diamond, may form cracks even in seemingly perfect diamond bulk. Creation of an inclusion by HPHT treatment inside inclusion-free diamond is not a frequent event, and the majority of inclusions observed in the treated stones are those initially present in them before treatment. However diamonds may have some extended irregularities of crystal lattice invisible in optical microscope. Such irregularities are the "weak" places, which may trigger development of more pronounced lattice destruction and convert the initially invisible defects in visible inclusions.

Fingerprint-like inclusions are the most common ones to encounter with in HPHT-treated diamonds (Fig. 5.4). They are formed in diamonds of different types. Although the "fingerprint" inclusions are associated with HPHT treatment, they can be also found in natural untreated type IIa diamonds of high color (Breeding 2006). Natural and HPHT-induced "fingerprint" inclusions look quite identical. Yet some minor differences in their structure can be recognized. In particular it concerns the "fingerprint" inclusions formed in the diamond interior.

HPHT treatment may result in mirror-like cleavages, etch channels and pinpoint inclusions (Hainschwang et al. 2002). Further examples of the inclusions, which are characteristic of HPHT-treated diamonds and which are not usually seen in natural untreated stones can be found in (Moses et al. 1999).

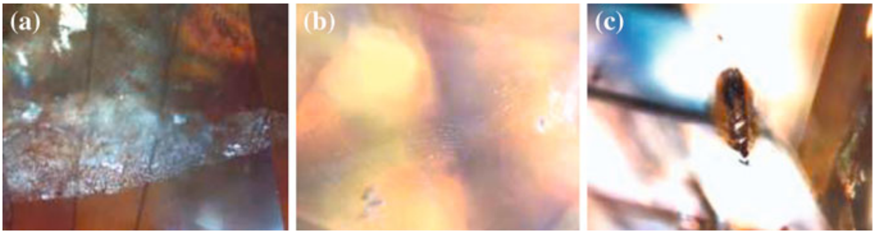


Fig. 5.4 **a**, **b** Fingerprint-like inclusions found in a *brownish-orangey-yellow* HPHT-treated diamond. The inclusions of this type can be also seen in untreated colorless to near-colorless diamonds [for further examples, see e.g., (Moses et al. 1999; Breeding 2006)]. **c** This fringed inclusion found in HPHT-treated diamond is a typical result of high temperature annealing of an included diamond. Inclusions of this type can be found in untreated natural diamonds too. Yet, their appearance in treated and untreated diamonds is usually different

5.3 Graining

Sometimes HPHT treatment induces in natural diamonds specific graining of greenish, yellowish, brownish and whitish colors. Appearance of this graining is different from the natural color graining observed in untreated natural diamonds. In HPHT-treated "apple green" diamonds, yellow or green graining may be seen along octahedral facets (Shigley 2001; Kitawaki 2007). Similar graining pattern, but in brown to yellow colors can be also observed along octahedral directions in many HPHT-treated type Ia diamonds (Reinitz 2007). Diamonds of yellow to green color dark in tone with brown to yellow planar graining oriented along octahedral directions are very likely HPHT-treated stones.

A whitish internal graining is also observed in HPHT-treated diamonds (Dale and Breeding 2007). This graining may lower the clarity grade of otherwise very high clarity diamonds (e.g., from IF to VVS1) (King et al. 2006; Dale and Breeding 2007). The whitish graining is detected in most HPHT-treated type IIa diamonds. Occasionally, along with the whitish graining, a specific brown graining can be seen too. This brown graining, however, is different in appearance from the natural brown graining and is often seen as a parallel banded pattern. Because of this graining, half of HPHT-treated type IIa diamonds may look slightly hazy when viewed in microscope (Moses et al. 1999).

The whitish graining can be seen in type IIa brown diamonds, which are used as starting material for HPHT treatment. This graining are not noticeably changed after treatment. Since the whitish/silvery graining is rather rare in untreated colorless type IIa diamonds (Smith et al. 2000), the stones revealing this graining must be checked for possible HPHT treatment. It is interesting that the diamonds with dense "cottony" whitish graining show also high lattice distortions in the X-ray topograms (Smith et al. 2000).

5.4 Surface Modification

Surface modification was one of the first features recognized in HPHT-treated diamonds. In 1997 Reinitz and Moses described a yellow-green treated-color diamond, which showed spectroscopic and microscopic features of HPHT treatment. That time, little was known about HPHT treatment and a conclusion was made that a "new" diamond treatment had been used during which the diamond had been "burned" (frosted areas on some facets, heavily bearded girdle). Indeed, HPHT annealing causes severe damage to the diamond surface. As-annealed diamonds always look translucent (Fig. 5.5), etched, pitted and carved with numerous graphitized micro-fractures. Frosted and pitted naturals, frosted feathers and frosted faceted girdles were reported in (Buerki et al. 1999; TM and IR 1999; Reinitz et al. 2000) as features of HPHT-treated diamonds (Fig. 5.6).

HPHT-treated diamonds are always repolished. If well done, the repolishing removes the damaged surface completely. Yet, sometimes the traces of etching can be recognized even on the repolished surfaces (Reinitz et al. 2000; Okano 2006) (Fig. 5.6c). Irrespective of the medium in which diamonds are HPHT annealed, their surface becomes damaged (Collins et al. 2000; Hainschwang et al. 2005; Okano et al. 2006). In contrast, natural surface of rough diamonds almost never have the appearance of the HPHT-treated surface. Therefore, when fused mark is recognized on the surface of a diamond, this diamond is suspected to be HPHT-treated. In contrast, if a diamond bears on its facets the remnants of naturals (natural growth surfaces) without traces of the high temperature etching, this diamond may be confidently reported as untreated (Reinitz et al. 2000; Shigley 2001; Okano 2006). However, some naturals may look similar to the HPHT-etched

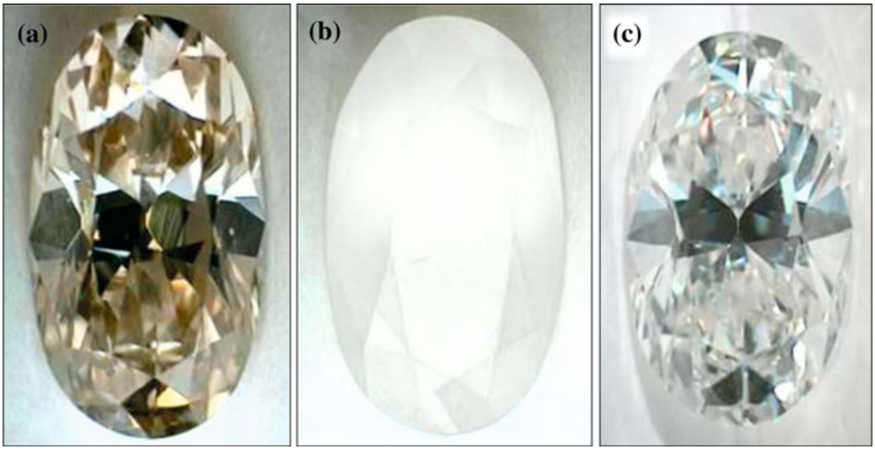


Fig. 5.5 HPHT processing of a type IIa natural brown diamond by Suncrest Diamonds USA **a** before processing, **b** as-treated, **c** after repolishing. (with permission of Suncrest Diamonds USA)

Fig. 5.6 **a** The facet junctions on either side of the upper girdle facets of this 0.59 ct HPHT-treated *green-yellow* diamond have a frosted, burned appearance, **b** strongly etched surface of non-repolished sites is an indicator of a high temperature HPHT treatment. Such a coarse etching is unlikely to encounter with on diamond naturals, **c** junctions of this small facet of an HPHT-treated diamond show traces of the frosted surface, which has not been completely removed by repolishing

facets. Therefore, "experience is necessary to distinguish burned features from the many textures that natural etching produces in diamond" (Reinitz et al. 2000).

Some HPHT-treated and repolished diamonds reveal the traces of the original facet junctions, which were etched during high temperature annealing. They are seen in microscope in polarized light as light lines stretching along the new facet junctions. These lines are more pronounced when viewed in fluorescence microscope under UV excitation (Fig. 5.7).

Surface etching is a very strong evidence of HPHT treatment and even alone it allows secure reporting of treatment. However, it can be found only on the surface of diamonds of poor cut and is almost never observed on well-cut stones. Hence, the detection of the surface modification has very limited applicability as the method of recognition of HPHT treatment.

5.5 Internal Stress

The development of internal stress during HPHT treatment is a complex process, which depends on the initial structural perfection of diamond, its type, the treatment temperature, and the hydrostaticity of the applied pressure. In many cases, commercial HPHT treatment may cause internal plastic deformations in diamond bulk. These deformations can be detected as internal stress, which causes strong birefringence patterns when viewed in polarized light (Kanda et al. 2005; Howell 2009) (Fig. 5.8).

Stress patterns of HPHT-treated type IIa diamonds are rather strong revealing first- and second-order interference of gray, blue or orange colors. The dominating colored interference is a feature of HPHT treatment (Chalain et al. 1999). In contrast, the birefringence patterns of natural untreated diamonds are usually less intense with dominating gray and brown colors. Although different in strength, the birefringence patterns of type IIa treated and untreated diamonds may look very

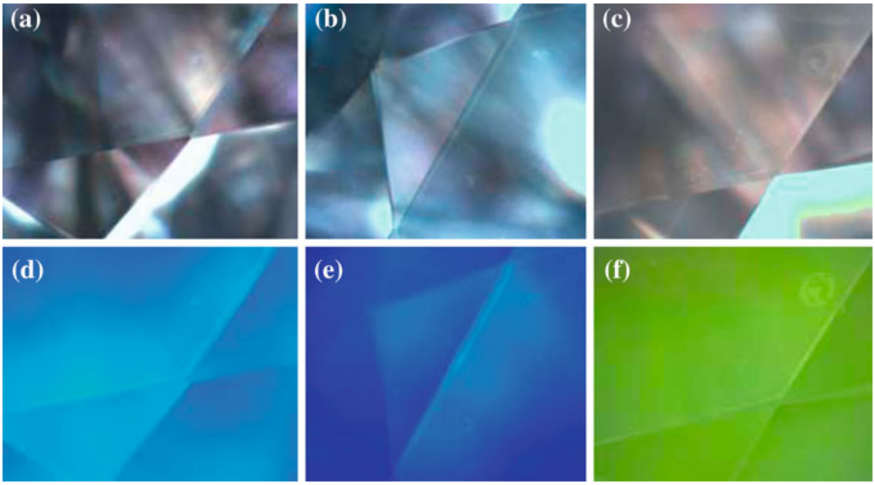


Fig. 5.7 The traces of original facet junctions seen on repolished HPHT-treated diamonds **a**, **b**, **c** images taken in polarized light, **d**, **e**, **f** same sites but viewed in fluorescence light under UV excitation of a mercury lamp. In the latter case, the whitish fluorescence lines running parallel to the new facet junctions are more distinct and may resemble "fluorescence cage" pattern (see Sect. 7.4. "Fluorescence Cage")

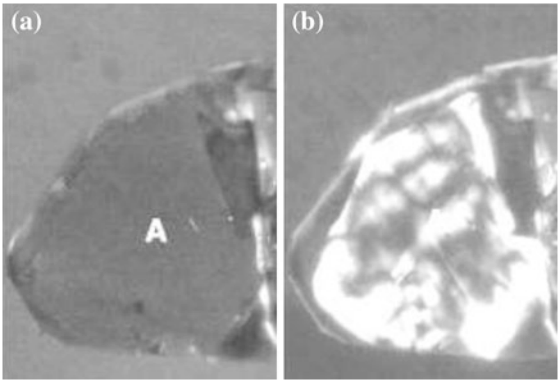


Fig. 5.8 Images of a synthetic type IIa diamond taken in polarized light before (**a**), and after (**b**) HPHT treatment performed at a temperature of 1,600 °C and a pressure of 6 GPa for 2 h. The image taken after HPHT processing reveals strong birefringence pattern due to internal strain produced by plastic deformation (Kanda et al. 2005) (with permission of Diamond and Related Materials magazine)

similar in terms of spatial distribution. For instance, the "tatami" strain pattern typical for natural type IIa diamonds is also a feature of many HPHT-treated diamonds (Moses et al. 1999). Thus, the recognition of the treated stones based on the birefringence method requires careful comparison of diamonds in treated and untreated states.

HPHT annealing may also cause the reverse process of reduction of internal stress in highly deformed diamonds. This effect was demonstrated on HPHT-treated polycrystalline CVD diamond. Because of the grain structure, as-grown polycrystalline CVD diamonds are highly stressed. HPHT annealing can considerably reduce this stress to a level of single crystal diamond (Kanda et al. 2003). Reduction of internal stress after HPHT treatment of natural brown type IIa diamonds was also shown spectroscopically as the reduction of non-homogeneous broadening of ZPLs of optical centers (Fisher et al. 2006). Comparative studies of the non-homogeneous broadening of ZPL of the GR1 center in untreated and HPHT-treated type IIa diamonds of brown color and colorless showed that brown diamonds are more internally stressed, and this stress is only partially relieved by HPHT treatment performed at a temperature of 2,500 °C. One may conclude that stress in natural brown type IIa diamonds is caused not only by the defects responsible for brown color (vacancy clusters). Dislocations and other defects extended defects are involved too. Destruction of vacancy clusters at high temperature does not result in their complete dissolving into single vacancies. Instead, the release of single vacancies is probably a side effect of the growth of large vacancy clusters at the expense of small ones and their collapse into dislocation loops and staking faults. These extended defects may well cause mechanical stress.

In case of nitrogen-containing diamonds, the evolution of internal stress during HPHT treatment can be considerably modified by the aggregation/dissociation processes of nitrogen defects. Unfortunately we do not possess any reliable data, which would allow us to predict this influence. Yet, we expect that in high-nitrogen brown diamonds, the internal stress increases after HPHT treatment. An example of this increase in type IaB diamonds is shown in Fig. 5.9. However, there is an opposite example of the unchanged internal stress in type IaA diamonds subjected to HPHT treatment (Fig. 5.10).

So far, not much information is available on the birefringence of HPHT-treated diamonds. Thus this method cannot be considered as a confident one for reporting HPHT treatment. However a strong, mottled strain pattern with high order interference observed in a high-color type IIa diamond is very unusual and can be considered as an indicator of HPHT treatment (Moses et al. 1999; Smith et al. 2000).

5.6 Dislocations

TEM studies revealed no significant changes in the density of dislocations, or dislocation distribution in initially brown type IIa diamonds upon HPHT treatment at temperatures up to 2,500 °C (Willems et al. 2006). A conclusion has been made that brown diamonds do not owe their color to dislocations (Fisher et al. 2006). This result is in a strong contradiction with the observations of other researchers who reported a drastic decrease of the dislocation density in natural brown diamonds after HPHT annealing (Mora et al. 2005; Vins et al. 2006; Vins et al. 2008).

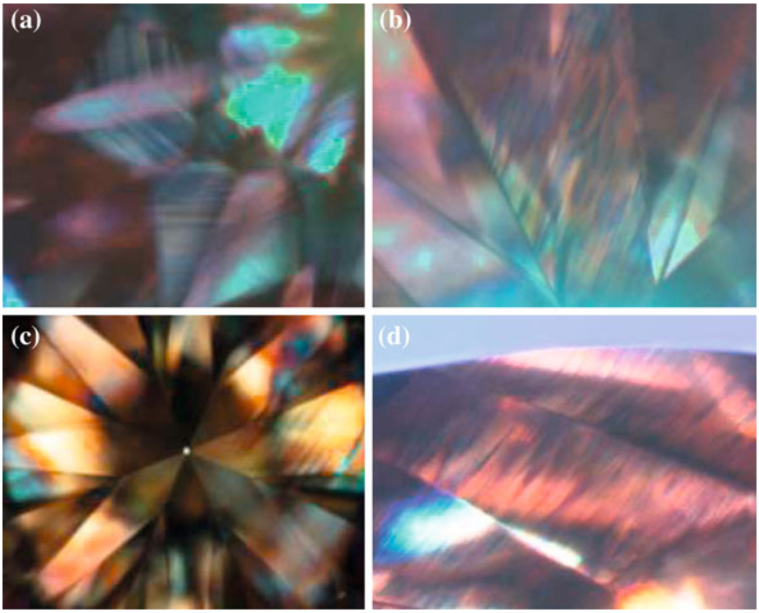


Fig. 5.9 Images of HPHT-treated diamonds taken in polarized light from the table side. Birefringence patterns due to the HPHT-induced internal stress are clearly seen **a**, **b**—two type IaB fancy purplish pink diamonds, **c**—type IIa, D color diamond, **d**—type IIa, brown-pink diamond. It is interesting that this diamond also shows the "fluorescence cage" effect—a very rare occasion for treated type IIa diamonds

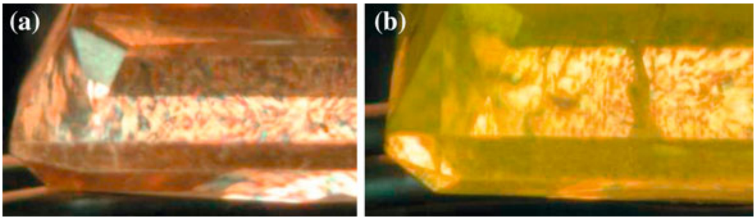


Fig. 5.10 Birefringence patterns of a type IaA > B diamond before (**a**), and after (**b**) HPHT treatment (courtesy of D. Simic). HPHT treatment has not changed the strength and distribution of the internal stress

Dislocation density may decrease by three to five orders of magnitude after HPHT treatment performed at temperatures from 2,300 to 2,500 °C (Mora et al. 2005; Vins and Yelisseyev 2008a).

It was found that dislocations in diamond become mobile at a temperature of 1,800 °C (Vins et al. 2006). Vins and colleagues (Vins et al. 2008) discussed the role of dislocations in formation of brown color diamonds and showed that the mobility of dislocations could be very different in different diamonds and especially in diamonds with different level of internal plastic deformation. The activation energy of motion of dislocations was found to be as high as 6.4 eV in plastically deformed diamonds and only 2.2–2.6 eV in non-deformed diamonds. Thus the very different behavior of dislocations in HPHT-treated diamonds is probably not due to the differences in the annealing temperature used for treatment, but very likely due to the presence of other defects, which work as dislocation stoppers. Thus the influence of HPHT treatment on the dislocation density must be considered taking into account the presence of other defects.

Natural type IIa, IIb and IaB diamonds are characterized by dislocation networks spreading in different directions (three-dimensional networks). These networks can be observed under short wavelength UV excitation in DiamondView luminescence microscope. HPHT-grown synthetic diamonds reveal much more perfect crystal structure as compared with that of natural diamonds and they do not exhibit the dense dislocation networks. CVD diamonds have dislocations aligned parallel to the growth directions (De Corte et al. 2006). Since HPHT treatment at high temperatures may reduce the dislocation density drastically, the observation of dense dislocation networks speaks in favor of untreated diamond.

Chapter 6
Spectroscopic Features of HPHT-Treated Diamonds

Optical properties are the most important characteristics of gem diamond. The unique optical transparency and high refraction index are the optical properties, which make diamond the premium gemstone. Color is also a very important parameter of gem diamond, and the color enhancement of diamond is the subject of HPHT treatment.

Color of diamond is determined by the optically active defects, which absorb light in the visible spectral range. When performing HPHT treatment, the parameters of the HPHT annealing are set at values optimal for generation of the desirable defects and/or removal of undesirable ones.

In absorption and/or luminescence spectra, optically active defects produce specific spectral bands, which are called optical centers. The optical centers in the visible spectral range and the corresponding defects are known as color centers. The absorption and luminescence spectral bands usually spread over a spectral range of a few tens of nanometers and frequently have complex structure. This spectral structure is unique for each optical center. Structure of the spectral bands of most color centers are determined by electron–phonon interaction and therefore these bands are frequently called electron–phonon bands. Usually, each electron–phonon band has one characteristic narrow line, which is known as zero-phonon line (ZPL). Frequently, ZPL is also the most intense feature in the spectrum when recorded at cryogenic temperatures. Commonly, optical centers are labeled by the spectral positions of their ZPLs. Spectral position of ZPL of any optical center coincides in absorption and luminescence spectra. However, the spectral position (as well as the spectral structure) of the electron–phonon band of a center recorded in absorption and luminescence are very different. In absorption, the electron–phonon band spreads from ZPL towards shorter wavelengths, whereas it spreads from ZPL towards longer wavelength in luminescence. For instance, NV^--center (also known as the 638 nm center) has ZPL at a wavelength of 638 nm. ZPL of the NV^- center is accompanied by an electron–phonon band spreading from 638 to about 800 nm in luminescence and from 638 nm to about 500 nm in absorption.

Optically active defects in diamond can be of different origin. Intrinsic defects are composed of carbon atoms in irregular lattice sites (interstitials) and/or vacant

I. A. Dobrinets et al., *HPHT-Treated Diamonds*, Springer Series in Materials Science 181, DOI: 10.1007/978-3-642-37490-6_6,

lattice sites (vacancies). Extrinsic (or impurity-related) defects contain impurity atoms. Intrinsic/extrinsic nature of the optically active defects is the key factor in understanding their transformations during HPHT processing, and consequently, in understanding HPHT-induced color changes.

Commonly, intensity of an optical center is used for the estimation of content of the corresponding defects. In general, intensity of an optical center measured in absorption and luminescence do not correlate. The intensity in absorption uniquely depends on the defect concentration. In contrast, the intensity in luminescence strongly depends on many other parameters and as such it may not follow the defect concentration. An example of this divergence is very different luminescence efficiency of NV centers in type IaB and IaA diamonds. Nitrogen A defects are very effective luminescence quenchers. Thus, equal concentration of NV defects produces high luminescence intensity of the NV centers in type IaB diamonds and much lower in type IaA diamond. However, their absorption intensities are equal. The quenching efficiency of the A defects fast increases with their concentration. A 15 % decrease in luminescence intensity is expected in diamonds containing 100 ppm A defects, whereas the presence of A defects in a concentration of 300 ppm may quench luminescence by two orders of magnitude.

The changes produced in the defect structure of diamond by HPHT treatment can be readily detected as changes in optical spectra. In most cases, it relates to the changes in intensity of optical centers. In some cases, the changes in electron–phonon structure are observed too. Since many of these changes are very specific of HPHT annealing, optical spectroscopy appears to be the most reliable method of identification of HPHT-treated diamonds. The luminescence spectroscopy is of special importance. It is the most sensitive and informative technique of all spectroscopic methods. Some centers are very effective in luminescence and they can be used for detection of the corresponding defects in concentrations as low as 1 ppb. This uniquely high sensitivity is a great advantage of the luminescence spectroscopy in recognition of HPHT-treated type IIa diamonds with very low impurity content. Even when used alone, luminescence spectroscopy allows to make confident conclusion in the most challenging cases, e.g. in case of structurally perfect type IIa diamonds.

By now, many optical centers are known as relevant to HPHT treatment. They are the centers either directly involved in the HPHT-induced color changes, or the centers used for characterization and recognition of HPHT treatment by spectroscopic methods. Below a detailed discussion of these centers is given.

6.1 Optical Centers in UV-Vis-NIR Spectral Range

The optical centers relevant to HPHT treatment are detected in a broad spectral range covering wavelengths from 230 to 20,000 nm. However, the most populated spectral range is UV-Vis-NIR spreading from 230 to 1000 nm. Most of the optical centers in this range are active both in luminescence and absorption.

236 nm (the N9 center)

The 236 nm line is the strongest feature of the N9 nitrogen-related optical system. The N9 center is almost always detected in HPHT-treated diamonds, even in those of the highest color. The presence of the N9 center is an evidence that nitrogen impurity is in a highly aggregated state, which takes place in most HPHT-treated diamonds. When observed in type IIa diamonds, it can be considered as an indicator of HPHT treatment (Smith et al. 2000). However, natural type IIa diamonds frequently reveal a weak type IaB character, so these diamonds can show the N9 center even when untreated.

251.2 and 254.2 nm

These two lines are observed in PL spectra of brown type IIa diamonds. They are destroyed by HPHT treatment at relatively low temperatures (in the range of temperature stability of the NV centers) (Smith et al. 2000). Presence of the 251.2 and 254.2 nm centers is an indicator of untreated diamonds.

260, 270 and 285 nm (the 2DB center)

The 2DB center is a characteristic feature of brown natural diamonds. HPHT treatment induces the 2DB center, which is readily detected in CL spectra. The 2DB center is probably related to defects produced by plastic deformation (Kanda et al. 2005). The center is frequently seen in natural type IIa diamonds. The 2DB center has moderate temperature stability. However, the 2DB center may be induced by HPHT treatment performed at low temperatures of 1,600 °C. The 2BD center (as well as the 5RL center, see below) disappears from CL spectra of type IIa natural diamonds after HPHT treatment at moderate and high temperatures (Kanda and Watanabe 2004). The 2DB and 5RL centers, when observed simultaneously with the free exciton emission, can be considered as a proof that diamond has not been HPHT-treated at high temperature. This is especially relevant for diamonds showing evidence of plastic deformation (Kanda and Watanabe 2004) (Fig. 6.1).

263.9, 265.1, 267.3, 277.4, 286.0 and 291.6 nm

These multiple lines are observed in PL spectra of brown type IIa diamonds. They are destroyed by HPHT treatment at relatively low temperatures (in the temperature range of stability of the NV centers) (Smith et al. 2000). Presence of these lines in PL spectrum of a natural diamond can be considered as indication that this diamond is not HPHT-treated.

270 nm Band

A broad absorption band with maximum intensity at a wavelength of 270 nm is produced by electronic transitions from the valence band to the nitrogen C defects (Fig. 6.2). Traces of this band are detected in almost all HPHT-treated diamonds, even in type IIa diamonds of D color. Although the 270 nm band may be occasionally found in untreated type IIa diamonds, this feature is a strong indicator of HPHT treatment (Smith et al. 2000). The 270 nm band is induced by HPHT treatment even in very low-nitrogen diamonds. Since the electronic optical

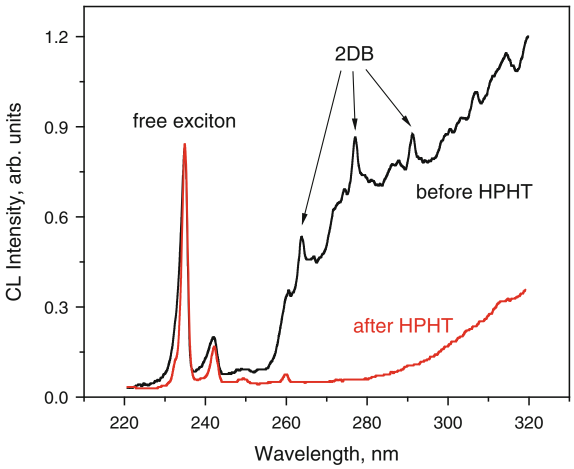
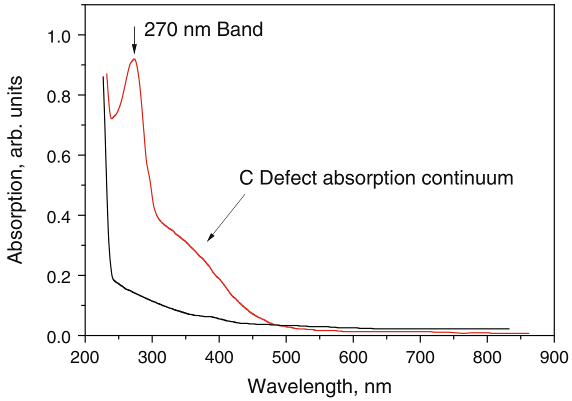


Fig. 6.1 Cathodoluminescence spectra of a natural type IIa diamond before (*black curve*) and after (*red curve*) HPHT treatment performed at a temperature of 2,000 °C under pressure 6 GPa [based on data from (Kanda and Watanabe 2004)]. Narrow free-exciton line observed after treatment suggests the reduction of internal stress

Fig. 6.2 Room temperature absorption spectrum of an initially brown type IIa diamond before treatment (*black curve*) and after HPHT treatment (*red curve*). After treatment, the spectrum is dominated by the 270 nm band [based on the data from (Fisher et al. 2006)]



transitions are much more effective than the phonon optical transitions, the 270 nm band can be seen in diamonds with concentration of C defects as low as 0.01 ppm, what is much below the detection limit of C defects by IR absorption spectroscopy. Normally, untreated type IIa brown diamonds do not reveal the 270 nm band, whereas after HPHT treatment at temperature of 2,500 °C, 60 % of them may exhibit the 270 nm band of an intensity corresponding to a concentration of C defects at a level of 0.1 ppm (Fisher et al. 2006). Thus, the detection of the 270 nm band in colorless or near colorless type IIa diamonds can be considered as a strong evidence of HPHT treatment.

It is most difficult to prove the origin of color of initially brown type IIa diamonds, which have been converted by HPHT treatment into colorless. Fortunately, many of

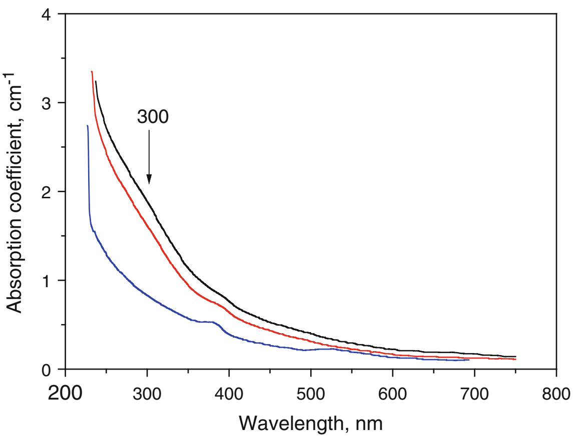


Fig. 6.3 Absorption spectra of a type IIa brown diamond before treatment (*black curve*) and after HPHT annealing at a temperature of 1,850 °C for 1 h (*red curve*) and a temperature of 2,080 °C for 1 h (*blue curve*) [re-plotted from (Fisher et al. 2009)]. The 300 nm band stands temperature 1,850 °C, but it is destroyed by temperature 2,080 °C

these diamonds contain small amount of nitrogen predominantly in form of B defects and do not reveal dispersed nitrogen detectable by optical spectroscopy. HPHT treatment generates enhanced concentration of C defects, which is evidenced by the 270 nm band absorption (Collins 2003). Simultaneous presence of traces of B-center, rather developed 270 nm band and a detectable A-center is very unnatural for untreated diamonds and therefore implies HPHT treatment. On the other hand, high-color low-nitrogen diamonds, which have no 270 nm center and yet exhibit a weak IR absorption of A- and B-defects, are definitely non-treated (Smith et al. 2000).

300 nm Band

A broad absorption band with maximum at a wavelength of 300 nm is observed on the background of the Brown absorption continuum in spectra of brown type IIa diamonds (Fig. 6.3). The 300 nm band stands HPHT treatment at temperatures of 1,850 °C, but disappears after treatment at temperatures of 2,080 °C and above (Fisher et al. 2009). The presence of the 300 nm band indicates that diamond has not been subjected to high temperature HPHT treatment.

389 nm center

The 389 nm center is a nitrogen-related, interstitial-type center frequently excited in cathodoluminescence spectra of natural and synthetic diamonds (Fig. 6.4). The 389 nm center may also relate to dislocations. The center is easily destroyed by HPHT treatment at temperatures 1,800 °C and above (Kanda and Jia 2001). A possible reason for this destruction is strong reduction of concentration of dislocations after HPHT treatment. In some cases, however, HPHT annealing may not affect the dislocation content in originally brown diamonds. Therefore in these diamonds, the 389 nm center may be observed after treatment too. In natural type IIa diamonds, the 389 nm center can survive short time annealing in vacuum at temperatures up to 1,650 °C. The presence of the 389 nm center is an indicator that diamond has not been subjected to high temperature HPHT treatment.

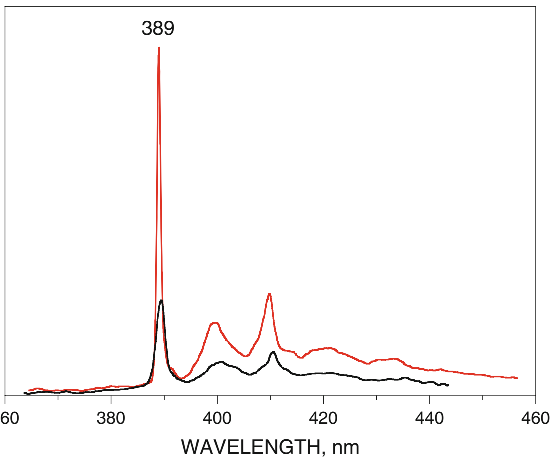


Fig. 6.4 Luminescence spectra of the 389 nm center measured on irradiated diamond at room temperature (*black curve*) and LNT (*red curve*). The center has a very characteristic electron–phonon band with two main maxima at wavelengths 400 and 410 nm

400 nm (3.1 eV) center

The 400 nm center is observed in absorption spectra. It relates to a Ni-containing defect. The 400 nm center anneals out at a relatively low temperature of 1,700 °C (Yelisseyev and Kanda 2007). Thus this center is an indicator of untreated diamond.

404.8, 405.5 (406), 409.6 and 412.3 nm centers

These four centers are active in PL of natural diamonds. They are frequently observed in natural type IIa diamonds (Gaillou et al. 2010; Titkov et al. 2010; Simic and Zaitsev 2012). Many natural untreated brown type IaA diamonds may exhibit the 406 nm center (Fig. 6.5a). The 406 nm center is also a common feature of natural pink type IaAB diamonds (Gaillou et al. 2010) (Fig. 6.5b). All these

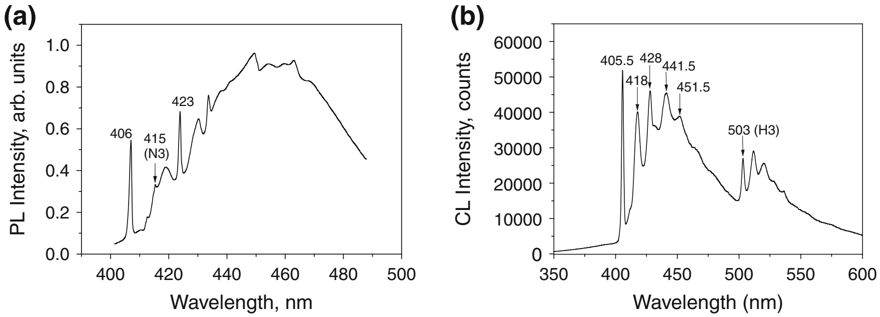


Fig. 6.5 **a** PL spectrum of an untreated natural type IaA brown diamond exhibiting dominating 406 and 423 nm centers. All the features of the spectrum but a weak 415 nm line (the N3 center) are vibronic replica of the 406 and 423 nm centers [re-plotted from (Nadolinny et al. 2009)]. **b** CL spectrum taken from the area of an individual pink grain in a natural pink diamond of type IaAB. The 406 nm center is one of the dominating features. All marked lines but 503 nm line (the H3 center) are vibronic features of the 406 nm center [re-plotted from (Gaillou et al. 2010)]

centers are destroyed by HPHT treatment at relatively low temperatures. Although the maximum temperature of stability of these centers is unknown, it is believed that their presence is a signature of untreated natural diamonds (Smith et al. 2000; Nadolinny et al. 2009).

415.2 nm (the N3 center)

The N3 center is one of the first optical centers of diamond studied spectroscopically. Atomic structure of the N3 center is well known. It includes three neighboring substitutional nitrogen atoms bound to a common vacancy (N_3V defect) (Fig. 6.6).

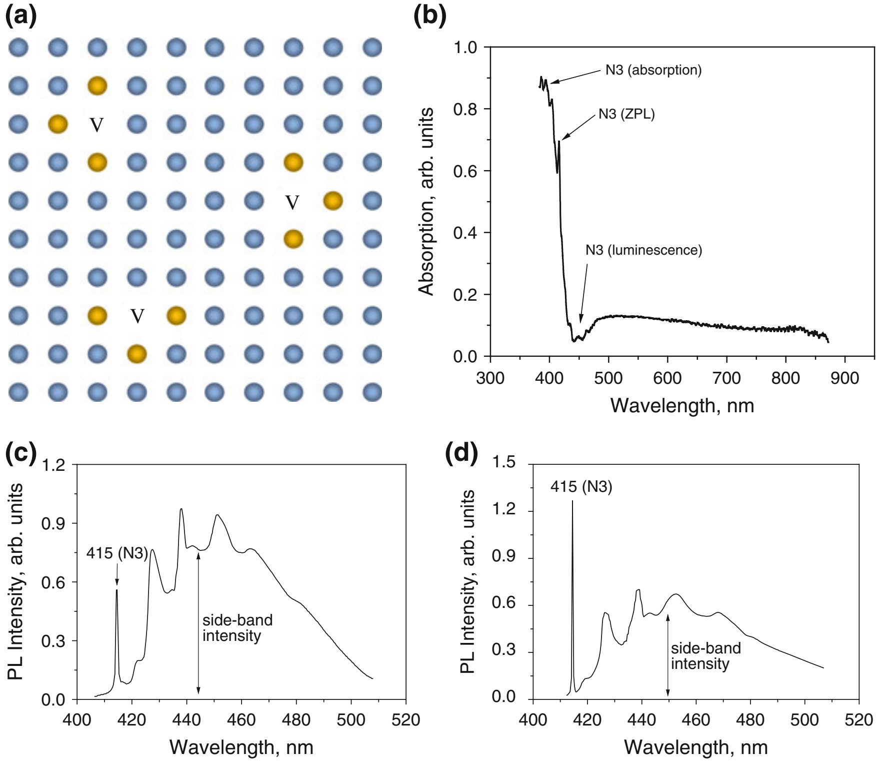


Fig. 6.6 **a** Atomic model of the N3 center: three adjacent substitutional nitrogen atoms bound to a common vacancy. *Blue* and *yellow circles* denote carbon and nitrogen atoms respectively. **b** Absorption spectrum of a natural diamond showing strong N3 center in regime of absorption and luminescence ("blue transmission" effect). High color (F) of this diamond is partially due to blue luminescence of the N3 center. **c** PL spectrum of the N3 center in natural untreated type IaB diamond. ZPL intensity in its maximum is lower than that of the side-band because of considerable non-homogeneous internal stress in this diamond. **d** PL spectrum of the same diamond as in (**c**), but after HPHT treatment performed at a temperature of 2,000 °C [re-plotted from (Nadolinny et al. 2009)]. Now ZPL intensity in its maximum is stronger than that of the side-band. This seeming increase in the intensity of ZPL occurs because of its spectral narrowing after treatment

Vast majority of natural diamonds exhibit N3 center in optical spectra, both in regimes of absorption and luminescence. Along with the N3 center, the N_3V defects produce optically active vibronic transitions at a wavelength of 477.6 nm. This feature at 477.6 nm, known as the N2 center, is active in absorption only. The N3 and N2 centers are observed together with correlated intensities. The absorption of the N3 and N2 centers cause a characteristic yellow color and the diamonds of this color are known as “cape yellow” diamonds. The N3 center is very effective in luminescence and it is the major contributor to the blue luminescence of most natural diamonds excited with UV light. Some diamonds with high intensity of the N3 center exhibit visible blue luminescence even under daylight illumination. This luminescence may be strong enough to cause diamond look bluish. Occurrence of this effect is similar to the effect of “green transmission” of the H3 center (see below) and therefore can be termed as “blue transmission” for the N3 center.

Behavior of the N3 center during annealing is typical for diamond optical centers related to impurity-vacancy complexes: its intensity first increases with temperature and then the center may anneal out. This behavior is especially pronounced in natural brown diamonds subjected to HPHT treatment. The N3 center may be completely quenched after heating at a temperature of 2,500 °C (Mora et al. 2005). However, no change in intensity of the N3 center is observed in type IaA initially colorless diamonds after HPHT treatment at a temperature of 2,100 °C (Vins and Yelisseyev 2008). Also in colorless (without plastic deformation) type Ia diamonds, HPHT treatment performed at temperatures 1,800–2,300 °C does not change intensity of the N3 center (Vins and Yelisseyev 2010). Equally, formation and enhancement of the N3 center was not observed in CO_2 and pseudo CO_2 diamonds after HPHT treatment at a temperature of 2,000 °C (Hainschwang et al. 2005).

In type Ia diamonds, some increase in intensity of the N3 center can be observed after low temperature HPHT treatment at about 1,800 °C, when strong H3 center is generated but no H2 center is formed yet (Collins 2001). The N3 center is considerably enhanced in type IaA gray diamonds after HPHT treatment at temperatures 1,800–2,100 °C: the higher the temperature the stronger the increase (Vins and Kononov 2003; Nadolinny et al. 2009). The N3 center is also generated and strongly increases in intensity in type Ib synthetic diamonds at temperatures of 1,800 °C and above (Kanda and Jia 2001). In originally brown type IIa diamonds, a considerable increase in the luminescence intensity of the N3 center is observed after treatment at a temperature of 2,300 °C and above (simultaneously with the removal of the H3 center). This increase may be particularly strong in type Ia diamonds (Collins et al. 2005). Simultaneously with the generation of the N3 center a little reduction of absorption intensity of the B defects is observed too (Vins 2002; Vins and Kononov 2003). Thus the vacancies released in plastically deformed brown diamonds during HPHT treatment may be one of the main reasons of the formation of the N3 center.

Although N3 center may change its intensity after HPHT annealing and it can be even annealed out at very high temperatures, commercial HPHT treatment does not influence considerably intensity of the N3 center. At least, these changes are small enough to influence the yellow color of HPHT-treated type Ia diamond (Vins et al. 2008).

Irradiation destroys the N3 center. High-nitrogen type IaAB diamonds heavily irradiated with electrons or neutrons and then HPHT annealed at a temperature of 2,300 °C exhibit too low concentration of N_3V defects to be detected in absorption as the N3 center. However, the concentration of N_3V defects can be sufficient to produce luminescence. Hence some diamonds treated with irradiation and HPHT annealing may still exhibit considerable N3 center in cathodoluminescence (Collins et al. 2005).

A slight narrowing of ZPL of the N3 center (from about 0.42 to 0.35 nm, when measured at liquid nitrogen temperature) occurs after HPHT treatment. This effect is obvious in diamonds treated at temperatures of 2,000 °C and above (Smith et al. 2000; Nadolinny et al. 2009). However, it must be kept in mind that the spectral width of ZPL of optical centers strongly depends on the structural perfection of crystal lattice. Therefore the numbers given above should be taken as qualitative parameters. Indeed, perfect untreated diamonds may exhibit very narrow ZPL of the N3 center, the spectral width of which is within the range characteristic for treated stones. Yet a very broad ZPL of the N3 center (over 0.45 nm) is a solid indicator of untreated diamonds. Spectral broadening reduces the peak intensity of narrow lines. Therefore broadened ZPL always shows lower relative intensity in its maxima as compared with their narrow counterparts. Practically, one may consider ZPL of N3 center as well broadened when its pick intensity is less than the intensity of the vibrational side-band. Correspondingly, ZPL, the pick intensity of which is well above the intensity of the vibrational side-band, is very narrow and this fact should be considered as an indication of possible HPHT treatment (Fig. 6.6c, d).

The increased intensity of the N3 center and its narrow ZPL (as well as broad ZPL of the 638 nm center) are not a very reliable means of detection of HPHT treatment (Smith et al. 2000). Yet the diamonds with strong and well resolved N3 center must be thoroughly tested for possible HPHT treatment.

Concentration of N_3V defects in ppm (N3[ppm]) can be estimated using the following relations [based on the original data of the authors and the data taken from (Davies 1999; Davies et al. 1992)]:

$$\mathrm{N3[ppm]} = 0.2\ \mathrm{I}_{\mathrm{ZPL-N3}}\left[\mathrm{cm}^{-1}\right],$$

where $\mathrm{I}_{\mathrm{ZPL\text{-}N3}}[\mathrm{cm}^{-1}]$ is the absorption intensity of ZPL of the N3 center in cm^{-1} recorded at LNT, or,

$$\mathrm{N3[ppm]} = 0.2\ \mathrm{I}_{393\,\mathrm{nm}}\left[\mathrm{cm}^{-1}\right],$$

where $\mathrm{I}_{393\ \mathrm{nm}}$ is the absorption intensity of the N3 center in cm^{-1} at a wavelength of 393 nm measured at RT. When using this formula, the background absorption underlying the N3 center absorption must be subtracted.

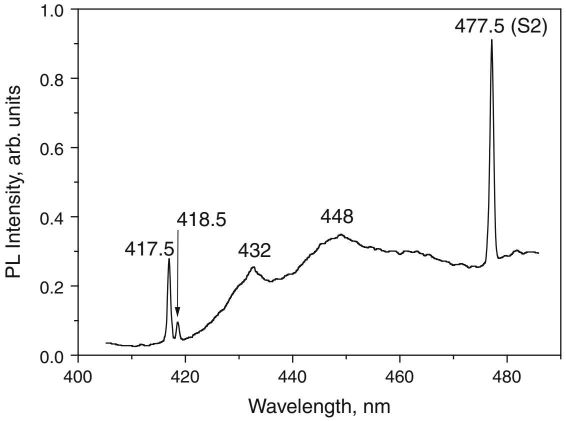


Fig. 6.7 PL spectrum of a synthetic diamond HPHT-treated at a temperature of 1,700 °C. The 417.5 nm center and S2 center are dominating features in the spectrum [re-plotted from (Yelisseyev and Kanda 2007)]

417.5 nm center

A center with doublet ZPL at wavelengths 417.5 (major line) and 418.5 nm is observed in spectra of untreated natural and synthetic diamonds (Fig. 6.7). This center is described as optical transitions on Ni-related defects (Yelisseyev and Kanda 2007). In PL spectra of natural diamonds, the 417.5/418.5 nm center usually accompanies the N3 center. The 417.5 nm center is stimulated by HPHT treatment performed at a temperature of 1,700 °C. However, it is destroyed at temperatures of 1,900 °C and above (Yelisseyev and Kanda 2007).

421.3, 423.0 and 430.9 nm centers

These three lines are observed in PL spectra of brown type IIa diamonds. They are destroyed by HPHT treatment at relatively low temperatures (in the range of temperature stability of NV centers). Presence of these centers is a good indicator of non-treated type IIa diamond (Smith et al. 2000) (Fig. 6.5).

439 nm center

The 439 nm center is observed in luminescence spectra of natural type I diamonds. It is especially pronounced in CL. The 439 nm center can be created, or, when naturally present, strongly enhanced by HPHT treatment. In type Ib diamonds, this center is enhanced simultaneously with the N3 center (Collins et al. 2005).

467 nm center

The 467 nm center is observed in PL spectra of CVD-grown and some natural diamonds. The center anneals out after low temperature HPHT treatment (Crepin et al. 2012). The 467 nm center is a feature of untreated diamonds.

470 nm (the TR12 center)

The TR12 center is a characteristic intrinsic radiation center of diamond. Its temperature stability is rather low, not exceeding 800 °C. The TR12 center is observed both in absorption and luminescence spectra. However, luminescence, and especially cathodoluminescence, is the most sensitive technique for detection of the TR12 center. It is believed that the presence of the TR12 center is a reliable indicator that diamond has not been heated at temperatures above 800 °C (De Weerdt and Van Royen 2000; Zaitsev 2002). Though, it must be kept in mind that the TR12 center can be re-introduced in HPHT-treated diamonds by low dose electron irradiation and subsequent annealing at temperatures 400–600 °C.

473.5 nm center

The 473.5 nm center relates to a nickel-containing defect. It is observed in absorption spectra of natural untreated diamonds (Chalain 2003). The 473.5 nm center is readily generated in Ni-containing diamonds by low temperature HPHT treatment at temperatures of 1,700 °C and its intensity increases with further HPHT treatment at temperatures over 1,900 °C (Yelisseyev and Kanda 2007). Presence of an intense 473.5 nm center is an indicator of possible HPHT treatment.

477.6 nm (the N2 center)

The N2 center is a vibronic transition at N_3V defect otherwise detected as the N3 center (see the 415 nm center) (Fig. 6.8). The N2 center is active in absorption only. Strong N2 center causes intense yellow color of type Ia diamonds (so-called “cape yellow” diamonds). The N2 center is not considerably affected by HPHT treatment, however, an increase in the intensity of the N2 center can be observed in HPHT-treated diamonds.

477.5 nm (the S2 center)

The S2 center is an optical transition at a complex defect containing Ni and N atoms. Secondary ZPLs related to the S2 center are at wavelength 489.1 and 523.3 nm. The S2 center is observed in PL and absorption spectra of untreated natural and synthetic diamonds (Chalain 2003) (Fig. 6.9). It has been established that the S2 center is generated during high temperature annealing (both in nature and in laboratory) (Lang et al. 2007; Yelisseyev and Kanda 2007). The center is

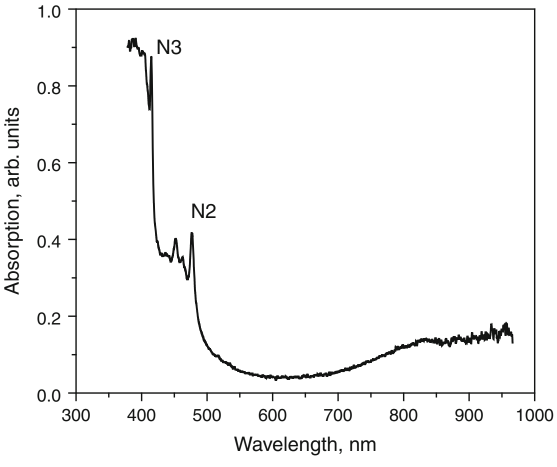


Fig. 6.8 Absorption spectrum of a fancy intense yellow type IaAB diamond showing strong absorption of the N2 and N3 centers. The spectrum was measured at liquid nitrogen temperature

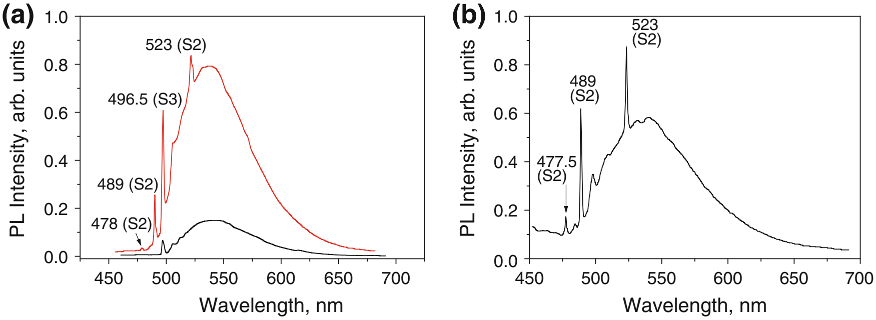


Fig. 6.9 **a** PL spectra of two synthetic diamonds: as-grown (*black curve*) and after HPHT annealing at temperature 1,900 °C and pressure 6.5 GPa for 16 h (*red curve*) [re-plotted from (Mudryi et al. 2004)]. HPHT annealing increases intensity of the S3 center and induces pronounced S2 center. **b** PL spectrum of the S2 center excited in a natural diamond. Note relatively structureless phonon side-band of the S2 center [based on data from (Lang et al. 2007) and (Yelisseyev and Kanda 2007)]

readily seen in diamonds heated at a temperature of 1,700 °C and its intensity increases with further HPHT treatment at temperatures over 1,900 °C (Yelisseyev and Kanda 2007; Mudryi et al. 2004). Although frequently seen in spectra of natural untreated diamonds, the S2 center of high intensity is an indication of possible HPHT treatment.

479 nm center

The 479 nm center is ascribed to a Ni-related defect. It is detected in absorption. The 479 nm center is generated by heating at 1,700 °C and it increases in intensity with further HPHT treatment at temperatures over 1,900 °C (Yelisseyev and Kanda 2007). Intense 479 nm center is an indicator of possible HPHT treatment.

480 nm (2.6 eV) Band

The 480 nm absorption band is a structureless broad feature showing no ZPL (Fig. 6.10). The 480 nm band is tentatively ascribed to electronic transitions on substitutional oxygen atoms (Hainschwang et al. 2008). Theory predicts a 480 nm optical band to be generated by positively charged substitutional oxygen atoms in diamond lattice (Gali et al. 2001). The 480 nm band is a common absorption feature of highly saturated orangey-yellow to yellowish-orange type I diamonds with moderate concentration of A- and C-defects. This band is also seen in spectra of chameleon and canary-yellow diamonds (Collins and Mohammed 1982; Neal 2007; De Weerdt and Van Royen 2001).

The defects responsible for the 480 nm absorption band are also active in PL producing a broad band with a maximum at 680 nm and a characteristic multi-peak vibronic structure (Fig. 6.10b) (Hainschwang et al. 2012). The 680 nm band is very effective in luminescence and is readily observed even in low-nitrogen colorless diamonds in which the 480 nm absorption band is below the detection limit. Both the 480 nm absorption band and the 680 nm luminescence band are

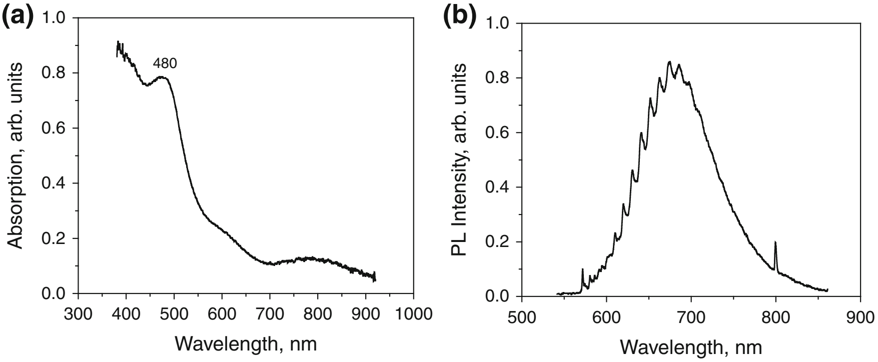


Fig. 6.10 **a** FSI absorption spectrum of a natural diamond showing strong 480 nm absorption band. Note that the band does not show any fine structure and covers a spectral range from 440 to 550 nm. A decrease in absorption intensity at wavelengths about 680 nm is the luminescence analog of the 480 nm band. **b** PL spectrum of a deep brownish orangey-yellow natural diamond with 680 nm structured band, which is the luminescence analog of the 480 nm band

observed in spectra of CO_2 and pseudo-CO_2 diamonds. ZPL of the 680 nm band is vanishingly small and cannot be detected directly. However, its position is expected to be at a wavelength of 565 nm.

In natural diamonds, the defects causing the 480 and 680 nm bands are confined to brown zones. In colorless zones these defects are not present. It is interesting, that the colorless zones without 480/680 nm bands may exhibit weak GR1 center.

All diamonds with well developed 480 nm band exhibit bright yellow luminescence under long wave UV excitation (Collins 1982). This luminescence is not attributed to the 480 nm band, but to a different center which is weak in absorption but always accompanies the 480 nm band. The 680 nm band, when strong, is observed in absorption spectra in the luminescence mode ("transmitter" effect) (Fig. 6.10a). Thus the luminescence of the 680 nm band can add red modifying tint to diamond color. Luminescence of the 680 nm band can be especially strong in Ni-containing natural diamonds.

In CO_2 and pseudo-CO_2 brown diamonds, the 480 nm absorption band increases in intensity after HPHT treatment performed at a temperature of 2,100 °C. In natural diamonds exhibiting pronounced Y-center, the absorption 480 nm band and the luminescence 680 nm band can reveal high intensity after irradiation and high temperature HPHT annealing (Hainschwang et al. 2012) (Fig. 6.11b). This behavior is in contrast with that observed in plastically deformed brown diamonds (Hainschwang et al. 2008). Enhancement of the 480 nm band during heating at high temperature may be accounted for by the transfer of oxygen into interstitial positions. The 680 nm band stands HPHT treatment at 2,100 °C (Hainschwang et al. 2008).

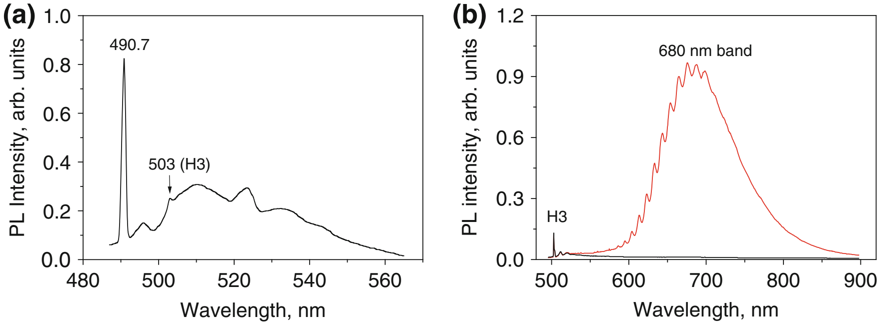


Fig. 6.11 **a** PL spectrum of a natural type IaA brown diamond exhibiting intense 491 nm center. All features of the spectrum but weak 503 line (the H3 center) are vibronic replica of the 491 nm center [re-plotted from (Nadolinny et al. 2009)]. **b**. PL spectra of a type Ib natural diamond exhibiting dominant Y center in IR absorption, before (*black line*) and after (*red line*) treatment by electron irradiation and HPHT annealing at a temperature of 2,250 °C [re-plotted from (Hainschwang et al. 2012)]

482 nm center

The 482 nm absorption center is attributed to a Ni-containing defect. This center is destroyed by HPHT treatment performed at a temperature of 1,800 °C (Lawson and Kanda 1993). The 482 nm center can be considered as an indication of untreated diamonds.

488 center

The 488 nm Ni-related center is observed in PL spectra of untreated natural and synthetic diamonds. It can be generated by HPHT treatment performed at a temperature of 1,700 °C and its intensity increases after further HPHT treatment at temperatures over 1,900 °C (Yelisseyev and Kanda 2007). Intense 488 nm center is an indication of possible HPHT treatment.

489.1 nm (the S2 center)

See 477.8 nm (the S2 center).

490.7 nm (the 491 nm center)

Many brown type IIa (with traces of B defects), IaB and IaAB diamonds exhibit luminescence of the 491 nm center, which can be especially strong in CL spectra (Figs. 6.11, 6.13a). The 491 nm center is always present in PL spectra of untreated natural type IaA diamonds. This center originates from some defects formed in plastically deformed diamonds (Collins 2001; Collins et al. 2005). The 491 nm center is observed only in diamonds showing the presence of B defects. In natural untreated plastically deformed type IaA diamonds, the 491 nm center is always accompanied by the 423 and 406 nm centers, which disappear after HPHT treatment (Nadolinny et al. 2008).

The 491 nm center considerably reduces its intensity after HPHT treatment even performed at low temperatures (in the range of temperature stability of the

NV centers). At temperatures of 1,700–1,800 °C, the 491 nm center anneals out completely. Pressure does not change temperature stability of the 491 nm center. In brown type Ia diamonds, the center anneals out at the same temperature of 1,700 °C, when heated in vacuum or atmospheric pressure (Collins et al. 2005). Decrease in intensity of the 491 nm center is accompanied by strong growth of the H3 and N3 centers and reduction of a broad band with maximum at 740 nm (Collins et al. 2000, 2005; Collins 2001, 2003; Nadolinny et al. 2009).

Generation of the 491 nm center in type IaB diamonds by plastic deformation at high temperature was shown in (Brookes et al. 1993). However, the creation or enhancement of the 491 nm center during commercial HPHT treatment is unlikely. Hence, the 491 nm center can be considered as a good indicator of untreated diamonds (Smith et al. 2000; Van Royen and Palyanov 2002; Nadolinny et al. 2009).

491.5 nm center

The 491.5 nm center is observed in absorption. It relates to a Ni-containing defect. The 491.5 nm center is destroyed by HPHT treatment performed at a temperature of 1,800 °C (Lawson and Kanda 1993). Presence of this center is an indicator of untreated diamonds.

494 nm (2.51 eV) center

The 494 nm absorption center relates to a Ni-containing defect. It is destroyed by HPHT treatment at a temperature of 1,700 °C (Lawson and Kanda 1993; Yelisseyev and Kanda 2007). However, 494 nm center was found in absorption spectra of synthetic diamonds, which might be exposed to HPHT treatment performed at much higher temperatures in the range 2,000–2,200 °C (Shigley et al. 1993). So far the 494 nm center cannot be considered as an indicator of untreated diamonds.

494.5 nm center

The 494.5 nm center is observed in PL spectra of untreated brown diamonds. The center is destroyed by HPHT treatment and it is not re-introduced by subsequent irradiation and conventional annealing (Simic and Zaitsev 2012) (Fig. 6.12). The 494.5 nm center is a good indicator of untreated diamonds.

496.2 nm, the H4-center

When nitrogen B defect captures a vacancy, it is converted into a N_4V_2 defect, which, when in neutral charge state, produces the H4 center. These defects in negative charge state are known as the H5 center (Vins et al. 2011b). Spectrum of the H4 center are similar to that of the H3 center with the exception of the positions of their ZPLs (496 nm for the H4 center and 503 nm for the H3 center) (Fig. 6.13). ZPL of the H4-center in absorption must not be confused with the first vibrational replica of the H3 center: both lines almost coincide at a wavelength of 495 nm. The spectral similarity of the H3 and H4 centers is especially obvious in luminescence.

The H3 center is a very frequent and distinctive feature of spectra of natural diamonds, whereas the H4 center is usually very weak. The H4 center is especially weak in absorption and it is not detected in absorption spectra of most natural

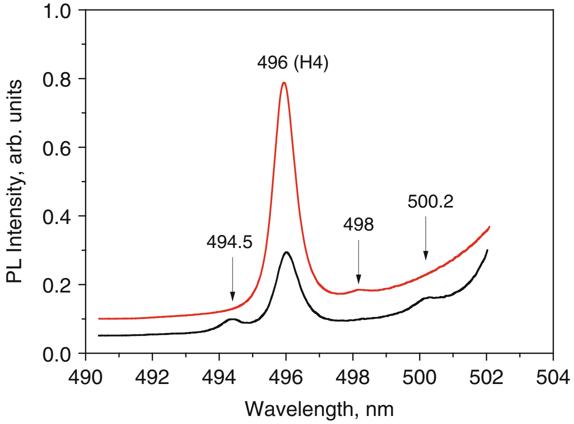


Fig. 6.12 PL spectra of a treated "pink" diamond showing change in intensity of the 494.5, 496 (H4), 498, and 500.2 nm centers after multi-process treatment (*black curve*—before treatment, *red curve*—after treatment). The 494.5 nm center is not seen after treatment. In contrast, a weak 498 nm center is generated by irradiation and annealing. These spectra were recorded at liquid nitrogen temperature with excitation at a wavelength of 488 nm (Simic and Zaitsev 2012)

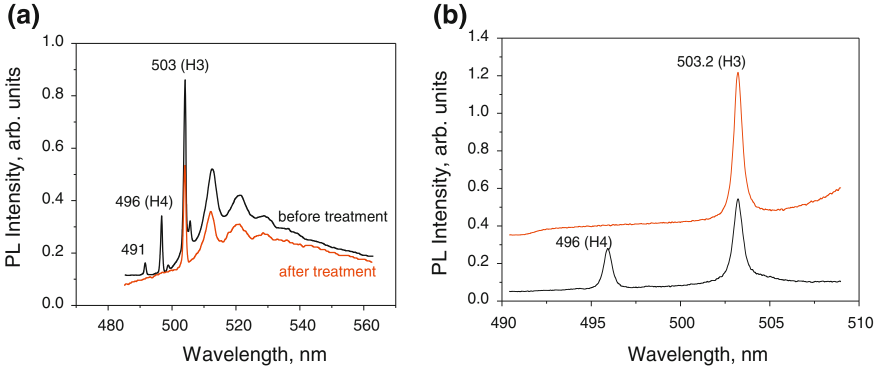


Fig. 6.13 PL spectra of a type Ia (**a**) and type IIa (**b**) diamonds before (*black curves*) and after (*red curves*) HPHT treatment. The H4 center completely disappears after treatment [re-plotted from (Anthony et al. 1999; Simic and Zaitsev 2012)]

diamonds. Naturally colored diamonds, even those of type IaB, never show intense H4 center in absorption (Collins et al. 2000; Collins 2003). In contrast, in PL spectra, the traces of the H4 center are detected in eventually every natural diamond (Anthony et al. 1999).

In natural diamonds, the defects responsible for the H4 center are located preferentially close to the surface, which could be irradiated. Thus the center is almost never observed in absorption of cut diamonds after their "skin" has been removed (Collins 1982). The influence of the H4 center on diamond color is similar to that of the H3 center, save for the “green transmission” effect, which has never been reported for the H4 center. Intense absorption of the H4 center contributes to yellow, orange and brown colors (Collins et al. 2000).

Temperature stability of the H4 center is about 1,500 °C. At higher temperatures, the H4 center is destroyed and the released nitrogen contributes to the formation of H3- and NV-defects (Collins et al. 2000; Collins 2001, 2003; Vins and Yelisseyev 2008; Vins and Yelisseyev 2010). Annealing of the H4 center also produces absorption centers with ZPLs at 536, 576, 454 and 439 nm. The 536 and 576 nm centers are frequently seen in PL spectra of brown diamonds (Collins et al. 2005).

Because of its low temperature stability, the H4 center disappears after HPHT treatment and it is not observed in the treated diamonds even in those with high content of B defects (Collins et al. 2000, 2005; Collins 2003; Okano 2006). It is believed that the H4 center converts into H3 center. This conversion occurs very fast and may not exceed 30 s at temperatures over 1,600 °C (Vins et al. 2008). The absence of the H4 center and the 491 nm center in PL spectra of a natural diamond is a strong evidence of HPHT treatment. Only rare type IIa diamonds with total nitrogen content below 0.01 ppm may show no detectable luminescence of these centers [based on results of (Anthony et al. 1999)].

The H4 center is readily created in diamonds containing B defects, when they are irradiated and subsequently annealed at temperatures over 800 °C. Therefore the H4 center is frequently seen in absorption and PL spectra of diamonds after multi-process treatment (Erel 2009). For instance, the H4 center is a common feature of PL spectra of Imperial Red diamonds (Wang et al. 2005). Yellow/green diamonds, which exhibit appreciable absorption of the centers H4, H2, H1b, H1c or 594 nm, are almost certainly color treated by irradiation (Collins 2003).

The H4 center can be also formed from B defects, when they are destroyed by moving dislocations (Nadolinnyi et al. 2004). Due to this, the H4 center is expected to be present, at least in trace concentration, in brown diamonds treated by low temperature HPHT annealing. Particular attention should be paid to type IaB diamonds with brown coloration. Since commercial treatment is not performed at low temperatures, the presence of H4 center can be considered as a good indicator of untreated diamonds. The H4 center is especially indicative of untreated diamonds with low-nitrogen content (Smith et al. 2000). However, one must be aware of the possibility of the re-introduction of the H4 center by subsequent irradiation followed by conventional annealing.

Concentration of the defects responsible for the H4 center in ppm (H4[ppm]) can be estimated using the following relations [based on original data of the authors and that from (Davies 1999; Davies et al. 1992)]:

$$\mathrm{H4[ppm]} = 0.25\ \mathrm{I_{ZPL-H4}}\left[\mathrm{cm}^{-1}\right],$$

where $\mathrm{I_{ZPL\text{-}H4}}[\mathrm{cm}^{-1}]$ is the absorption intensity of ZPL of the H4 center in cm^{-1} recorded at LNT.

496.7 nm (the S3 or NE1-center)

The S3 center relates to a defect comprising Ni and N atoms. The S3 center is observed in PL spectra of natural and synthetic diamonds (Fig. 6.9). The S3-center forms in diamonds during high temperature annealing in nature and in lab (Lang et al. 2007; Yelisseyev and Kanda 2007). This center is generated by heating at temperatures about 1,700 °C and increases in intensity with further HPHT treatment at temperatures over 1,900 °C (Yelisseyev and Kanda 2007). The presence of the S3 center is not an evidence of HPHT treatment, however, diamonds exhibiting the S3 center of high intensity must be checked for possible treatment.

498 nm center

The 498 nm center is observed in PL spectra of natural diamonds with brown coloration (Simic and Zaitsev et al. 2012). The 498 nm center is destroyed by HPHT treatment, but can be re-introduced by irradiation followed by conventional annealing (Fig. 6.12). The defects responsible for the 489 nm center are tentatively ascribed to modified H4 defects trapped in brown lamellae. Hence the 498 nm center is destroyed with removal of brown color. If a diamond reveals in PL spectra the 498 nm center and has no signs of artificial irradiation, this diamond can be confidently reported as untreated.

501 nm center

This Ni-related absorption center is destroyed by HPHT treatment at a temperature of 1,800 °C (Lawson and Kanda 1993). Presence of the 501 nm center is an evidence of untreated diamonds.

500 nm center

This Ni-related PL center is generated by heating at a temperature of 1,700 °C and it is destroyed by HPHT treatment at a temperature of 1,900 °C (Yelisseyev and Kanda 2007). The presence of the 500 nm center may evidence possible low temperature HPHT treatment. However, the possibility of high temperature HPHT treatment should be excluded.

500 nm band

A broad band with maximum at a wavelength of 500 nm is observed in phosphorescence spectra of type IIb diamonds (Fig. 6.44). The 500 nm band relates to the 660 nm phosphorescence band (see below). The 500 nm band is tentatively ascribed to a donor–acceptor radiative recombination involving boron acceptors and some defects with substitutional nitrogen atoms, which act as deep donors (Watanabe et al. 1997; Eaton-Magana and Lu 2011). In contrast to the 660 nm band, the 500 nm band, originates from temperature stable defects and it stands HPHT treatment. The dominance of the 500 nm band in phosphorescence of HPHT-treated type IIb diamonds is their characteristic feature and the main criterion of their recognition.

500.2 nm center

The 500.2 nm center is observed in PL spectra of untreated natural brown diamonds (Fig. 6.12). The center is destroyed by HPHT treatment and it is not re-introduced by subsequent irradiation and annealing used for multi-process treatment (Titkov et al. 2010; Simic and Zaitsev 2012). The presence of the 500.2 nm center in PL spectrum of a natural diamond strongly suggests that this diamond is untreated.

502.5 nm (2.468 eV) center

This Ni-related center is observed in PL spectra. The 502.5 nm center anneals out at a temperature of 1,700 °C (Yelisseyev and Kanda 2007). The presence of the 502.5 nm center is an evidence of untreated diamond.

503.2 nm, the H3 center

The H3 center is one of the most well studied optical centers of diamond. The H3 center is also one of the most common nitrogen-related optical centers involved in the process of HPHT treatment. The H3 center is observed in any nitrogen-containing diamonds: natural untreated, HPHT-grown synthetic, CVD-grown, natural HPHT-treated. The atomic structure of the defect responsible for the H3 center is NVN—two substitutional nitrogen atoms bound to a common vacancy. Absorption spectrum of the H3 center, when measured at liquid nitrogen temperature, is represented by a broad structured vibronic band with maximum at a wavelength about 480 nm and ZPL at a wavelength of 503.2 nm. In absorption spectra recorded at room temperature, ZPL and the vibronic band structure almost disappear and the spectrum reveals a broad structureless band spreading from 420 to 510 nm. Since the H3 center absorbs green–blue light, it contributes to yellow, orange or brown color of diamond (Collins et al. 2000). Intense absorption of the H3 center (rare for natural untreated diamonds) makes diamond virtually opaque in green and blue spectral ranges and this makes diamond orange. The orange color induced by H3 center looks different from the "natural" orange color and thus it can be recognized visually (Collins 1982). This color modification is frequently observed in the irradiated and annealed type Ia diamonds.

The NVN defects may exist in diamond lattice in neutral and negative charge states. Both charge states are optically active. The neutral NVN defects give rise to the H3 center, whereas the negatively charged NVN defects result is the H2-center (see below). The charge state of the NVN defects is determined by the presence of the donor defects, which may deliver free electrons at room temperature. The most common donor defects of this type in natural diamonds are nitrogen C defects. Thus considerable concentration of C defects increases relative intensity of the H2-center and simultaneously decreases relative intensity of the H3 center.

The H3 center has high quantum efficiency and therefore it is very effective in luminescence. The H3 center is detected in luminescence of almost any diamond even when nitrogen is present in trace concentrations. However, the H3 center is not readily observed in absorption. Strong absorption of the H3 center is a rare event for untreated natural diamonds. Natural pristine diamonds with the absorption intensity of H3 center of a few cm^{-1} have never been observed (Collins 2003). Yet natural brown diamonds often show a weak absorption of the H3 center, what can be considered as a common feature of these diamonds. Some brown and yellow untreated type I diamonds may exhibit naturally-occurring H3 absorption of considerable intensity (Collins 1982, 2003; Collins et al. 2000). The H3 center of lower intensity is also seen in pink natural diamonds (De Weerdt and Van Royen 2001).

The H3 center is particularly strong in natural diamonds with high internal mechanical stress and in plastically deformed diamonds (e.g. at the coat/core boundary of coated diamonds) (Yelisseyev et al. 2004). Majority of natural diamonds, which exhibit the H3 center, are brown diamonds with evidence of strong plastic deformation (with brown graining). These diamonds may not reveal the "green transmission" effect (Collins et al. 2000). The enhanced intensity of the H3 center in plastically deformed diamonds is explained by the interaction of A defects with moving dislocations producing vacancies (Kiflawi and Lang 1976; Van Enckevort and Visser 1990).

The H3 center is a typical radiation center. In irradiated diamonds, NVN defects are formed of nitrogen A defects, when they capture the irradiation-induced vacancies. Any high energy irradiation followed by annealing at temperatures over 500 °C results in formation of the H3 centers in nitrogen-containing diamonds (Fig. 6.14). The role of the irradiation and annealing is the creation and delivery of single vacancies to already available A defects.

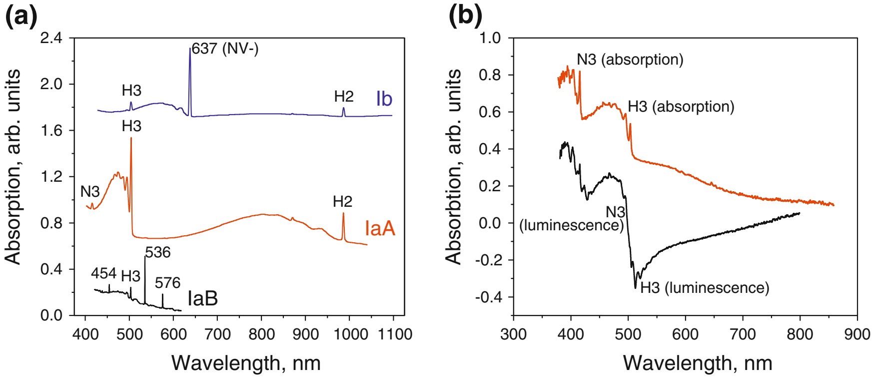


Fig. 6.14 **a** Absorption spectra of type IaA (*red curve*), IaB (*black curve*) and Ib (*blue curve*) diamonds after irradiation and conventional annealing at temperatures of 1,600–1,650 °C [replotted from (Collins 2007)]. The dominating centers in the spectra are H3 and H2 in type IaA, 536 nm in type IaB, and 638 nm (NV- center) in type Ib. **b** FSI absorption spectra of two HPHT-treated diamonds showing equally strong absorption of the H3 center: high-nitrogen diamond with 340 ppm A defects and 450 ppm B defects exhibits no "green transmission" (*red curve*); moderate nitrogen diamond with 10 ppm A defects and 310 ppm B defects exhibits very pronounced "green transmission" effect due to the H3 center and "blue transmission" effect due to the N3 center (*black curve*). The reason of the strong "transmission" effect is the low content of A defects, which are very effective quenchers of luminescence

Besides irradiation, single vacancies can be also created in plastically deformed brown diamonds by heating at temperatures, at which the vacancy clusters dissolve. The formation and enhancement of the H3 center is characteristic of HPHT-treated regular brown diamonds. The generation of the H3 center during plastic deformation at high temperatures in type IaA diamonds is shown in (Brookes et al. 1993). In most cases, HPHT treatment of brown type Ia diamonds at temperatures below 1,900 °C does not cause considerable changes in their color and the intensity of the H3 center increases only slightly. With temperature increase to 2,100 °C, brown color anneals out and the intensity of the H3 center increases drastically (De Weerdt et al. 2004). In these diamonds, the intensities of the H3 center and the Pink Band correlate, what suggests that the vacancies delivered by the "Pink Band defects" and the "Brown absorption continuum defects" are the primary reason of the enhancement of the H3 center after HPHT annealing (De Weerdt and Collins 2007). Brown color is crucial for the production of the H3 center. In cape yellow diamonds without brown color modifier, HPHT treatment does not produce the H3- and H2-centers. However, C defects are formed in these diamonds during HPHT treatment and their concentration is sufficient to intensify the original yellow color and to induce the IR absorption peak at a wavenumber of 1,344 cm^{-1} (Collins 2001; Collins et al. 2005). In contrast to brown diamonds, the intensity of the H3 center is not enhanced in CO_2 and pseudo-CO_2 diamonds after HPHT treatment performed at a temperature of 2,000 °C (Hainschwang et al. 2005).

In high-nitrogen type IaA HPHT-treated diamonds, the H3 center may not form at all, if these diamonds have no vacancy-related defects (no brown color). Therefore, no change in intensity of the H3 center is observed in type IaA colorless diamonds after HPHT treatment (Vins and Yelisseyev 2008). Similarly, these diamonds may show only very low intensity of the NV-center, although they can exhibit substantial amount of C defects. In contrast, the diamonds with considerable content of A defects, when plastically deformed during HPHT processing, show H3 center of very high intensity. Diamonds with considerable content of B defects, when plastically deformed during HPHT processing, also show enhanced intensity of the H3 center. Note that the H4 center, because of its low temperature stability, is not observed in type IaB diamonds after HPHT treatment (Brookes et al. 1993).

Pressure is not an important factor for the generation of the H3 center. The H3 center may readily form in brown type Ia diamonds, when annealed at a temperature of 1,700 °C in vacuum or at ambient pressure. The usual result of such a heating is the removal of the 491 nm and the H4 centers and enhancement of the H3 center. Further annealing at 1,750 °C may increase the H3 center intensity by an order of magnitude (Collins et al. 2005).

Due to high quantum efficiency, the H3 center, when excited by daylight, produces visible green luminescence. In some diamonds, this luminescence is strong enough to make them look green. The diamonds with the green component of color resulting from the green luminescence of the H3 center are known as "green transmitters". The "green transmission" of the H3 center can be seen in FSI absorption spectra of many type Ia HPHT-treated diamonds as a negative absorption band in the spectral range from 500 to 600 nm (De Weerdt and Van Royen 2000) (Fig. 6.14b). “Green transmission” of a strength that may affect the face-up color of an untreated cut diamond of brown to yellow color is quite rare (Moses 1997; Buerki et al. 1999; Fritsch 1998; Reinitz et al. 2000). In contrast, “green transmission” is a very characteristic feature of HPHT-treated type Ia diamonds. The “green transmission” effect was one of first characteristic features found in HPHT-treated yellow/green diamonds and it was used for the recognition of treatment. Brown type Ia diamonds become almost always “green transmitters” after HPHT-treatment (TM and IR 1999; Haske 2000; Reinitz et al. 2000; Collins et al. 2000).

Natural “green transmitters” usually reveal very weak H2-center (Buerki et al. 1999; Wang and Moses 2004). Rarely, natural type Ib diamonds exhibiting “green transmission” effect may show absorption of the H2 and 638 nm centers. This peculiarity was observed in both high and low-nitrogen type Ib diamonds (Hainschwang and Notari 2004). In contrast, HPHT-treated “green transmitters” reveal enhanced H2-center (Haske 2000). Although the H2 center is a characteristic feature of “green transmitters”, the diamonds exhibiting the “green transmission” effect and no H2-center have been also reported (Buerki et al. 1999).

The luminescence of the H3 center does not depend on the process of its formation. However, the visual appearance of a “green transmitter” may be different for natural and HPHT-treated stones. It has been noticed that the bright green emission in daylight is characteristic of natural “green transmitters”, whereas HPHT-induced “green transmitters” may exhibit strong chalky yellowish green emission under LW- and SW-UV excitation followed by afterglow (Collins 2003; Tretiakova 2009).

In initially brown diamonds, the “green transmission” effect becomes strong after HPHT treatment performed at temperatures above 2,000 °C (Collins et al. 2000; Collins 2001), when considerable amount of A defects are destroyed. If temperature of the treatment is not high enough, e.g. about 1,800 °C, the H3 center may produce strong absorption, but reveal relatively low luminescence (Collins 2001) and almost no “green transmission”. Thus, “green transmission” is a feature of HPHT treatment performed at moderate temperatures.

Effect of “green transmission” is significantly quenched by A defects (Wang and Moses 2004; Hainschwang 2002). Therefore, “green transmitters” have low to moderate amount of A defects (Collins 2003). Quenching action of A defects strongly increases with their concentration. If the A defect concentration is less than 50 ppm, almost all color centers in diamond are isolated from A defects and no measurable quenching of luminescence is observed (Davies et al. 1978; Anthony et al. 1999). A 100 ppm concentration of A-centers decreases luminescence intensity by about 15 %. The increase in A defect concentration to 300 ppm reduces the luminescence intensity of diamond by two orders of magnitude. Although in high-nitrogen type Ia diamonds the “green transmission” effect is suppressed, the absorption of the H3 center remains very strong. A feature of such high-nitrogen diamonds is a dark green color, which is deeper than the green color typically observed in HPHT-treated type Ia diamonds (Wang and Hall 2007).

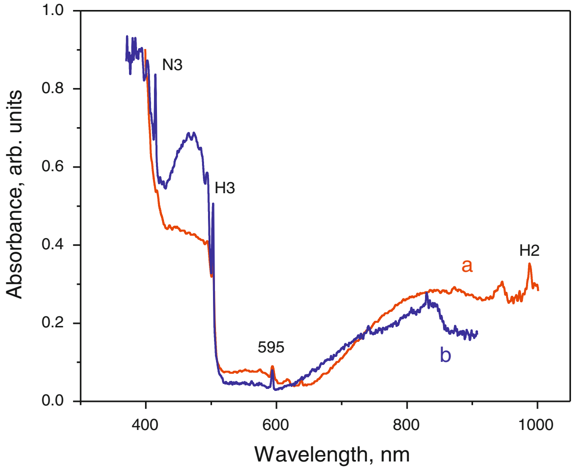


Fig. 6.15 Absorption spectrum of a diamond reported as HPHT-treated (*a*, *red curve*). The presence of the 595 nm center suggests that after HPHT annealing, an irradiation and low temperature annealing were applied too [based on the data from (Hainschwang et al. 2002)]. Absorption spectrum of an irradiated and annealed high-nitrogen type Ia diamond exhibits strong H3 center (*b*, *blue curve*). Both diamonds show no noticeable "green transmission" effect

Hence, the absence of the "green transmission" effect in a high-nitrogen diamonds with strong H3 center absorption does not imply that these diamonds are not HPHT-treated.

"Green transmission" effect, while strong after HPHT, can be weak or even absent in diamonds treated by irradiation and conventional annealing. The residual radiation damage, which remains in diamond even after annealing, suppresses the H3 center luminescence (Fig. 6.15).

Temperature stability of the H3 center is relatively high. In brown type Ia diamonds, the H3 center may form during HPHT annealing at temperatures starting from 1,700 °C. In brown type IaB diamonds, HPHT treatment induces the H3 center at temperatures of 1,800 °C and above (Vins and Yelisseyev 2010). In type Ib synthetic diamonds, the H3 center is generated and its intensity strongly increases after treatment at a temperature over 1,800 °C (Kanda and Jia 2001). Strong green luminescence of the H3 center is produced in nitrogen-doped CVD diamonds by HPHT annealing at temperatures of 1,900 °C and above (Twitchen et al. 2003). After treatment at a temperature of 2,025 °C, strong H2 and H3 centers are seen simultaneously (Collins et al. 2000) (Fig. 6.16). In brown type Ia diamonds, 2,000 °C is a temperature threshold for the formation of the H3 center during HPHT treatment. Below this temperature, intensity of the H3 center increases progressively with time. At temperatures over 2,000 °C, the H3 center can be formed during the first few minutes and after that is gradually destroyed. At temperatures above 2,100 °C, intensity of the H3 center decreases considerably (Vins and Yelisseyev 2008; Vins et al. 2008). Annealing of the H3 center during HPHT treatment is especially pronounced in originally brown type IIa diamonds, where the complete removal of the H3 center can occur (Smith et al. 2000). The temperature threshold of activation and destruction of the H3 center depends on HPHT treatment duration: the longer the treatment time the lower the threshold of the temperature stability of the H3 center. If heating is performed for a short time, the H3 center can survive very high temperatures. For instance in brown type Ia diamonds, when HPHT treatment is

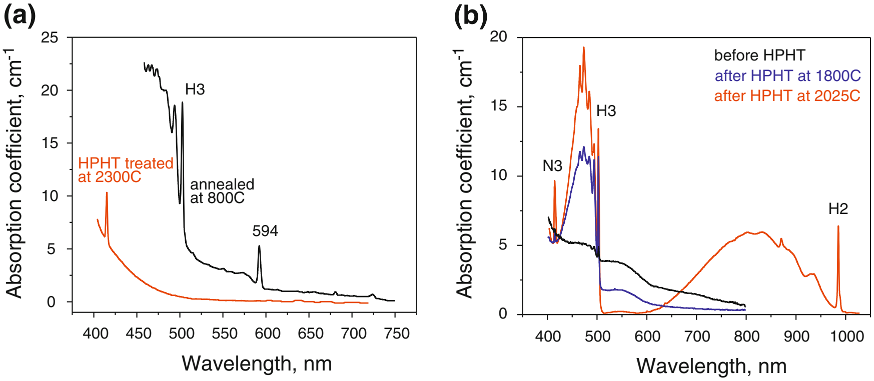


Fig. 6.16 **a** Absorption spectra of a neutron-irradiated diamond after conventional annealing at a temperature of 800 °C (*black curve*) and HPHT annealing at a temperature of 2,300 °C under pressure 5 GPa (*red curve*) [based on the data from (Collins et al. 2005)]. **b** Absorption spectra of initially brown type Ia diamond: before treatment (*black curve*) and after HPHT treatments at a temperature of 1,800 °C (*blue curve*) and 2,025 °C (*red curve*). The first step of HPHT treatment at 1,800 °C converted brown color into yellow–brown. The second treatment at 2,025 °C essentially removed the Brown absorption continuum and produced green color with some remaining brown modifier [based on the data from (Collins et al. 2001)]

performed in "pulse regime", the intensity of the H3 center may increase with temperature up to 2,300 °C. Hoewever, in general, the H3-ceneter does not stand high temperature annealing. In most diamonds, a 10 min HPHT treatment at a temperature 2,300 °C destroys the H3 center (Fig. 6.17). In diamonds with comparable brown color, the H3 center intensity increases with the increase in the B defect concentration (De Weerdt and Collins 2007).

Irradiation stimulates the destruction of the H3 center at high temperatures. For instance, high-nitrogen type IaAB diamonds heavily irradiated with electrons or neutrons and then HPHT annealed at a temperature of 2,300 °C display in their spectra no H3 center (Collins et al. 2005).

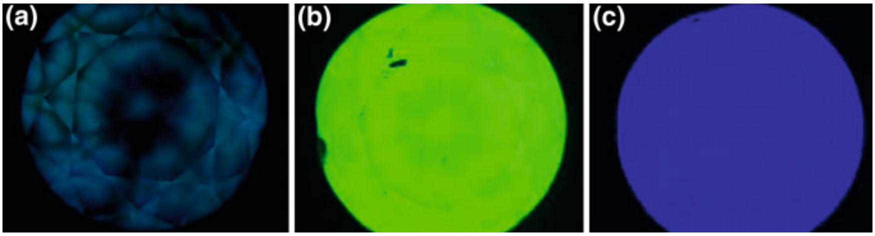


Fig. 6.17 Fluorescence images of a natural type Ia initially *brown diamond* before treatment (**a**), after first HPHT treatment at a temperature of 1,900 °C (**b**) and after second treatment at a temperature of 2,400 °C (**c**). After the first low temperature treatment, the diamond exhibits very strong *green* fluorescence of the H3 center, which disappears after the heating at 2,400 °C

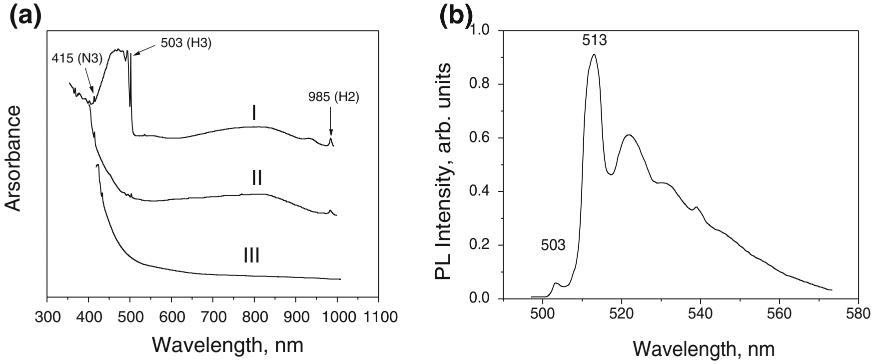


Fig. 6.18 **a** Absorption spectra of type Ia HPHT-treated diamonds with resulting yellow to green color. *I*—the most common spectrum exhibiting strong H3 and H2 centers and minor N3 center. This type of spectra is typical for type Ia diamonds HPHT-treated at temperatures below 2,300 °C. *II*—spectrum of some HPHT-treated diamonds. Type Ia diamonds HPHT-treated at temperatures of 2,300 °C and above can show this type of spectra. *III*—typical spectrum of HPHT-treated diamonds of yellow to brownish-yellow color. This is a common spectrum of nitrogen-containing diamonds HPHT-treated at high temperature [based on the data from (Reinitz et al. 2000)]. **b** PL spectrum of an initially brown type IaA diamond after HPHT treatment performed at a temperature of 1,850 °C. The H3 center is the main feature of the spectrum. Intensity of ZPL line is strongly suppressed because of the effect of re-absorption [based on the data from (Nadolinny et al. 2009)]. Relatively weak ZPL of the H3 center is a feature of HPHT-treated initially brown type IaA diamonds

The activation energy of formation of the H3 center in brown diamonds varies from 2 to 4 eV decreasing with the intensity of brown color. The activation energy of dissociation of the H3 center is much higher amounting 8 eV.

The H3 center is a typical product of HPHT treatment in colored type I diamonds. However, the presence of the H3 center can be considered as an indication of HPHT treatment only under the following conditions: (1) the center has high intensity in absorption (Collins 2003), (2) it shows considerable effect of "green transmission" and (3) it is seen in combination with the H2 center. Since the H3 center may anneal out at temperatures over 2,000 °C, it must be kept in mind that the presence of intense H3 center and strong "green transmission" effect is the manifestation of HPHT treatment performed at low to moderate temperatures (Fig. 6.18).

Concentration of neutral NVN defects (the H3 defects) in ppm (H3[ppm]) can be estimated using the following relations [based on original data and the data from (Davies 1999; Davies et al. 1992)]:

$$\mathrm{H3[ppm]} = 0.25\ \mathrm{I}_{\mathrm{ZPL-H3}}\left[\mathrm{cm}^{-1}\right],$$

where $\mathrm{I}_{\mathrm{ZPL\text{-}H3}}[\mathrm{cm}^{-1}]$ is the absorption intensity of ZPL of the H3 center in cm^{-1} recorded at LNT, or

$$\mathrm{H3[ppm]} = 0.5\ \mathrm{I}_{485\,\mathrm{nm}}\left[\mathrm{cm}^{-1}\right],$$

where $I_{485\ \mathrm{nm}}$ is the absorption intensity of the H3 center in cm^{-1} at a wavelength of 485 nm measured at RT (when using this formula, the background absorption underlying the H3 center absorption must be subtracted correctly).

503.5 nm (3H center)

Along with the GR1 and TR12 centers, the 3H center is a typical feature of irradiated diamonds. About 70 % of all as-mined natural diamonds may exhibit the 3H center in their spectra. In particular, the 3H center is detected in natural untreated type IIa and IIb diamonds (Eaton-Magaña and Lu 2011).

The 3H center is observed both in absorption and luminescence. The diamonds with the 3H center also reveal in PL spectra a line at a wavelength of 540.7 nm, which is believed to relate to the 3H center (Choi et al. 2011). Possibly the feature at 540.7 nm is a 170 meV local vibration of the 3H center.

The 3H-center relates to an intrinsic defect containing interstitials, therefore its temperature stability is low. Presence of the 3H center is a reliable indicator of diamonds that have not been heated at temperatures above 800 °C, e.g. have not been HPHT-treated (De Weerdt and Van Royen 2000; Zaitsev 2002). 3H center can be created in diamond by mechanical damage (grinding, polishing) and ion beam polishing (Mora et al. 2005). Hence it is possible to encounter weak H3 center in spectra of HPHT-treated and recut diamonds. It is also known that weak 3H center (along with the GR1 center) is deliberately induced in HPHT-treated diamonds by low dose electron irradiation—a trick which is used to conceal HPHT treatment.

505 nm center

The 505 nm center is observed in PL spectra of natural brown diamonds (Gaillou et al. 2010; Titkov et al. 2010; Simic and Zaitsev 2012). The 505 nm center is destroyed by HPHT treatment. However, it can be well re-introduced by electron irradiation followed by conventional annealing (Simic and Zaitsev 2012) (Fig. 6.19). The 505 nm center is tentatively ascribed to a modified H3 center trapped in brown lamellae. Thus the 505 nm center is destroyed with removal of brown color. If a diamond reveals in PL spectra the 505 nm center and has no signs of artificial irradiation, it can be confidently reported as untreated.

511 nm center

The 511 nm Ni-related absorption center is created by HPHT treatment performed at a temperature of 1,700 °C. The center is destroyed by further treatment at temperatures above 1,800 °C (Lawson and Kanda 1993; Yelisseyev and Kanda 2007). Thus, the 511 nm center can be considered as a manifestation of HPHT treatment performed at low temperatures. However, HPHT treatment at moderate and high temperatures must be excluded.

515 nm center

This Ni-related center is observed in PL spectra. The 515 nm center is destroyed by HPHT treatment at a temperature of 1,700 °C (Lawson and Kanda 1993;

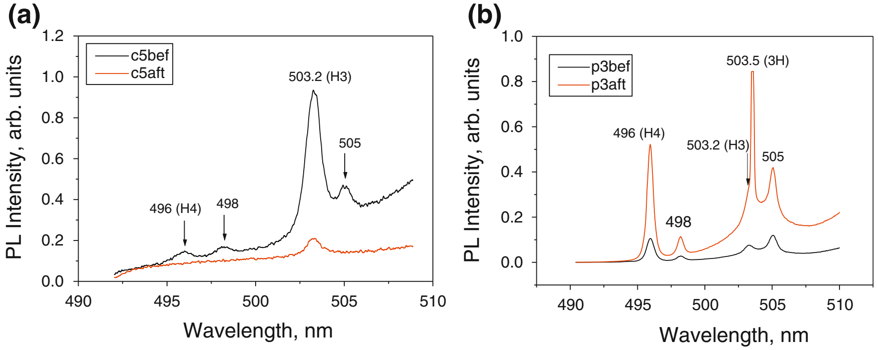


Fig. 6.19 PL spectra of two diamonds showing characteristic change in relative intensity of the 496 (H4), 498, 503.2 (H3), 503.5 (3H), 500.2 and 505 nm centers after HPHT (**a**) and multi-process (**b**) treatments. The resulting color of the diamonds is “colorless” (**a**) and “pink” (**b**). Note that the treated pink diamond exhibits 3H center and 505 nm center, which have been created by irradiation and conventional annealing following HPHT annealing. The spectra were recorded at liquid nitrogen temperature with excitation at a wavelength of 488 nm (Simic and Zaitsev 2012)

Yelisseyev and Kanda 2007). The presence of the 515 nm center indicates that diamond has not been HPHT-treated. However, in order to exclude low temperature HPHT treatment with confidence, the presence of the 515 nm center must be analyzed in combination with other optical centers.

516 nm center

This Ni-related absorption center is generated by heating at a temperature of 1,700 °C and destroyed by further HPHT treatment at a temperature of 1,900 °C (Yelisseyev and Kanda 2007). Presence of the 516 nm center can be considered as a manifestation of HPHT treatment performed at low temperatures.

518.5 nm center

This Ni-related absorption center is destroyed by HPHT treatment at a temperature of 1,800 °C (Lawson and Kanda 1993). The 518.5 nm center is a feature of untreated diamonds.

519.7 nm center

This center is present in some natural brown diamonds. Nature of the 519.7 nm center is not known. The 519.7 nm center anneals out during HPHT treatment at temperatures 1,700–1,800 °C (Collins et al. 2000). Its presence may confirm that diamond has not been HPHT-treated.

520.5 nm center

This Ni-related absorption center is destroyed by HPHT treatment performed at a temperature of 1,800 °C (Lawson and Kanda 1993). The presence of the 520.5 nm center may confirm that diamond has not been HPHT-treated.

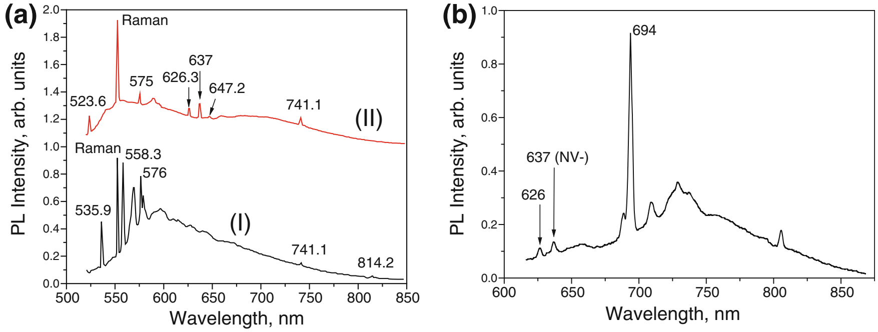


Fig. 6.20 **a** PL spectra of type IIa brown diamond before treatment (*I*), and after HPHT treatment and subsequent irradiation (*II*). Both spectra show weak GR1 center. The 536 nm (ZPL at 535.9 nm) and 558 nm (ZPL at 558.3 nm) centers are completely destroyed by treatment [re-plotted from (Fisher et al. 2006)]. Spectrum of the treated diamond exhibits 523.6 and 626.3 nm centers. **b** PL spectrum of a HPHT-treated fancy brown greenish yellow diamond exhibiting three optical centers characteristic of HPHT treatment: 626, 638 and 694 nm

523.3 nm (the S2 center)

See 477.5 nm center.

523.6 and 626.3 nm centers

The 523.6 (524) and 626.3 (626) nm centers are observed in absorption and PL spectra of type Ib diamonds after electron irradiation (Collins and Rafique 1979; Fisher et al. 2006). These centers are two different charge states of a nitrogen-interstitial complex. Both centers are effective in PL and are readily observed in type IIa diamonds with low concentration of C defects after low dose electron irradiation. The presence of the 523.6 and 626.3 nm centers in spectra of colorless type IIa diamonds may be considered as a strong indicator of HPHT-treatment followed by a low dose irradiation. A weak GR1 center is expected to be detected in PL spectra of these treated diamonds too (Fig. 6.20).

527.5 nm center

This Ni-related absorption center is generated by heating at a temperature of 1,700 °C and is destroyed by HPHT treatment at a temperature of 1,900 °C (Yelisseyev and Kanda 2007). The 527.5 nm center can be considered as a manifestation of HPHT treatment performed at low temperatures.

536 nm center

Many untreated brown and pink type IaAB diamonds have in absorption and PL spectra a line at a wavelength of 536 nm, which can be rather strong in some diamonds (Fig. 6.21). The 536 nm center is a frequent feature of spectra of Argyle pink diamonds (Gaillou et al. 2010). The 536 nm center manifests the presence of B defects and their derivatives (Iakoubovskii and Adriaenssens 2002). In brown diamonds, the 536 nm center is frequently accompanied by the 575 nm (NV^0) center. The 536 nm center can be created by heating at temperatures of 1,500 °C

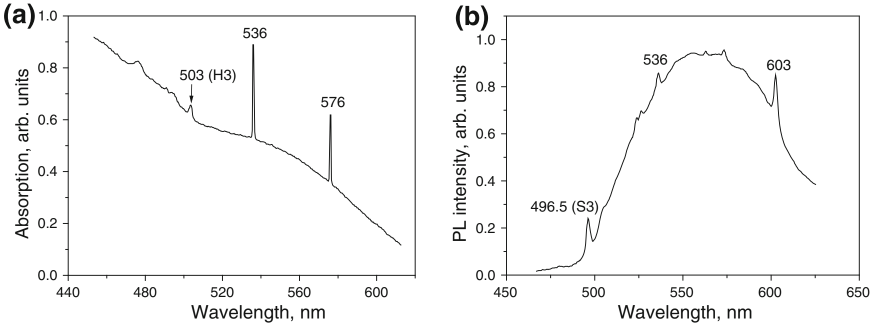


Fig. 6.21 **a** Absorption spectrum of an untreated natural brown diamond measured at LNT [re-plotted from (Collins and Ly 2002)]. The 536 nm center is one of the main features of the spectrum. **b** PL spectrum taken from an untreated green-gray Argyle diamond [re-plotted from (Iakoubovskii and Adriaenssens 2002)]

(Collins 1982). The center is also strong in type IaAB diamonds HPHT-treated at temperatures up to 2,000 °C. In contrast, the 536 nm center is weak in HPHT-treated type IIa stones (Shiryaev et al. 2001; Tretiakova and Tretyakova 2008), what suggests that the 536 nm center relates to nitrogen-containing defects. The 536 nm center is a feature of natural green transmitters (Tretiakova 2009). High temperature HPHT treatment destroys the 536 nm center. Because of this, the 536 nm center is considered as an indicator of non-treated type IIa diamond (Smith et al. 2000). However, the presence of the 536 nm center does not exclude low temperature HPHT treatment and/or HPHT treatment combined with irradiation and annealing. For instance, the 536 nm center is a common feature of Imperial Red diamonds (Wang et al. 2005).

The 536 nm center belongs to a defect of rigid atomic structure. Unlike many other optical centers, the 536 nm center does not change spectral width of its ZPL in diamonds with varying internal stress (Eaton-Magana 2011).

537.5 and 549 nm centers

These two independent Ni-related PL centers are generated by heating at a temperature of 1,700 °C and are destroyed by HPHT treatment performed at a temperature of 1,900 °C (Yelisseyev and Kanda 2007). The presence of these centers can be considered as an indication of low temperature HPHT treatment. However, their absence does not exclude HPHT treatment with confidence. Vice versa, the absence of the 537.5 and 549 nm centers from PL spectra of a Ni-containing diamond can be considered as an indicator of high temperature HPHT treatment (Fig. 6.22).

550 nm (the Pink Band)

A broad absorption band with a maximum at a wavelength of 550 nm is a very characteristic feature of pink and some brown plastically deformed natural diamonds (Collins 1982) (Fig. 6.23). This band is responsible for pink color of natural

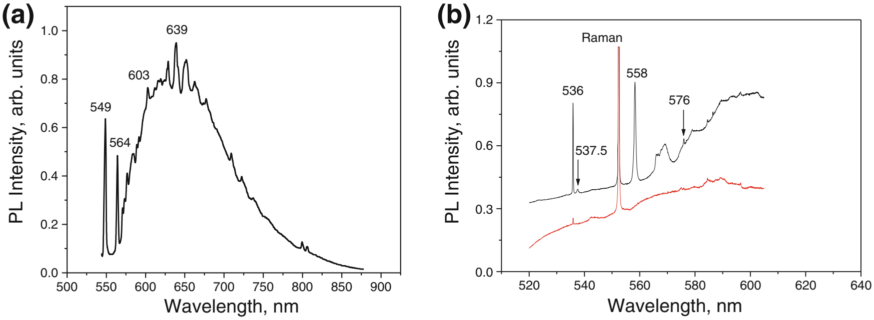
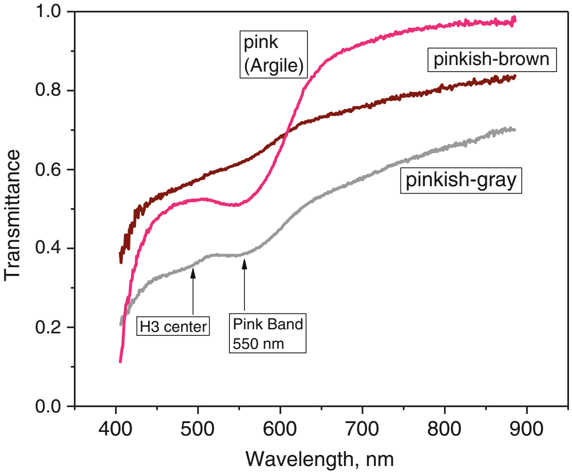


Fig. 6.22 **a** PL spectrum of an HPHT-treated type IaAB diamond showing intense 549 nm center and other Ni-related centers with ZPLs at 603.5 and 639.5 nm. Presence of these centers suggests that the HPHT treatment was performed at a low temperature (about 1,800 °C). This stone exhibits distinctive "fluorescence cage", which is an indicator of HPHT treatment. **b** PL spectra of an initially brown type IIa diamond (*black curve*) converted by HPHT treatment into colorless (*red curve*). Treatment has suppressed the 536, 537.5 and 576 nm centers (Simic and Zaitsev 2012)

Fig. 6.23 Room temperature transmission spectra of three diamonds of different color exhibiting the *Pink Band*



diamonds. Atomic model of the defect generating the Pink Band is not known, although its vacancy nature is assumed in (De Weerdt and Collins 2007). There is an opinion that the Pink Band relates to the paramagnetic M2 center produced by plastic deformation (Titkov et al. 2008; Titkov et al. 2010). The Pink Band and the Brown absorption continuum (see below) are closely related features. Theoretical modeling of the Brown absorption continuum predicts its multiband structure. One of these bands might be the Pink Band. The Pink Band, observed in natural brown and pink diamonds, can be bleached by cooling or SW UV irradiation (De Weerdt and Van Royen 2001). This bleaching suggests that the intensity of the Pink band depends on the charge state of the related defects. Because of this charging effect,

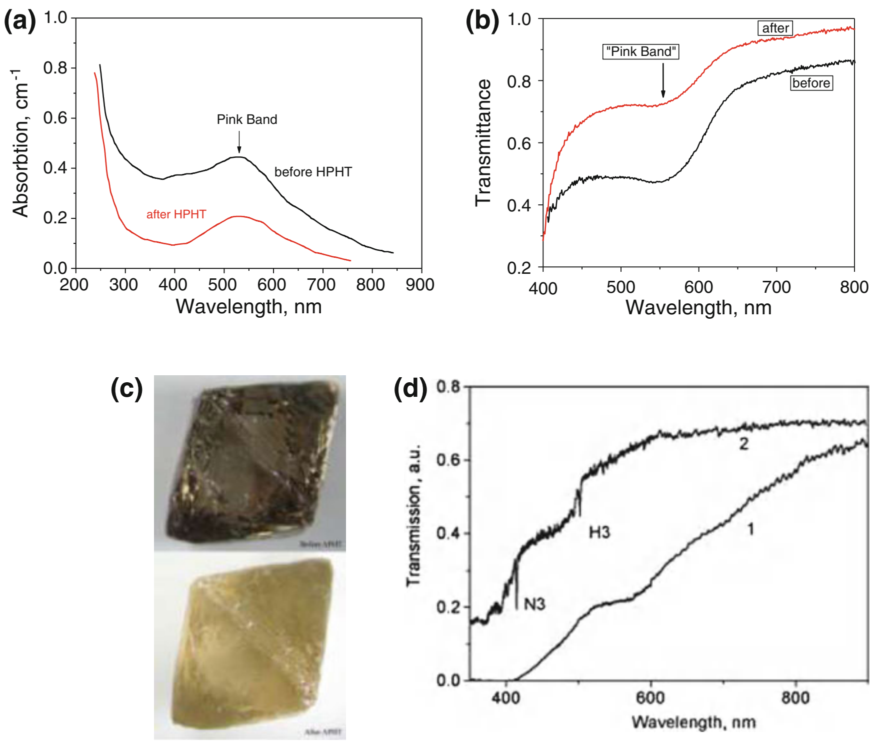


Fig. 6.24 **a** This initially *brown* diamond of type IIa exhibits the *Pink* Band in its absorption spectra recorded before (*blue curve*) and after (*red curve*) HPHT treatment at a temperature of 2,200 °C. Intensity of the *Brown* absorption continuum is strongly reduced by the treatment, whereas the intensity of the *Pink* Band remains almost unchanged [re-plotted from (Vins and Yelisseyev 2010)]. **b** Transmission spectra of a fancy *pink* natural diamond before annealing (*black curve*) and after annealing (*red curve*) in vacuum at a temperature of 1,580 °C for 2 h. Intensity of the 550 nm *Pink* Band is reduced after HPHT treatment and the final color of the diamond is *light pink*. **c** Photos of a rough *brown* diamond before and after APHT treatment at a temperature of 2,000 °C for 15 s (with permission of the Diamond and Related Materials journal). **d** Transmission spectra of a diamond before (*1*) and after (*2*) HPHT treatment. Before treatment, the *Pink* Band is clearly seen. The treatment destroyed the *Pink* Band completely [re-plotted from (Vins et al. 2010)]

intensity of the Pink Band in HPHT-treated type Ia diamonds can be manipulated via controlled generation of C defects.

The Pink Band is a temperature stable feature and normally it stands medium temperature HPHT treatment (Fig. 6.24a). However, in some diamonds, a partial reduction in intensity of the band is observed after annealing at ambient pressure or in vacuum at a temperature as low as 1,600 °C (Fig. 6.24b). The Pink Band strongly reduces in intensity after high temperature HPHT treatment and may be annealed out completely at temperatures over 2,200 °C (De Weerdt and Van Royen 2000; Hainschwang et al. 2008) (Fig. 6.24d). Presence of the Pink Band is a

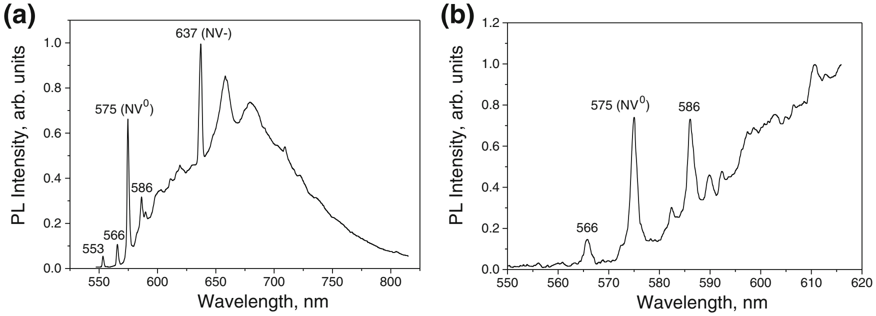


Fig. 6.25 **a** PL spectrum of a HPHT-treated fancy deep *brownish yellow* diamond showing many optical centers characteristic of HPHT treatment: lines at wavelengths 553, 566, 575, 586 and 638 nm. Note that intensity of the 638 nm (NV$^-$) center is much higher than that of the 575 nm (NV^0) center—a typical feature of HPHT-treated diamonds. **b** PL spectrum of a HPHT-treated fancy deep *brownish orangey yellow* diamond exhibiting the 566 and 586 nm centers. This diamond also exhibits strong luminescence of the NV centers (spectrum of the NV$^-$ center is not shown)

proof that diamond has not been HPHT treated at high temperatures. However, low and moderate temperature HPHT treatment is quite possible. Moreover, HPHT treatment at moderate temperatures intensifies the Pink Band over the Brown absorption continuum and converts natural brown color diamond into pink stones (Fig. 6.24a). Therefore brownish pink diamonds and especially these of pale pink color should be carefully checked for possible HPHT treatment.

The Pink Band does not exhibit high absorption strength neither in natural untreated nor in treated diamonds. Hence, the Pink Band does not cause intense pink color. In order to obtain noticeable pink color after HPHT treatment, type IIa diamond must have intensity of the Pink Band at least 0.5 cm^{-1} over the Brown absorption continuum background.

553 nm (554) center

This Ni-related center is observed in PL spectra of natural and synthetic diamonds (Fig. 6.25a). The 553 nm center may be generated by HPHT treatment at a temperature of 1,700 °C and its intensity increases with further HPHT treatment at temperatures over 1,900 °C (Yelisseyev and Kanda 2007). Intense 553 nm center is an indicator of HPHT treatment.

555.8 nm center

A minor line at a wavelength of 555.8 nm can be generated by electron irradiation followed by HPHT annealing at a temperature of 2,250 °C in type Ib natural diamonds showing presence of the nitrogen-related Y-center (Hainschwang et al. 2012).

558 nm center

Untreated brown type IaAB diamonds frequently exhibit in PL spectra a line at a wavelength of 558 nm (Tretiakova and Tretyakova 2008; Fisher and Spits 2000;

Fisher et al. 2006) (Figs. 6.22, 6.32, 6.36). This line is also observed in natural untreated type IIa diamonds. The 558 nm center is destroyed by HPHT treatment at relatively low temperatures (in the range of stability of the NV centers). The presence of the 558 nm center is an indicator of untreated natural diamonds (Smith et al. 2000).

559.6 nm center

A minor line at a wavelength of 559.6 nm can be generated by electron irradiation followed by HPHT annealing at a temperature of 2,250 °C in type Ib natural diamonds showing the presence of the nitrogen-related Y-center (Hainschwang et al. 2012).

563 nm center

The 563 nm center is observed in PL spectra of CVD-grown and some natural diamonds. The center anneals out after low temperature HPHT treatment (Crepin et al. 2012). Presence of the 563 nm center is a feature of untreated diamonds.

566 nm (565) center

The 566 nm center is observed in PL spectra of natural diamonds exhibiting Ni-related centers (Figs. 6.25, 6.26). The 566 nm center is frequently seen in type IIa untreated natural diamonds and it is detected in HPHT-treated diamonds too (Epelboym et al. 2011). The 566 nm center is accompanied by the 553 and 586 nm centers, although their intensities do not correlate. If pronounced, the 565 nm center may be considered as an indicator of possible HPHT treatment.

567 and 569 nm centers

These PL centers can be found in spectra of some natural type IIa diamonds (Figs. 6.26). The 567 and 569 nm centers are destroyed by HPHT treatment. Their presence is an indicator of untreated type IIa diamond (Smith et al. 2000). However, the 567 nm center can be seen in some diamonds exhibiting strong evidence of HPHT treatment. We assume that these diamonds were subjected to a low temperature short-time treatment (Figs. 6.26, 6.27).

575 nm (the NV^0 center)

The 575 nm center relates to the nitrogen-vacancy defect in neutral charge state: NV^0 defect. When the migrating vacancies meet single nitrogen atoms they may form nitrogen-vacancy complexes (NV defects). The NV defects are optically active when being in two charge states: neutral (NV^0 defects) and negative (NV^- defects). The NV^0 defects produce an optical center with ZPL at a wavelength of 575 nm. The NV^- defects produce an optical center with ZPL at a wavelength of 638 nm (Fig. 6.27).

The charge state of the NV defects is controlled by the presence of the defects working as donors and/or acceptors. For instance, nitrogen C defects, which are deep donors, charge NV defects negatively. Both 575 and 638 nm centers absorb light in yellow and green spectral ranges and, if present in sufficient concentrations, add to diamond red and/or pink color (Collins et al. 2000). Usually

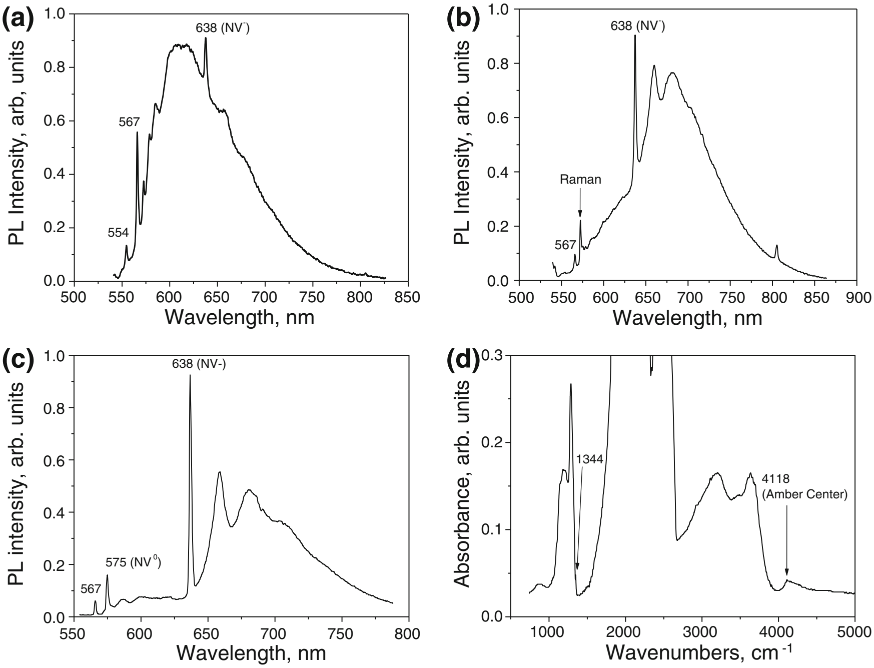


Fig. 6.26 **a**, **b** PL spectra of two ABC natural diamonds exhibiting the 567 nm Ni-related center. Although the 638 nm (NV^-) center is strong (**b**), it is not an indicator of HPHT treatment in this case. Along with the 567 nm center, the untreated nature of this stone has been confirmed by the presence of the Amber Center and deep brown coloration. The absence of the 575 nm (NV^0) center in both spectra indicates an appreciable concentration of C defects. (**c**, **d**) PL and IR absorption spectra of a fancy deep *brownish yellow* HPHT-treated diamond. The treatment of this stone has been confirmed by simultaneous presence of the 638 nm (NV^-) and 575 nm (NV^0) centers in PL spectrum ($NV^- \gg NV^0$), by the presence of the NV^- center in absorption spectrum, by the presence of the 1,344 cm^{-1} line (C defects) in IR absorption spectrum and by two small "frosted" facets. This diamond shows the 567 nm center. One can assume that this stone was HPHT treated at a low temperature

absorption of the 638 nm center is much stronger than that of the 575 nm center. However, in luminescence, both centers are highly active.

In natural diamonds, intensity of the NV centers is usually weak and in most diamonds the 575 and 638 nm centers can be detected in luminescence spectra only. In contrast, in HPHT-treated diamonds, the centers are frequently well seen both in luminescence and absorption spectra. The 575 and 638 nm centers may be particularly strong in absorption spectra of type Ia diamonds after multi-process treatment.

In untreated diamonds, relative PL intensity of the 575 nm center is usually stronger than that of the 638 nm center (Collins 2003; Vins 2008). In untreated type IIa brownish diamonds, the 575 nm center is frequently observed alone and the 638 nm center is not detected (Sriprasert et al. 2007). The preferential neutral

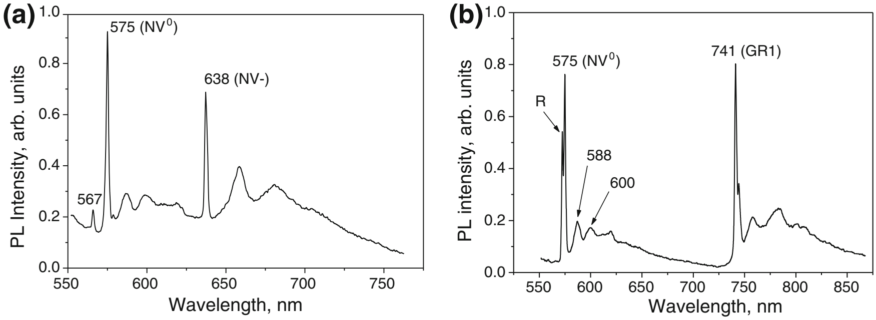


Fig. 6.27 PL spectra of two treated diamonds showing intense 575 nm (NV^0) center: **a** HPHT-treated low-nitrogen type IaAB fancy intense *greenish yellow* diamond. Note that the spectrum of this diamond shows the presence of the 567 nm center, what suggests low temperature HPHT treatment. Relatively strong NV^0 center is an indication that the HPHT annealing has not produced many C defects. **b** Irradiated low nitrogen diamond (about 4 ppm B defects and 0.5 ppm A defects). After irradiation, the NV$^-$ center is completely suppressed and the NV defects are presented by the NV^0 center only. The bands at wavelengths 588 and 600 nm are vibronic features of the 575 nm center. Very strong GR1 center suggests that the diamond has not been annealed

charge state of the NV defects in untreated type IIa diamonds could be due to high concentration of dislocations, which are deep acceptors in diamond lattice (Samsonenko et al. 2010). Thus the influence of dislocations on the charge state of defects is opposite to that of C defects, which are donors and therefore charge defects negatively.

Strong intensity of the 575 nm center in PL spectra is an indicator of untreated natural type IIa diamonds. Although this criterion should be considered with caution, for in low-nitrogen HPHT-treated diamonds, the intensity of the NV^0 center can also be stronger than the intensity of the NV$^-$ center. In type Ib diamonds with high-nitrogen content (about 200 ppm C defects), the NV defects are present predominantly in negatively charged NV$^-$ state and are detected as the 638 nm center. However, in low-nitrogen type Ib diamonds (below 10 ppm C defects) about half of the NV centers are neutral producing 575 nm center of considerable intensity (Collins et al. 2005).

NV defects have rather low temperature stability and may anneal out completely at temperatures above 1,500 °C. Thus their presence in PL spectra of natural type IIa diamonds can be considered as an indicator that these diamonds were not exposed to high temperature HPHT treatment (Smith et al. 2000). This criterion, however, should not be applied to type Ia diamonds, in which HPHT treatment, along with annealing of existing NV centers, results in generation of new ones. This effect is especially clearly seen in diamonds after short-time HPHT treatment, when the resulting defect structure remains in highly non-equilibrium state and many defects of low temperature stability survive.

In brown type IaA diamonds treated at a temperature of 2,100 °C, A defects dissociate into C defects and produce high concentration of NV centers. The deeper the brown color the higher the dissociation rate of the A defects (Vins and Yelisseyev 2008). No intensity change of the NV centers is observed in IaA colorless diamonds after HPHT treatment (Vins and Yelisseyev 2008), what can be the result of dynamic equilibrium of two competing processes—annealing and generation of NV defects. The 575 nm center is also strongly generated in type Ib synthetic diamonds after treatment at a temperature of 1,800 °C and above (Kanda and Jia 2001). Generation of the 575 nm center during plastic deformation at high temperatures in diamonds containing C defects was shown in (Brookes et al. 1993). Thus diamonds with Ib component, which have been plastically deformed during HPHT treatment, are expected to reveal enhanced intensity of the 575 nm center.

Although strong 575 nm center is a feature of HPHT-treated diamonds, it may be completely destroyed by HPHT treatment performed at high temperatures, even after short time exposure. The removal of the NV centers at high temperatures is strongly stimulated by prior irradiation. For instance, it has been noticed that high-nitrogen type IaAB diamonds heavily irradiated with electrons or neutrons and then HPHT-annealed at a temperature of 2,300 °C display in their spectra no NV centers (Collins et al. 2005).

In treated diamonds, the 575 nm center is frequently observed in FSI absorption spectra in regime of luminescence (negative absorption). The negative absorption of the 575 nm center is rarely observed in spectra of untreated diamonds (Fig. 6.28).

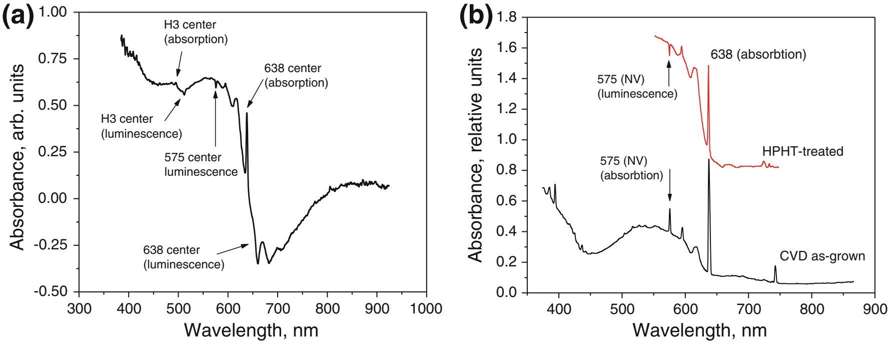


Fig. 6.28 **a** FSI absorption spectrum of an Imperial *Red* diamond of fancy deep *purple* color. Very strong 638 nm center (NV^- center) is seen in regimes of absorption and luminescence ("*red* transmission" effect)—a typical feature of HPHT-treated diamonds of *red color*. A weak H3 center also shows "*green* transmission" effect. The 575 nm center is seen in the regime of emission, not absorption—a typical feature of FSI absorption spectra of Imperial *Red* diamonds. **b** Comparison of absorption spectra of a natural HPHT-treated diamond of *red color* and an as-grown CVD diamond of *pink color*. Both diamonds exhibit dominating 638 nm (NV^-) center and minor 575 nm (NV^0) center. In the HPHT-treated diamond, the 575 nm center is observed in the regime of luminescence, whereas it shows absorption in as-grown CVD diamond [based on data from (Wang 2009b; Johnson and Breeding 2009)]

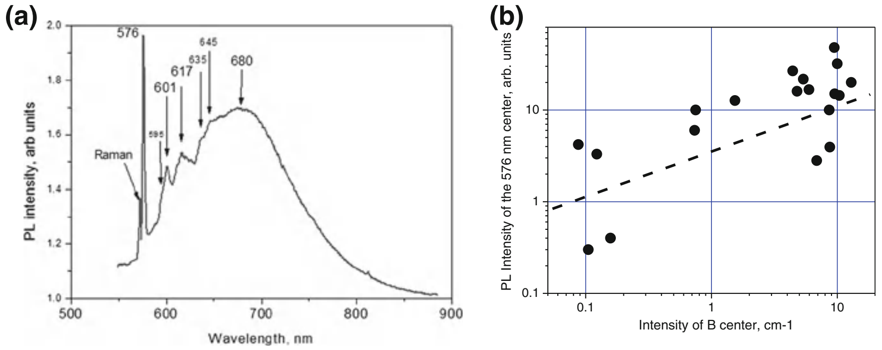


Fig. 6.29 **a** PL spectrum of the 576 nm center taken from a natural *pink* diamond at LNT. The main features of the center are ZPL at a wavelength of 576 nm and two distinctive phonon replica at 601 nm (acoustic phonons) and 617 nm (optical phonons). These phonon replicas are the main features distinguishing the 576 nm center from the 575 nm (NV^0) center, which has very different phonon-assisted bands (see the 575 nm center, Fig. 6.27b). **b** PL intensity of the 576 nm center plotted versus absorption intensity of B defects in brown untreated diamonds. *Dashed line* shows linear dependence

A useful feature, which can be used for the recognition of HPHT treatment, is the intensity ratio of the 536 and 575 nm centers. It has been reported that in HPHT-treated diamonds of “apple green” color, the intensity ratio I_{536}/I_{575} measured in PL spectra excited at a wavelength of 514 nm is smaller than that in natural untreated stones (Kitawaki 2007). This criterion, however, should be taken cautiously for it is not clear whether the contribution of ZPL of the 576 nm center was properly extracted from the intensity of ZPL of the 575 nm center.

576 nm center

The 576 nm center is a very characteristic PL feature of natural diamonds of brown and pink colors (Collins 1982; Smith et al. 2000; Epelboym et al. 2011) (Fig. 6.29). Untreated brown type IaAB diamonds frequently exhibit strong 576 nm center (Tretiakova and Tretyakova 2008). The 576 nm center is observed only in diamonds with nitrogen B defects. Almost always the diamonds exhibiting strong 576 nm center are of types IaB or IaB > A. Formation of the 576 nm center requires the presence of vacancies, which are available in brown diamonds or in irradiated diamonds (Collins and Ly 2002). Despite of the obvious relation between B defects and the 576 nm center, their intensities do not well correlate (Fig. 6.29b). This suggests that the defects responsible for the 576 nm center may comprise both B defect and some unknown component, e.g. vacancy.

In natural type IIa diamonds, the 576 nm center stands HPHT treatment at temperatures up to 1,800 °C (Shiryaev et al. 2001). High temperature HPHT treatment destroys the 576 nm center. Smith and colleagues (Smith et al. 2000) observed traces of the 576 nm center in HPHT-treated diamonds. Thus we believe, that the 576 nm center can survive commercial short-time, low temperature HPHT treatment. However, in vast majority of cases, the presence of intense 576 nm

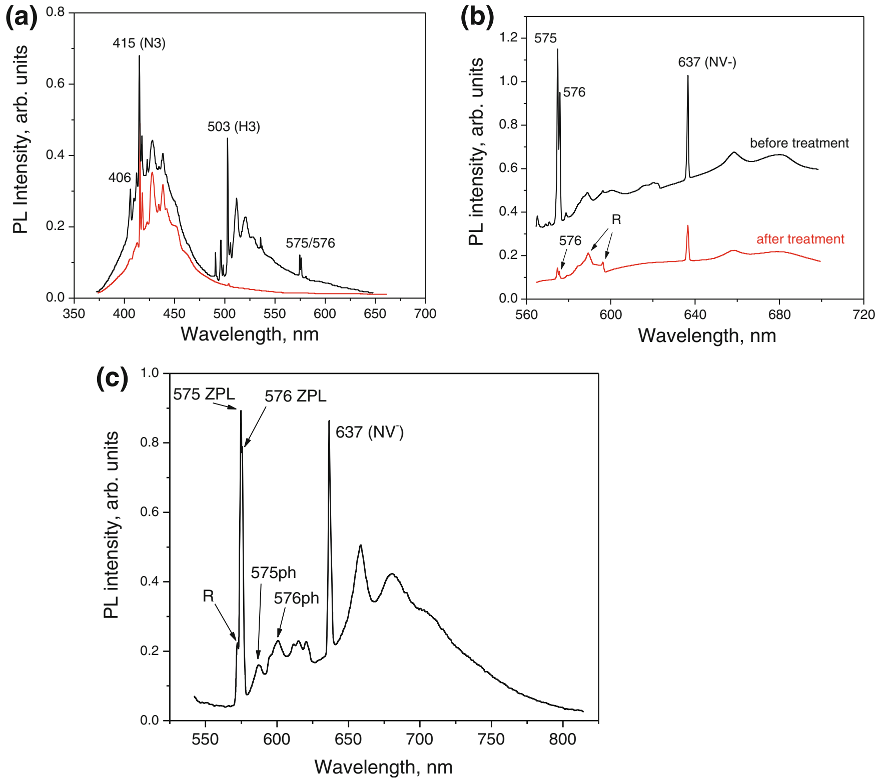


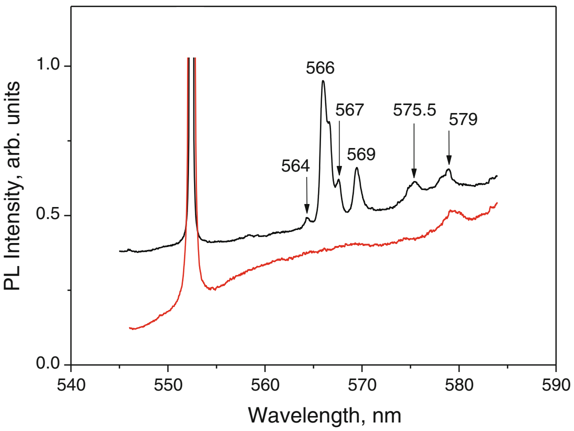
Fig. 6.30 (**a**, **b**) PL spectra of natural diamonds recorded before (*black curves*) and after (*red curves*) HPHT treatment [based on data from (Smith et al. 2000)]. Almost all centers, but the N3 center, are destroyed by the treatment. Yet traces of the 576 nm center are detected in the treated diamond in (**b**). **c** PL spectrum of a HPHT-treated low-nitrogen type IaB diamond showing simultaneously 575 nm (NV^0) and 576 nm centers. Positions of ZPLs and the main acoustic phonon replica of the centers are indicated

center in PL spectra is a reliable indicator of untreated diamonds. Yet, the treatment in this case should be understood as high temperature HPHT treatment (Fig. 6.30).

579 nm

The 579 nm center is observed in PL spectra of some natural brown type IIa diamonds. It can be accompanied by a number of narrow lines in the spectral range 560–580 nm. HPHT treatment destroys all these centers but the 579 nm center (Fig. 6.31). The solitary 579 nm center in the spectral range 560–580 nm can be considered as a feature of colorless type IIa HPHT-treated diamond.

Fig. 6.31 PL spectra of originally *brown* type IIa natural diamond (*black curve*) converted by HPHT treatment into colorless (*red curve*). A complex spectral structure with major lines at 566 and 569 nm is completely removed by the treatment. The 579 nm center is the only feature in the spectral range from 560 to 585 nm (Simic and Zaitsev 2012)



580 nm center

This PL center is observed in natural brown type IIa diamonds (Fisher and Spits 2000) (Fig. 6.32). The center is destroyed by HPHT treatment at temperatures in the range of stability of NV centers. The 580 nm center is probably mentioned as a Ni-related center with ZPL at 2.136 eV (580.5 nm) in (Yelisseyev and Kanda 2007). The 2.136 eV center anneals out at a temperature of 1,700 °C. Possibly the 580 nm center is mentioned in (Smith et al. 2000) as the 578.8 nm center, where it was shown as a good indicator of untreated type IIa diamonds.

586 nm center

This center is observed in PL spectra of natural brown type IIa diamonds and diamonds of yellow color (Fig. 6.32). The 586 nm center is destroyed by HPHT treatment at relatively low temperatures (in the range of thermal stability of the NV centers). Rarely, the 586 nm center can be detected in PL spectra of HPHT-

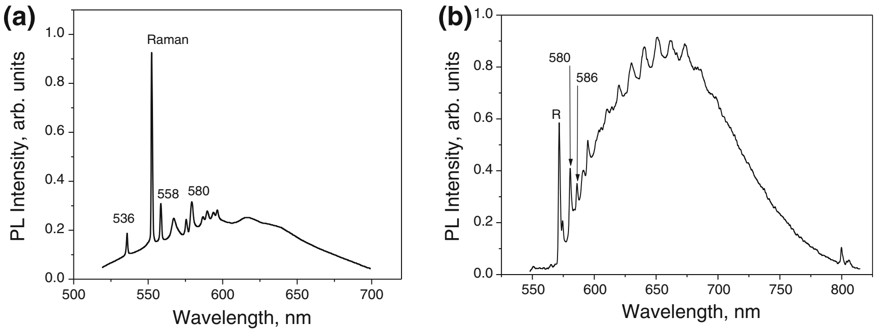


Fig. 6.32 **a** PL spectrum of a natural *brown* untreated type IIa diamond showing 536, 558 and 580 nm centers. **b** PL spectrum of a natural untreated fancy *yellow* diamond showing the 580 and 586 nm centers. Both centers are features of untreated diamonds

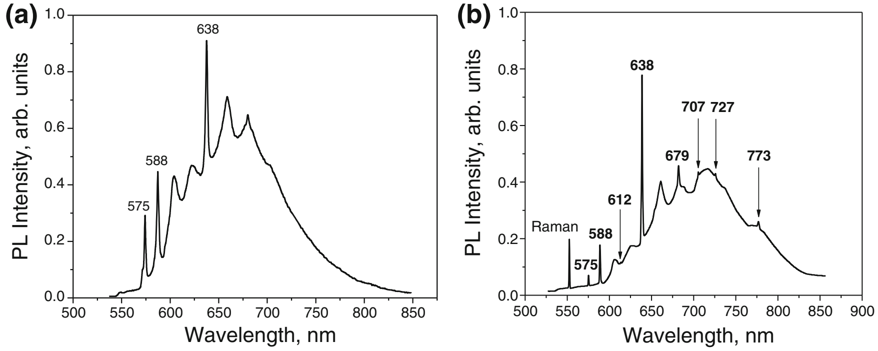


Fig. 6.33 **a** PL spectrum of a natural diamond of intense *greenish-yellow* color treated with irradiation and annealing. The spectrum exhibits three major centers 575 nm (NV^0), 588 nm and 638 nm (NV^-). This diamond does not show obvious evidence of HPHT treatment save for the high intensity ratio I_{638}/I_{575}, which is about 4. **b** PL spectrum of a *greenish-yellow* HPHT-treated diamond [re-plotted from (Zhonghua Song et al. 2009)]. High ratio of intensities of the 638 and 575 nm centers I_{638}/I_{575} suggests HPHT treatment. However the presence of the 588 nm center and traces of the centers 612, 679, 707, 727 and 773 nm can be considered as an indication that the treatment was performed at low temperatures not exceeding 1,800 °C

treated diamonds exhibiting strong NV centers. The presence of the 586 nm center is considered as an indicator of untreated type IIa diamond (Smith et al. 2000).

588 nm center

This center is frequently observed in PL spectra of nitrogen-containing and/or Ni-containing HPHT-treated natural diamonds (Fig. 6.33). It is a common feature of Imperial Red diamonds (Wang et al. 2005). The 588 nm center is also observed in high-nitrogen diamonds subjected to irradiation followed by conventional annealing at temperatures up to 1,000 °C. The center 588 nm can be considered as an evidence of multi-process treatment.

594.4 nm (the 595 nm center)

This absorption center is a typical radiation-induced optical feature of nitrogen-containing diamonds (Fig. 6.34). The 595 nm center is not excited in PL. The 595 nm center relates to a temperature unstable defect. It anneals out at a temperature of 1,000 °C. Annealing of the 595 nm center is accompanied by creation of the 2,024 nm (H1b) center and the 1,934 nm (H1c) center, which involve A- and B-defects respectively (Collins 2001; Collins et al. 2005). The 595 nm center is rarely seen in natural untreated diamonds. In vast majority of natural colored diamonds exhibiting the H3 center absorption (diamonds with yellow component in color), the 595 nm center is absent (Collins 2003). The center is especially rarely detected in spectra of cut diamonds (Collins 1982). However, the 595 nm center can be seen in spectra of untreated type Ia(B > A) diamonds from eastern Zimbabwe, which have greenish and brownish overtones (Breeding 2011).

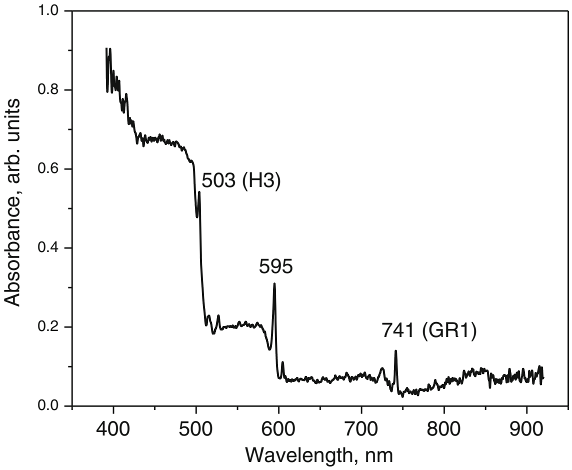


Fig. 6.34 Absorption spectrum of a fancy deep *brownish yellow* diamond, which exhibits an intense 595 nm center. This diamond has been reported as treated by multi-process treatment. Based on the intensity and phonon structure of the GR1 center, one can conclude that the final annealing used for the treatment was performed at a temperature below 700 °C

The 595 nm center is a typical feature of treated diamonds. It is frequently seen in spectra of diamonds treated by combination of HPHT annealing, irradiation and low temperature annealing. For instance, this center is a feature of Imperial Red diamonds. It is a very rare event to encounter 595 nm, H1b and H1c centers in spectra of natural untreated diamonds; therefore their presence is a strong indicator of treatment (Collins 2001; Hainschwang et al. 2002; Hainschwang et al. 2009).

596 nm center

We have no detailed information about the 596 nm center save for the fact that it is observed in PL spectra of some Ni-containing HPHT-treated natural diamonds (Fig. 6.35).

599 nm center

This Ni-related PL center is generated by HPHT treatment at a temperature of 1,700 °C and it is destroyed by HPHT treatment at a temperature of 1,900 °C (Yelisseyev and Kanda 2007) (Figs. 6.42b, 6.43). We believe that the presence of the 599 nm center is a feature of untreated diamonds. However, low temperature treatment cannot be excluded.

601 nm center

This center is observed in PL spectra of brown type IIa diamonds. It is destroyed by HPHT treatment at relatively low temperatures (in the temperature range of stability of the NV centers). Presence of the 601 nm center is an indicator of untreated type IIa diamonds (Smith et al. 2000).

603.5 nm

The 603.5 nm Ni-related center frequently accompanies the 700.5 nm center in PL spectra of Ni-containing diamonds. This center is a characteristic feature of the

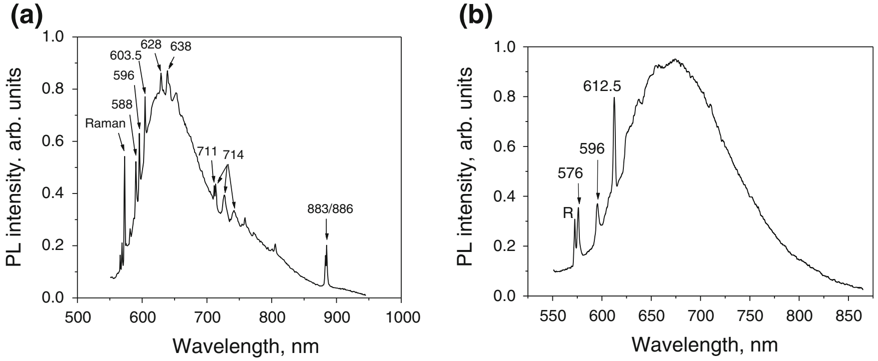


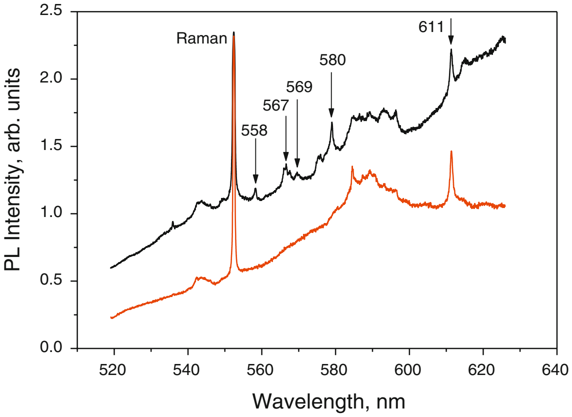
Fig. 6.35 **a** PL spectrum of a low-nitrogen, fancy *orangey yellow* diamond measured at LNT. Many Ni-related centers characteristic of HPHT treatment are seen. This stone showed *yellow* color "fluorescence cage", which is frequently observed in type Ia Ni-containing HPHT-treated natural diamonds. **b** PL spectrum of an untreated fancy dark yellow brown natural diamond showing the 596 nm center. The presence of the 576 and 711 nm centers and the narrow Platelets Peak (FWHM of 8.8 cm^{-1}) confirm that the diamond is untreated. In this diamond, the 711 nm center is very strong when excited at a wavelength of 658 nm

natural yellow diamonds, which owe their color to Ni-related centers (Tretiakova 2009). The 603.5 nm center is destroyed by high temperature HPHT treatment. However, it may be observed in diamonds HPHT-treated at low temperatures (Fig. 6.35a).

611 nm center

The 611 nm center is observed in some brown type IIa diamonds. This center stands commercial HPHT treatment and cannot be used for identification of treated diamonds (Simic and Zaitsev 2012) (Fig. 6.36).

Fig. 6.36 PL spectra of a type IIa originally *brown* natural diamond (*black curve*) converted by HPHT treatment into colorless (*red curve*). Spectrum of this diamond is more complex before treatment exhibiting several optical centers, which disappear after annealing. After HPHT treatment, the 611 nm line remains unchanged



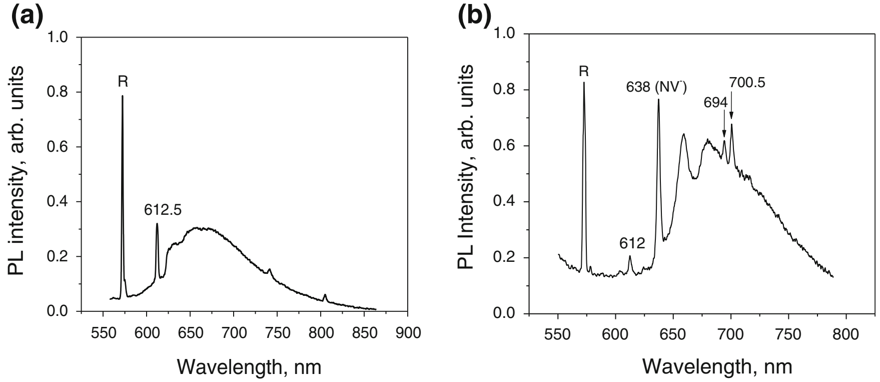


Fig. 6.37 PL spectra taken from an untreated type IaB natural diamond (**a**) and untreated high-nitrogen type IaAB diamond (**b**). A well-developed 638 nm center (NV^-) in spectrum (**b**) has natural origin and it is not an indicator of HPHT treatment. The presence of sole NV^- center without any trace of the 575 nm (NV^0) center is a feature of a diamond with an appreciable content of C defects

612.5 nm center

Untreated brown and pink type IaAB diamonds frequently reveal strong line at a wavelength of 612.5 nm in PL spectra (Tretiakova and Tretyakova 2008; Gaillou et al. 2010) (Fig. 6.37). The 612.5 nm center and the accompanying broad band with maximum at a wavelength of 720 nm is also a common feature of natural purple diamonds (Titkov et al. 2008). The 612.5 nm center is destroyed by HPHT treatment performed at temperatures of 2,000 °C and above (Tretiakova and Tretyakova 2008; Hainschwang et al. 2005; Tretiakova 2009).

613–617 and 620 nm

These multiple lines are observed in PL spectra of brown type IIa diamonds. They are destroyed by HPHT treatment at relatively low temperatures (in the temperature stability range of the NV centers). Presence of these lines is an indicator of untreated type IIa diamonds (Smith et al. 2000).

626.3 nm

(see the 523.6 nm center)

628 nm

The 628 nm center is observed in PL spectra of natural Ni-containing diamonds subjected to HPHT treatment at moderate temperatures (Fig. 6.35a).

638 nm (NV^- center)

The 638 nm center is the manifestation of the negatively charged nitrogen-vacancy NV defect (see also the 575 nm center for the neutral NV defect). The 638 nm center is a common optical feature of type Ib diamonds, the crystal lattice of which is damaged by plastic deformation, irradiation, micro-cleavage, micro-fracture etc.

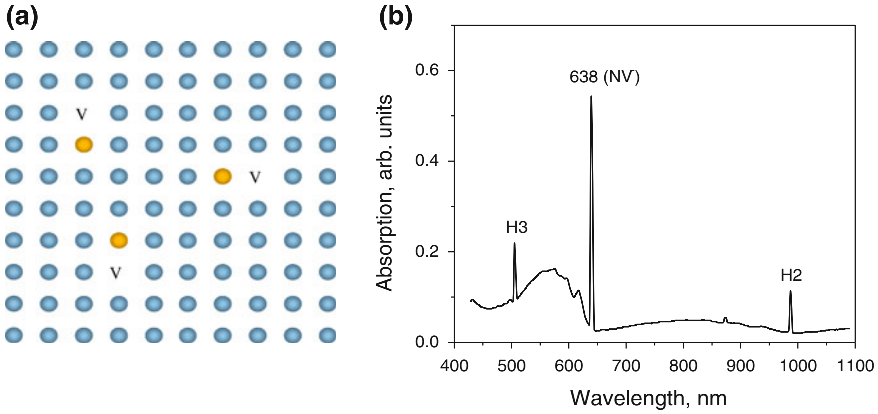


Fig. 6.38 **a** Atomic model of the nitrogen-vacancy defect responsible for the NV$^-$ center. *Blue* and *yellow circles* denote carbon and nitrogen atoms respectively. **b** Absorption spectrum of an electron-irradiated type Ib synthetic diamond after annealing at a temperature of 1,600 °C. The dominating feature is the 638 nm (NV$^-$) center

(Fig. 6.38). The 638 nm center is also the most prominent absorption and luminescence spectral feature involved in the process of HPHT treatment. In low-nitrogen type Ib diamonds, the center may cause natural color of very rare red hue (Wang 2009).

The 638 nm center can be detected in PL spectra of almost every untreated natural brown diamond of any type. The 638 nm center can be rather strong in absorption spectra of natural type Ib diamonds (Hainschwang et al. 2005) and especially strong in PL spectra of pristine type Ib brown diamonds. The 638 nm center of moderate intensity is seen in PL spectra of pristine brown type IIa diamonds (Smith et al. 2000). The 638 nm center is also a feature of PL spectra of natural type IIb diamonds (Eaton-Magaña and Lu 2011). The NV$^-$ center can be strong in PL spectra of brown-yellow stones, which exhibit features characteristic of type Ib diamonds and exhibit the H2 center in absorption. No luminescence of the 638 nm center is seen in diamonds with no absorption of the H2 center (Hainschwang et al. 2005, 2006a; De Weerdt and Van Royen 2000). Correspondingly, the H3 center is not seen in absorption spectra of the diamonds exhibiting absorptions of the 638 nm center and the H2 center. Nevertheless, the H3 center can be observed in luminescence of these diamonds (De Weerdt and Van Royen 2000).

In natural colorless untreated diamonds, PL intensity of the NV$^-$ center is usually less than that of the NV^0 center (Vins et al. 2008). Intensity of the naturally-occurring 638 nm center decreases with reduction in nitrogen content, and the center is hardy seen in PL spectra (laser excitation at a wavelength of 514 nm) of colorless type IIa untreated diamonds. Its intensity in such stones is less than 1/100th of the intensity of the second-order Raman scattering of diamond (Chalain et al. 2000).

The naturally-occurring 638 nm center is not strong enough to influence the diamond color (Collins 1982). These few natural diamonds, the body color of which has pink component due to the 638 nm center, are unique. Therefore, practically any diamond colored via NV^- center is rightfully reported as treated.

Luminescence of the NV^- center in some diamonds can be so high that it adds considerably red hue to the color of these diamonds, when these diamonds are viewed under daylight illumination. This effect is similar to that of "green transmission" known for the H3 centers and, by analogy, can be referred to as "red transmission".

The NV^- center is a typical product of HPHT treatment of initially brown diamonds. Since any natural diamond contains at least traces of nitrogen impurity, NV defects always form at high temperatures during the destruction of vacancy clusters. Even high color HPHT-treated type IIa very low-nitrogen diamonds (obtained from brown stones) show in PL spectra at least traces of the 638 nm center, ZPL intensity of which, when measured at RT, may be comparable with that of the second-order Raman band (Chalain et al. 2000). Regular brown type IIa diamonds always show in PL spectra the 638 nm center after HPHT treatment (Chalain et al. 1999; Fisher and Spits 2000; Collins 2001). Natural brown to yellow type Ia diamonds do not reveal in PL spectra remarkable 638 and 575 nm centers, whereas both centers are usually intense in these diamonds after HPHT treatment (Sriprasert et al. 2007). Irradiation of HPHT-treated natural diamonds increases intensity of the 638 nm center drastically. The 638 nm center is the main feature of PL and absorption spectra of Imperial Red diamonds (Wang et al. 2005; Vins et al. 2008).

In initially brown diamonds, the NV^- center is produced by HPHT treatment performed at temperatures of 2,000 °C and above (Collins 2003). In type Ia brown diamonds, the 638 nm center can be rather strong after a few minutes of treatment at a temperature of 2,300 °C (De Weerdt and Collins 2007). In brown (plastically deformed) type IaA diamonds, HPHT treatment performed at temperatures of 2,100 °C and above results in dissociation of the A defects and massive formation of the NV defects. In these diamonds, the 638 nm center is strong enough to be seen in absorption spectra (Vins and Yelisseyev 2010).

The production of the NV defects during HPHT annealing occurs only in plastically-deformed diamonds, which have at least slight component of brown color. In structurally perfect diamonds, HPHT treatment does not induce NV centers. Thus the source of vacancies (vacancy clusters, dislocations) is essential. For this reason, the 638 nm center is not enhanced in irregular brown CO_2 and pseudo CO_2 diamonds after HPHT treatment (Hainschwang et al. 2005).

In natural type Ib diamonds, initially intense 638 nm center can be strongly reduced by HPHT treatment performed at a temperature of 2,000 °C. The reduction in intensity of the 638 nm center is explained by the conversion of type Ib into type Ia (Hainschwang et al. 2005). HPHT treatment performed at very high temperature may destroy the NV defects completely (Fig. 6.39a). Usually this destruction is observed at temperatures 2,300 °C and above. The exact mechanism

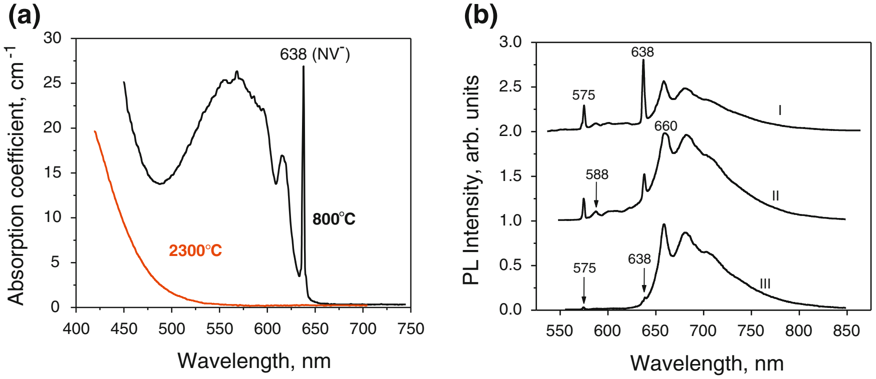


Fig. 6.39 **a** Absorption spectra from an electron-irradiated type-Ib synthetic diamond after annealing in vacuum at a temperature of 800 °C (*black curve*) and after subsequent HPHT annealing at a temperature of 2,300 °C under pressure 5 GPa (*red curve*) [based on data from (Collins et al. 2005)]. **b** PL spectra of HPHT-treated diamonds showing different spectral shape of the 638 nm center. (*I*)—A diamond showing 575 and 638 nm centers of "regular" spectral shape. Peak intensity of ZPL of the 638 nm center is considerably stronger than that of the phonon side band. (*II*)—A diamond showing the 638 nm center, ZPL intensity of which is reduced due to the effect of self-absorption. (*III*)—PL spectrum of the 575 and 638 nm centers taken from an Imperial Red diamond. Due to very strong self-absorption, ZPL of the 638 nm center almost disappears. Since ZPL intensity of the 638 nm center strongly depends on self-absorption, it is important that the intensity ratio of the centers NV^- and NV^0 is measured not in their ZPLs, but in the phonon sidebands, e.g. at a wavelength of 588 nm (the first phonon replica of the 575 nm center) and 660 nm (the first phonon replica of the 638 nm center). Thus, the true intensity ratio of the centers I_{638}/I_{575} in spectrum (II) is about 10, whereas it is only 0.9, when measured in their ZPLs

of the annealing of the NV defects is not clear. Though, it is believed that the NV defects become mobile and aggregate into larger nitrogen complexes.

HPHT-treated diamonds can reveal both formation of NV centers and their destruction (Fig. 6.41b). This seeming inconsistency suggests that the concentration of NV defects and, consequently, the intensity of the 638 and 575 nm centers in HPHT-treated diamonds is a result of complex aggregation/dissociation processes of nitrogen-vacancy defects. Since NV defects are not stable at temperatures of commercial HPHT treatment, their presence in HPHT-treated diamonds suggests that the defect transformations occurring during HPHT annealing were not completed and the sources of formation of NV defects were not worked out. Typical example of this situation is the incomplete removal of brown color in initially dark brown diamonds. The vacancy clusters in brown diamonds are the source of vacancies for the NV defects. Since HPHT annealing always produces a certain concentration of C defects in natural diamond, the NV centers are generated as long as the vacancy clusters are present. When the vacancy clusters are completely annealed out and brown color disappears, the NV centers anneal out too. Thus, strong NV centers are a typical feature of spectra of HPHT-treated diamonds, which exhibit in their color remnants of brown hue.

Irradiation reduces intensity of the 638 nm center and increases relative intensity of the 575 nm center. Thus, the presence of the 638 nm center in strongly irradiated diamonds may be considered as an indicator of HPHT treatment performed prior to irradiation.

Spectral width of ZPL of the NV^- center increases after HPHT treatment. FWHM of the 638 nm line in spectra of type IIa diamonds measured at LNT is about 0.45 nm and below in untreated stones and about 0.53 nm and above in HPHT-treated ones. This increase suggests that HPHT treatment increases the internal strain in the vicinity of the NV defects (Haenni et al. 2000; Collins 2001; Smith et al. 2000; Chalain et al. 2001). The 575 nm center exhibits similar broadening of its ZPL after HPHT treatment, and it can be also used for recognition of HPHT treatment. Unfortunately, some overlap of the FWHM ranges for treated and untreated diamonds does not allow to use the ZPL-width criterion as a reliable proof of HPHT treatment for all diamonds. However, based on the data from (Wang et al. 2009b), the diamonds, which exhibit the 638 and 575 nm centers with ZPLs broader than 0.7 nm, can be reported as treated with confidence. Correspondingly, the diamonds with NV centers, ZPLs of which are narrower than 0.4 nm, can be confidently reported as untreated.

In PL spectra of natural untreated diamonds, intensity of the 638 nm center is usually minor as compared with that of the 575 nm center. In contrast, the 638 nm center is stronger than the 575 nm in PL spectra of HPHT-treated diamonds. The NV^- center can be much stronger than the NV^0 center in treated diamonds of any type (Chalain et al. 2001; Wang and Gelb 2005). Strong PL of the 638 nm center and rather weak PL of the 575 nm center is a typical result of HPHT treatment of brown diamonds (Hainschwang et al. 2005; Tretiakova and Tretyakova 2008; Collins 2001). It is important that the intensity ratio of the NV^- and NV^0 centers (I_{638}/I_{575}) is measured in spectra obtained with the excitation at a wavelength in the range 500–550 nm (e.g. with 514 nm Ar-laser line, or 532 nm laser line). If a shorter excitation wavelength is used (e.g. 488 nm argon laser line), this ratio must be corrected by a factor of 2–5. The criterion of recognition of HPHT-treated diamonds based on the intensity ratio $I_{638}/I_{575} > 1$ is not valid for the excitation wavelengths shorter than 400 nm, for the 638 nm center is not excited directly in this spectral range. Although the intensity ratio of the NV centers $I_{638}/I_{575} > 1$ works well for many HPHT-treated diamonds, in general it is a rough criterion providing a 75 % fidelity (Collins 2003).

The intensity ratio I_{638}/I_{575} increases with the nitrogen content (Fig. 6.40b). For instance, this ratio increases with the increase in the intensity of the 270 nm absorption band. Also, in type IIa HPHT-treated diamonds, there is a tendency: the better color the less the ratio I_{638}/I_{575}, e.g. it is of 3.0 for M-color diamonds and it drops to 1.2 for K-color diamonds. In type Ia diamonds this ratio is much greater than in type IIa diamonds and can be as high as 30 in yellow color diamonds. It has been found that in type Ia HPHT-treated diamonds, the higher absorption intensity of the H3 center the greater intensity ratio I_{638}/I_{575} (Sriprasert et al. 2007). Type Ib

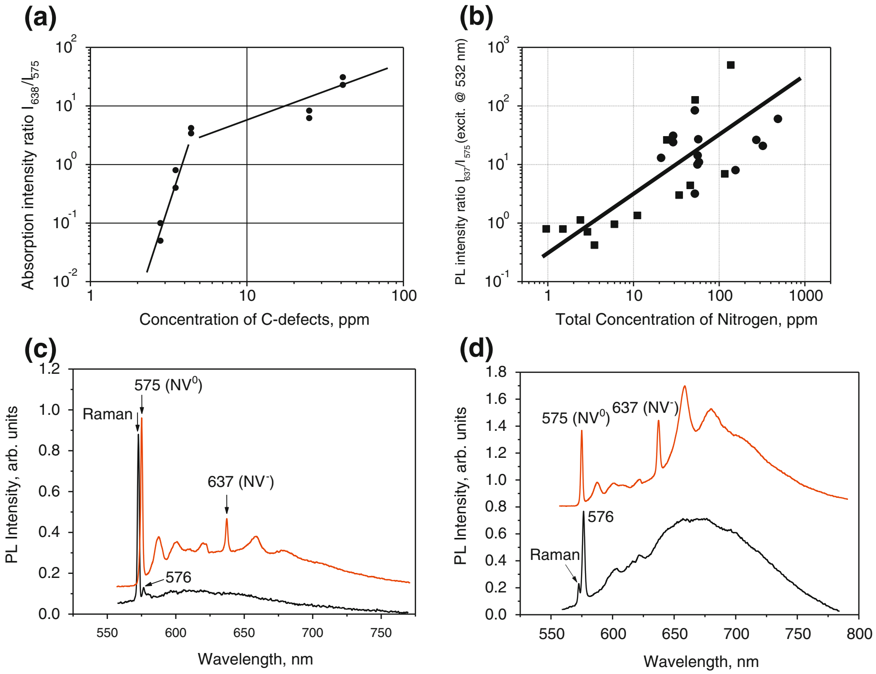


Fig. 6.40 Intensity ratio of the 638 nm (NV$^-$) and 575 nm (NV^0) centers in treated diamonds versus nitrogen content. **a** Absorption intensity ratio I_{638}/I_{575} versus concentration of C defects in synthetic type Ib diamonds irradiated with electrons of energy 3 MeV at a dose of 10^{18} cm^{-2} and subsequently annealed at a temperature of 1,000 °C. The NV$^-$ center dominates in diamonds with C defect content over 5 ppm, whereas the relative intensity of the NV^0 center is greater in low-nitrogen diamonds (Vins et al. 2008, 2011a). **b** Intensity ratio I_{638}/I_{575} in PL spectra of HPHT-treated diamonds versus total nitrogen content. Diamonds were treated by HPHT annealing (*circles*) and multi-process treatment (*squares*) (Simic and Zaitsev 2012). **c**, **d** PL spectra of two initially *brown* type IaB diamonds measured at LNT with laser excitation at a wavelength of 532 nm before (*black curves*) and after (*red curves*) milti-process treatment: **c** a low-nitrogen diamond (3 ppm B defects) exhibits the intensity ratio of the NV-centers $I_{638}/I_{575} = 0.6$; **d** a diamond with 25 ppm B defects exhibits the intensity ratio of the NV-centers $I_{638}/I_{575} = 5.5$. Note that the intensities of the centers have been measured in their phonon side-bands, not in ZPLs. Before treatment, the dominating feature of both diamonds is the 576 nm center. After treatment, only the NV$^-$ and NV^0 centers are seen

diamonds have particularly great intensity ratio I_{638}/I_{575} due to high concentration of C defects, which charge most NV defects negatively. However, with the compensation of the donor nitrogen by other defects (e.g. by vacancies in irradiated diamonds) the intensity ratio I_{638}/I_{575} decreases. For instance, in type IIa diamonds implanted with nitrogen ions and subsequently annealed at a temperature of 1,400 °C, the intensity ratio I_{638}/I_{575} is less than one. After HPHT annealing of the implanted diamond at a temperature of 2,000 °C, relative intensity of the NV$^-$ center becomes again much stronger than that of the NV^0 center (Orwa et al. 2011; Acosta et al. 2009).

In low-nitrogen HPHT-treated diamonds, the intensity ratio $I_{638}/I_{575} > 1$ may reverse (Fisher and Spits 2000) (Fig. 6.40). This effect is explained by too low concentration of C defects, which cannot charge majority of NV defects negatively. A detailed analysis of the influence of the donor action of C defects upon the absorption intensity of the NV-centers is given in (Vins et al. 2011a). The absolute and relative intensities of the NV centers were studied in diamonds irradiated with 3 MeV electrons and subsequently annealed at a temperature of 1,000 °C for 2 h (Fig. 6.40a). It is seen that the ratio I_{638}/I_{575} becomes less than one (both in absorption and photoluminescence) in diamonds with nitrogen content below 4 ppm.

When using the value of the ratio I_{638}/I_{575} for recognition of HPHT-treated diamonds, it is important to understand, that the influence of nitrogen content on the relative intensities of the NV centers has a statistical nature and must be treated as a tendency rather than an exact dependence. The donor energy level of the C defects is very deep in the bandgap and the C defects do not produce free electron concentration high enough to establish the uniform Fermi level all over the diamond. Hence, different areas of one and the same diamond may exhibit considerably different values I_{638}/I_{575}. As a result, even very low-nitrogen HPHT-treated diamonds may show $I_{638}/I_{575} > 1$ despite the tendencies shown n Fig. 6.40a,b.

High power of the laser excitation used for recording PL spectra also decreases the ratio I_{638}/I_{575}. For instance, a power increase from 0.01 to 3 mW can reduce the ratio in an irradiated type Ib diamond 40 times (excitation at a wavelength 532 nm, measurements at LHeT). This reduction is explained by the photoionization of the NV^- centers and conversion them into NV^0 centers. A faster intensity saturation of the NV^- center than that of the NV^0 center can be another reason too. The laser power has a significant effect on the charge state of the NV defects in high-nitrogen diamonds. However, it does not affect the intensity ratio in low-nitrogen diamonds (Manson and Harrison 2005; Waldermann et al. 2006; Acosta et al. 2009). The decrease of the I_{638}/I_{575} ratio is especially pronounced in the low power range. Thus the excitation intensity must be always taken into account when measuring I_{638}/I_{575} ratio in PL spectra.

Detection of NV centers using laser-induced PL spectroscopy is one of the main methods traditionally used for recognition of HPHT-treated diamonds. It is especially helpful for type IIa diamonds, HPHT treatment of which is particularly difficult to recognize. Although, the intensity ratio $I_{638}/I_{575} > 1$ works well for vast majority of type Ia HPHT-treated diamonds and for many type IIa diamonds, this criterion cannot be used as a reliable proof of treatment. Since in many HPHT-treated type IIa diamonds the ratio I_{638}/I_{575} is less than one, a more reliable indication of treatment seems to be the total strength of the NV centers irrespective of their relative intensities.

Concentration of negatively charged NV defects in ppm (NV^-[ppm]) can be estimated using the following relations [based on original data and that from (Davies 1999; Davies et al. 1992)]:

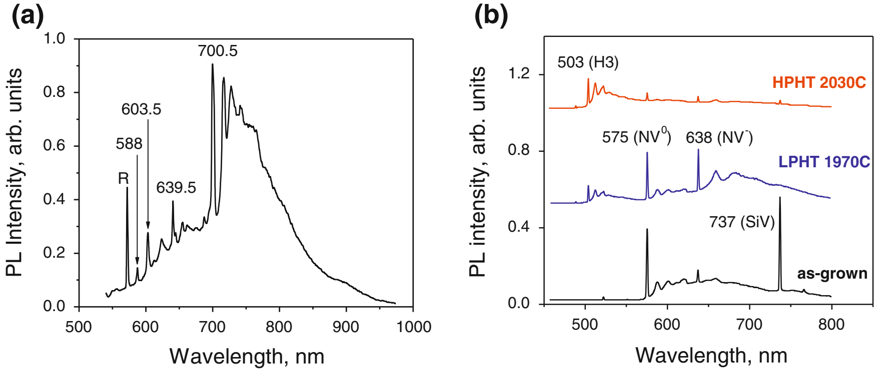


Fig. 6.41 **a** PL spectrum of a fancy *greenish yellow brown* diamond treated by irradiation and annealing at a temperature of 1,500 °C. The centers 588, 603.5, 639.5 and 700.5 nm remain intact after this treatment. **b** PL spectra of three pieces of a CVD diamond measured at LNT: as-grown (*black curve*), after LPHT annealing at a temperature of 1,970 °C (*blue curve*), and after HPHT annealing at a temperature of 2,030 °C (*red curve*) (Meng Yu-Fei et al. 2008). The NV centers are considerably suppressed by high temperature annealing. The intensities of the spectra are normalized to the intensity of the Raman peak

$$\mathrm{NV^-[ppm]} = 0.06\ \mathrm{I_{ZPL-NV-}}\left[\mathrm{cm^{-1}}\right],$$

where $\mathrm{I_{ZPL\text{-}NV\text{-}}[cm^{-1}]}$ is the peak absorption intensity of ZPL of the $\mathrm{NV^-}$ center in $\mathrm{cm^{-1}}$ recorded at LNT, or

$$\mathrm{NV^-[ppm]} = 0.12\ \mathrm{I_{584\,nm}}\left[\mathrm{cm^{-1}}\right],$$

where $\mathrm{I_{584\ nm}}$ is the absorption intensity of the $\mathrm{NV^-}$ center in $\mathrm{cm^{-1}}$ measured at a wavelength of 584 nm at RT (when using this formula, the background absorption underlying the $\mathrm{NV^-}$ center absorption must be subtracted).

639.5 nm (640 nm center)

This Ni-related PL center is generated by heating at 1,700 °C and is destroyed by HPHT treatment performed at a temperature of 1,900 °C (Fig. 6.41a). The 640 nm center is frequently seen together with the 700.5 nm Ni-related center (Yelisseyev and Kanda 2007). Possibly the 640 nm center is reported in (Tretiakova 2009) in spectra of natural diamonds of yellow color as the 640.6 nm center. The 640 nm center is a feature of untreated diamonds. However, if strong, the 640 nm center may be considered as an indicator of HPHT treatment performed at low temperatures (below 1,800 °C).

645.5 nm (1.921 eV) center

This Ni-related center is observed in PL spectra of synthetic and some natural diamonds. The 645.5 nm center can be generated by heating at a temperature of 1,700 °C and its intensity increases after further HPHT treatment performed at

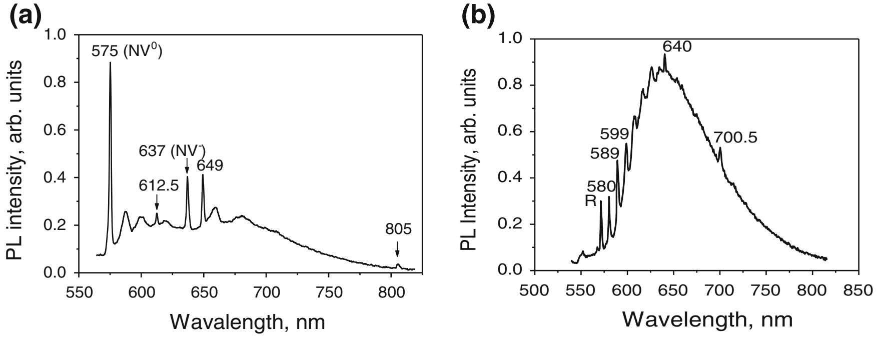


Fig. 6.42 **a** PL spectrum of a fancy intense *greenish yellow* diamond showing the 649 nm center. This diamond was HPHT-treated at a moderate temperature. **b** PL spectrum of the 650 nm Ni-related band taken from an untreated natural diamond. The short wavelength wing of the band overlaps with 580, 589, and 599 nm Ni-related centers, which, however, do not cause considerable distortion of the spectral shape of the 650 nm band. The 640 and 700.5 nm centers are seen too. All these centers and the 650 nm band are features of untreated natural diamonds

temperatures over 1,900 °C (Yelisseyev and Kanda 2007). Strong 645.5 nm center can be considered as an indication of HPHT treatment.

648 nm center

The 648 nm center is observed in PL spectra of some natural diamonds. This center is reported in untreated pink diamonds (Gaillou et al. 2010). The 648 nm center is also observed in HPHT-treated diamonds (Fig. 6.42a). A boron-related origin of the 648 nm center is proposed in (Emerson and Wang 2010). The 648 nm center relates to a defect with a very rigid atomic structure. Unlike many other centers in diamond, the 648 nm center does not change spectral width of its ZPL with increasing stress of the crystal lattice (Eaton-Magana 2011). Alone, the presence of the 648 nm center is not an indicator of treatment.

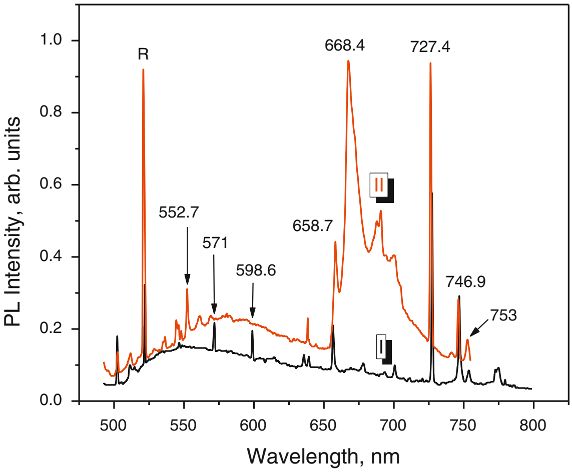
650 nm (the 650 nm band)

The 650 nm Ni-related broad band is observed in PL spectra of some natural diamonds (Fig. 6.42b). This band anneals out at a temperature of 1,700 °C (Yelisseyev and Kanda 2007). Presence of the 650 nm band is a good indicator of untreated natural diamonds.

658.5 and 668.5 nm (659 nm center)

These are the most intense features of a complex Ni-related center observed in PL and absorption spectra of synthetic diamonds and some natural diamonds (Fig. 6.43). The 668.5 nm line may be strong in spectra of untreated Argyle pink diamonds (Iakoubovskii and Adriaenssens 2002; Gaillou et al. 2010). This line is generated by HPHT treatment at a temperature of 1,700 °C and it increases in intensity with further HPHT treatment at temperatures over 1,900 °C (Yelisseyev and Kanda 2007). Although the 659 nm center is created at high temperatures, its

Fig. 6.43 PL spectra of a synthetic diamond taken at a temperature of 5 K with laser excitation at a wavelength of 488 nm. *I*—as-grown; *II*—HPHT-annealed at a temperature of 1,950 °C (Yelisseyev et al. 2003)



destruction by HPHT-treated in synthetic diamonds is reported in (Shigley et al. 1993).The presence of this center can be considered as an indication of treatment.

660 nm band

The 660 nm red band is observed in phosphorescence spectra of nearly all natural type IIb blue diamonds (Fig. 6.44). The 660 nm band is most effectively excited via electronic transitions from the conduction band and therefore it is intense in PL when excited with light of wavelengths shorter than 230 nm or with electrons (CL). The 660 nm band can be observed simultaneously with the greenish-blue band with maximum emission at a wavelength of 500 nm (see the 500 nm band). Synthetic type IIb blue diamonds do not show strong 600 nm band, but the 500 nm band and sometimes the 575 nm center can be present (Eaton-Magana et al. 2006, 2008; Watanabe et al. 1997). A tentative mechanism of the 660 nm band phosphorescence is a donor–acceptor radiative recombination involving boron acceptors and some defects related to plastic deformation. The latter act either as deep donors or deep traps (Watanabe et al. 1997; Eaton-Magana and Lu 2011). The 660 nm band is destroyed by HPHT treatment (Breeding et al. 2006). Therefore the observation of the red phosphorescence caused by the 660 nm band is a reliable indicator of natural untreated blue diamonds.

676.5 nm center

The 676.5 nm Ni-related center is observed in absorption and PL spectra of synthetic and natural untreated diamonds. The 676.5 nm center is a feature of untreated pink diamonds (Gaillou et al. 2010). This center is destroyed by HPHT treatment performed at temperatures of 1,800 °C and above (Lawson and Kanda 1993). However, the 676.5 nm center can be seen in diamonds treated by irradiation and conventional annealing (Fig. 6.45a). Presence of the 676.5 nm center speaks in favor of the diamonds, which were not treated by HPHT annealing.

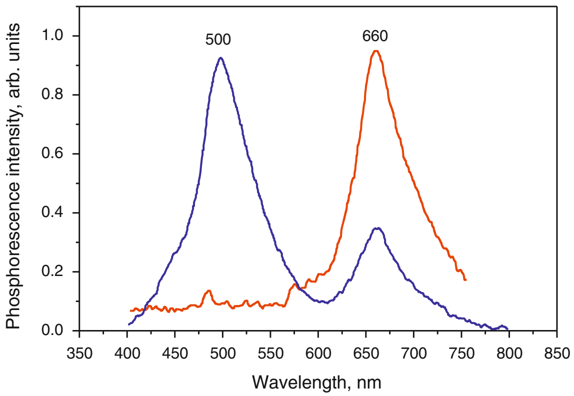


Fig. 6.44 Phosphorescence spectra of natural type IIb diamonds: a fancy intense blue diamond exhibiting dominating "Red Band" (*red curve*) and a very light blue diamond exhibiting "Blue Band" and "Red Band" (*blue curve*). Lifetime of the emission of the "Blue Band" is shorter than that of the "Red Band". Therefore, if the two bands are present with comparable intensities, the "Red Band" dominates in visual phosphorescence [based on the data from (Eaton-Magana and Lu 2011)]

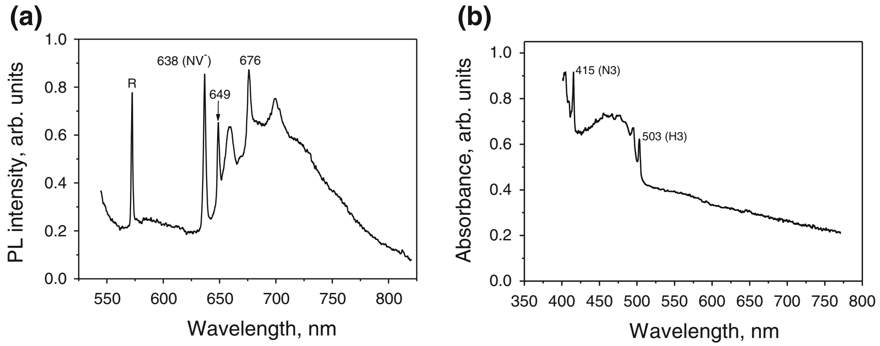
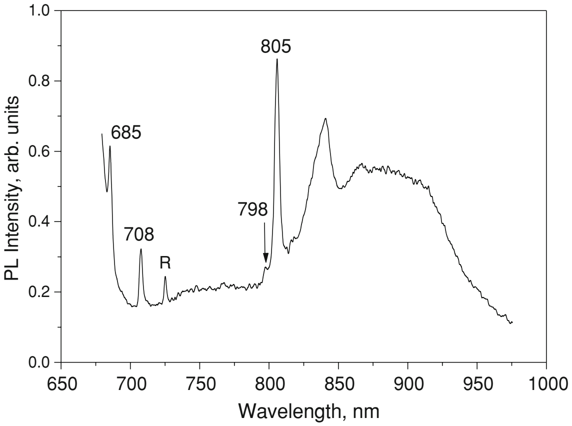


Fig. 6.45 **a** PL spectrum (taken at LNT) of an irradiated and subsequently annealed natural diamond (no HPHT treatment). The spectrum is dominated by the 638, 649 and 676.5 nm centers. **b** Absorption spectrum of the same diamond. Although the H3 center is strong in absorption, it does not reveal the "green transmission" effect. Strong absorption without "green transmission" is a characteristic behavior of the H3 center in diamonds treated by irradiation followed by annealing at temperatures below 1,400 °C

679 nm center

This Ni-related center is observed in PL spectra of synthetic and some natural diamonds. The 679 nm center is generated by heating at temperatures about 1,700 °C and it is destroyed by HPHT treatment at temperatures above 1,900 °C (Yelisseyev and Kanda 2007). The presence of the 679 nm center is an indication that diamond has not been exposed to high temperature HPHT treatment.

Fig. 6.46 PL spectrum of a low-nitrogen type IaB fancy deep purplish *pink* diamond processed by multi-process treatment. The centers 685, 708 and 805 nm are the major features of the spectrum



680 nm band

This broad structured band is observed in PL spectra of some natural diamonds The 680 nm band is the luminescence replica of the 480 nm absorption band (see the 480 nm band).

685 nm center

The 685 nm center is observed in PL spectra of type IaB diamonds after multi-process treatment. This center may be especially pronounced after complete annealing of the GR1 center. The 685 nm center is frequently seen together with the 708 and 805 nm centers (Fig. 6.46).

694 nm center

The 694 nm Ni-related center is observed in PL spectra of untreated natural and synthetic diamonds (Chalain 2003) (Fig. 6.47a). This center is generated by heating at temperatures about 1,700 °C and it is destroyed by HPHT treatment performed at temperatures of 1,900 °C and above (Yelisseyev and Kanda 2007). The 694 nm center should not be confused with the hydrogen-related 694 nm center, which differs from its Ni-related counterpart by a very different vibronic sideband (Fig. 6.47b). Strong 694 nm Ni-related center may be an indicator of HPHT treatment performed at low and moderate temperatures. In contrast, the hydrogen-related 694 nm center stands HPHT treatment. In PL spectra of HPHT-treated diamonds, the 694 nm Ni-related center is frequently accompanied by relatively strong 638 nm (NV^-) center. In contrast, in untreated diamonds, the hydrogen-related 694 nm center is rarely seen together with strong 638 nm center.

700.5 nm (1.770 eV) center

The 700.5 nm center is observed in PL spectra of natural and synthetic diamonds (Chalain 2003) (Fig. 6.48). This center is tentatively ascribed to a nickel-nitrogen defect. The 700.5 nm center is a common feature of type Ia nickel-containing diamonds. The 700.5 nm center is frequently present in spectra of Argyle diamonds. This center is a feature of some natural type Ia yellow diamonds which

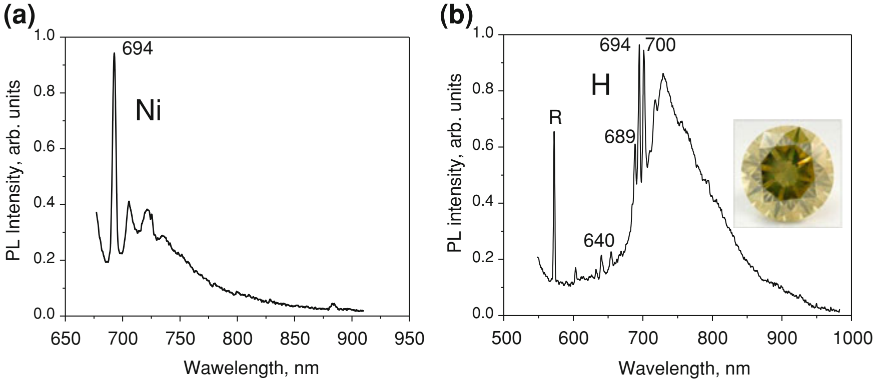
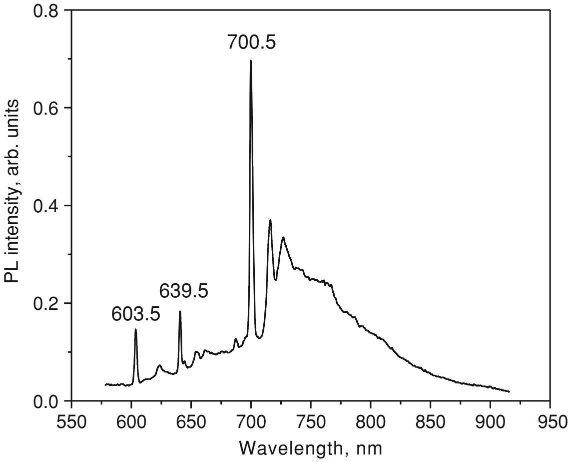


Fig. 6.47 **a** PL spectrum of the 694 nm Ni-related center taken from an HPHT-treated diamond. The dominating 694 nm center is an indicator of low temperature HPHT treatment. **b** PL spectrum of the 694 nm hydrogen-related center taken from an HPHT-treated diamond of *yellowish green* color. Presence of the characteristic hydrogen-related centers 640, 689 and 700 nm (Emerson 2009) confirms the presence of hydrogen in this stone

Fig. 6.48 PL spectrum of a light *brownish yellow* natural untreated diamond revealing 700.5, 639.5 and 603.5 nm Ni-related centers



owe their color to Ni impurity. In these diamonds, the 700.5 nm center is always accompanied by the Ni-related centers with ZPLs at 496.7 nm (S3), 489 nm and 523.3 nm (S2) (Plotnikova et al. 1980; Tretiakova 2009). The 700.5 nm center is a common PL feature of natural gray diamonds (Eaton-Magana 2011).

The 700.5 nm center can be generated by HPHT annealing. Increase in intensity of this center in natural diamonds after HPHT treatment at temperatures over 1,700 °C may occur due to generation of single nitrogen atoms (Hainschwang et al. 2005; Iakoubovskii and Adriaenssens 2001; Yelisseyev and Kanda 2007). The enhancement of this center can be especially pronounced in brown type Ia diamonds HPHT-treated at a temperature of 2,000 °C (Hainschwang et al. 2005).

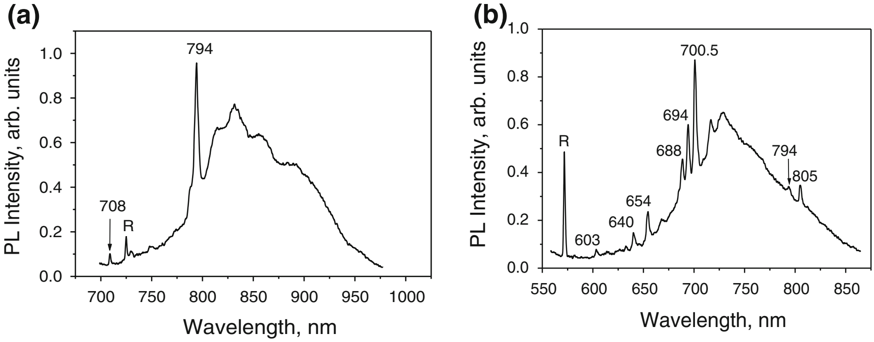


Fig. 6.49 PL spectra of an untreated high-nitrogen fancy deep *brownish greenish yellow* diamond taken with laser excitation at wavelengths 532 nm (**a**) and 658 nm (**b**). Almost all PL centers in the spectra, including a weak 708 nm center, are features of untreated diamonds

Formation of the 700.5 nm center in Ni-containing synthetic diamonds after HPHT annealing has been reported too (Yelisseyev et al. 2002). The 700.5 nm center may be also strong in nitrogen-containing diamonds subjected to irradiation followed by conventional annealing at temperatures over 1,000 °C.

707.5 nm (708 nm) center

The 708 nm Ni-related PL center is generated by heating at 1,700 °C and is destroyed by HPHT treatment performed at a temperature of 1,900 °C (Yelisseyev and Kanda 2007) (Fig. 6.49a).

710 nm Band

A structureless broad band with maximum at a wavelength of 710 nm is observed in absorption spectra of HPHT-treated synthetic diamonds (Fig. 6.50a). In some publications, the 710 nm band is referred to as a band with maximum at a

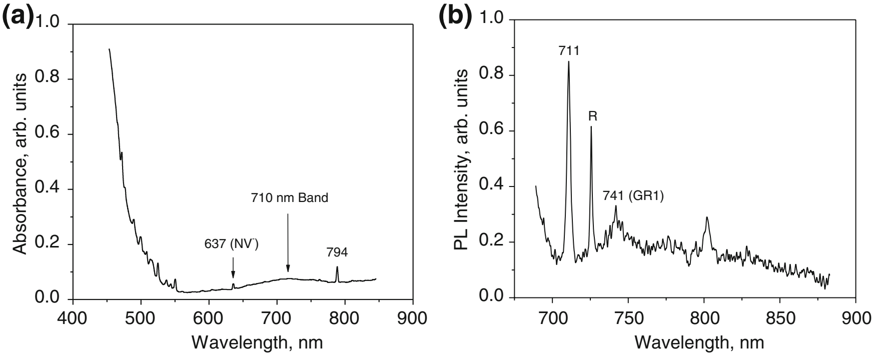


Fig. 6.50 **a** Absorption spectrum of a HPHT-treated synthetic diamond showing the 710 nm Band and the 794 nm Ni-related center (Shigley et al. 1993). **b** PL spectrum of the 711 nm Ni-related center taken from a natural untreated fancy dark*orangey brown* diamond

wavelength of 690 nm. This band may be associated with the vibronic side-band of the 794 nm Ni-related center (Shigley et al. 1993). It is not clear whether the 710 nm band is generated by HPHT treatment. However, the band can considerably increase its relative intensity after HPHT annealing because of the reduction of the absorption background in the spectral range 600–800 nm.

711 nm center

This Ni-related center is observed in absorption and PL spectra of Ni-containing diamonds (Fig. 6.50b). The 711 nm center anneals out completely at temperatures over 1,700 °C (Yelisseyev and Kanda 2007). Presence of the 711 nm center is a reliable indicator of untreated diamonds.

714 nm center

This Ni-related center is observed in PL spectra of Ni-containing diamonds. The 714 nm center is frequently detected in spectra of HPHT-treated stones. The center is generated by heating at temperatures of 1,700 °C and it increases in intensity with further HPHT treatment performed at temperatures over 1,900 °C (Yelisseyev and Kanda 2007). The 714 nm center has a distinctive vibrational side-band with dominating 32 meV vibration. Presence of the 714 nm center can be considered as an indication of HPHT treatment.

723/721 nm center

This Ni-related center with doublet ZPL is observed in PL spectra of untreated natural and synthetic diamonds. The 723/721 nm center is generated by heating at temperatures of 1,700 °C and it is partially destroyed by HPHT treatment performed at a temperature of 1,900 °C (Yelisseyev and Kanda 2007) (Fig. 6.51). The 723/721 nm lines can be observed in diamonds after multi-process treatment.

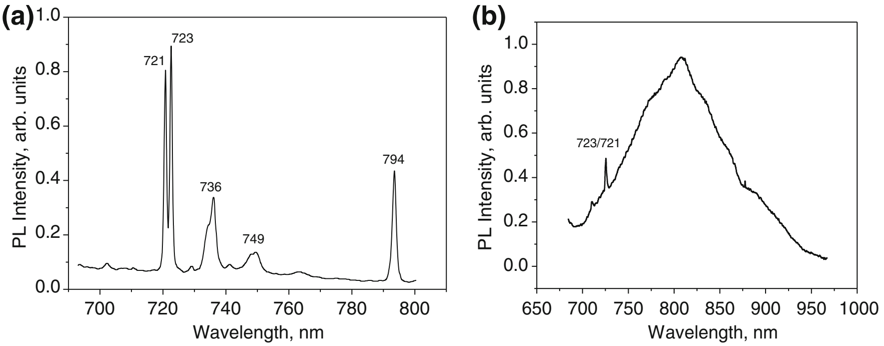


Fig. 6.51 **a** PL spectrum of a synthetic diamond HPHT-treated at a temperature of 1,700 °C. The dominating optical features of the spectrum are the 723/721 nm and 794 nm centers [re-plotted from (Yelisseyev and Kanda 2007)]. **b** PL spectrum of a HPHT-treated intense yellow diamond showing 723/721 nm Ni-related center. HPHT treatment of this diamond has been confirmed by the presence of strong H3 and H2 centers in absorption spectrum, observation of the "green transmission" effect and by strong 638 and 575 nm centers (intensity ratio I_{NV-}/I_{NV0} is about 3) in PL spectrum

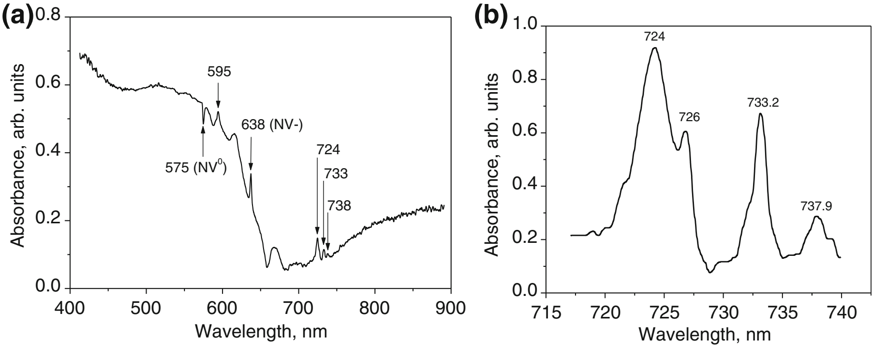


Fig. 6.52 **a** FSI absorption spectrum of an Imperial Red diamond. Strong 638, 575 and 595 nm centers are typical features of type Ia diamonds after multi-process treatment. The centers with ZPLs at 724, 733 and 738 are seen too. **b** Absorption spectrum of a treated diamond of red color showing 724, 726, 733.2 and 738 nm lines. The visible absorption spectrum of this diamond is dominated by 638 nm (NV^-) center [re-plotted from (Johnson and Breeding 2009)]

724, 726, 733.2 and 737.0 nm centers

These centers are observed in absorption spectra of some red diamonds after multi-process treatment (Johnson and Breeding 2009) (Fig. 6.52).

727.5 nm center

This Ni-related PL center is generated by heating at temperature 1,700 °C and it is destroyed by HPHT treatment performed at temperatures over 1,800 °C (Lawson and Kanda 1993; Yelisseyev and Kanda 2007). The 727.5 nm center can be considered as an indication that diamond has not been HPHT-treated at high temperature.

732.4 nm center

This Ni-related center is observed in absorption spectra of synthetic and some natural diamonds. It is generated by heating at temperature 1,700 °C and it is destroyed by HPHT treatment performed at temperatures over 1,900 °C (Yelisseyev and Kanda 2007) (Fig. 6.53). The 732.4 nm center can be considered as an indication that diamonds has not been subjected to high temperature HPHT treatment.

730 nm band

The 730 nm band is an intense feature of a complex absorption spectrum observed in some hydrogen-rich natural diamonds. The other accompanying bands are less intense and have maxima at wavelengths 520, 552 and 840 nm (Fig. 6.54). All these features are strong in spectra of high-nitrogen, high-hydrogen diamonds when measured at room temperature. The bands are always present together, although they do not correlate perfectly in intensity, what suggests that they may originate from similar, yet different hydrogen-related defects. It is believed that these bands cannot be created by any known treatment of diamond including HPHT treatment.

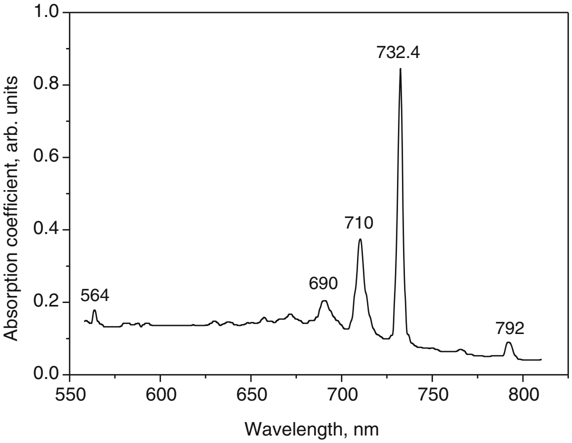


Fig. 6.53 Absorption spectrum of the 732.4 nm center in high-nitrogen synthetic diamond HPHT-treated at a temperature of 1,900 °C [re-plotted from (Yelisseyev and Kanda 2007)]

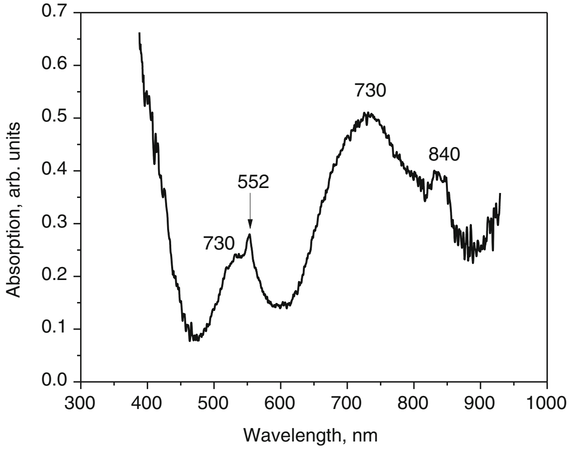


Fig. 6.54 Absorption spectrum of a natural high-hydrogen, high-nitrogen diamond of fancy violetish gray color. Broad bands at 540 and 730 nm as well as relatively narrow bands at 552 and 840 nm are hydrogen-related features. All these bands can be present in absorption spectra of hydrogen-rich natural diamonds

737 nm (the SiV center)

The 737 nm silicon-related center is a common feature of PL spectra of CVD diamond and can be found in some natural diamonds too (Breeding and Wang 2008). The SiV center stands HPHT treatment performed at low temperature (Crepin et al. 2012). ZPL of this center may considerably increase its width after HPHT treatment (Anthonis et al. 2006). This broadening of ZPL of the SiV center can be used as a criterion of recognition of HPHT treatment. However, accurate measurements of the broadening of ZPL of this center must be performed at low temperatures using a high resolution spectrometer.

741 nm (the GR1 center)

The GR1 center is the most common intrinsic center of diamond. The primary reason of generation of the GR1 center is irradiation. The GR1 center is created in

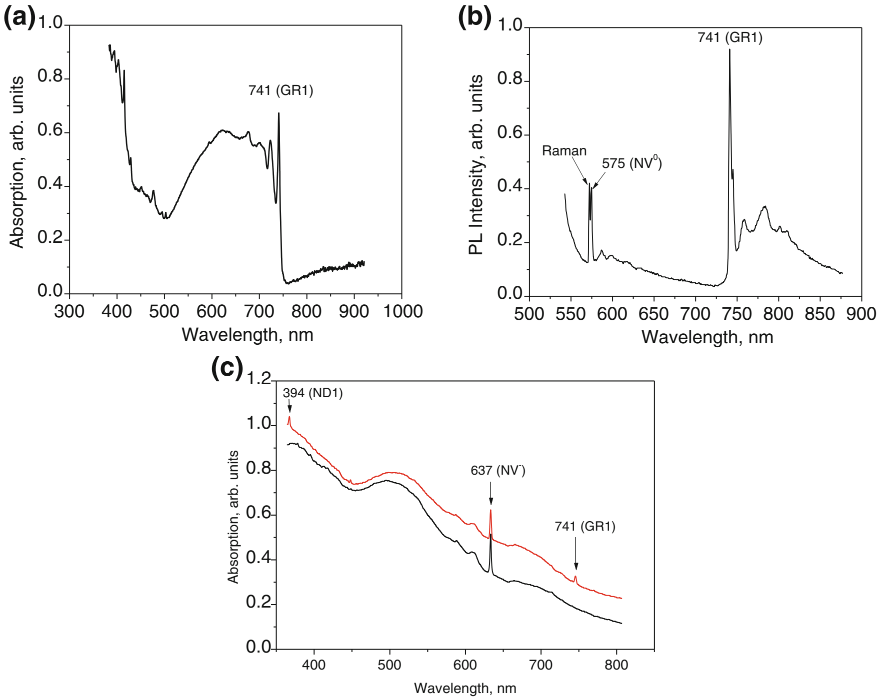


Fig. 6.55 **a** Vis absorption spectrum of an irradiated natural diamond of a deep greenish blue color. The GR1 center is the main feature of the spectrum. **b** PL spectrum of a dark brown yellow diamond treated by irradiation followed by annealing at a temperature of 500 °C. The GR1 center is strong both in PL and Vis absorption spectra of this diamond. When induced in brown diamonds, the GR1 center can add a yellowish component to their color. This color is particularly noticeable after annealing at a temperature of 500 °C. **c** Absorption spectra of a CVD diamond, color of which has been converted by HPHT treatment (1,600 °C, 5 min) from brown to pink (*black line*). After subsequent low-dose irradiation, minor GR1 and ND1 centers appear. No change in color was observed after this irradiation [based on (Crepin et al. 2012)]

any diamond by any high energy irradiation with electrons, gamma-rays, neutrons and ions. The GR1 center may also naturally occur in diamonds of any type. The GR1 center is active both in absorption and luminescence giving rise to broad structured bands (see the Fig. 6.55). The defects responsible for the GR1 center are isolated neutral vacancies.

Isolated vacancies in diamond produce two characteristic optical centers when in two different charge states: neutral vacancies—the GR1 center and negatively charged vacancies—the ND1 center (ZPL at a wavelength of 393.6 nm).

The GR1 and ND1 centers are observed in absorption spectra of as-grown pink CVD diamonds (Wang 2009b). The GR1 center can be also created in small concentrations during plastic deformation of diamond lattice. In highly deformed polycrystalline carbonado diamonds, the GR1 center can be of high intensity (Wang et al. 2009b). Untreated brown diamonds of types IIa and IaAB frequently show weak line at 741 nm (Fisher et al. 2006; Tretiakova and Tretyakova 2008). This observation support the assumption that the vacancy clusters, which are the reason of brown color, can partially dissolve during long time natural annealing and produce a measurable concentration of isolated vacancies.

In most natural diamonds exhibiting strong GR1 center, the vacancies responsible for this absorption are concentrated in thin "skin" at the surface, whereas the vacancy concentration in the bulk is much lower. The vacancy-rich "skin" may have green to brownish green color. Natural diamonds, which have vacancy concentration in the bulk high enough to provide GR1 center measurable in absorption, are extremely rare. It is believed that the GR1 center absorption at a wavelength of 625 nm of strength over 0.3 cm^{-1} is a fairly safe proof of radiation treatment (Collins 2003). All rough greenish diamonds from Zimbabwe (Marange) exhibit green and orange radiation stains on their surface and the GR1 center in absorption spectra—typical features of natural irradiation. Some rough diamonds show also features of subsequent annealing at low temperatures (Crepin et al. 2011).

Vacancies in diamond lattice are very temperature unstable defects. They start moving at temperatures over 500 °C. Therefore the GR1 center has low temperature stability and it anneals out gradually in a temperature range 600–1,000 °C. The kinetic of annealing of the GR1 center may vary in diamonds of different perfection and impurity content. However, in any diamond, the GR1 center anneals out completely at temperatures 900–1,000 °C. Yet rapid heating may not result in full annealing of the GR1 center and traces of it can be observed in diamonds treated with pulse heating at temperatures above 1,000 °C. Migration of single vacancies in diamond lattice occurs when they are primarily in neutral charge state. The activation energy of this migration is about 2.3 eV (Davies et al. 1992).

Because of low temperature stability, HPHT treatment destroys the GR1 center completely (Fisher et al. 2006). Based on this fact, the presence of the GR1 center is commonly considered as a reliable indicator that diamond has not been heated at temperatures above 1,000 °C (e.g. is not HPHT-treated) (De Weerdt and Van Royen 2000). PL spectroscopy in this case is the most sensitive technique capable of detection of traces of GR1 center. However, it must be always kept in mind that GR1 center can be easily re-introduced in HPHT-treated diamonds by subsequent irradiation (Fig. 6.55c). Remnants of the GR1 center along with the 535 and 588 nm centers are common features of Imperial Red diamonds (Wang et al. 2005), which were processed by HPHT annealing followed by electron irradiation and final annealing at temperatures below 800 °C. The intentional re-introduction of the GR1 center in HPHT-treated diamonds is becoming a common procedure aimed at concealing the fact of treatment. This method works very well and the recognition of the artificial origin of this post-irradiation is a challenging task. If the irradiation is performed with low doses, the irradiated diamond does not change its color at all and the induced GR1 center has very low intensity. In this case, it is almost impossible with available spectroscopic techniques to get a reliable proof that the GR1 center has been created artificially (Kitawaki 2007; Crepin et al. 2011; Crepin et al. 2012).

Discussing the problem of recognition of artificial low dose irradiation, we would like to draw attention to the fact that vacancies in diamond can be detected in different charge states. This unique property has never been considered in terms of recognition of treatment. We speculate that the intensity ratio of the GR1 and ND1 centers I_{GR1}/I_{ND1} could be very helpful in this regard and, in particular, for recognition of artificial post-irradiation of HPHT-treated type IIa diamonds. Indeed, in untreated colorless type IIa diamonds, nitrogen is present preferentially in aggregated forms. In HPHT-treated colorless diamonds, considerable portion of nitrogen is converted into C defects. Hence, in the ratio I_{GR1}/I_{ND1} is expected to be very different: high in untreated diamonds and low in HPHT-treated diamonds.

The spectral width of ZPL of the GR1 center in HPHT-treated diamonds is less than it is in untreated natural diamonds. This suggests that the crystal lattice surrounding neutral vacancies in diamond improves with HPHT annealing. This decrease, however, is small and amounts on average to only 0.5 meV when measured at LNT. Thus the measurements of the spectral width of ZPL of the GR1 center cannot be practically used for recognition of HPHT treatment (Fisher et al. 2006). Besides, it must be taken into account that the spectral width of ZPL of the GR1 center strongly increases with concentration of nitrogen defects. FWHM of ZPL of the GR1 center can be of 1–2 meV in type IIa diamonds, and it increases to about 7 meV in diamonds containing 1,000 ppm nitrogen (Kiflawi et al. 2007). Since the spectral width of ZPL of the GR1 center is not sensitive to type of nitrogen defects, it does not change with nitrogen defect transformations induced by HPHT treatment and, consequently, is not indicative of treatment.

Concentration of isolated neutral vacancies V^0(ppm) in ppm can be estimated using the following relations [based on the original data of authors and that from (Davies 1999; Davies et al. 1992)]:

$$V^0[\mathrm{ppm}] = 0.1\, I_{ZPL-GR1}\left[\mathrm{cm}^{-1}\right],$$

where $I_{ZPL\text{-}GR1}[\mathrm{cm}^{-1})$ is the absorption intensity of ZPL of the GR1 center in cm^{-1} recorded at LNT, or

$$V^0[\mathrm{ppm}] = 0.4\, I_{693\,\mathrm{nm}}\left[\mathrm{cm}^{-1}\right],$$

where $I_{693\ \mathrm{nm}}$ is the absorption intensity of the GR1 center in cm^{-1} at a wavelength of 693 nm measured at RT (when using this formula, the background absorption underlying the GR1 center absorption must be subtracted correctly).

747 and 759 nm centers

These two Ni-related centers are observed in PL spectra. The 747 and 759 nm centers are frequently seen together and their intensities correlate (Fig. 6.56). Both centers can be generated by heating at a temperature of 1,700 °C and they are destroyed by HPHT treatment performed at a temperature of 1,900 °C (Yelisseyev and Kanda 2007). Strong 759 nm center is a feature of natural diamonds, which have not been HPHT-treated at high temperatures.

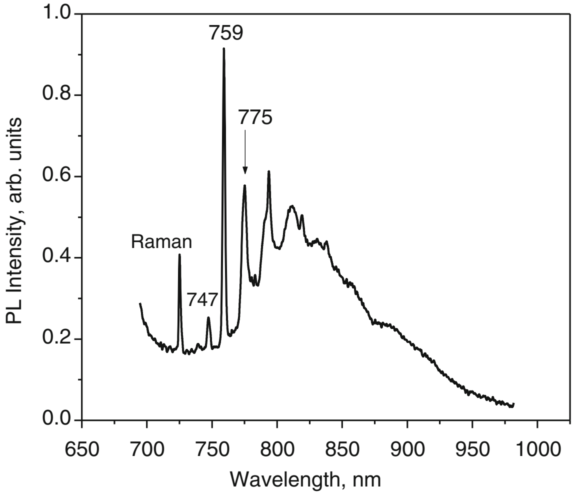


Fig. 6.56 PL spectrum of an untreated natural diamond exhibiting dominating 759 and 747 nm centers. A prominent feature of the 759 nm center is the interaction with a quasi-local vibration of energy 35 meV (*arrow* points to 775 nm line)

753 nm center

This Ni-related center is observed in absorption and PL spectra of synthetic and some natural diamonds. The center is generated by heating at temperature 1,700 °C and it increases in intensity with further HPHT treatment performed at temperatures over 1,900 °C (Yelisseyev and Kanda 2007) (Fig. 6.43). Strong 753 nm center can be considered as an indication of HPHT treatment.

759 nm center (see 747 and 759 nm centers)

774.5 nm center

This Ni-related PL center is generated by heating at temperature 1,700 °C and it is destroyed by HPHT annealing at a temperature of 1,900 °C (Yelisseyev and Kanda 2007). Irradiation can re-introduce the 774.5 nm center. The 774.5 nm center can be observed in diamonds after multi-process treatment.

787 nm center

The 787 nm center is a typical feature of PL spectra of some natural type Ia diamonds. This center always accompanies the Ni-related centers with ZPLs at 496.7 nm (S3), 488.9 nm and 523.2 nm (Plotnikova et al. 1980). The 787 nm center is a common PL feature of gray natural diamonds (Eaton-Magana 2011). The 787 nm center is a PL feature of pink diamonds (Gaillou et al. 2010). This center seen in spectra of synthetic diamonds grown in the presence of Ni, and HPHT-treated at high temperatures (Yelisseyev et al. 2002). Possibly, the 787 nm center is mentioned in some publications as a Ni-related PL center with ZPL at 788.5 nm. The latter one is generated by heating at 1,700 °C and it is destroyed by HPHT treatment at a temperature of 1,900 °C (Yelisseyev and Kanda 2007).

794 nm center

This Ni-related optical center is observed in absorption and PL spectra of natural diamonds. The 794 nm center is a common PL feature of gray natural diamonds (Eaton-Magana 2011). The 794 nm center may be particularly intense in type IaB diamonds. It is also effectively created in nitrogen- and nickel-containing synthetic diamonds by electron irradiation and subsequent annealing at a temperature of 900 °C (Osvet et al. 1997). The 794 nm center is generated by heating at temperatures over 1,600 °C and its intensity increases with further HPHT treatment at temperatures over 1,900 °C (Yelisseyev and Kanda 2007; Lawson and Kanda 1993a). In PL spectra, the 794 nm center may dominate in diamonds annealed at temperatures above 2,200 °C. The center is very stable and it stands HPHT treatment at temperatures over 2,500 °C. If strong, the 794 nm center gives a greenish color to HPHT-treated synthetic diamonds (Yelisseyev et al. 1996). Probably this center was reported as the 792 nm center in absorption spectra of synthetic diamonds HPHT-treated at temperatures of 2,000 °C and above (Shigley et al. 1993). Intense 794 nm center can be considered as an indicator of HPHT treatment (Fig. 6.57).

798 and 845 nm centers

These two centers are observed in PL spectra. The 798 and 845 nm centers can be formed in natural diamonds by HPHT treatment (Fig. 6.58). Intensity of these centers strongly increases after HPHT treatment performed at a temperature of 2,100 °C (Hainschwang et al. 2008).

805.2 nm (the 805 nm center)

The 805 nm center is observed in PL and absorption spectra. The 805 nm center can be easily recognized via its characteristic phonon side-band with a prominent quasi-local vibration feature at a wavelength of 840 nm in PL spectra and at a wavelength of 768 nm in absorption spectra (Fig. 6.59). The center is rarely seen in spectra of natural untreated diamonds. Yet it is a feature of synthetic diamonds grown in the presence of silicon. The 805 nm center is observed in some HPHT-treated diamonds showing Ni-related optical centers. The center is also observed in spectra of type Ia diamonds after multi-process treatment. This center is a feature of ABC diamonds treated by irradiation and conventional annealing. In these diamonds, the 805 nm center is frequently accompanied by the 708 and 798 nm centers (Fig. 6.58).

Intensity of the 805 nm center correlates with that of the H4 center and there is an opinion that the 805 nm center is the manifestation of the H4 defect in the negatively charged state. Hence the 805 nm center is strong in diamonds containing nitrogen C defects acting as electron donors.

808.5 and 822.5 nm center

A Ni-related center with doublet ZPL at 808.5 and 822.5 nm is observed in PL spectra. This center anneals out at a temperature of 1,700 °C (Yelisseyev and

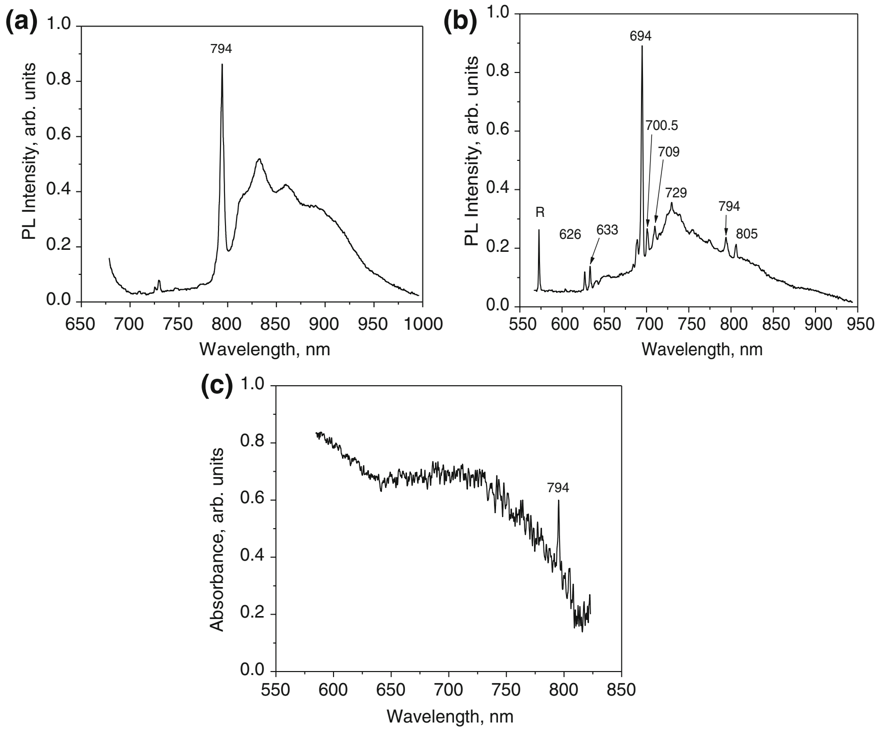


Fig. 6.57 PL spectra taken from an HPHT-treated deep brown greenish yellow diamond with laser excitation at wavelengths 658 nm (**a**) and 532 nm (**b**). Strong 794 nm center and absence of 787 nm center are indications of HPHT treatment. **c** Absorption spectrum of this diamond. Absorption of the phonon side-band of the 794 nm center in the red spectral range (650–800 nm) improves green component in the color of this diamond

Kanda 2007). The presence of the 822/808 nm center is a good indicator of untreated diamonds.

837 nm center

The 837 nm line is the main feature of a center with a triplet ZPL observed in PL spectra of some Imperial Red diamonds after multi-process treatment (Fig. 6.60). The center is tentatively ascribed to a Ni-containing defect.

877 nm center

This Ni-related PL center is generated by heating at 1,700 °C and it is destroyed by HPHT treatment at a temperature of 1,900 °C (Yelisseyev and Kanda 2007). The 877 nm center is a feature of the diamonds, which have not been HPHT-treated at high temperatures.

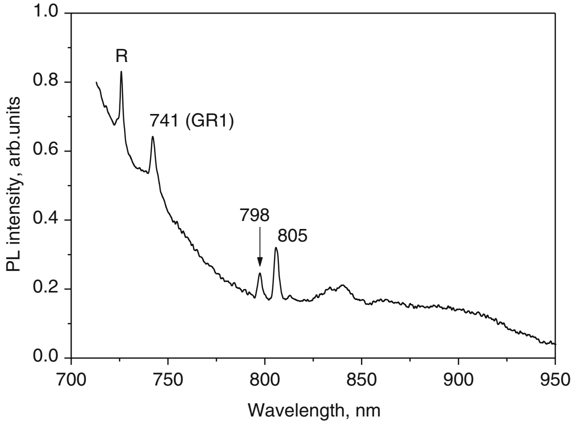


Fig. 6.58 PL spectrum of a low-nitrogen fancy intense orangey pink diamond after multi-process treatment. The dominating centers are GR1, 798 and 805 nm. Presence of the GR1 center either indicates that the final annealing step of the treatment was performed at a temperature below 800 °C, or that, after the multi-process treatment, the diamond was additionally irradiated with low dose of energetic electrons

882 nm band

HPHT-treated yellow synthetic diamonds can reveal in CL spectra a very strong broad band with maximum at a wavelength of 882 nm. This band is probably generated by a Ni-related defect (Lindblom et al. 2005). The 882 nm band can be also present in HPHT-treated natural diamonds of type Ib character.

884.2 nm center

A sharp line at a wavelength of 884.2 nm is observed in PL spectra of natural Ni-containing diamonds (Lang et al. 2007). This line is possibly related to a Ni-containing defect. Possibly, the 884.2 nm line is a manifestation of natural annealing at elevated temperatures.

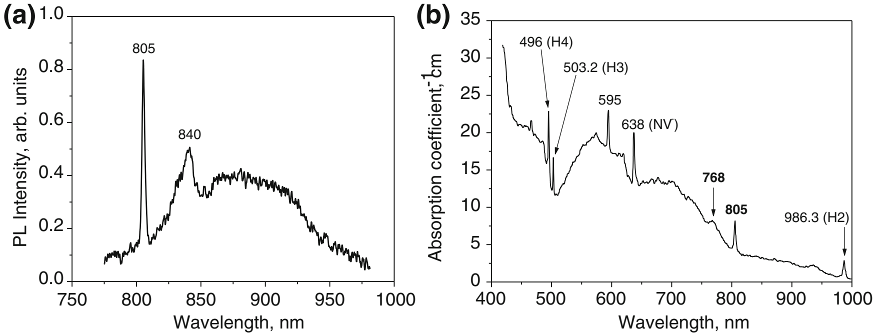


Fig. 6.59 **a** PL spectrum of the 805 nm center in a HPHT-treated fancy intense greenish yellow diamond. ZPL of the 805 nm center is accompanied by the vibrational sideband spreading from 800 to 950 nm, a characteristic feature of which is a peak at 840 nm due to interaction with acoustic phonons of energy 70 meV. **b** Absorption spectrum of a type Ia diamond after multi-process treatment. The treatment has converted the diamond into ABC diamond. Absorption of many optical centers characteristic of multi-process treatment can be seen. The 805 nm center is presented by its ZPL at 805.2 nm and phonon replica at wavelength of 768 nm (interaction with optical phonons of energy 116 meV) [re-plotted from (Vins et al., 2011b)]

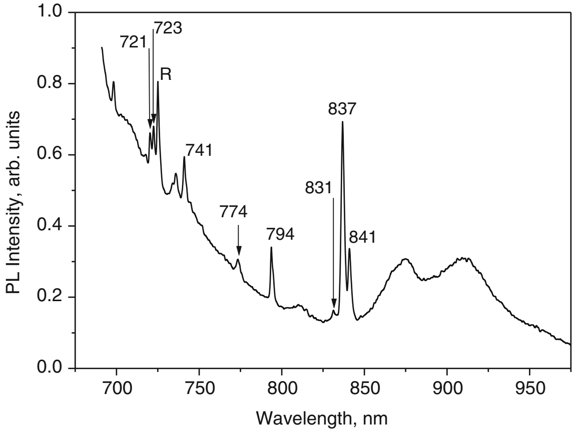


Fig. 6.60 PL spectrum of a fancy dark brownish red diamond sequentially treated by HPHT annealing, electron irradiation and conventional annealing. The dominating optical feature of the spectrum is the 837 nm center. The 794 nm center is also present confirming HPHT treatment. The doublet 721/723 nm and the 774 nm line are indicators of low-temperature HPHT treatment. Though, these features could be also stimulated by irradiation and subsequent conventional annealing, which were used for the treatment of this diamond

886/883 nm (the 885 nm or 1.40 eV center)

Well known 885 nm Ni-related center with the doublet ZPL is a common feature of synthetic Ni-containing diamonds. It is also present in some natural diamonds showing presence of Ni-related centers. The 885 nm center is active in absorption and luminescence (Fig. 6.61). The 885 nm center is not a very temperature stable one and can be completely annealed out after HPHT treatment at temperatures of

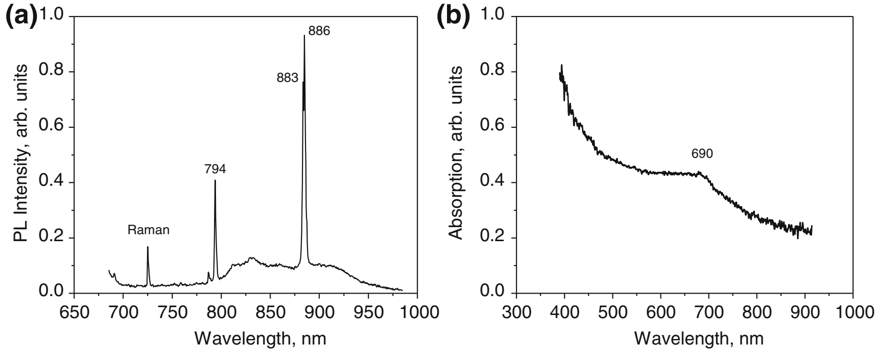


Fig. 6.61 **a** PL spectrum of an untreated fancy light yellowish green natural diamond showing 885 and 794 nm Ni-related centers. **b** Absorption spectrum of this diamond exhibits a broad band at 690 nm, which is the phonon replica of the 886/883 nm ZPL. In absorption, the 690 nm band is much stronger than ZPLs and it is clearly seen even when ZPLs are undetectable. The 690 nm band can add a green component to the color of Ni-containing natural diamonds

1,700 °C and above (Lawson and Kanda 1993; Yelisseyev and Kanda 2007). The 885 nm center is a feature of untreated diamonds.

905 nm center

The 905 nm center is seen only in diamonds of Ib character. The center is excited in absorption and luminescence. The presence of the 905 nm center is an indication of enhanced content of C defects. The 905 nm center is ascribed to a hydrogen-related defect (Hainschwang et al. 2006a). Although the 905 nm center is seen in spectra of natural untreated diamonds, it could be considered as an indicator of enhanced concentration of C defects created by HPHT treatment when detected in combination with other optical centers characteristic of HPHT treatment.

926 nm center

HPHT treatment results in formation of the 926 nm center in brown type Ia diamonds. The center is seen in PL spectra (Fig. 6.62). The 926 nm center is clearly seen after HPHT treatment performed at a temperature of 2,000 °C (Hainschwang et al. 2005). However, the 926 nm center can be found in untreated diamonds too. If strong, the 926 nm center is an indication of possible HPHT treatment.

972 nm center

This Ni-related PL center is generated by heating at a temperature of 1,700 °C and it is destroyed by HPHT treatment performed at a temperature of 1,900 °C (Yelisseyev and Kanda 2007). The 972 nm center can be considered as a feature of untreated diamonds.

986.3 nm (the H2 center)

The H2 center is an optical electronic transition at nitrogen-vacancy-nitrogen (NVN) defect in negatively charged state (Collins et al. 2000; Mita et al. 1990).

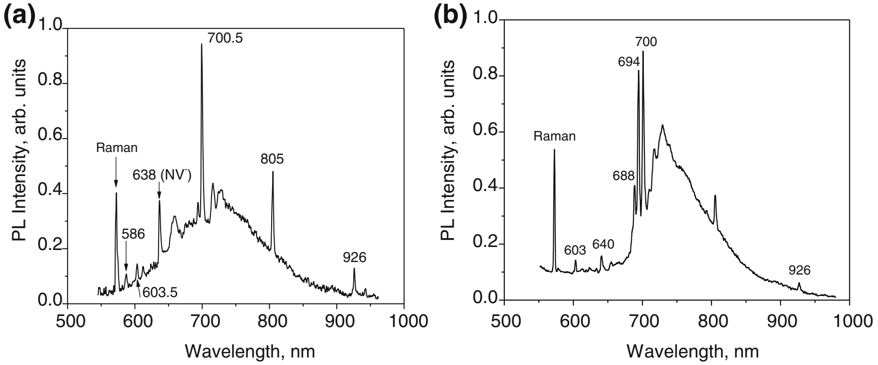


Fig. 6.62 **a** PL spectrum of a high-nitrogen, high-hydrogen fancy dark yellowish greenish gray diamond showing distinctive "fluorescence cage". The diamond has been identified as HPHT treated. **b** PL spectrum of a natural untreated diamond showing the presence of the 926 nm center. The spectrum is dominated by the hydrogen-related centers with ZPLs at 688, 694 and 700 nm

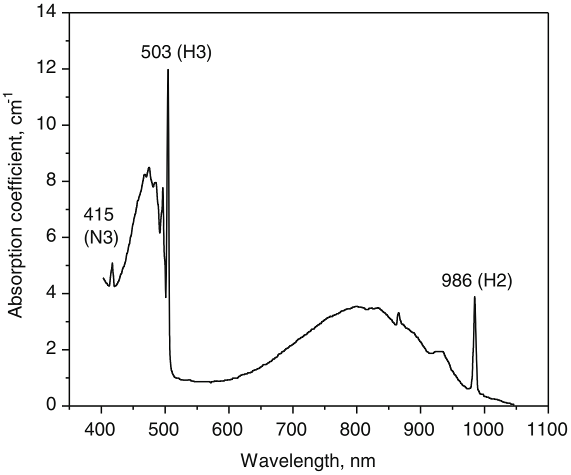


Fig. 6.63 Absorption spectrum of a neutron-irradiated type IaA diamond after annealing at a temperature of 1,600 °C at normal pressure [re-plotted from (Collins et al. 2005)]

NVN defects in neutral charge state produce the H3 center (see 503.2 nm center). The H2 center is effective in absorption. Absorption spectrum of the H2 center is characterized by ZPL at 986 nm and a broad electron-vibrational side-band spreading from near infrared to the red spectral range (Fig. 6.63). Because of this red absorption, strong H2 center produces yellow/green color. It is believed that the excited electronic state of the H2 center is in the conduction band (like for the negatively charged vacancy, the ND1 center) and, therefore, the efficiency of the radiative relaxation of its excited state is negligibly small. However, rarely, very weak H2 center can be seen in luminescence regime. The H2 center was reported in PL spectra of type Ia diamonds after HPHT treatment under excitation with laser of a wavelength 633 nm (Okano 2006).

The H2 center is pronounced in spectra of diamonds containing defects acting as donors, e.g. C defects. For instance, the H2 center may be noticeable in absorption spectra of natural type Ib diamonds and diamonds of type Ib character (Collins et al. 2000; Mita et al. 1990; De Weerdt and Van Royen 2000). These diamonds also exhibit the H3 center and strong 638 nm center (Hainschwang et al. 2005). The H2 center is frequently detected in spectra of low-nitrogen orange diamonds of type IaA + Ib, which exhibit strong “green transmission” effect and the 638 nm center in PL spectra (Hainschwang et al. 2006a; Chalain et al. 2005; Collins et al. 2000; Collins 2003). Absorption spectra of these diamonds usually have H3 and N3 centers. Occasionally, weak absorption of the H2 center can be observed in untreated natural pink and brown diamonds (De Weerdt and Van Royen 2001, 2000; Hainschwang et al. 2005; Reinitz et al. 2000).

Although some natural diamonds reveal the H2 center, vast majority of natural untreated diamonds does not have this center in their absorption spectra. In natural diamonds which do show the H2 center, its intensity is not high enough to influence the color of these diamonds.

The H2 center, like the H3 and NV centers, is a typical radiation center. As such, it is readily created in diamonds with the presence of donor-like defects by any irradiation and subsequent annealing. In diamonds with considerable presence of C defects, the H2 center can be detected after electron irradiation and subsequent annealing at temperatures above 800 °C. The H2 center is very common in nitrogen-containing diamonds after multi-process treatment involving irradiation. Moderate to strong H2 center absorption is always present in absorption spectra of Imperial Red treated diamonds (Wang et al. 2005). However, in type Ia diamonds, it becomes pronounced after annealing at higher temperatures, usually over 1,400 °C, when dissociation of A defects into C defects becomes noticeable. In the electron irradiated and annealed type Ia diamonds, intensity of the H2 center can be strong enough to make them green (Collins 2001). In type Ia diamonds irradiated with neutrons, formation of the H2 center occurs after annealing at moderate temperatures (Vins et al. 2008). However, the production of intense H2 center in neutron irradiated diamonds requires annealing at temperatures of 1,600 °C and above (Collins et al. 2005).

Strong absorption of the H2 center is a typical result of HPHT treatment of type Ia diamonds (De Weerdt and Van Royen 2000; Wang 2002). However, the H2 center is not observed in HPHT-treated CO_2 and pseudo CO_2 diamonds (Hainschwang et al. 2005). The H2 center requires for its creation A defects and therefore it is readily formed by HPHT treatment in type IaA diamonds. The H2 center is also detected in type IaB diamonds of initial brown color after they were HPHT treated at temperatures 1,900–2,100 °C. Formation of NVN defects during HPHT treatment is a complex process depending on the initial impurity-defect content of diamond and parameters of treatment. Since HPHT treatment is frequently performed for short time and the resulting defect structure of diamond is highly non-equilibrium in terms of defect concentration and the charge state of defects, the intensity of the H2 center in HPHT-treated diamonds is not well predictable.

Considerable formation of NVN defects in brown type Ia diamonds during HPHT treatment may occur at temperatures as low as 1,600 °C. However, usually the H2 center does not appear after treatment at temperatures below 1,800 °C, for these temperatures are too low to decompose a noticeable amount of A defects into C defects. Quite a number of HPHT-treated green–yellow diamonds do not reveal the H2 center in absorption (Kim and Choi 2005). One may assume that the absence of the H2 center in these diamonds is due to low temperature treatment. Reliable production of the H2 center by HPHT treatment requires temperatures of at least 2,000 °C and preferably at 2,100–2,200 °C. After annealing at these temperatures, the H2 center contributes to green/yellow color of the treated diamonds considerably. Rapid formation of the H2 center is observed at higher temperatures, when high concentration of C defects is formed (Collins et al. 2000). Although the H2 center can be destroyed by temperatures over 2,100 °C, the dominating H2 center can be seen in absorption spectra of type I diamonds even after very high temperature HPHT treatment. For instance, formation of the dominating H2 center after treatment at temperatures 2,400–2,500 °C was reported in (Smith et al. 2000; Hainschwang et al. 2006a). This seeming increase in the temperature stability of the H2 center is the manifestation of a strong process of formation of the NVN defects prevailing over the process of their destruction. The same behavior is observed for the H3 center too. Hence the presence of H2 center in diamonds HPHT-treated at high temperature is a signature of non-equilibrium defect structure and a strong indication of short-time treatment. If high temperature HPHT treatment is performed for a long time, the centers H2, H3 and NV anneal out completely in any diamond.

NVN defects are stable to a temperature of 2,100 °C. At higher temperatures, NVN defects decompose into A defects and individual vacancies (Vins et al. 2008; Vins and Yelisseyev 2010). Corresponding reduction of intensity of the H2 center in type IaA diamonds can be observed after HPHT treatment at temperatures of 2,150 °C (Vins and Yelisseyev 2008). Suppression of the H2 center after high temperature treatment occurs not only because of the direct destruction of NVN defects. Recharging of NVN defects from negative to neutral charge state is another reason. At temperatures over 2,200 °C, reverse process of aggregation of dispersed nitrogen into A defects occurs. Concentration of donors reduces and the H2 centers transform into H3 centers. Destruction of the H2 centers is also strongly stimulated by irradiation performed prior to HPHT treatment. Thus high-nitrogen type IaAB diamonds heavy irradiated with electrons or neutrons and then HPHT annealed at a temperature of 2,300 °C display in their spectra no H2 center (Collins et al. 2005).

Although H2 center is a typical feature of HPHT-treated brown diamonds, the presence of the H2 center in absorption spectra of natural diamonds cannot be used alone as a reliable proof of HPHT treatment. Yet, strong H3 center in absorption/luminescence spectra and the presence of the H2 center in absorption spectra can be considered as a strong indicator of HPHT treatment (De Weerdt and Van Royen 2000).

6.2 Optical Centers in IR Spectral Range

In diamond, optical centers in IR spectral range (wavelength over 1000 nm, or wavenumber below 10,000 cm^{-1}) are active only in absorption. The reason for this is very high energy of phonons of diamond lattice. Electron–phonon interaction with energetic phonons strongly reduces the probability of radiative relaxation of electrons on defects and, consequently, luminescence of corresponding optical centers. Since IR absorption spectrometers are about two orders of magnitude less sensitive than the luminescence ones, the absence of luminescence is a disadvantage of the IR optical centers, which limits their use in recognition of HPHT treatment. Below, the IR optical centers used for recognition of HPHT-treated and untreated diamonds are reviewed.

1,609 nm (6,214 cm^{-1}) center

A line at a wavenumber of 6,214 cm^{-1} is observed in absorption spectra of some natural diamonds. HPHT treatment destroys this center (Hainschwang et al. 2008). The presence of the 6,214 cm^{-1} line may speak in favor of untreated diamond. Diamonds revealing no 6,214 cm^{-1} center and strong H2 center are definitely HPHT-treated (Henn and Milisenda 1999; Buerki et al. 1999; Collins 2001; Moses and Reinitz 1999).

1,621 nm (6,170 cm^{-1}) center

Spectral position of this line in absorption spectra may vary from 6,172 to 6,168 cm^{-1}. The 6,170 cm^{-1} line is a feature of HPHT-treated diamonds. It is seen in spectra of Imperial Red diamonds and in diamonds treated by irradiation followed by conventional annealing. Although the 6,170 cm^{-1} line is also observed in some naturally irradiated diamonds (De Weerdt and Anthonis 2004; Wang et al. 2005), when strong, it can be considered as an indication of treatment.

1,934 nm (5,170 cm^{-1}), the H1c center and 2,024 nm (4,940 cm^{-1}), the H1b center

The H1c and H1b centers are observed as narrow lines in absorption spectra (Fig. 6.64). It is believed that the H1c center originates from a complex comprising nitrogen B defect, whereas the H1b center relates to a complex comprising nitrogen A defect. Both centers are formed from the defects responsible for the 594 nm center during annealing at temperatures above 800 °C. Thus, both centers are observed in type Ia diamonds only. During annealing at temperatures above 1,300 °C, the H1c and H1b centers further transform into H2 center. The H1c and

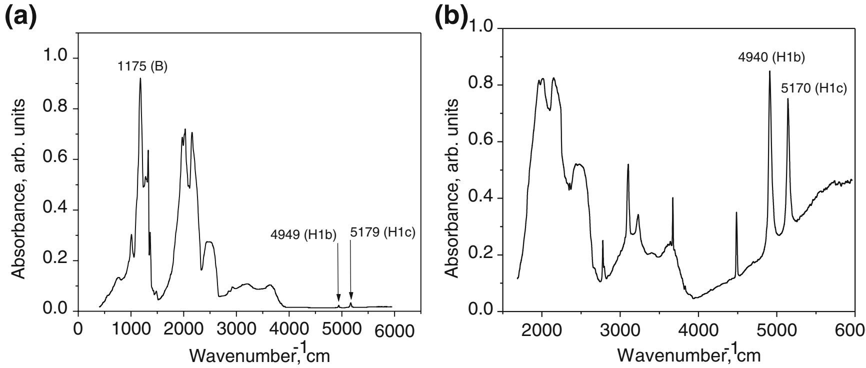


Fig. 6.64 **a** FTIR absorption spectrum of a fancy dark pink purple diamond which was identified as subjected to multi-process treatment. Weak H1c and H1b centers imply that the irradiation/annealing steps were performed after HPHT treatment. The H1c 1Hb centers are minor features used for the identification of treatment of this stone. The primary features are very intense 575 and 638 nm centers dominating in absorption and PL spectra. **b** FTIR absorption spectrum of an HPHT treated diamond showing strong H1b and H1c centers. In Vis absorption spectrum, this diamond also reveals the H3, 594 nm and strong H2 centers

H1b centers have equal temperature stability (Collins 2003). As transient defects formed at moderate temperatures, both centers are expected to completely anneal out in natural diamonds during their natural annealing in earth. Therefore, there are no reports on natural untreated diamonds containing H1b or H1c centers (Collins 2003). Based on this fact, it has been concluded that the presence of H1c and H1b centers in a diamond indicates that this diamond has been irradiated and annealed at temperatures below 1,400 °C (Hainschwang et al. 2002; Vins and Yelisseyev 2008a). In general, the H1c and H1b centers are a strong indicator of multi-process treatment. For instance, intense H1c and H1b centers are observed in spectra of Imperial Red diamonds (Wang et al. 2005).

Using the H1c and H1b centers as the indicators of treatment, it must be kept in mind that their atomic models have not been established yet. Even the relation of these centers to the B and A defects can be questioned. Our recent experiments with eight diamonds of pure type IaAB' (no detectable B defects and no detectable H4 centers) processed by 3 MeV electron irradiation followed by annealing at a temperature of 1,200 °C show that the H1c center (5,170 cm^{-1}) is present in spectra of all diamonds. Its intensity may vary from 10 to 25 cm^{-1} for different samples. The H1b center (4,940 cm^{-1}) is also present in spectra of all samples and its intensity closely follows the intensity of the A defect absorption. This finding strongly suggests that the H1b center is indeed one related to the A defects, whereas the H1c may be not (Vins and Yelisseyev 2012).

2,143 nm (4,668 cm^{-1}) and 2,225 nm (4,494 cm^{-1}) centers

These hydrogen-related lines are observed in regular brown type IaB diamonds (Fig. 6.65). They are reduced in intensity or destroyed by HPHT treatment performed at a temperature of 2,000 °C (Hainschwang et al. 2005). However, the 4,668 and 4,494 cm^{-1} centers can survive HPHT treatment at low temperatures. With some reservation, the 4,668 and 4,494 cm^{-1} centers may be considered as features of untreated diamonds.

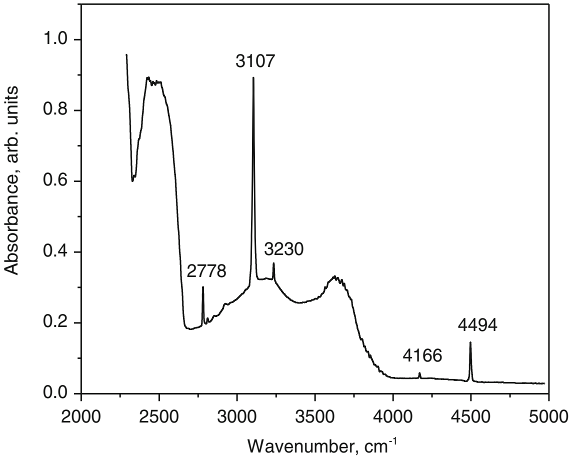


Fig. 6.65 FTIR absorption spectrum of an untreated high-nitrogen brown orange diamond showing 4,494 cm^{-1} center, the hydrogen-related 3,107 cm^{-1} center and the 4,166 cm^{-1} line of the Amber Center

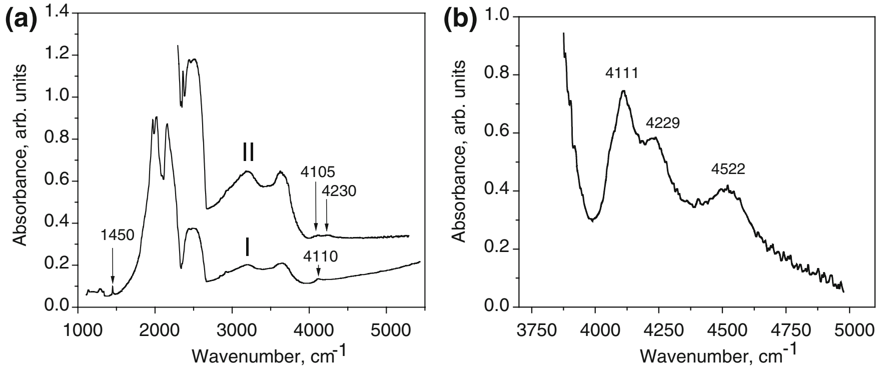


Fig. 6.66 **a** FTIR absorption spectrum of a fancy intense purple diamond treated by combination of HPHT annealing, irradiation and conventional annealing (*I*). The treatment of this diamond is confirmed by the presence of the H3 and H2 centers, strong NV^- center and its "red transmission" effect, the 1,450 and 1,344 cm^{-1} (C defect) centers. The Amber center is clearly seen in the spectrum too. FTIR absorption spectrum of a low-nitrogen HPHT-treated diamond, showing weak unresolved features of the Amber center in the spectral range 4,000–4,350 cm^{-1} (*II*). **b** FTIR spectrum of the Amber Center in an HPHT-treated diamond of fancy deep brown yellow color. The treatment of this diamond was confirmed by the simultaneous presence of C-, A-, B-defects, broad Platelets peak and pronounced "fluorescence cage" effect

4,168 (the most common line), 4,113, 4,073, and 4,067 cm^{-1} (the Amber center)

The Amber center is a term describing at least four different, yet closely related, optical centers characterized by optical absorption features in the spectral range from 3,900 to 9,000 cm^{-1} and a set of rather narrow lines near 4,100 cm^{-1} (Massi et al. 2005) (Fig. 6.66). The Amber center is a common feature of natural brown diamonds. However, it is not a common center of natural pink diamonds (De Weerdt and Van Royen 2001). Although the Amber center is not observed in diamonds without brown coloration, not all brown diamonds reveal this center. The Amber center is associated with brown graining. A tentative model of the Amber Center present in type Ia diamonds (the AC1 center) is a modified A defect with an atomic structure $NCCN^+$ (Massi et al. 2005).

The Amber centers of all types (4,168, 4,067 and 4,173 cm^{-1}) are destroyed by HPHT treatment (Hainschwang et al. 2005). However, the Amber centers can survive low-temperature, short-time HPHT treatments. Yet the amber center is completely destroyed by commercial HPHT treatment performed at temperatures over 2,000 °C (Hainschwang et al. 2005; De Weerdt and Van Royen 2000; Van Royen and Palyanov 2002). The presence of the Amber Center in FTIR absorption spectra of a diamond is not a reliable proof of its pristine nature. However, in many cases it can be considered as an indicator of untreated diamond.

2,879 nm (3,474 cm^{-1}) and 2,976 nm (3,360 cm^{-1}) centers

These centers are observed in absorption spectra of natural brown type Ib diamonds. They are destroyed by HPHT treatment performed at temperatures of

2,000 °C (Hainschwang et al. 2005). The 3,474 and 3,360 cm^{-1} centers can be considered as features of untreated diamonds.

3,024 nm (3,307 cm^{-1}) center

This hydrogen-related center is observed in absorption spectra of brown diamonds. The 3,307 cm^{-1} center is reduced in intensity or destroyed by HPHT treatment (Hainschwang et al. 2005). The center can be considered as a feature of untreated diamonds.

3,169 nm (3,156 cm^{-1}) center

HPHT treatment may create this center in natural diamonds (Hainschwang et al. 2008).

3,180 nm (3,145 cm^{-1}) and 3,144 nm (3,181 cm^{-1}) centers

These centers are features of heavily irradiated and annealed diamonds. So far they were not reliably observed in untreated stones (Fritsch et al. 2007). However, detection of the 3,145 and 3,181 cm^{-1} centers in natural untreated diamonds cannot be excluded (Fisher 2012). The 3,145 and 3,181 cm^{-1} centers relate to hydrogen-containing defects and they are detected in diamonds revealing the presence of C defects. The diamonds, FTIR spectra of which exhibit 3,145 and 3,181 cm^{-1} centers, are always of type IaA with very low intensity of B defect absorption (Hainschwang et al. 2006a; Woods and Collins 1983). These both lines are a strong indication of type Ib character of diamonds, and as such, they can be considered as an indication of HPHT treatment.

3,323 cm^{-1}

A sharp line observed in some natural and CVD-grown diamonds in IR absorption spectra. The center 3,323 cm^{-1} relates to a hydrogen-containing defect of low temperature stability. The center anneals out after HPHT treatment at a temperature of 1,600 °C (Crepin et al. 2012). The 3,323 cm^{-1} center is a feature of untreated diamonds.

3,219 nm (3,107 cm^{-1}) (the Hydrogen center)

The 3,107 cm^{-1} absorption center is the most prominent hydrogen-related center of diamond (Fig. 6.67). It is attributed to stretching vibrations of C–H bond (for bending vibration see the 1,405 cm^{-1} center). Hydrogen is a major impurity in natural and CVD diamonds and its concentration in natural diamonds may be as high as 1 %. Thus the 3,107 cm^{-1} center is frequently present in IR absorption spectra of diamonds of different types. Usually the center is stronger in diamonds containing considerable amount of B defects. In type IaB stones, the absorption strength in the 3,107 cm^{-1} line may reach a value of 60 cm^{-1}. The presence of B defects seems to be a required condition for the formation of the 3,107 cm^{-1} center. Diamonds of pure types IaA (no detectable B and B' centers) and IaAB' (no detectable B center) do not reveal the 3,107 cm^{-1} center of measurable intensity, whereas the diamonds of types IaA and IaAB' with traces of the B center (a few ppm B defects, absorption intensity of the B center of 0.3 cm^{-1}) may

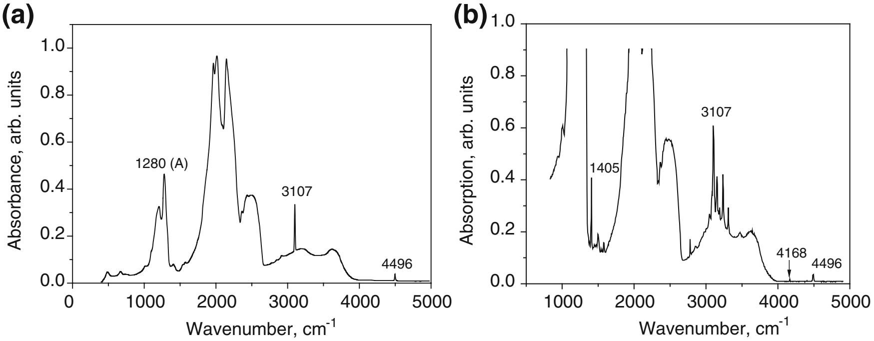


Fig. 6.67 FTIR absorption spectra of hydrogen-containing natural diamonds: **a** low-nitrogen type IaA diamond with moderate hydrogen content showing the 3,107 cm^{-1} line as the only hydrogen-related center; **b** high-nitrogen yellowish greenish gray diamond with high hydrogen content showing numerous hydrogen-related centers with the dominating 3,107 cm^{-1} center

already reveal weak 3,107 cm^{-1} line. About 50 % of diamonds of pure types IaB and IaBB' exhibit in their spectra the 3,107 cm^{-1} center.

In natural type IaAB diamonds, the 3,107 cm^{-1} center tends to increase with the increase in the nitrogen content (mostly in the form of B defects). The center can be negligibly weak at a nitrogen concentration of 200 ppm and very strong in diamonds with the total nitrogen content over 1,000 ppm (Lang et al. 2007). Yet, no direct correlation of the strength of the 3,107 cm^{-1} center with the concentration of the A and/or B defects (as well as with the total nitrogen content) in natural diamonds (both untreated and HPHT-treated) has been found (De Weerdt and Collins 2006). In type IIa diamonds, the 3,107 cm^{-1} center, if detected, is very weak. The center is rarely observed in natural and synthetic diamonds of types IIb. Also diamonds of type Ib character usually show very weak hydrogen-related absorption (Hainschwang et al. 2006a). Thus, the role of the aggregated nitrogen in the formation of the 3,107 cm^{-1} center is obvious.

There is no direct correlation between color of natural diamonds and the absorption strength of the 3,107 cm^{-1} center. However, the center is very strong in type Ia diamonds of violet-gray color, e.g. in Argyle diamonds (De Weerdt and Kuprianov 2002).

The hydrogen-related defects, including those producing the 3,107 and 1,405 cm^{-1} centers effectively interact with radiation defects. Both centers can be considerably suppressed or even completely destroyed in type Ia diamonds after electron irradiation and subsequent prolonged annealing at a temperature of 1,200 °C (Vins 2001). However, electron irradiation performed prior to HPHT annealing stimulates the formation of the 3,107 cm^{-1} center, which in this case forms at lower annealing temperatures (Kiflawi et al. 1996).

In contrast to the radiation damage, the mechanical stress and plastic deformation promote formation of the 3,107 cm^{-1} center. Thus the 3,107 cm^{-1} center is particularly strong in areas of low structural perfection (e.g. coat/core boundary of coated natural diamonds) (Yelisseyev et al. 2004). For this reason, the 3,107 cm^{-1} center is a frequent absorption feature of brown diamonds.

Complex behavior of the 3,107 cm^{-1} center during HPHT annealing is reported in (De Weerdt and Collins 2006; Vins and Yelisseyev 2008a). A ten-fold decrease or two-fold increase in the intensity of the 3,107 cm^{-1} center is observed as a result of high temperature heating under pressure. In type Ia diamonds with different content of A and B defects, intensity of the 3,107 cm^{-1} center usually reduces by a few times after a short-time HPHT treatment. For instance, a 10 min HPHT treatment at temperatures of 2,100–2,200 °C strongly reduces the 3,107 cm^{-1} center and can even destroy it completely (Vins and Yelisseyev 2008). In some diamonds, however, a strengthening of the 3,107 cm^{-1} center is observed after a short-time (1 min) HPHT treatment (De Weerdt and Collins 2007). An enhanced intensity of the 3,107 cm^{-1} line was observed in HPHT-treated Imperial Red diamonds with dominating absorption of B defects (Wang et al. 2005). This seemingly inconsistent behavior of the 3,107 cm^{-1} center during HPHT annealing is explained by involvement of some competing processes which increase and decrease the concentration of the hydrogen-related detects.

Analysis of the published data and that of our own experiments shows that in 80 % of cases, HPHT treatment strongly reduces the 3,107 cm^{-1} line (over an order of magnitude). In 20 % of cases, this line may slightly increase its intensity after HPHT treatment (not more than two times). With the increase in the HPHT annealing time, the 3,107 cm^{-1} line gradually decreases and eventually disappears. This up-and-down behavior is especially pronounced in gray diamonds, which owe their color to the presence of micro-inclusions of graphite. Micro-inclusions of graphite are saturated with hydrogen and retain it, if diamonds are not heated at high temperatures. Graphite micro-inclusions in natural diamonds contain a lot of hydrogen. High temperature HPHT treatment converts graphite into diamond and the released hydrogen atoms form different hydrogen-related defects including those responsible for the 3,107 cm^{-1} center. Simultaneously with the release of hydrogen, HPHT treatment increases concentration of B defects, what is also a stimulating factor for the formation of the 3,107 cm^{-1} center.

The defects responsible for the 3,107 cm^{-1} center are temperature stable ones. When alone, they can survive annealing at a temperature of 2,650 °C for 5 h (Kiflawi et al. 1996). However, the interaction with other defects produced by HPHT annealing may destroy the 3,107 cm^{-1} center and this destruction can be erroneously ascribed to low temperature stability. For instance, it has been shown that the 3,107 cm^{-1} center is stable in type IaAB diamonds, but it has lower stability in type IaB diamonds (De Weerdt and Kuprianov 2002). Although natural IaB and IaBB' diamonds almost always reveal the 3,107 cm^{-1} line, it is absent from spectra IaB stones transformed from IaA diamonds by high temperature (2,500 °C and above) HPHT treatment (Vins and Yelisseyev 2008; De Weerdt and Kuprianov 2002). Despite the fact that the defects responsible for the 3,107 cm^{-1} center survive at a temperature of 2,650 °C, long-time HPHT treatment results in gradual annealing out of the 3,107 cm^{-1} center even at temperatures as low as 2,100 °C (De Weerdt and Collins 2006). This process can be especially rapid in type IaB diamonds. Thus the absence of the 3,107 cm^{-1} center in natural type IaB diamonds is an indication of a high-temperature HPHT treatment (Vins and Yelisseyev 2010). However, it should be kept in mind that untreated natural type IaB diamonds with no 3,107 cm^{-1} can be found (Fisher 2012).

An atomic model of the 3,107 cm^{-1} center as a complex of the N3 defect and hydrogen atom—VN_3H defect has been recently proposed in (Goss et al. 2012). This model suggests that the 3,107 cm^{-1} center is a common feature in spectra of diamonds exhibiting presence of B defects and their derivatives N3 defects. This model may well explain why the intensity of the 3,107 cm^{-1} center correlates with the total nitrogen content in synthetic diamond after HPHT annealing (Kiflawi et al. 1996). Indeed, at temperatures over 2,000 °C, hydrogen distributes uniformly over the diamond volume, however, the concentration of the HPHT-induced B defects and N3 defects is proportional to the total nitrogen content. It is important to note that the hydrogen atoms participating in the formation of VN_3H defects do not diffuse into the diamond from the surrounding medium during HPHT annealing, but are captured into the crystal during its growth.

Formation of the 3,107 cm^{-1} center in diamonds with high hydrogen content (gray natural diamonds and CVD diamonds) during HPHT annealing can occur at a temperature as low as 1,800 °C (Vins and Kononov 2003; Twitchen et al. 2003). Hence the formation of B defects and the release and migration of hydrogen in these diamonds take place even during low temperature HPHT treatment.

The Hydrogen center reveals complex behavior during HPHT annealing, which strongly depends on the initial impurity-defect content of diamond. Yet the tendency is the suppression of the 3,107 cm^{-1} center and its removal with the increase in temperature and time of annealing. Since commercial HPHT treatment is not performed at very high temperatures and for a long time, the concentration of the hydrogen defects in treated diamonds does not come to the equilibrium value and the 3,107 cm^{-1} center may have very different intensity. Therefore, the presence of this center and its relative intensity cannot be used as criteria of recognition of HPHT treatment.

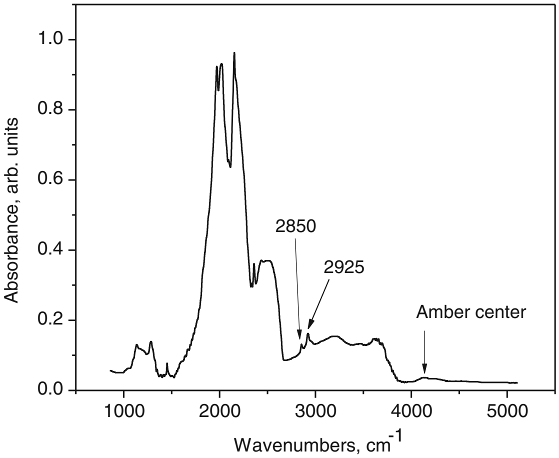
2,975, 2,925, 2,850 cm^{-1}

A set of absorption features with major lines at wavenumbers 2,975, 2,925, 2,850 cm^{-1} is observed in some natural and synthetic diamonds. These features are enhanced in HPHT treated diamonds, which exhibit considerable generation of C defects. These lines are common in spectra of diamonds treated by multi-process treatment, e.g. they are observed in spectra of Imperial Red diamonds (Fig. 6.68).

4,141 nm (2,415 cm^{-1}) and a broad band around 650–400 cm^{-1}

These two features are created and enhanced in spectra of pseudo-CO_2 diamonds by HPHT treatment performed at a temperature of 2,000 °C (Hainschwang et al. 2005).

Fig. 6.68 FTIR absorption spectrum of a fancy deep purple pink diamond showing 2,975, 2,925, 2,850 cm^{-1} centers. Note that the spectrum also shows the Amber center, which is the result of the irradiation and annealing steps performed after HPHT treatment



4,156 nm (2,406 cm^{-1}), 2,362 cm^{-1} and features from 658–645 cm^{-1}

HPHT treatment stimulates formation of CO_2 molecules from oxygen impurity commonly present in natural diamonds (Hainschwang et al. 2008; Hainschwang et al. 2005). The absorption bands at wavenumbers 2,406, 2,362 and in the spectral range from 658 to 645 cm^{-1} seen in IR absorption spectra of natural brown diamonds are ascribed to isolated CO_2 molecules integrated into diamond lattice (Hainschwang et al. 2006b), rather than to CO_2 inclusions. Considerable absorption of the CO_2-related centers is rarely observed in colorless type IIa diamonds. Intense CO_2 centers are characteristic of translucent natural diamonds with transparent undulatory graining (Wang et al. 2005b).

HPHT treatment performed at temperatures 2,000–2,100 °C (at a pressure of 60–65 kbar) does not change intensity of the 656 and 2,383 cm^{-1} bands in high CO_2 diamonds. However, low intensity CO_2-related lines may be enhanced by treatment. In pseudo-CO_2 diamonds, the CO_2-related lines can be re-created by treatment (Hainschwang et al. 2008).

6,532 nm (1,531 cm^{-1}), 1,548 and 1,523 cm^{-1}

Presence of this group of lines in the spectral range 1,520–1,580 cm^{-1} indicates that diamond was irradiated but not annealed at high temperature (Hainschwang et al. 2002). These lines are seen in natural untreated diamonds (Fig. 6.69a). They stand annealing at temperatures below 800 °C and can be observed in diamonds together with the 595 nm center, which is formed after low temperature annealing.

6,757 nm (1,480 cm^{-1})

HPHT treatment produces this line in regular brown type IaAB diamonds. For instance, it is produced by HPHT treatment in cape yellow diamonds (Collins 2001). The 1,480 cm^{-1} center can be detected in IR absorption spectra of high-nitrogen type Ia diamonds after HPHT treatment at temperatures below 1,950 °C (these diamonds acquire canary–yellow color) (Tretiakova 2009). The 1,480 cm^{-1}

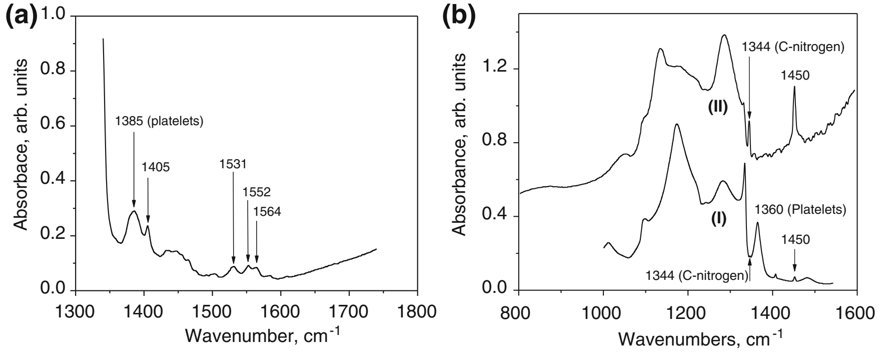


Fig. 6.69 **a** IR absorption spectrum of an untreated high-nitrogen light yellow diamond showing a set of lines in the range 1,520—1,580 cm^{-1}. High content of A defects (about 500 ppm) results in a very broad Platelets line at a wavenumber of 1,385 cm^{-1} (about 30 cm^{-1}). Therefore, for this diamond, the broad Platelets peak is not an indication of HPHT treatment. **b** The H1a and 1,344 cm^{-1} centers in FTIR absorption spectra of HPHT-treated diamonds: (I) a diamond showing very broad Platelets peak characteristic of HPHT-treated diamonds [re-plotted from (Wang et al. 2005)]; (II) an Imperial Red diamond showing a pronounced H1a and 1,344 cm^{-1} (C defect) centers

center is very rarely observed in pristine natural diamonds (Collins 2001; Hainschwang et al. 2005; Collins et al. 2000; Kiflawi et al. 1988; Okano et al. 2006). It is a very temperature stable center and it is not destroyed by annealing at a temperature as high as 2,750 °C (Kiflawi et al. 1998).

6,897 nm center, the H1a center (1,450 cm^{-1})

It has been shown that the H1a center relates to a defect containing interstitial nitrogen atoms: <001> dinitrogen split interstitial (N_{2I} defect) (Liggins et al. 2010). The presence of the H1a center indicates that diamond was irradiated and annealed at temperatures below 1,400 °C (Hainschwang et al. 2002; Vins and Yelisseyev 2008a). Strong H1a center is always observed in HPHT-treated Imperial Red diamonds (Wang et al. 2005) (Fig. 6.69b). The H1a center can be also seen together with intense GR1 center in diamonds treated by irradiation and subsequent annealing at temperatures below 800 °C.

Absorption intensity of the H1a center is used for the evaluation of concentration of interstitial nitrogen atoms (N_I):

$$N_I(\text{ppm}) = (3 \pm 0,6)\mu_{1,450},$$

where $\mu_{1,450}$ is the absorption coefficient of the line 1,450 cm^{-1} in cm^{-1} (Yelisseyev and Vins 2011).

Together with the 424 and 594 nm absorption centers, the H1a center is a reliable indicator of radiation treatment (Vins and Yelisseyev 2008a).

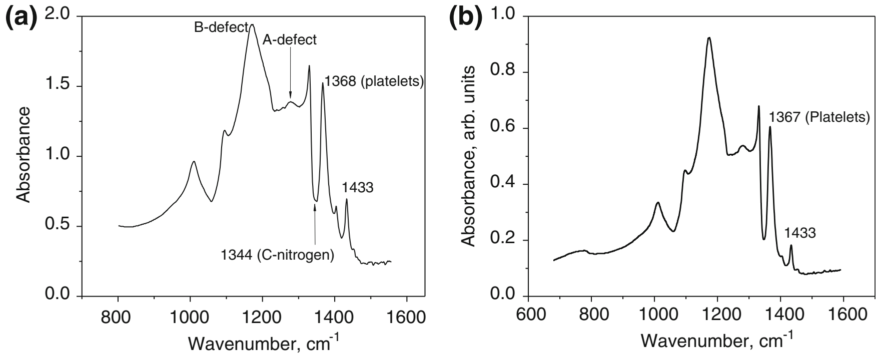


Fig. 6.70 **a** IR absorption spectra of a fancy *brownish pink* diamond HPHT-treated at moderate temperatures. Broad Platelets peaks and traces of 1,344 cm^{-1} line (C defects) are features of treatment. **b** FTIR absorption spectrum of a natural untreated *pink* diamond. Note very broad platelets peak—a feature of natural untreated plastically deformed *brown* and *pink* diamonds. Both spectra (**a**) and (**b**) are very similar and exhibit the 1,430 cm^{-1} line, relative intensity of which is greater in the untreated diamond. No sign of the 1,344 cm^{-1} peak is detected in the spectrum of the untreated diamond

6,993 nm (1,430 cm^{-1})

This hydrogen-related line is observed in spectra of natural untreated diamonds. It is reduced in intensity or destroyed by HPHT treatment performed at a temperature of 2,000 °C (Hainschwang et al. 2005). Low temperature treatment may leave the 1,430 cm^{-1} center without measurable changes (Fig. 6.70).

7117 nm (1405 cm^{-1})

This line is a typical hydrogen-related center of diamond. The 1,405 cm^{-1} center is the optical absorption on the bending vibrational mode of C–H atomic bond (for C–H stretching vibrations see the 3,107 cm^{-1} center). The 1,405 cm^{-1} center can be seen in spectra of any natural diamond (Fig. 6.71). However, it is probably more frequently observed in type IaA diamonds. The center is very temperature stable. It stands temperature of 2,650 °C for several hours (Kiflawi et al. 1998; Evans et al. 1995). However, the 1,405 cm^{-1} center can be reduced or destroyed in regular brown diamonds by treatment at a temperature of 2,000 °C (Hainschwang et al. 2005).

7283 nm (1373 cm^{-1})

The 1,373 cm^{-1} line is a feature observed in type IIa and may be in type IIb diamonds. This feature is attributed to vibrations of some hydrogen-containing complex. The line anneals out after HPHT treatment and can be considered as a feature of untreated natural diamonds (Simic and Zaitsev 2012) (Fig. 6.72).

7,270 nm (1,360 cm^{-1}), the B' center or the Platelets peak

The B' center is the manifestation of the B' defects (Platelets). The atomic model of Platelets has not been established with certainty, however, the mostly used

Fig. 6.71 FTIR absorption spectrum of an untreated type IaB diamond (F color) showing the 1,405 cm^{-1} center. This diamond reveals traces of natural irradiation: a weak GR1 center in Vis absorption and PL spectra and rather weak 575 and 638 nm centers in PL spectra. Intensity ratio of the NV centers I_{638}/I_{575} is about 0.1 supporting the conclusion that the diamond is in pristine untreated state

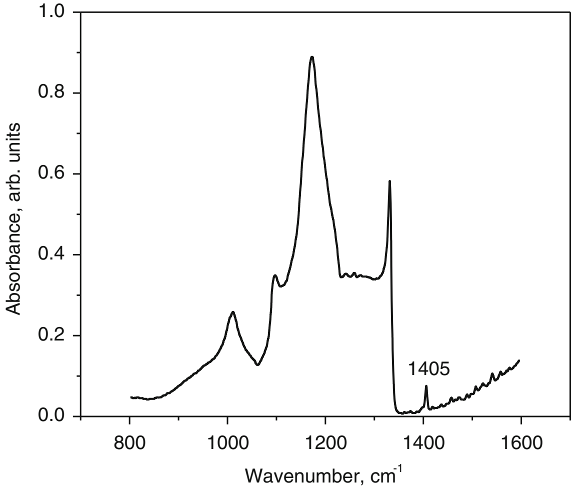
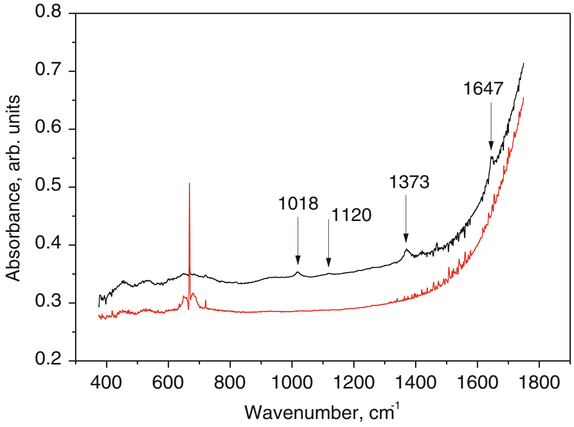


Fig. 6.72 FTIR absorption spectra of a type IIa initially brown diamond converted into colorless by HPHT treatment: *black curve*—before treatment, *red curve*—after treatment. The spectral lines, which change their intensity after HPHT treatment are indicated



model is a planar aggregations of interstitial carbon atoms decorated by nitrogen. Our working model of the Platelet is a planar aggregation of interstitial carbon atoms around nitrogen B defects, where the B defects serve as centers of condensation for carbon interstitials. It is not clear how much nitrogen is incorporated in the Platelets. However, the fact, that the platelets are formed only in nitrogen-rich diamonds, makes one to ascribe the B' defects to nitrogen-containing complexes. The Platelets are common defects in type Ia natural diamonds and are detected in IR spectra of almost all diamonds of type IaB > A.

The main spectral feature of the Platelets is a relatively narrow absorption peak, which, in many natural diamonds, can be found at a wavenumber of 1,360 cm^{-1}. Its spectral width is about 8 cm^{-1}. A weak line at a wavenumber of 382 cm^{-1} and a broad band with maximum at about 330 cm^{-1} are further IR absorption features

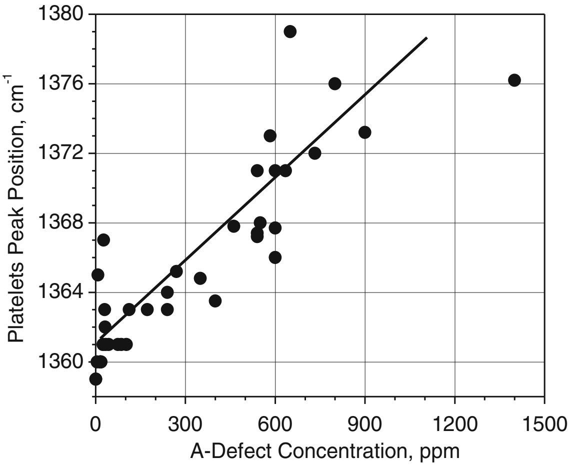


Fig. 6.73 Spectral position of the Platelets peak in untreated natural diamonds (without intense brown/gray coloration and without traces of natural irradiation) versus A defect concentration

of B' defects. B' defects are also active in UV spectral range producing absorption features at wavelengths 263.2, 266.8, 280.0 and 283.4 nm.

The spectral position and the spectral width of the B' peak may vary from 1,354 to 1,386 cm^{-1} and from 4 to 36 cm^{-1} respectively depending on the Platelets size (the smaller the Platelets the higher the Platelets peak energy) and the nitrogen content. The Platelets peak shifts considerably towards higher energies with the increase in concentration of A defects (Fig. 6.73). No noticeable influence of B defects on IR spectrum of Platelets is observed (Vasilyev and Sofroneev 2008).

Temperature stability of Platelets is moderate. With temperature increase, Platelets "evaporate" emitting carbon interstitials. Measurable destruction of Platelets starts at a temperature of 1,700 °C. Since Platelets are extended defects comprising thousands of atoms, their collapse is a slow process and Platelets can well survive short time annealing at temperatures much above 1,700 °C. Although Platelets are unstable defects at high temperatures, they can be produced by HPHT annealing. Formation of Platelets occurs at HPHT conditions, at which interstitial carbon atoms and B defects are produced. The main producer of carbon interstitials is the moving dislocations and the aggregation of A defects into B defects. In brown diamonds, both processes may be activated at temperatures as low as 1,800 °C. Thus HPHT treatment, performed practically at any temperature, may have considerable effect upon Platelets (Kiflawi and Lawson 1999; Hainschwang et al. 2008; Kupriyanov et al. 2008; Vins and Yelisseyev 2010). The processes of formation and destruction of Platelets depend on the nitrogen content and structural perfection of diamond. Therefore, in different diamonds, HPHT treatment may result in increase or decrease in the concentration of Platelets. However, if HPHT annealing is performed for a long time, the Platelets always anneal out in diamonds of any color: brown and colorless.

The A defects play important role in formation of Platelets. It has been found that in diamonds with A defect concentration below 400 ppm (the A center absorption intensity below 25 cm^{-1}), the Platelets peak decreases after HPHT treatment performed at any temperature. In contrast, in diamonds with the A defect content over 400 ppm and low initial intensity of the Platelets peak, HPHT treatment, performed at a temperature of 2,200 °C and above, increases the Platelets peak intensity, this increase occurring along with the increase in the B center intensity (Vins and Yelisseyev 2008). The temperature threshold 2,200 °C of the Platelets growth is the temperature of activation of the A- to B-defect aggregation and the release of the carbon interstitials contributing to the formation of the Platelets. If the A defect content is high, the concentration of carbon interstitials exceeds the equilibrium one and they condensate into Platelets. During long-time HPHT annealing, when the nitrogen defects reach their equilibrium concentrations and the production of carbon interstitials stops, small Platelets begin to "evaporate" releasing B defects and contributing to the growth of large Platelets. The described process explains why in any diamond of type I, the Platelets peak is considerably reduced together with the A center content after very high temperature HPHT treatment, and both features eventually disappear after long time treatment (Fig. 6.74).

Formation of diamonds of "pure" type IaAB' (about 6 % all type Ia natural diamonds) is explained by the aggregation of most C defects into A defects at a temperature just at the beginning of formation of B defects. The concentration of B defects still remains below the detection limit. Though, it is sufficient for the formation of a measurable concentration of Platelets. The source of most carbon interstitials involved in the growth of Platelets is not the process of the A- to B-defect aggregation. We believe that the moving dislocations are more efficient in emitting carbon interstitials. Hence, the formation of type IaAB' diamonds could occur at rather low temperatures, which are insufficient for conversion of A defects into B defects, but high enough for the activation of the dislocation motion.

Another important change, the Platelets peak exhibits after HPHT treatment, is its broadening. HPHT treatment may not necessarily change the spectral position of the Platelets peak, but it always makes the Platelets peak broader (Kiflawi and Lawson 1999) (Figs. 6.75, 6.76).

The HPHT-induced spectral shift of the Platelets peak always occurs towards smaller wavenumbers, suggesting the increase in the Platelets size (Clackson et al. 1990; Vins et al. 2008; Goss et al. 2003). Since the spectral position of the Platelets peak in natural diamonds varies considerably, it is not a straightforward indicator of HPHT treatment. However, the ranges of the spectral width of the Platelets peak in untreated and treated diamonds do not coincide and therefore the spectral width can be used as an indicator of HPHT treatment (Fig. 6.77).

In natural untreated brown diamonds and hydrogen-rich diamonds, the Platelets peak can be as broad as in HPHT-treated ones. Yet, the Platelets peak is never this broad in non-brown and/or low-hydrogen natural diamonds. Hence, the following simple rule works for most cut diamonds:

The Platelets peak width is less than 9 cm^{-1}—likely untreated diamond,
The Platelets peak width is over 12 cm^{-1}—likely HPHT-treated diamond,

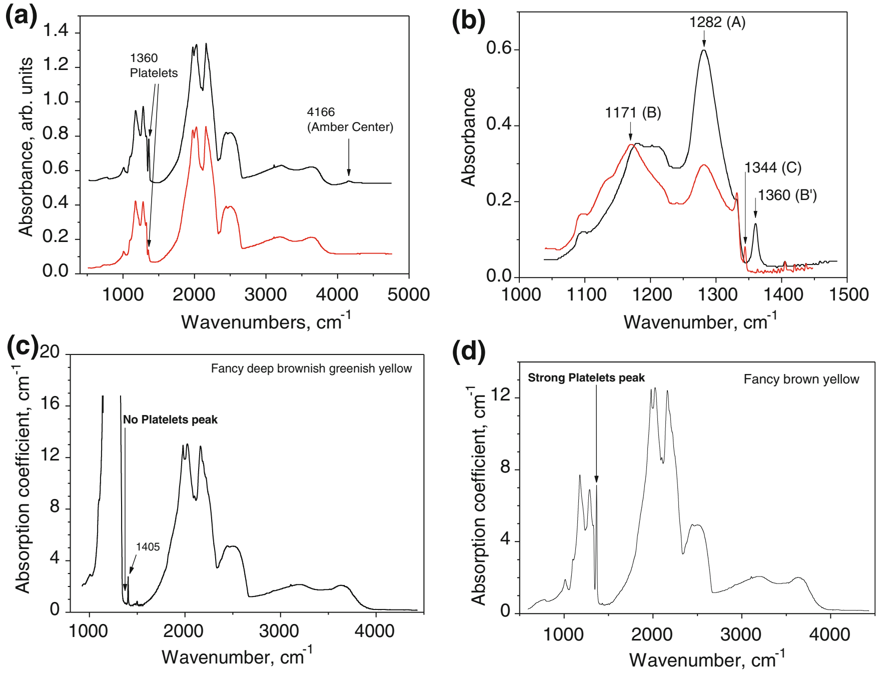


Fig. 6.74 **a** IR absorption spectra of a light brown type IaAB diamond HPHT-treated at moderate temperature: *black curve*—before treatment, *red curve*—after treatment. HPHT treatment did not cause significant change in the A/B intensity ratio. However, the intensity of the Platelets peak is reduced considerably. The Amber center is completely annealed out. **b** Typical transformations of IR absorption spectra of the major nitrogen defects in initially brown natural type IaA > B diamonds after HPHT treatment at a temperature of 2,300 °C. Before treatment (*black curve*), the A center is the dominating feature of the spectrum. The Platelets peak is quite pronounced. After treatment (*red curve*), the A center intensity is considerably reduced and the B center intensity is increased. The C center peak at wavenumber 1,344 cm^{-1} is clearly seen. The Platelets peak has been removed completely [based on the data from (Simic and Zaitsev 2012)]. **c** IR absorption spectra of type IaAB natural diamonds with high content of nitrogen A defects. The absence of the Platelets peak in a diamond with high concentration of A defects suggests untreated nature of this diamond. **d** IR absorption spectra of type IaAB natural diamonds with low concentration of A defects. Strong Platelets peak in a diamond with weak A defect absorption suggests untreated nature of this diamond

The Platelets peak width is less than 8 cm^{-1} and the spectral position of the peak is at wavenumbers over 1,358 cm^{-1}—definitely untreated diamond.

The Platelets peak width is over 9 cm^{-1} and the spectral position of the peak is at wavenumbers less than 1,360 cm^{-1}—definitely treated diamond.

The spectral position and width of the Platelets peak are not affected by irradiation and/or annealing performed at temperatures below 1,400 °C. Thus the spectral changes of the Platelets peak observed in spectra of diamonds subjected to multi-process treatment have been induced during HPHT annealing process and they cannot be altered during the following irradiation and conventional annealing steps.

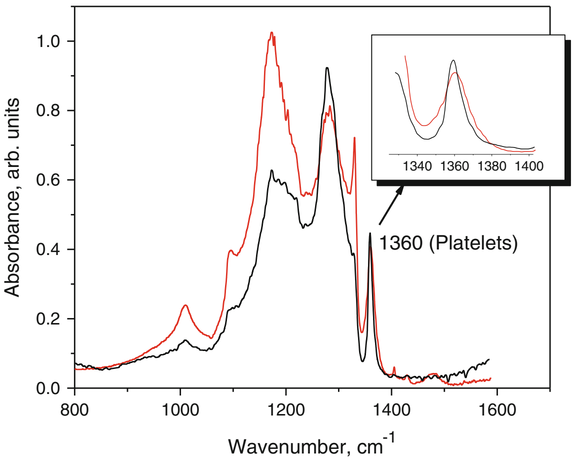


Fig. 6.75 FTIR absorption spectra of a natural type Ia diamond before HPHT treatment (*black curve*) and after HPHT treatment (*red curve*). HPHT treatment has not caused a noticeable change in intensity of the Platelets peak, however, the Platelets peak has become broader. The insert shows the Platelets peak in greater detail

Further impact of HPHT treatment on the B’ defects is the removal of the 382 cm^{-1} peak, which occurs if the treatment is performed at very high temperatures over 2,500 °C (Kiflawi and Lawson 1999).

7,440 nm (1,344 cm^{-1}), the C-center

The C-center is one of the most common IR optical centers of diamond. It has a characteristic spectral shape with two prominent features: a sharp peak at a wavenumber of 1,344 cm^{-1} and a band with maximum at a wavenumber of 1,130 cm^{-1} (Fig. 6.78). The C-center is a dominant IR absorption feature of type Ib diamonds and it can be detected in spectra of some type Ia natural diamonds, which in this case are referred to as type Ia + Ib diamonds, or type Ia diamonds of Ib character.

In nature, diamonds grow as type Ib. However, overwhelming majority of natural diamonds are type IaAB stones with comparable content of A and B defects and very low concentration of C defects. The concentration of C defects in most natural diamonds rarely exceeds 0.06 ppm (Vins and Yelisseyev 2008a). This difference in concentrations of the aggregated and dispersed nitrogen suggests that during natural HPHT annealing, the diffusion of single nitrogen atoms was fast enough to complete the first stage of the nitrogen aggregation: the aggregation of C defects into A defects (Collins et al. 2000). The equilibrium concentration of C defects is a strong function of temperature and at the geological temperatures (below 1,700 °C) is very low. Hence, the diamonds which spent long enough time deep in earth have hardly detectable concentration of C defects. Only rare diamonds, which were expelled to the earth surface shortly after their growth, retain dominating concentration of C defects.

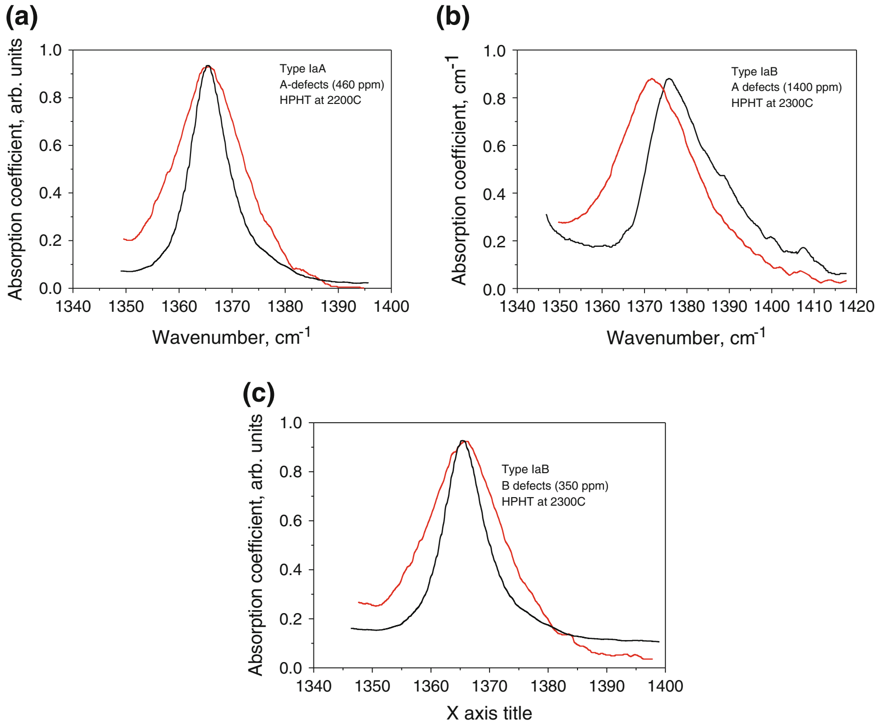


Fig. 6.76 Broadening of the Platelets peak after HPHT treatment. The HPHT-induced broadening of the Platelets peak occurs in diamonds of any type. The spectral shift of the peak may not occur. *Black curves* are the spectra before treatment, *red curves*—after treatment

The C defects are very common product of HPHT treatment (Fig. 6.78b). Temperature of commercial HPHT annealing is much higher than the geological temperatures. Consequently in type Ia diamonds, the concentration of C defects generated during HPHT treatment increases greatly and it continues to increase with the annealing time. Upon rapid cooling down, the treated type Ia diamond retain unproportionally high concentration of C defects, what eventually makes them ABC diamonds.

The main reason of formation of C defects during HPHT annealing is the dissociation of small nitrogen complexes like A and H3 defects. The intensity of the C-center, produced by HPHT treatment, strongly depends on the total nitrogen content and on the initial state of the nitrogen aggregation. Although after HPHT treatment the C-center intensity can increase by orders of magnitude, for about 90 % of HPHT-treated diamonds it still remains a minor feature in FTIR absorption spectra (Hainschwang et al. 2005; Sriprasert et al. 2007) (Fig. 6.78b). Usually, in order to be detectable in IR absorption spectra of type Ia diamonds as a peak at 1,344 cm^{-1}, the concentration of C defects should be of a few tenths of ppm. In high-nitrogen diamonds with intense A- and B-center absorptions, the

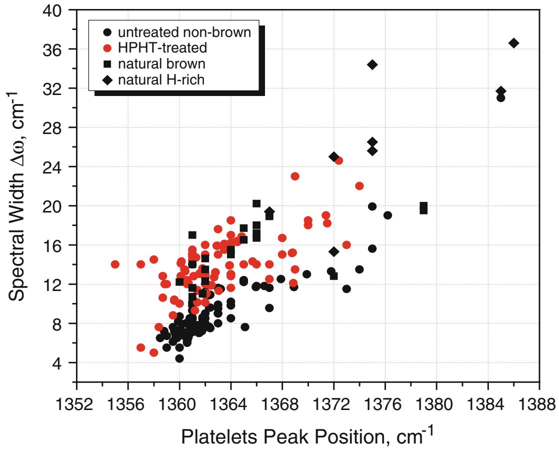


Fig. 6.77 Platelets peak width as a function of Platelets peak spectral position for untreated (*black symbols*) and HPHT-treated (*red circles*) diamonds [the data from (Fisher 2008) and other publications are combined with the original data of authors]. In HPHT-treated diamonds, the Platelet peak is significantly broader than in majority of untreated diamonds. However, high-nitrogen, high-hydrogen, as well as pink and brown untreated stones show the Platelets peak, the width and position of which are well in the range of “treated” diamonds. The Platelets peak can be also broad in spectra of diamonds with intense Amber Center

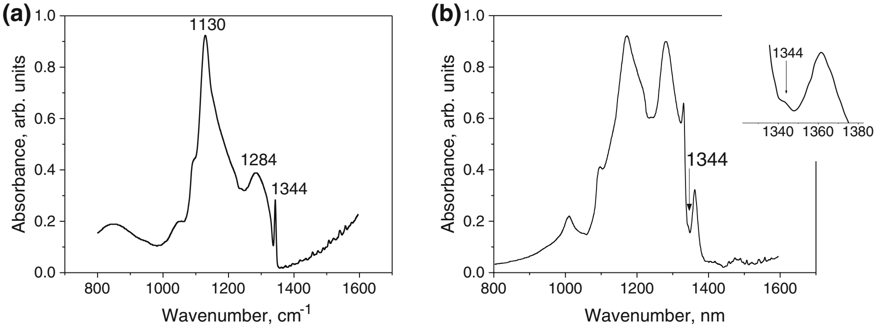


Fig. 6.78 **a** FTIR absorption spectrum of a fancy deep yellow orange synthetic diamond of a pure type Ib. The main features of C-center are sharp peak at 1,344 cm^{-1} and relatively narrow band at 1,130 cm^{-1}. A minor broad band at 1,284 cm^{-1} is also a feature of the C-center. **b** FTIR absorption spectrum of a diamond of red color after multi-process treatment. A tiny feature at a wavenumber 1,344 cm^{-1} manifests the presence of the C defects at a concentration of 2 ppm. The insert shows the 1,344 cm^{-1} line is greater detail. The Platelets peak is characteristically broad. This type of spectrum is very common for HPHT-treated type IaAB diamonds. Although the intensity of C-center in IR absorption is negligibly weak, Vis absorption and PL spectra of this diamond show very strong 638 nm center, which is a direct derivative of the C defects

detectable concentration limit of the C defects is of 1 ppm. In these diamonds, the C-center absorption is very weak and is detected as a tiny hump at a wavenumber of 1,344 cm^{-1} (Reinitz et al. 2000; Collins 2001; De Weerdt and Van Royen 2000; Fisher et al. 2006). In many cases, HPHT treatment does not produce C defects in concentrations detectable in IR absorption (De Weerdt and Van Royen 2000). In HPHT-treated diamonds, the C defects can be detected via absorption of the 1,344 cm^{-1} peak, when the color grade of these diamonds is I and below (Fisher and Spits 2000; Collins 2001).

The C defects are not produced during low temperature HPHT treatment (e.g. at a temperature of 1,800 °C) in concentrations high enough to be detected in Vis and IR absorption spectra. The optically detectable concentration of C defects appears after treatment performed at temperatures of 2,000 °C and above (Collins 2001; De Weerdt and Collins 2007). The production efficiency of C defects fast increases with temperature. After HPHT treatment at a temperature of 2,500 °C, the concentration of C defects may be as high as 5 ppm. Thus high temperature HPHT treatment converts type Ia diamonds into type Ia diamonds of Ib character, which show strong C defect absorption continuum and a well-developed IR peak at wavenumber 1,344 cm^{-1} (Fisher et al. 2006).

Dissociation of the aggregated nitrogen into C defects is strongly stimulated by radiation. Irradiation of an average natural type Ia diamonds with reactor neutrons at a dose of 10^{17} cm^{-2} followed by conventional annealing at a temperature of 1,500 °C may create C defects in concentration of 5 ppm (Vins and Yelisseyev 2008a). Initial brown color is also a factor stimulating the nitrogen dissociation (Vins and Yelisseyev 2010). Thus one may assume that the interaction with the vacancies, which are created by irradiation or released form vacancy clusters, is the reason of the stimulated dissociation. However, the enhanced production of C defects in type Ia brown diamonds during HPHT treatment has not been observed in (Fisher et al. 2006).

If C defects are present in high concentration, HPHT treatment aggregate them into A and B defects. In type Ib diamonds, almost complete transformation of the C defects into A and B centers is achieved during high temperature HPHT treatment (Hainschwang et al. 2005). This suggests that a diamond, IR absorption spectrum of which is dominated by C-center, is definitely untreated (Hainschwang et al. 2006a; Shigley et al. 1993). Practically, the 1,344 cm^{-1} peak of intensity over 5 % of the total intensity of the nitrogen-related IR absorption is a reliable indicator of untreated natural diamonds.

The probability of detection of C-center in spectra of natural nitrogen-containing diamonds decreases with the level of nitrogen aggregation. Thus the C-center is more frequently seen in type IaA diamonds than in diamonds with dominating B defects. Also the natural diamonds with intense N3 center absorption do not reveal absorption of C-center and if they do, these diamonds are probably HPHT-treated with the aim of intensification of their original pale yellow color (Collins 2003).

It is well known that natural type IIa diamonds may contain traces of aggregated nitrogen and no dispersed nitrogen. Thus the presence of single nitrogen in type IIa diamonds is an indication of possible HPHT treatment (Wang and Gelb 2005).

Concentration of C defects can be estimated measuring absorption intensities of the main line of C-center (1,130 cm^{-1}), sharp peak at wavenumber 1,344 cm^{-1}, the C defect absorption continuum at a wavelength of 477 nm, and the 270 nm band:

$$\begin{aligned}\mathrm{Nc(ppm)} &= (25 \pm 2)\mu_{1,130},\\ \mathrm{Nc(ppm)} &= (25\,\mathrm{to}\,50)\mu_{1,344},\\ \mathrm{Nc\ (ppm)} &= (18 \pm 2)\mu_{477},\\ \mathrm{Nc(ppm)} &= (0.6 \pm 0.1)\mu_{270},\end{aligned}$$

where μ is the absorption coefficient in cm^{-1}. When using the peak at 1,344 cm^{-1}, one must make sure that the spectral resolution of the spectrometer is good enough to ensure the correct measurement of the peak intensity.

Generation of C defects in type Ia diamonds is a very characteristic feature of HPHT treatment of these diamonds. Any type I diamond, which does not exhibit in its spectra any centers related to C defects is definitely untreated. Although one must be aware that in many HPHT-treated diamonds, the IR optical centers related to C defects can be too weak to be detected by conventional FTIR spectrometers. In these cases a comprehensive spectroscopy over the UV-Vis-IR spectral range must be performed with the aim of detection of all optical centers directly related to C defects and the centers related to the primary derivatives of C defects (e.g. NV centers).

7,800 nm (1,282 cm^{-1}), the A-center.

The A-center is one of the most common nitrogen-related optical centers of diamond. The A-center is the manifestation of the nitrogen A defects. The absorption spectrum of the A-center in natural type IaA diamond is shown in Fig. 6.79.

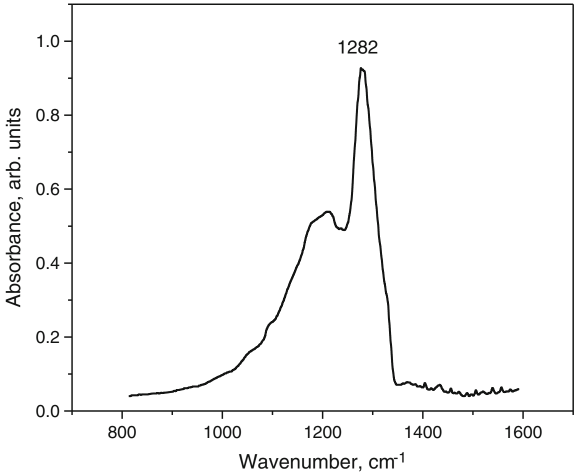


Fig. 6.79 FTIR absorption spectrum of a natural diamond of pure type IaA showing sole A-center spectrum. The main feature of the A-center is the peak at a wavenumber of 1,282 cm^{-1}

A defects are responsible for the so-called “secondary” absorption edge with the onset at a wavelength of 300 nm. The secondary absorption edge is present in UV spectra of all type IaA and IaAB diamonds (Fig. 6.81).

The A defects are actively involved in the processes of transformation of nitrogen defects during HPHT treatment. However, their presence or absence alone does not say anything definite about the treatment history of a diamond. Yet when considered in combination with other nitrogen-related defects, the relative intensity of the A center may provide reliable proof of treatment or its absence.

The A defects are an intermediate form of nitrogen aggregates involved in the aggregation/dissociation processes occurring during HPHT annealing. HPHT annealing of type Ib diamonds at a temperature of 2,300 °C converts about 75 % of C-nitrogen into aggregated forms (Collins et al. 2005), which are mostly A defects.

In brown type IaA diamonds, noticeable dissociation of the A defects into C defects occurs at temperatures 2,100 °C and above. At temperatures above 2,200 °C, the A defects start to associate into B defects and platelets. The deeper the initial brown color the greater the rates of these reactions. In contrast, the A defects do not form in brown type IaB diamonds treated at temperatures in the range from 1,800 to 2,300 °C under pressure of 7 GPa (range of phase stability of diamond) (Vins and Yelisseyev 2010). However, the A defects can form in these diamonds during HPHT treatment performed at lower pressures corresponding to the range of stability of graphite.

The A defects are very effective quenchers of luminescence and their high concentration may considerably reduce the luminescence intensity of any optical center in diamond (Collins 1982). This quenching effect must be always taken into account when analyzing the luminescence intensity of the centers used as criteria of HPHT treatment. For instance, the 638 nm center can be rather weak in PL spectra of some HPHT-treated type IaA diamonds, whereas it is well detectable in Vis absorption spectra. The A defects also strongly suppress the “transmission” effect. The diamonds with high concentration of A defects are never blue, green and/or red “transmitters”.

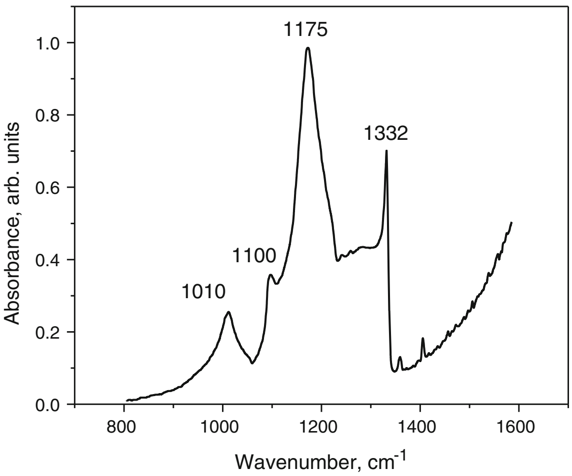
In type IaA and IaA > B diamonds, the concentration of A defects in ppm can be found measuring the coefficient of absorption of the main band at wavenumber 1,282 cm^{-1} using the formula (Boyd et al. 1994):

$$\mathrm{N_A(ppm)} = 16.5\,\mu_{\mathrm{A.}}$$

In type IaAB diamonds with comparable intensities of A- and B-center absorptions, the concentration of A defects can be found measuring the absorption coefficient of the band 1,282 cm^{-1} (for A-center) and of the band 1,175 cm^{-1} (for the B-center):

$$\mathrm{N_A(ppm)} = 16.5\left(1.2\,\mu_{1,282} - 0.488\,\mu_{1,175}\right).$$

Fig. 6.80 FTIR absorption spectrum of natural diamond of a pure type IaB showing sole absorption of the B-center. The features of the B-center are at 1,010, 1,100, 1,332 and 1,175 cm^{-1}, the latter being the most intense



8,511 nm (1,175 cm^{-1}), the B-center

The B-center is one of the most common nitrogen-related optical centers of diamond. The B-center is the manifestation of the nitrogen B defects. In IR absorption spectra, the B-center has the main peak at a wavenumber of 1,175 cm^{-1}, sharp line at a wavenumber of 1,332 cm^{-1}, minor features at 1,100, 1,010 cm^{-1} and a characteristic plateau from 1,290 to 1,210 cm^{-1} (Fig. 6.80). There is a correlation between B-center and the absorption centers N9 (UV features at wavelengths 236 and 234.8 nm) and N10 (UV features at wavelengths 240 and 248 nm). The N9- and N10-centers can be seen only in diamonds with low content of A defects (below 30 ppm). However, the B-center and the N9-, N10-centers do not belong to one and the same defect (Shiryaev et al. 2001).

B defects are found in all natural untreated and HPHT-treated type Ia diamonds. Thus, the presence or absence of the B-center in IR spectra of a diamond does not say anything definite about its HPHT treatment history. However, it is more common that HPHT-treated type Ia diamonds exhibit a stronger B-center absorption than the A-center absorption (Reinitz 2007; Sriprasert et al. 2007) (Fig. 6.78b).

The B defects are actively involved in the processes of transformation of nitrogen defects during HPHT treatment. They are the final form of point defects involving the aggregated nitrogen. B defects are the most temperature stable nitrogen complexes and the transformation of nitrogen defects during HPHT annealing goes in the direction of formation of B defects. Because of very high activation energy, the natural formation of B defects at geological temperatures is a very slow process. Fast aggregation requires temperatures over 2,200 °C (Vins et al. 2008; Vins and Yelisseyev 2010). It is believed that HPHT treatment, if performed at the temperatures and pressures within the area of stability of diamond, does not dissociate B defects. Therefore the formation of C defects in type

IaB diamonds after HPHT treatment occurs probably due to dissociation of residual A defects, which are always present in small amounts in any type Ia diamond.

In type IaB and IaB > A diamonds, the concentration of B defects in ppm N_B (ppm) can be found measuring the coefficient of absorption of the main feature of the B-center at 1,175 cm^{-1} ($\mu_{1,175}$) (Boyd et al. 1995):

$$N_B[\text{ppm}] = 35\,\mu_{1,175}.$$

In type IaAB diamonds with comparable intensities of A- and B-center absorptions, the concentration of B defects can be found measuring the absorption coefficients of the band at 1,282 cm^{-1} (for the A center) and of the band at 1,175 cm^{-1} (for the B center):

$$N_B[\text{ppm}] = 35\left(1.2\,\mu_{1,175} - 0.59\,\mu_{1,282}\right).$$

1,018 cm^{-1} line

The 1,018 cm^{-1} line is observed in some natural type IIa brown diamonds. The 1,018 cm^{-1} line is destroyed by HPHT treatment and can be considered as a feature of untreated diamonds (Simic and Zaitsev 2012) (Fig. 6.72).

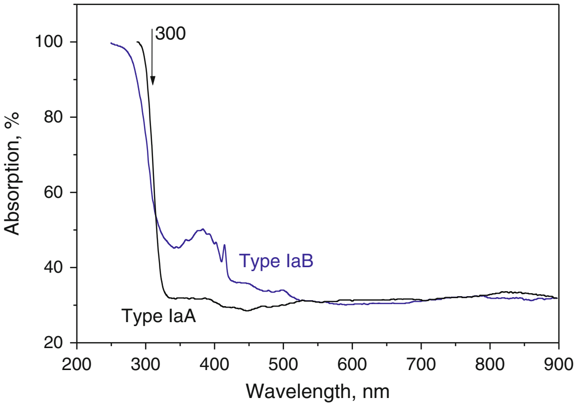
6.3 Optical Continua

6.3.1 The Secondary Absorption

The Secondary Absorption is a strong absorption starting at a wavelength of 300 nm and spreading towards shorter wavelengths (Fig. 6.81). The onset of the Secondary Absorption at 300 nm (the secondary absorption edge) is very sharp in diamonds with moderate and high concentration of A defects and resembles the intrinsic absorption edge at a wavelength of about 230 nm. The reason of the Secondary Absorption is A defects. The Secondary Absorption is the most characteristic spectral feature of all type Ia diamonds. However, natural type IaB diamonds with low concentration of A defects, can exhibit no Secondary Absorption (Fisher 2012). The Secondary Absorption is present in spectra of untreated and treated diamonds. Therefore it is not used as an indicator of diamond treatment. However, it plays an important role in revealing the "fluorescence cage" effect induced in type Ia diamonds by HPHT treatment.

Because of the secondary absorption, type Ia diamonds with the A defect concentration over 100 ppm are completely opaque in UV spectral range. If the concentration of A defects is below 30 ppm ($\mu_A < 2$ cm^{-1}), the diamonds are partially transparent for UV light.

Fig. 6.81 Typical UV-Vis absorption spectra of natural type IaA and IaB diamonds. The dominating feature of both spectra is the Secondary Absorption with the edge at about 300 nm. The A defects, even present in low concentrations in type IaB diamonds, produce strong Secondary Absorption



Concentration of A defects can be evaluated form the strength of the Secondary Absorption measured at a wavelength of 306.5 nm using the following relation:

$$N_A[\text{ppm}] = 66\,\mu_{306.5}\left[\text{cm}^{-1}\right].$$

6.3.2 The Brown Absorption Continuum

The Brown absorption continuum is a continuous, almost structureless absorption starting in the near IR spectral range and steadily rising towards shorter wavelengths over the whole visible spectral range (Fig. 6.82). This continuum is responsible for brown color of natural diamonds and as-grown CVD diamonds. The nature of the Brown absorption continuum has not been established unambiguously yet. However, it is believed that different types of extended defects are responsible for this absorption, the vacancy clusters and dislocations being the most important ones (Hounsome et al. 2006, 2007; Jones 2009; Fujita et al. 2009; Vins et al. 2008). Because of the nitrogen-vacancy interaction, the vacancy aggregation and formation of the vacancy clusters occurs more readily in type II diamonds and in low-nitrogen areas of type I diamonds (Jones et al. 2007). Because of this, percentage of brown type IIa diamonds is higher than that of type Ia diamonds.

The spectrum of the Brown absorption continuum does not vary noticeably with diamond type. However, some features can be added by other optical centers like H3 center and Pink Band (Fig. 6.83a). The spectra of the Brown absorption continuum taken from two brown diamonds of the lowest and highest color saturation are shown in Fig. 6.82b.

The Brown absorption continuum has relatively high temperature stability and in some diamonds it stands temperature over 1,900 °C. Since the Brown absorption continuum originates from different defects, its temperature stability varies in different diamonds. HPHT treatment at temperatures over 1,900 °C considerably

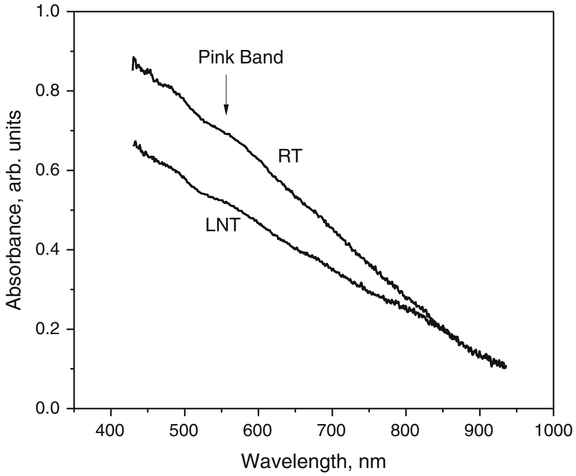


Fig. 6.82 Absorption spectra of an untreated fancy dark brown diamond exhibiting uniform Brown absorption continuum. A trace of the Pink Band (a weak broad feature with maximum at a wavelength of 560 nm) can be recognized. The spectra were taken at RT and LNT

reduces intensity of the Brown absorption continuum in most diamonds. Annealing at temperatures over 2,100 °C may remove the Brown absorption continuum completely (Fig. 6.24). The Brown absorption continuum can be also considerably reduced by irradiation (neutrons) and vacuum annealing at a temperature of 1,600 °C (Collins et al. 2005).

The concentration of vacancies N_V in the vacancy clusters responsible for the Brown continuum can be found from the absorption coefficient μ_{500} measured at a wavelength of 500 nm (Hounsome et al. 2007):

$$N_V[\mathrm{ppm}] = 20\,\mu_{500\,\mathrm{nm}}\left[\mathrm{cm}^{-1}\right].$$

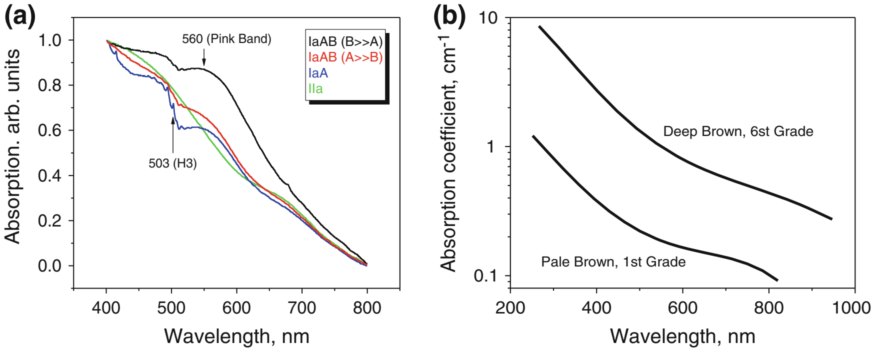


Fig. 6.83 **a** Absorption spectra of brown diamonds of different types measured at LNT: type IaB > A, type IaA > B, type IaA, type IIa [re-plotted from (De Weerdt and Van Royen 2001)]. **b** Room temperature absorption spectra of two brown type IIa diamonds representing the 1st grade of brown color (*the palest brown*) and the 6th grade of brown color (*the deepest brown*) according to DTC color grades (Fisher 2009)

In deep brown diamonds, the concentration of vacancies can be very high amounting to over 200 ppm.

6.3.3 The C Defect Absorption Continuum

The C defect absorption continuum is one of the features of the absorption spectrum of C defects. The others are the C-center and the 270 nm band. The C defect absorption continuum is the manifestation of electronic transitions from C defects to the conduction band. It is a gradually increasing absorption typically staring at wavelengths of 500–600 nm and spreading towards shorter wavelengths (Fig. 6.84). In some natural diamonds this absorption may start at longer wavelengths and rise slower towards UV range (Collins et al. 2000; Hainschwang et al. 2006a).

The C defect absorption continuum is a dominant feature of absorption spectra of natural type Ib diamonds and nitrogen-containing HPHT-grown synthetic diamonds and it is almost never seen in Vis absorption spectra of type Ia natural untreated diamonds. However, the C defect absorption continuum is a common absorption feature of HPHT-treated type Ia and some type IIa diamonds. If a type Ia natural diamond exhibits simultaneously the C Defect Absorption continuum and the A- and B-centers, it is very likely HPHT-treated one (Collins et al. 2000).

Generation of C defects in type Ia diamonds during HPHT treatment occurs mainly due to dissociation of A defects (see above 1,282 cm^{-1}, the A-center). The HPHT-induced decomposition of A defects occurs at any temperature. However, it becomes remarkable only at temperatures over 2,000 °C. Thus the C defect absorption continuum is a feature of type Ia diamonds HPHT-treated at moderate and high temperatures. In the initially colorless or cape yellow type Ia diamonds, the HPHT-induced C defect absorption continuum is the main reason of the final yellow color (Collins et al. 2000).

The C defect absorption continuum can be detected when the C defect concentration is above 0.1 ppm. Thus, the observation of this continuum may reveal the presence of trace concentrations of C defects even in high-nitrogen HPHT-treated diamonds, FTIR spectra of which do not explicitly reveal the 1,344 cm^{-1} peak. The C defect absorption continuum can be recognized particularly well when comparing absorption spectra taken at room and liquid nitrogen temperatures (Fig. 6.85).

Concentration of C defects in ppm (N_C) can be evaluated from the absorption strength of the C defect absorption continuum measured at a wavelength of 400 nm ($\mu_{400\ \mathrm{nm}}$) (De Weerdt and Collins 2008):

$$\mathrm{N_C}[\mathrm{ppm}] = 2\mu_{400\ \mathrm{nm}}\left[\mathrm{cm}^{-1}\right].$$

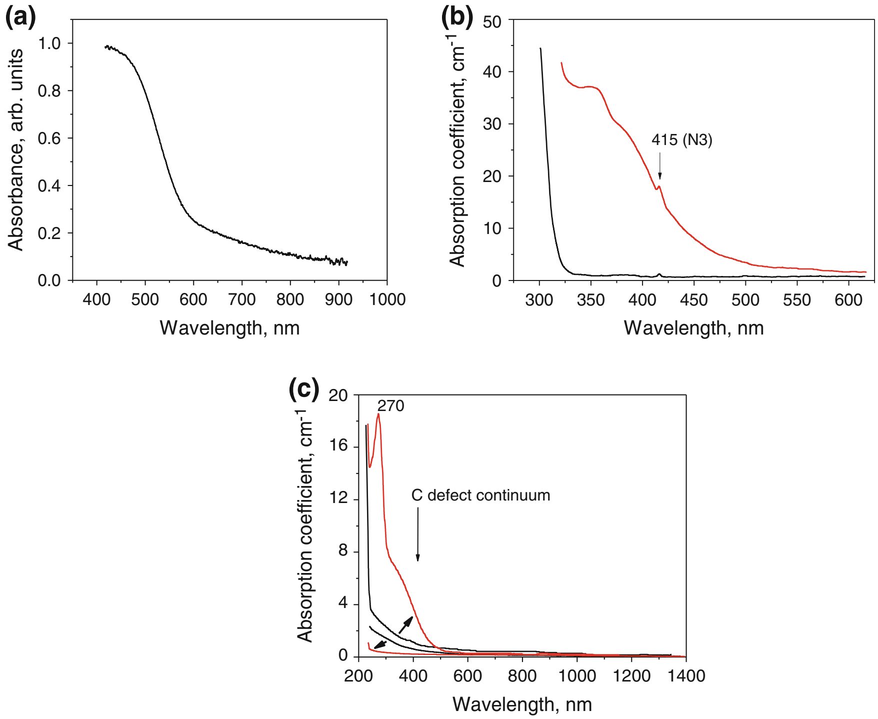
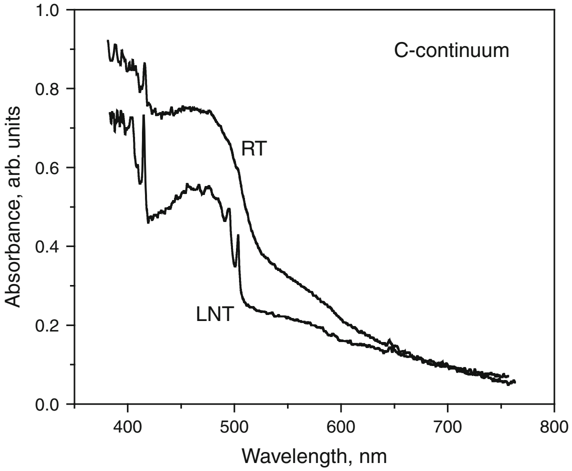


Fig. 6.84 **a** Vis absorption spectrum of a fancy deep yellow orange synthetic diamond of a pure type Ib. **b** UV-Vis absorption spectra of a type Ia natural diamond before (*black curve*) and after (*red curve*) HPHT treatment performed at a temperature of 2,600 °C [re-plotted from (Evans and Qi 1982)]. Before treatment, the spectrum exhibits only the secondary absorption edge, whereas after treatment, it is dominated by the C defect absorption continuum. **c** UV-Vis-IR absorption spectra of initially brown type IIa diamonds before (*black curves*) and after (*red curves*) HPHT treatment (measurements at RT). The initial color of both diamonds was of the 3rd grade of brown color. After HPHT treatment (2,500 °C, 1 h), one diamond shows decrease in absorption all over the spectrum, whilst the other diamond reveals pronounced absorptions of C defects: the C defect absorption continuum and the 270 nm band [based on the data from (Fisher et al. 2006)]

6.3.4 The Boron Absorption Continuum

The Boron absorption continuum starts in the IR spectral range at a wavenumber of 2,400 cm^{-1} as a multiline structure and spreads to the blue range of Vis spectrum gradually reducing in intensity. The Boron absorption continuum is the reason of blue color of type IIb diamonds. IR absorption spectra of type IIb diamonds are shown in Fig. 6.86. The defects responsible for the Boron absorption continuum are substitutional single boron atoms (boron acceptors). The Boron absorption continuum is a very stable optical feature and it does not change after HPHT treatment performed at any temperature.

Fig. 6.85 UV-Vis absorption spectra of a high-nitrogen type Ia diamond after low temperature HPHT treatment. The spectra were recorded at RT and LNT. The C defect absorption continuum is stronger at RT. FTIR absorption spectrum of this diamond exhibits vanishingly small 1,344 cm^{-1} peak. In this diamond, the concentration of the HPHT-generated C defects is about 0.2 ppm



HPHT treatment of some gray and brownish gray diamonds converts them into blue. The initial gray color of these diamonds is due to superposition of the absorptions of the Boron absorption continuum and the Brown absorption continuum. HPHT annealing removes the Brown absorption continuum and reduces the electron compensation of the boron acceptors. As a result, the diamonds become more transparent in UV and blue spectral range and the intensity of the Boron absorption continuum increases (Fig. 6.87). The reduction of the Brown absorption continuum and the increase in intensity of the Boron absorption continuum well correlate (Fisher et al. 2009). The final color of these diamonds is blue.

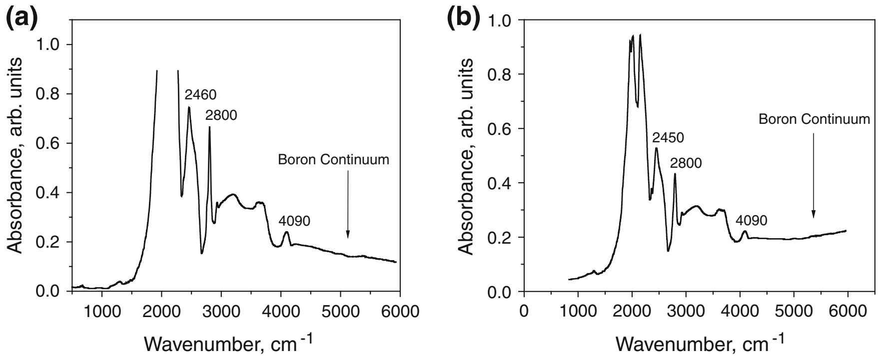


Fig. 6.86 **a** FTIR absorption spectrum of natural blue diamond (**a**) and synthetic boron-doped blue diamond (**b**). Major peaks of the boron-related absorption and the Boron absorption continuum are indicated

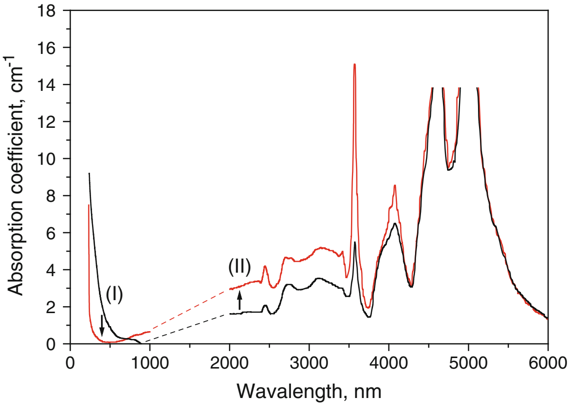


Fig. 6.87 Absorption spectra of a brown-gray type IIb diamond before (*black curve*) and after (*red curve*) HPHT treatment at a temperature of 2,500 °C for 1 h [based on the data from (Fisher et al. 2009)]. HPHT treatment removes the Brown absorption continuum (*arrow I*) and increases intensity of the Boron absorption continuum (*arrow II*)

6.4 Combinations of Optical Centers and Continua

It is rare that the confident reporting of HPHT treatment is done based on the analysis of one spectroscopic feature. In vast majority of cases, many spectroscopic features have to be compared and analyzed. Below, some specific combinations of optical centers used for recognition of HPHT-treated and untreated natural diamonds are discussed.

Canary-yellow diamonds with low-nitrogen content (20–40 ppm) revealing in IR absorption spectra only C and A defects and strong C defect absorption continuum in Vis absorption are likely HPHT-treated type Ia diamonds of originally pale yellow (cape yellow) color. However, such spectra are known for untreated diamonds too. Thus, this combination of the optical centers alone is not sufficient to report treatment with confidence (Collins 2001).

In natural type IaA/B diamonds, relative absorption intensities of H3 and H4 centers produced by irradiation followed by conventional annealing well correlate with relative absorption intensities of A and B defects, that is $I_{H3}/I_{H4} = I_A/I_B$ (Davies 1972). However, this correlation is not valid for the naturally occurring H3 and H4 centers. Usually, in untreated stones, the intensity of the H3 center is overproportionally strong (Collins 2001). Low intensity of H4 center in pristine diamonds is the result of long time natural annealing of diamonds in earth. Thus, the correlating intensities of H3/H4 and A/B centers is an indication of a possible treatment involving irradiation and annealing treatment, e.g. multi-process treatment.

After high temperature HPHT treatment (above 2,300 °C) of type Ia diamonds, the peak at wavenumber 1,344 cm^{-1} is frequently observed together with A- and

B-centers. Thus type Ia diamonds annealed at high temperatures are always ABC diamonds. Simultaneous presence of all three forms of nitrogen is extremely unlikely for natural green to yellow to orange diamonds and can be considered as a reliable indication of the treatment (Hainschwang et al. 2005; Chalain et al. 2005; Hainschwang et al. 2006a). Very rarely A, B and C centers are observed simultaneously in spectra of natural untreated diamonds. Fortunately, these diamonds have very different properties compared to those of HPHT-treated stones (Hainschwang et al. 2005). Even stronger proof of HPHT treatment is the observation of combination of A, B, C, NV and H2 centers in type Ia diamonds (De Weerdt and Van Royen 2000). Simultaneous presence of A, B, C, H3 and H2 centers is also a very characteristic manifestation of HPHT treatment (Kim and Choi 2005).

In some natural diamonds, high temperature HPHT treatment performed at temperatures 2,400–2,500 °C eliminates the PL lines at wavelengths 566, 579, 586, 601, 612/616 nm. These diamonds could also exhibit in absorption spectra intense H2 center and no H3 and N3 centers (Smith et al. 2000; Hainschwang et al. 2006a).

Simultaneous presence of the C- and B-centers is not observed in spectra of natural untreated diamonds and it can be considered as a strong evidence of HPHT treatment (Wang et al. 2005a). We observed the C- and B-centers in diamonds of pinkish-orange color, which also showed the GR1 and ND1 centers together with the NV^0 and NV^- nm centers. It is very likely that these diamonds were irradiated and annealed after HPHT treatment (multi-process treatment). Especially noticeable formation of C defects from B defects can occur during HPHT treatment of plastically deformed brown diamonds. The HPHT-treated diamonds with C and B defects may also have enhanced intensity of the N3 center (Vins et al. 2008). It is interesting that a natural diamond with B and C defects was reported in (Chalain et al. 2005). Nevertheless, the simultaneous presence of C defects in IaB diamonds is a reliable indicator of HPHT treatment.

In absorption spectra of “Imperial Red diamonds”, the N3, H3, NV^- and NV^0 centers are dominating. The NV^- center is usually the strongest one. Weak H4 center and 595 nm center are also seen in spectra of these diamonds. Weak GR1 and ND1 centers can be occasionally present too (Wang et al. 2005).

A type IaAB diamond exhibiting weak Platelets peak and strong 638 nm center, which is much stronger that the 575 nm center, is very likely HPTH-treated. If in addition, the H2 center is detectable in absorption spectra, this diamond is definitely HPHT-treated (Hainschwang et al. 2005).

PL spectra showing simultaneously NV^- (NV^0), 701 and 926 nm centers have not been reported for natural diamonds (Hainschwang et al. 2005). Thus this combination of optical centers is a strong evidence of HPHT treatment.

Simultaneous presence of intense centers N3, H3 and H2 is a characteristic feature of HPHT-treated diamonds. No such spectra have been reported for natural stones (Serov and Viktorov 2007).

Simultaneous presence of the centers H4, H3, H2, H1a, H1b, H1c, NV^0, NV^- and 595 nm has never been observed in spectra of natural untreated diamonds. In contrast, this combination is common for Imperial Red diamonds (Wang et al.

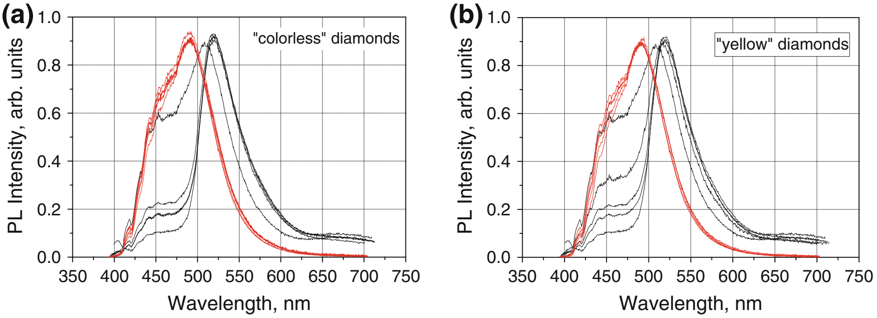


Fig. 6.88 PL spectra of initially brown type IIa (**a**) and type IaA (**b**) diamonds before treatment (*black curves*) and after high temperature HPHT treatment (*red curves*). Before treatment, all diamonds show maximum PL intensity at a wavelength of about 520 nm. One of type IIa diamonds has maximum luminescence intensity at a wavelength of 510 nm. After treatment, PL intensity maximum shifts to 480-490 nm. The measurements were taken at RT with excitation at a wavelength of 365 nm. Intensities of all spectra were adjusted to one and the same level for better comparison

2005). A similar observation was reported in (Tretiakova 2009), where it was shown that simultaneous presence of the centers C, H1b, N1c and H2 is a strong indication of HPHT treatment.

It is extremely unusual to find untreated natural diamond containing simultaneously the C, N3 and B defects all over the bulk. The exceptions are the coated stones, which have "old" core containing highly aggregated nitrogen and "young" coat containing C and A defects. Such a zoning is a feature distinguishing HPHT-treated and untreated stones (Fisher 2009).

Room temperature PL spectra of many initially brown diamonds of types IIa and IaAB, when excited with SWUV light, have dominating broad band with maximum at about 520 nm. After high temperature HPHT or multi-process treatment, the spectral position of this band shifts to 490 nm. This effect is not obvious for type IaB diamonds (Haske 2005; Simic and Zaitsev 2012) (Figs. 6.88, 7.3b).

Chapter 7
Visual Luminescence and Luminescence Imaging

The observation of visual luminescence under UV excitation and the examination of luminescence images in fluorescence microscope are very useful techniques for preliminary recognition of HPHT-treated diamonds. The luminescence color alone can give the first alarm about possible HPHT treatment. As to the luminescence imaging, in some cases even alone, it can provide sufficient information for the confident reporting of treatment.

There are no non-luminescent natural diamonds. Even the diamonds graded as "none-fluorescent" always exhibit weak luminescence when examined in fluorescence microscope. The reason of this luminescence activity is various defects, which are inevitably present in natural diamonds. HPHT-grown synthetic diamonds, like natural diamonds, are also always luminescence active. The only example of "absolutely" luminescence-inert diamonds is ultra-pure CVD diamonds (so-called "electronic grade" diamonds), the defect content of which can be below 0.1 ppb.

Most luminescence effective defects in diamond contain nitrogen impurity. The number of nitrogen-related optical centers may exceed 500. The second-best activator of luminescence in diamond is nickel. The number of the nickel-related optical centers is in the order of 100. It is not exaggeration to say that almost all optical centers of diamond are the manifestation of the defects containing nitrogen and/or nickel in different combinations and in combination with intrinsic defects like vacancies and/or carbon interstitials. Impurity-free defects are commonly not active in the visible luminescence of natural diamond. The luminescence of intrinsic defects in natural diamonds can be detected only spectroscopically.

Luminescence intensity of natural diamonds is particularly sensitive to the content of the nitrogen A defects. The A defects are very strong luminescence quenchers and the diamonds with high concentration of A defects usually exhibit weak luminescence (Crossfield et al. 1974; Davies 1978; Anthony et al. 1999). In contrast, the diamonds with low content of A defects are strongly luminescing ones. However, the diamonds with very low content of nitrogen (type IIa diamonds) also reveal weak luminescence, for they have too low concentration of optically active defects. Hence, the most intense luminescence is excited in natural type I diamonds with moderate content of nitrogen.

I. A. Dobrinets et al., *HPHT-Treated Diamonds*, Springer Series in Materials Science 181, DOI: 10.1007/978-3-642-37490-6_7,

HPHT annealing considerably changes the defect composition and, consequently, the set of the optical centers in diamond. This change is revealed as the changes in the visible luminescence color and as specific features of the distribution of luminescence over the diamond surface and bulk. Example of these changes in type Ia diamond are shown in Fig. 7.1.

The luminescence color and its intensity of diamond depend on the wavelength of the excitation light. Thus, the color and intensity of the luminescence excited by LWUV and SWUV radiation are usually different. In most cases, LWUV excitation is more effective. The reason for this is that most optical centers, which are active in the visible spectral range, are excited in the blue and near UV spectral range. SWUV is away from this range and, because of this, ineffective.

HPHT-treated diamonds, including type IIa diamonds, are usually highly luminescent. About 50 % of natural diamonds reveal strong enhanced luminescence after HPHT treatment (Fig. 7.2). On average, HPHT treatment increases intensity of the visible luminescence by an order of magnitude. The reason of this increase is the reduction of concentration of A defects, which are converted at high temperatures into H3 defects.

Electron irradiation, which is used an intermediate step in multi-process treatment also influences the luminescence intensity and the luminescence image of diamond considerably. The irradiated diamonds always exhibit weaker luminescence (Fig. 7.2c). Besides, irradiation is very effective in generating the "fluorescence cage" effect (Boillat et al. 2001) (Fig. 7.1aIII).

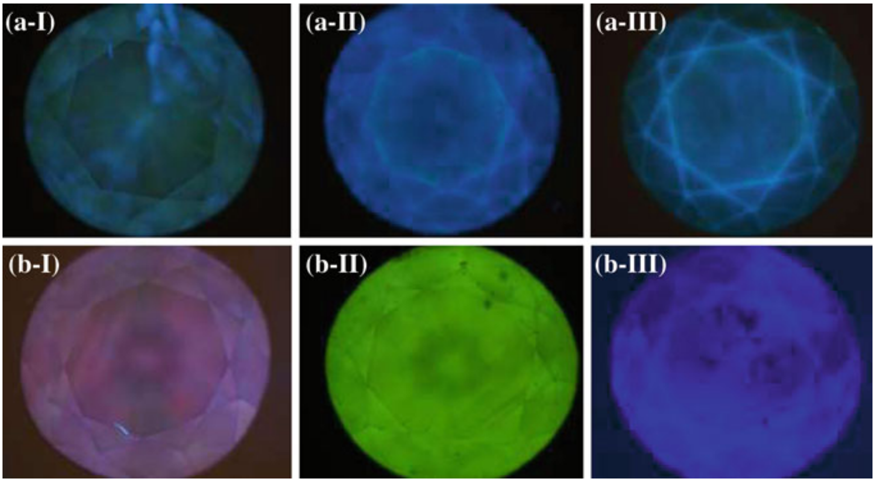


Fig. 7.1 Luminescence images of two type Ia diamonds at different stages of treatment. **a** I—before treatment, II—after HPHT annealing at a temperature of 1,900 °C, III—after subsequent irradiation with electrons. **b** I—before treatment, II—after first HPHT annealing at a temperature of 1,900 °C, III—after second HPHT annealing at a temperature of 2,400 °C. It is seen that treatment changes strongly color, intensity and distribution of luminescence. All images were taken under LWUV excitation. The "fluorescence cage" effect (see below) is pronounced on the irradiated diamond and after high temperature HPHT treatment

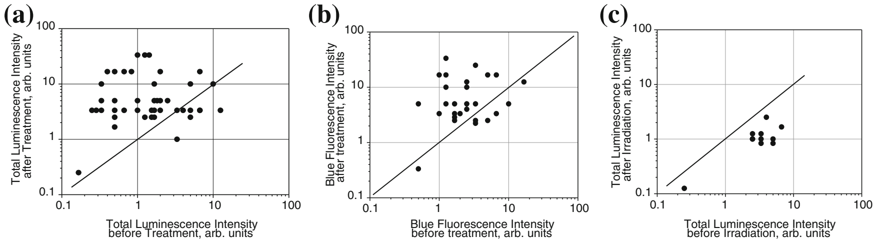


Fig. 7.2 Change in intensity of the visual luminescence of type Ia diamonds at different stages of multi-process treatment. **a** Total luminescence intensity before and after HPHT annealing at a temperature of 1,900 °C for 10 min. **b** Intensity of blue luminescence before and after HPHT annealing at a temperature of 2,300 °C for 10 min. **c** Total luminescence intensity after HPHT annealing at a temperature of 2,300 °C and after subsequent electron irradiation. The points above the *red line* indicate the intensity increase after treatment, whereas the points below the lines indicate the intensity decrease. In most cases, HPHT treatment increases the luminescence intensity. Irradiation always decreases luminescence intensity. The luminescence was excited with LWUV light

Natural diamonds can reveal luminescence of different colors. However, the most common colors are blue, green and red. Below, the features of the visible luminescence related to HPHT treatment are discussed. Almost always, the visible luminescence of diamond is fluorescence. The only case of phosphorescence, which is relevant to the problem of recognition of HPHT treatment, is the phosphorescence of type IIb diamonds. However, since the time-resolved luminescence is not used as a method of recognition of HPHT treatment, the differences between the fluorescence and phosphorescence imaging will not be discussed in this book.

7.1 Blue Fluorescence

Fluorescence of majority of natural diamonds is blue. Different optical centers can contribute to the blue fluorescence. However, primarily, the blue fluorescence is the emission of the N3 center, which is present in most natural type Ia diamonds. Due to the N3 center, blue fluorescence is especially pronounced in cape yellow diamonds. Since the maximum absorption of the N3 center is at a wavelength of 360 nm, the most effective excitation of the blue fluorescence is achieved with LWUV illumination.

In most diamonds, commercial HPHT treatment does not change concentration of N3 defects considerably. However, high temperature HPHT treatment usually increases the N3 center luminescence intensity. This increase is the result of the reduction in concentration of A defects and, consequently, the increase in the efficiency of N3 center luminescence (Fig. 7.2b). The change of the fluorescence color, e.g., to green or red, which is frequently observed after HPHT treatment at moderate temperatures, is the result of a more intense fluorescence of the H3 and NV^{-} centers (Fig. 7.1b).

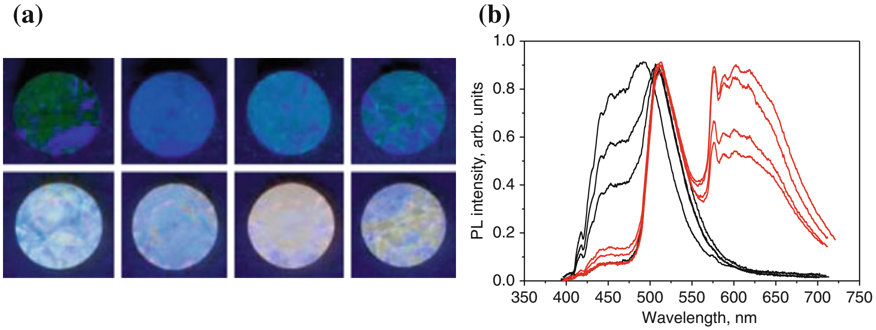


Fig. 7.3 **a** Fluorescence images of four low-nitrogen type IaB diamonds of initial brown color before treatment (*upper row*) and after multi-process treatment (*lower raw*). The treatment has changed the *brown color* to *pink*. All *diamonds* show *red* component in their fluorescence. **b** PL spectra of these diamonds. After treatment, the spectra reveal strong NV-center emission, which is the reason of the *red* component of the fluorescence color. For one diamond, the maximum intensity of the dominating broad band shifts from 520 to 490 nm (Simic and Zaitsev 2012) (courtesy of D. Simic)

Type Ia diamonds used for HPHT treatment are preferentially those of brown color. In pristine state they exhibit fluorescence with dominating blue color. After HPHT treatment performed at moderate temperatures, their fluorescence color is converted to green. The resulting color of the diamonds is yellow/green with a slight brown modifier. Thus if a diamond of green-yellow color exhibits blue fluorescence, it can be considered as an evidence of its untreated nature, whereas a diamond of this color exhibiting strong green fluorescence is likely HPHT-treated.

Weak blue fluorescence, observed in many natural type IIa diamonds, is not changed noticeably in intensity after HPHT treatment (Moses et al. 1999). However, its color may acquire a light pink modifier due to formation of the NV^0 center (Fig. 7.3).

7.2 Green/Yellow Fluorescence

Green fluorescence is also quite common for natural untreated diamonds. Its most probable origin is the H3 center, which is extremely effective in luminescence. In contrast to the N3 center, HPHT treatment influences the concentration of H3 defects very much and, consequently, the intensity of the H3 center. Moderate temperature HPHT treatment strongly increases the H3 center fluorescence in initially brown type Ia diamonds, whereas high temperature treatment destroys it completely (Fig. 7.4). However, fluorescence of CO_2 and pseudo CO_2 brown diamonds does not change after HPHT treatment (Hainschwang et al. 2005). Thus, strong green fluorescence of green-yellow diamonds is an indication of their

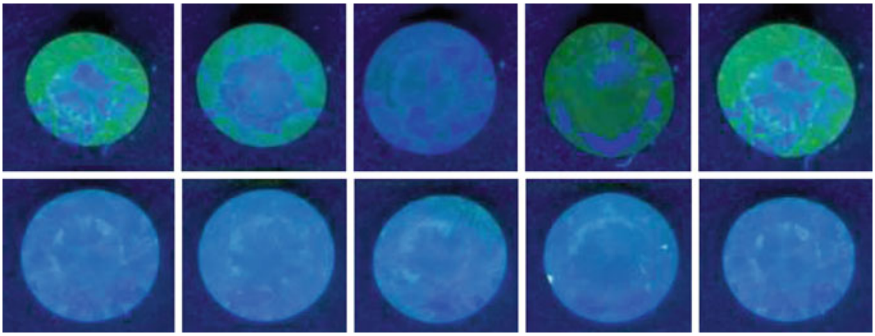


Fig. 7.4 Fluorescence images of five type IaA diamonds of initial brown color before treatment (*upper row*) and after high temperature HPHT treatment (*lower raw*). The treatment has changed the *brown color* into *yellow*. *Green* component of fluorescence has disappeared after treatment (Simic and Zaitsev 2012) (courtesy of D. Simic). Room temperature PL spectra of these diamonds are shown in Fig. 6.88b

possible HPHT treatment, whereas the absence of green fluorescence in yellow diamonds may also suggest HPHT treatment, though high temperature one.

Frequently, fluorescence of the H3 center is accompanied by red–orange fluorescence of the NV centers. The result of this combination is a yellowish green fluorescence.

The fluorescence of the H3 center can be excited at any wavelength from blue through deep UV. However, like for the blue fluorescence of the N3 center, it is particularly strong when excited with LWUV illumination (Kim and Choi 2005; Reinitz et al. 2000).

Moderate to strong chalky, greenish-yellow to yellowish-green fluorescence to both LWUV and SWUV excitation is very common for yellow to green HPHT-treated diamonds. This chalky appearance is the result of strong green fluorescence of the H3 center with some blue fluorescence of the N3 center. A yellowish tint can be added by fluorescence of the NV^- center. The observation of greenish chalky fluorescence is a simple method of preliminary selection of HPHT-treated diamonds (Reinitz et al. 2000; Kammerling and McClure 1994). Although green luminescence can be seen in natural yellowish green diamonds (Anthony et al. 2000), intense green fluorescence in greenish-yellow diamonds is an indicator of HPHT treatment. Non-treated yellow to brown diamonds show combination of blue and yellow fluorescence, often with the yellow component concentrated in brown graining and typically with no chalkiness (Reinitz et al. 2000; Kammerling and McClure 1995).

DiamondView imaging shows a homogeneous distribution of greenish-yellow luminescence in type IIa HPHT-treated diamonds, which is very different from that observed in natural-color type IIa or type Ib diamonds (Wang and Gelb 2005). The green luminescence may be especially strong in the areas, which were luminescence-inert before HPHT treatment (Van Royen and Palyanov 2002). The inert areas usually contain high concentration of A defects, which quench luminescence. After HPHT annealing, the A defects are converted into the H3 defects producing strong luminescence.

High temperature HPHT treatment considerably reduces concentration of the H3 and A defects. This decreases the green fluorescence intensity, but strengthens the "green transmission" effect. Thus strong green luminescence under UV excitation cannot be observed in originally brown type Ia diamonds after they have been subjected to HPHT treatment at moderate temperatures. However, these diamonds may exhibit "green transmission", which clearly seen in FSI Vis transmission spectra (Hainschwang et al. 2005).

The "green transmission" effect is a frequent result of HPHT treatment of type Ia diamonds with moderate nitrogen content. A feature of the "green transmission" observed in HPHT-treated diamonds is its concentration in yellow graining (Deljanin et al. 2003). Natural "green transmitters" reveal more homogeneous distribution of green luminescence. Strong "green transmission" effect is rare in natural diamonds and, therefore, is indicative of HPHT treatment. However, it is less reliable indicator than the strong green fluorescence under UV irradiation (Reinitz et al. 2000; Kane 1980).

Some HPHT-treated type Ia diamonds exhibit simultaneously strong "transmission" effect in blue and green color, what gives these diamonds neon-like appearance. This two-color "transmission" effect is a strong evidence of HPHT treatment (Anthony et al. 1999).

Some HPHT-treated diamonds exhibit bright yellow to lemon yellow fluorescence, which is the result of enhanced nickel-related centers. Before treatment, the nickel-containing diamonds usually have blue fluorescence. The defects responsible for this yellow fluorescence are those producing the S2 and S3 centers. The S2 and S3 centers are very temperature stable ones and the nickel-related yellow-green fluorescence is not destroyed even by very high temperature HPHT treatment.

Although strong green luminescence (green "transmission") and yellow-green fluorescence of type Ia diamonds are indicators of possible HPHT treatment, alone they are not a proof of HPHT treatment (Anthony et al. 2000).

7.3 Orange/Red Fluorescence

Orange to red fluorescence is also frequently observed in HPHT-treated diamonds. The most probable origin of this fluorescence is the emission of NV centers. Often it is accompanied by blue and green emissions from other nitrogen-related centers.

Imperial Red diamonds are examples of the treated stones with red fluorescence. Fluorescence of HPHT-treated Imperial Red diamonds under UV excitation exhibits very chalky blue, red, yellow and green emissions. Most of these diamonds show moderate-to-strong pinkish-orange to red and yellow fluorescence under SWUV excitation (Wang et al. 2005). When excited with LWUV light, the fluorescence of Imperial Red diamonds can be strong yellow, green, blue and red (Fig. 7.5a, b).

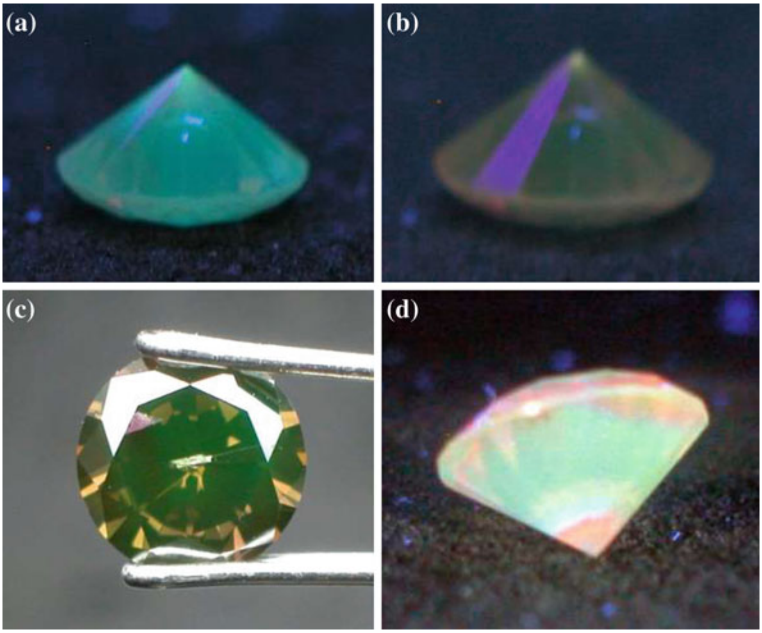


Fig. 7.5 Fluorescence images of Imperia Red diamonds. **a** *Moderate green* fluorescence under LWUV excitation. **b** Very weak fluorescence under SWUV excitation. **c** *Strong green* luminescence ("green transmission" effect) excited by daylight. **d** Zoned fluorescence is typical for Imperial Red diamonds (courtesy of S. Z. Smirnov)

When excited with visible light, Imperial Red diamonds exhibit green and orange-red luminescence ("green transmission" and "red transmission" effects), which is not observed in natural untreated diamonds (Wang et al. 2005).

Most Imperial Red diamonds are green transmitters (Fig. 7.5c). In these diamonds, the green luminescence of the H3 center is distributed unevenly and sometimes alternates with the red luminescence of the NV centers (Fig. 7.5d). Red luminescence is not typical for natural nitrogen-containing diamonds. Thus it is a feature of Imperial Red diamonds.

SWUV excitation of some natural gray/blue type IIb diamonds produces red phosphorescence (Wang et al. 2003a). High temperature HPHT treatment of these stones makes them blue, it destroys their red phosphorescence and produces blue phosphorescence. The observations of this phosphorescence is usually performed with DiamondView microscope (Breeding et al. 2006). An example of conversion of the red phosphorescence into blue phosphorescence by HPHT treatment is given in (Wang 2010; Breeding et al. 2006).

The 660 and 500 nm broad bands (Fig. 6.45) are responsible for the red and blue phosphorescence respectively. Actually both bands are present in spectra of type IIb diamonds simultaneously, the red 660 nm band being usually stronger. HPHT annealing destroys the 660 nm band, but not the 500 nm band. Hence, the

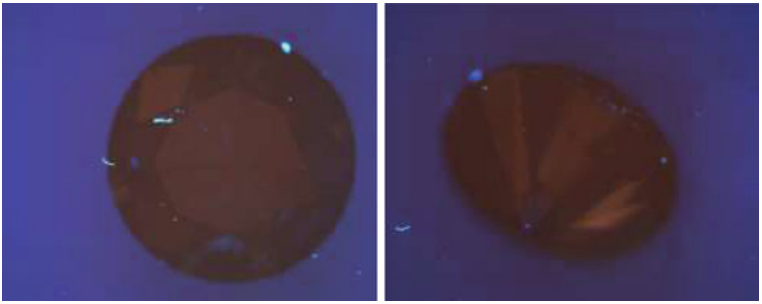


Fig. 7.6 Images of a synthetic type IIb diamond under SWUV irradiation of a mercury lamp. The *diamond* produces very weak *red* phosphorescence

remaining 500 nm band makes the phosphorescence of the treated type IIb diamonds blue. It has been also found that the 500 nm band dominates in phosphorescence of synthetic type IIb diamonds too. Therefore, the phosphorescence of red color of type IIb diamonds is considered as a good indicator of untreated natural type IIb diamonds. Yet, this criterion, like many others, is not perfect. Some natural untreated diamonds may exhibit dominating blue phosphorescence (Eaton-Magana et al. 2008). Moreover, some synthetic type IIb blue diamonds show weak red phosphorescence when excited by mercury lamp (Fig. 7.6).

7.4 Fluorescence Cage

“Fluorescence Cage” is a specific fluorescence pattern of intersecting bright lines observed on the surface of cut diamonds under UV excitation. Most of these lines run along the junctions of the facets shaping cut diamond. Sometimes, these lines can be seen along some internal extended defects. The effect of the enhanced fluorescence on the facet junctions was first discovered on irradiated diamonds (Boillat et al. 2001; Hainschwang et al. 2009; Fritsch et al. 2009), and then found on HPHT-treated diamonds (Dobrinets and Zaitsev 2009). Most natural untreated cut diamonds exhibit more or less even distribution of fluorescence over the bulk and surface (Fig. 7.7). Some untreated diamonds show non-homogeneous distribution of fluorescence. However, this non-homogeneity has a patchy appearance and rarely looks like “fluorescence cage”.

The most frequent color of “fluorescence cage” is blue (Fig. 7.8). However, its color can be very different (Fig. 7.9). On treated diamonds, the “fluorescence cage” is seen all over the diamond, but can be more distinctive on the pavilion side.

No systematic studies of the “fluorescence cage” have been performed so far and the origin and the mechanism of activation of this effect have not been established yet. By now, we have examined about 300 diamonds for the “fluorescence cage”.

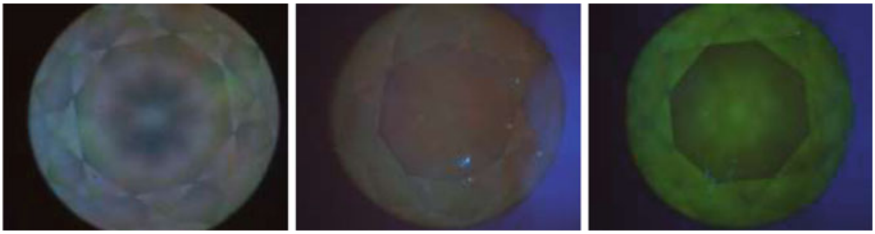


Fig. 7.7 Typical fluorescence images of natural untreated diamonds. There is no sign of enhanced fluorescence on the facet edges

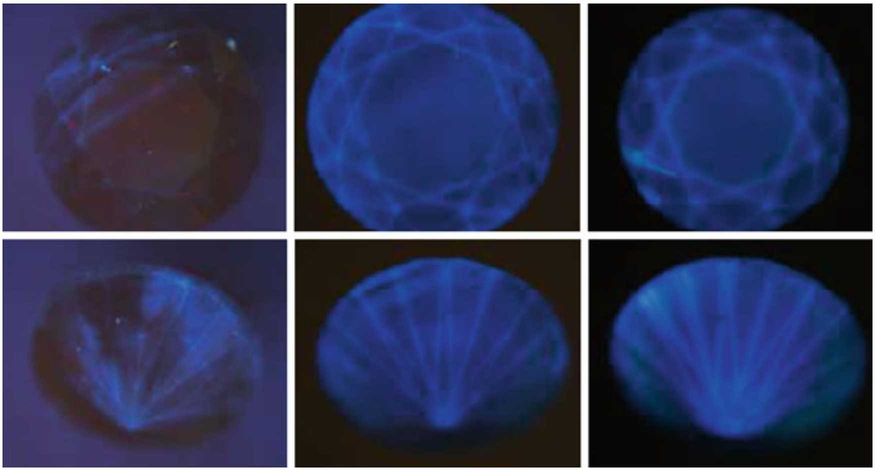


Fig. 7.8 Fluorescence images of type Ia diamonds after HPHT treatment at a temperature of 2,300 °C. The “fluorescence cage” is seen from table and pavilion sides. The diamond on the *left pictures* also exhibits bright fluorescence lines along slip planes (Simic and Zaitsev 2012a)

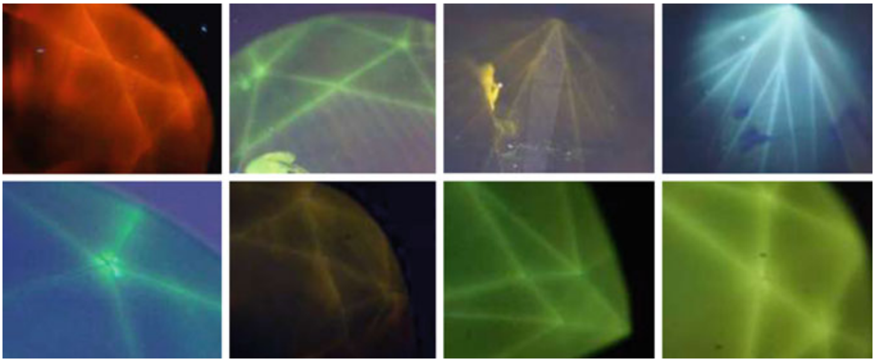


Fig. 7.9 ”Fluorescence cage” patterns of different colors observed on HPHT-treated diamonds

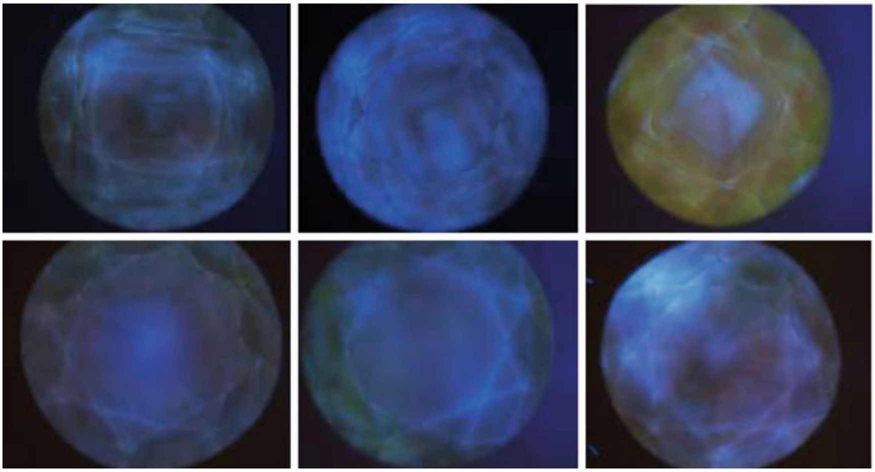


Fig. 7.10 These natural untreated cut diamonds exhibit fluorescence patterns resembling those of the "fluorescence cage" of treated stones. The *upper row* shows the patterns which do not have highlighted facet edges and therefore can be easily distinguished from the "fluorescence cage". The *lower row* shows the patterns with the fragments, which look like "fluorescence cage" of treated diamonds (Simic and Zaitsev 2012a)

Based on this statistics, we have found that natural untreated diamonds do show "fluorescence cage", but rarely. In these rare cases, the fluorescence patterns of untreated diamonds show many growth features and look different from the "fluorescence cage" patterns characteristic for treated diamonds. Yet, we have found a few untreated diamonds, which reveal the "fluorescence cage" patterns similar to those observed on treated diamonds (Fig. 7.10).

"Fluorescence cage" appears on treated diamonds of type I only. There is a tendency: the higher nitrogen content the stronger the "fluorescence cage" effect. The "fluorescence cage" is always present in the fluorescence images of Imperial Red diamonds, which are the result of multi-process treatment involving HPHT annealing and irradiation (Fig. 7.11).

The observation of "fluorescence cage" is sensitive to the parameters of excitation (wavelength, intensity, direction of the exciting beam) and direction of observation. Thus the cage pattern may be hardly seen when viewed at non-optimal conditions (e.g., Eaton-Magaña and Chadwick 2009).

The "fluorescence cage" is excited in treated type I diamonds and particularly well in those rich with A defects. The diamonds of type IaB show weak "fluorescence cage", suggesting that the formation of A defects in type IaB diamonds during HPHT annealing is a minor effect. It might be that the role of A defects in the activation of the "fluorescence cage" is opposite to that the A defects do for the "transmission" effect: A defects enhance the "fluorescence cage" effect, but suppress the "transmission" effect.

The observation of the "fluorescence cage" effect has several important advantages when considered as a method of recognition of treated diamonds.

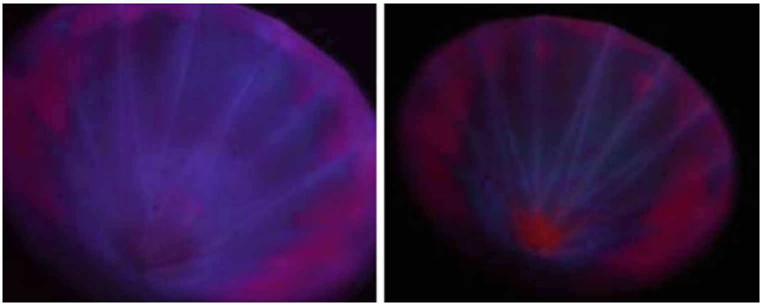


Fig. 7.11 Fluorescence images of two "Imperial Red diamonds" taken from the culet side. Both diamonds show preferential *blue* fluorescence with some areas of *red* fluorescence. The "fluorescence cage" has *blue color* and is observed all over the pavilion surface but the culet tips, the fluorescence of which differs in color from the fluorescence of diamond body

Firstly, it is applicable for the recognition of HPHT and irradiation treatments. Secondly, it is suitable for diamonds of any size and shape and it does not require unmounting of diamond from its setting. Thirdly, the "fluorescence cage" test is simple, inexpensive and fast.

Although the fluorescence patterns resembling the "fluorescence cage" can be observed on natural untreated diamonds, the cut diamonds showing uniform bright "fluorescence cage" along facet junctions are certainly treated.

7.5 Fluorescence of Macrodefects

The areas surrounding macro-defects (e.g., cracks, inclusions and growth boundaries) are the most vulnerable places, where the luminescence active defects can be generated by mechanical damage especially effectively. In this case, mechanical damage works similarly to the irradiation damage. For instance, the formation of nitrogen NV and H3 defects at cracks is well known.

The macro-defects and cracks with enhanced luminescence can be well seen in fluorescence microscope either as bright areas, or as areas of different color (Fig. 7.12). Typically, the luminescence of fresh cracks created during HPHT treatment is stronger than that observed on naturally occurring features. The reason of this difference is the very different annealing time, the damaged diamond spends in nature in earth and during HPHT treatment. Very long time of annealing in earth results in almost complete elimination of the excessive concentration of the point defects formed at cracks. In contrast, after short annealing time of HPHT treatment, the concentration of the optically active defects remains essentially non-uniform. This difference is analogous to that between the natural nitrogen-containing brown diamonds and HPHT-treated green-yellow diamonds. In both cases, the diamonds were heated to temperatures sufficient for at least partial decomposition of vacancy clusters and creation of H3 defects. However, the natural low temperature HPHT

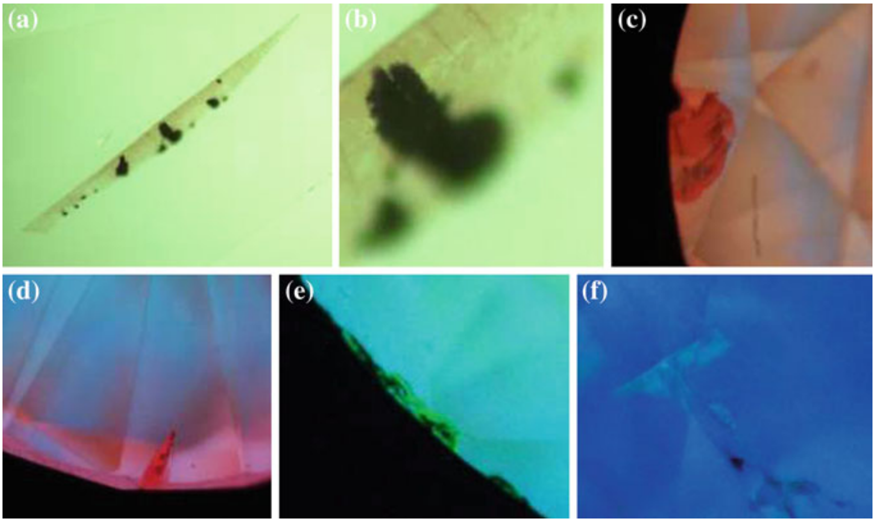


Fig. 7.12 Fluorescence images of cracks in HPHT-treated diamonds. Typically, the fluorescence color of the HPHT-induced cracks differs from the color of the luminescence of the diamond bulk. **a** The *pink color* component of the luminescence excited within this crack suggests the enhanced formation of NV centers. The *green* luminescence of the bulk is due to dominating H3 center. The crack exhibits *black* graphitized inclusions. **b** Fragment of the image (**a**) showing the distribution of the *pink* luminescence over the crack. **c** Fluorescence image of a crack in HPHT-treated type IIa *pink diamond*. **d** Type IIa HPHT-treated diamond of *light brownish pink color*. *Bright red cracks* at girdle indicate formation of intense NV centers. **e** Fluorescence image of girdle of this HPHT-treated diamond shows *bright green crack* on the *blue background* of the diamond bulk. **f** This HPHT-treated diamond of *light yellow color* reveals crack, luminescence of which has a slight greenish modifier, which suggests the formation of enhanced concentration of H3 defects

annealing for a long time destroys the H3 center almost completely, whereas the HPHT annealing performed at much higher temperature and much shorter time cannot remove the H3 defects. Due to this reason, naturally occurring cracks and inclusions usually do not show enhanced fluorescence (Fig. 7.13).

The H3 and NV defects are the most common luminescence-active point defects created in diamond by mechanical damage. Thus the most common fluorescence colors of the features created and/or modified by HPHT treatment are green and red. Sometimes strong yellow color due to nickel-related centers can be seen too. The primary defects created by mechanical damage are vacancies and carbon interstitial atoms which alone do not result in the color centers within Vis spectral range. However, vacancies trapped on nitrogen defects form visible luminescence centers, of which the H3- and NV-centers are the major ones. The luminescing micro-defects are the feature of type I HPHT-treated diamonds. However, they can be detected in type IIa diamonds too (Fig. 7.12c, d).

Activation of strong green luminescence along growth directions in HPHT-treated greenish yellow diamonds was reported in Van Bockstael (1998), Henn and

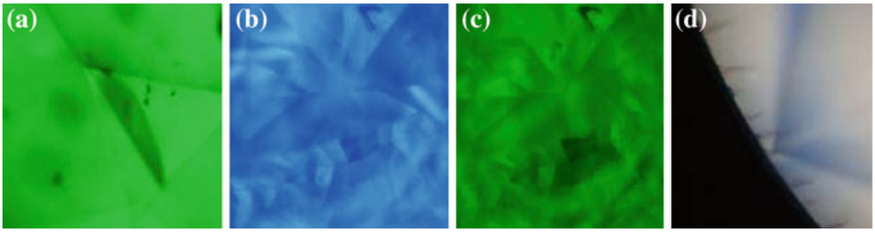


Fig. 7.13 **a** This half-moon "crescent"-type crack on the surface of a polished untreated diamond does not show enhanced luminescence or luminescence of different color—typical feature of natural cracks. **b**, **c** This natural *pink diamond* shows natural "feather" crack. No enhanced luminescence is observed in this crack neither in *blue* (**b**) nor in *green* (**c**) spectral range. **d** Fluorescence image of girdle of an HPHT-treated diamond, which exhibits numerous micro-cracks made by rough grinding. None of these cracks produce enhanced fluorescence

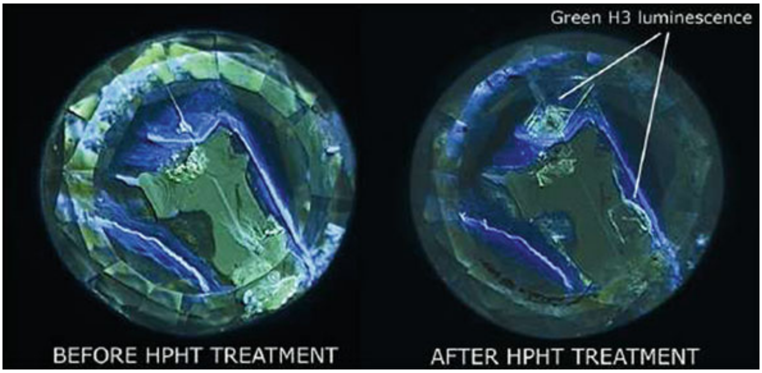


Fig. 7.14 Diamond view luminescence images of an CO_2 *brown diamond* before and after HPHT treatment. Treatment reduces the luminescence intensity throughout the diamond including the *central green area* (after treatment, this area is colored with *brown*). Formation of new localized narrow zones of *strong green* luminescence is clearly seen (Hainschwang et al. 2008). These new zones are most probably the HPHT-induced cracks and the growth boundaries

Milisenda (1999). The distribution of green luminescence in type Ia HPHT-treated diamonds correlates with the strain pattern viewed in polarized light. Untreated type Ia stones frequently show uniform N3 center blue fluorescence, whereas the treated ones display the H3 center green emission correlating with the growth features (De Weerdt and Van Royen 2000).

An example of the luminescence images, which reveal characteristic distribution of the H3 center luminescence in HPHT-treated diamonds, is given in Hainschwang et al. (2008). Figure 7.14 shows that HPHT annealing forms green luminescence lines along (111) growth planes. Shapeless bright green lines are most probably HPHT-induced micro-cleavages.

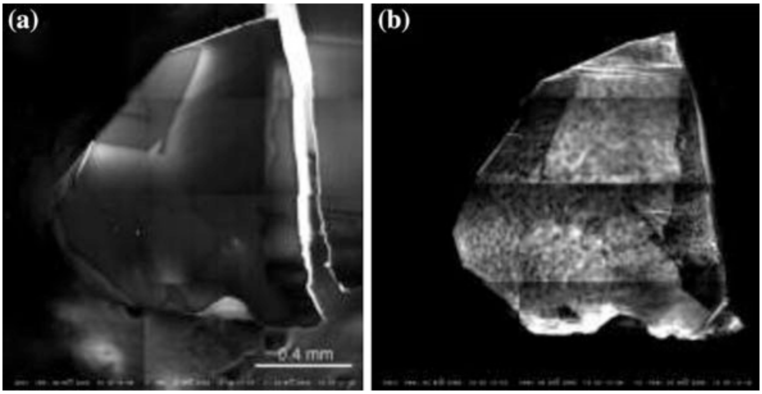


Fig. 7.15 CL images of distribution of luminescence of the A-band (maximum intensity at a wavelength of 430 nm) in a synthetic diamond before (**a**) and after (**b**) HPHT treatment performed at a temperature of 1,600 °C under pressure 6 GPa for 2 h. Note the grainy distribution of luminescence at a scale of 10–20 μm. This grainy pattern resembles that observed in natural IIa diamonds (Kanda et al. 2005) (with permission of Diamond and Related Materials journal)

HPHT treatment of synthetic IIa diamonds may generate internal strain and enhance the intensity of the A-band excited in CL. The HPHT-induced mosaic CL pattern is similar to that observed in natural IIa diamonds (Fig. 7.15) (Kanda et al. 2005).

Chapter 8
Technology and Business of HPHT Treatment

Fundamental research of HPHT annealing of diamond has been carried out for over 50 years. For the last 20 years, HPHT annealing has been also used commercially for color enhancement of gem diamonds. The advantages of HPHT annealing as a method of treatment are the true bulk modification of the impurity-defect structure and very high stability of the resulting changes. These advantages, together with the fact that high temperature heating is essentially a “natural” process for natural diamond, were the reason that the HPHT processing of gem diamonds was originally presented as “natural improvement”.

A huge difference in the prices of brown and colorless (especially pink) diamonds was and remains the main driving force of commercial HPHT treatment, which may become a big industry when the major sources of type IIa brown diamonds will become accessible. Technology principles of HPHT treatment are well known and any company or laboratory possessing high pressure, high temperature equipment could easily start commercial HPHT treatment of diamond. Indeed, after the public disclosure of HPHT treatment by General Electric and De Beers, the HPHT treatment business was rapidly taken over by many other companies in USA, Russia, Ukraine, Germany, India, South Korea, Belarus and China. It has been shown that any type of high pressure, high temperature equipment is suitable for HPHT treatment: Belt, Toroid, BARS, Cubic (Schmetzer 2010).

8.1 Basics of HPHT Treatment Technology

Below we give brief description of technology of HPHT treatment with HPHT apparatus BARS-300 (Fig. 8.1).

The central and the most essential part of an HPHT apparatus is the HPHT cell, in which diamond undergoes HPHT annealing. The quality of the HPHT cell is crucial for the successful treatment. Every type of HPHT apparatuses has its own specific design of HPHT cell. Figure 8.2 shows typical design of the HPHT cell

I. A. Dobrinets et al., *HPHT-Treated Diamonds*, Springer Series
in Materials Science 181, DOI: 10.1007/978-3-642-37490-6_8,

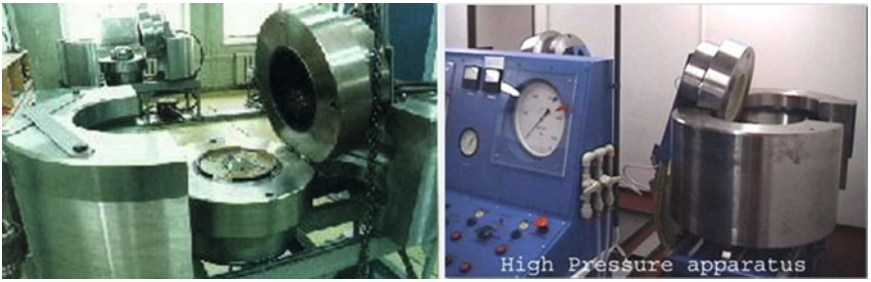
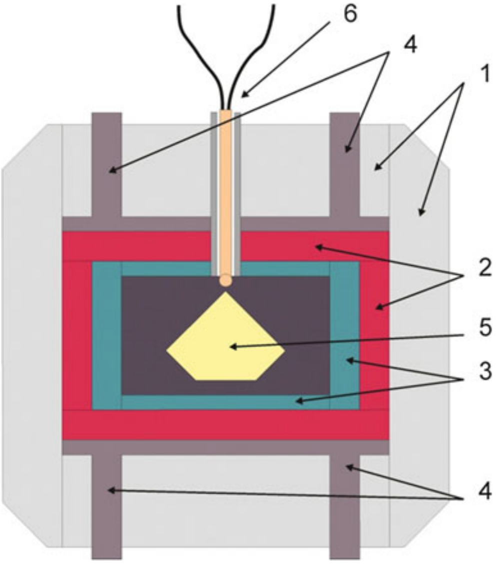


Fig. 8.1 BARS-300 apparatus used for commercial HPHT treatment

Fig. 8.2 Design of a typical HPHT cell used in BARS-300 apparatuses. *1*—cell housing made of zirconia ceramic, *2*—tubular graphite heater, *3*—insulator, *4*—metallic high current connectors, *5*—diamond surrounded by inert medium (e.g., graphite, potassium bromide, sodium chloride, potassium chloride, cesium chloride, cesium bromide, copper chloride, copper bromide), *6*—thermocouple



used in BARS-300 apparatuses. In order to ensure reliable treatment of natural diamond, HPHT cell must meet several requirements, the most important of which are the chemical inertness to diamond surface, good hydrostaticity, low sintering ability and the absence of phase transitions in the medium surrounding diamond.

Many different substances are used as media for HPHT cells. For instance, they are halide salts (chlorides and bromides) proposed by DeBeers technologists. Their advantage is a good solubility in water, which retains after HPHT annealing (Burns and Fisher 2001). It is very beneficial for safe recovery of the processed diamond from the medium. Alternative HPHT media are graphite and mixtures of graphite with oxides (magnesium oxide, zirconium oxide, aluminum oxide).

Control of pressure is the most difficult technological task. The traditional approach is the calibration of the pressure inside the HPHT cell against the force applied to the external anvils of the press. This calibration is usually carried out at room temperature using materials which undergo phase transitions at known pressures. Since the anvils deform with time, the pressure calibration has to be carried out regularly. The re-calibration is also required with any change in the design of the HPHT cell or changes in the HPHT medium. The pressure control using the calibration against the applied force has a limited accuracy. Usually, commercial HPHT treatment is performed at pressures set with an accuracy of 10 %.

The correct measurement of temperature is also a serious challenge. Temperatures up to 1,700 °C can be measured directly using Pt–Re thermocouple, which is directly inserted into the HPHT cell. The temperatures over 1,700 °C are measured indirectly using the calibration against the power released by the graphite heater. Usually, this method provides an accuracy of temperature measurements of 50 °C.

The HPHT cell of BARS-300 apparatus is made in a shape of a cube with side length of 20 mm. This cell allows processing of diamonds of a size up to 12 mm (up to 15 carats) for a few hours at a pressures up to 8 GPa and temperatures up to 2,000 °C, or for a half an hour at the same pressure and temperatures up to 2,500 °C. 2,500 °C is the maximum temperature, which can be practically achieved with BARS-300 apparatus. The standard parameters of commercial treatment of diamonds with BARS-300 apparatus are: temperature from 1,800 to 2,300 °C, pressure 7 GPa, time 10 min. HPHT cells of bigger models of BARS apparatuses (e.g. BARS-500) allow secure HPHT treatment of 20 carat diamonds.

The design of HPHT cells is ongoing process. Although the general principles of the HPHT cell design are well known, their actual structures vary from lab to lab and even from technologist to technologist. The internal structure of HPHT cell is a matter of know-how and it is rarely disclosed in publications and patents.

8.2 Selection and Preparation of Diamonds for HPHT Treatment

Correct selection of diamonds and correctly pre-shaping them are crucial steps of HPHT treatment technology. Natural diamonds are rarely exposed to HPHT treatment in the as-mined state. Instead, firstly the diamonds are carefully examined and possibly all inclusions and cracks on the diamond surface are removed by rough cutting (pre-shaping). Afterwards the pre-shaped diamonds undergo cleaning and they are ready for HPHT annealing. The structural imperfections on the surface of diamond considerably increase probability of the fracture of diamond under high pressure. Therefore, the removal of these “weak” places is crucial for successful HPHT treatment. Unfortunately, the removal of the surface imperfections does not guarantee against failure even for diamonds of high clarity. The internal stress in diamond and its unpredictable change during HPHT annealing may cause the fracture as well. Uncontrollable redistribution of stress in the media surrounding diamond during HPHT annealing may also cause cleavage and fracture.

8.2.1 Selection and Pre-Shaping

Usually diamonds are selected by visual examination using loupe with x10 magnification. In some cases, the microscopic examination in polarized light is required. The parameters which are taken into account are size, color, shape, visual imperfections and internal stress. The ranges of size and color, which are recommended for commercial HPHT treatment, are 3–12 carat and light brown to medium brown respectively. Dark brown diamonds are not good choice for two reasons. Firstly, dark brown color is difficult to remove completely. Brown color of intensity Br1 to Br2 can be easily removed at a temperature of 2,200 °C, whereas brown color of intensity Br3 to Br4 requires temperatures of at least 2,300 °C. Secondly, very strong H3/H2 centers induced in type Ia initially dark brown diamonds make the final green-yellow color of these diamonds too dark.

In terms of shape, rounded diamonds with convex facets are the most preferable. These diamonds may have rounded facets of cube and octahedral. It is important that the pre-shaped diamonds do not have sharp extended features, deep cavities and concave deeps with reflex negative angles between the adjacent facets. The presence of these features may considerably reduce the uniformity of the applied stress and result in fracture.

The initial clarity of diamonds must be high enough to ensure the final clarity of the treated stone of SI2 and better. Inclusions of any character are not desirable for HPHT treatment. The most unwanted inclusions are stressed cracks, thin half-transparent fractures with convex and/or jagged front (so called "feathers" and similar to them), as well as the fractures with specula reflections. Surface cracks and surface caverns with cracks are also very undesirable inclusions. The defects, which normally do not cause further damage and which can be left in pre-shaped diamonds, are widely open shallow cracks, small caverns without cracks, little inclusions in the bulk.

The diamonds with many flaws, the removal of which would result in considerable loss of weight, are not suitable for HPHT treatment. Also, it is not advisable to saw diamonds and/or make pre-shape perimeter before HPHT treatment. These operations may generate additional cracks and increase the probability of fracture.

8.2.2 Cleaning of Pre-Shaped Diamonds

Cleaning of the pre-shaped diamonds is an important step of the HPHT treatment technology. Its aim is the removal of possibly all contaminations present on the open surfaces and in the surface features. If not removed, these contaminations, when under HPHT conditions, may become additional sources of stress, graphitization and surface macro-defects (Vins 2011a).

The best cleaning of diamond known for us is that performed in mixtures of acids at high temperature and pressure. The standard procedure of this cleaning, however, is not capable of removal of many types of contaminations. An advanced procedure of the acid cleaning at temperatures up to 350 °C at pressures up to 450 bar has been developed in the lab of one of the authors (V. V.) (Fig. 8.3). At such high temperature and pressure, the acid vapors become very aggressive and penetrating and are capable of etching all non-diamond materials including those, which cannot be removed by the traditional cleaning methods. The new method allows cleaning of very deep and narrow cracks and, because of this, is termed “deep cleaning”. The method works even at submicron level and it can remove the features less than one micron in size. It has been found that the crucial factor of the cleaning quality is temperature, which must be kept above 235 °C.

The following inclusions are the most common for natural diamonds. Syngenetic sulphide inclusions, which were trapped during diamond growth. These inclusions are the most hard-to-reach. They are located in closed fractures and so-called “veils” deep inside the diamond. Another type of inclusions is iron-containing inclusions. They are readily accessible iron oxide and hydroxide inclusions typical for diamonds mined from residual soils. Fine-dispersed graphite inclusions are also quite common in natural diamonds. They can be found both in open accessible fractures (rarely) and in inaccessible fractures scattered in the diamond bulk. Other inclusions, such as silicates and oxides, are also frequent in natural diamonds, and usually they are readily accessible. Every type of the inclusions has different chemistry and its complete removal requires corresponding composition of the acid mixture.

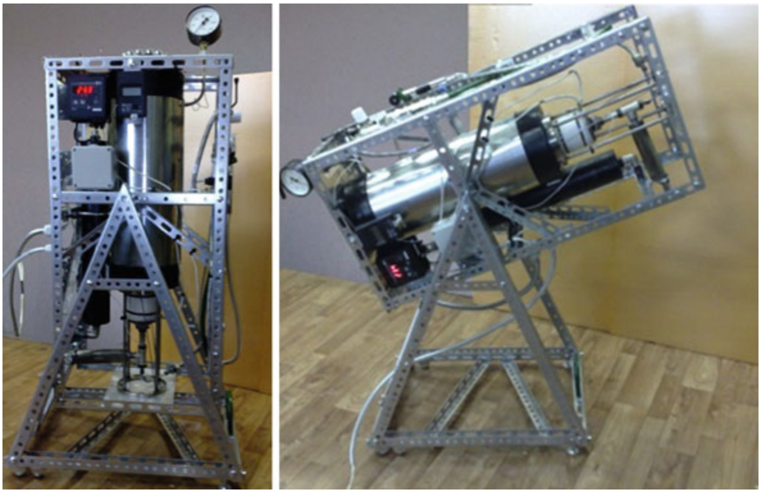


Fig. 8.3 Apparatus for “deep cleaning” developed in Siberian Innovation and Technology Company, Ltd., Novosibirsk, Russia

The removal of the surface contaminants and accessible inclusions (in open fractures) usually requires 1–1.5 h cleaning (Fig. 8.4). In order to clean "veils" and tiny closed fractures seen in microscope, it may take 3–5 cleaning cycles.

Below, some examples of failure of HPHT treatment (loss of weight, considerable reduction in clarity, total destruction) due to the neglect of required pre-shaping and cleaning procedures are presented in Figs. 8.5 and 8.6.

The indicator of the quality of selection, pre-shaping and cleaning is the final yield, which is evaluated as the mass ratio of the finally cut stone versus the initial rough diamond and the clarity of the finally cut stone. Strict compliance with the rules of selection and pre-shaping allows to reach average yield up to 32 % with clarity SI to VS for 80 % of stones. Otherwise the yield may drop to 5 % with clarity SI to VS for not more than 30 % of stones.

8.2.3 Characterization of Pre-Shaped Diamonds

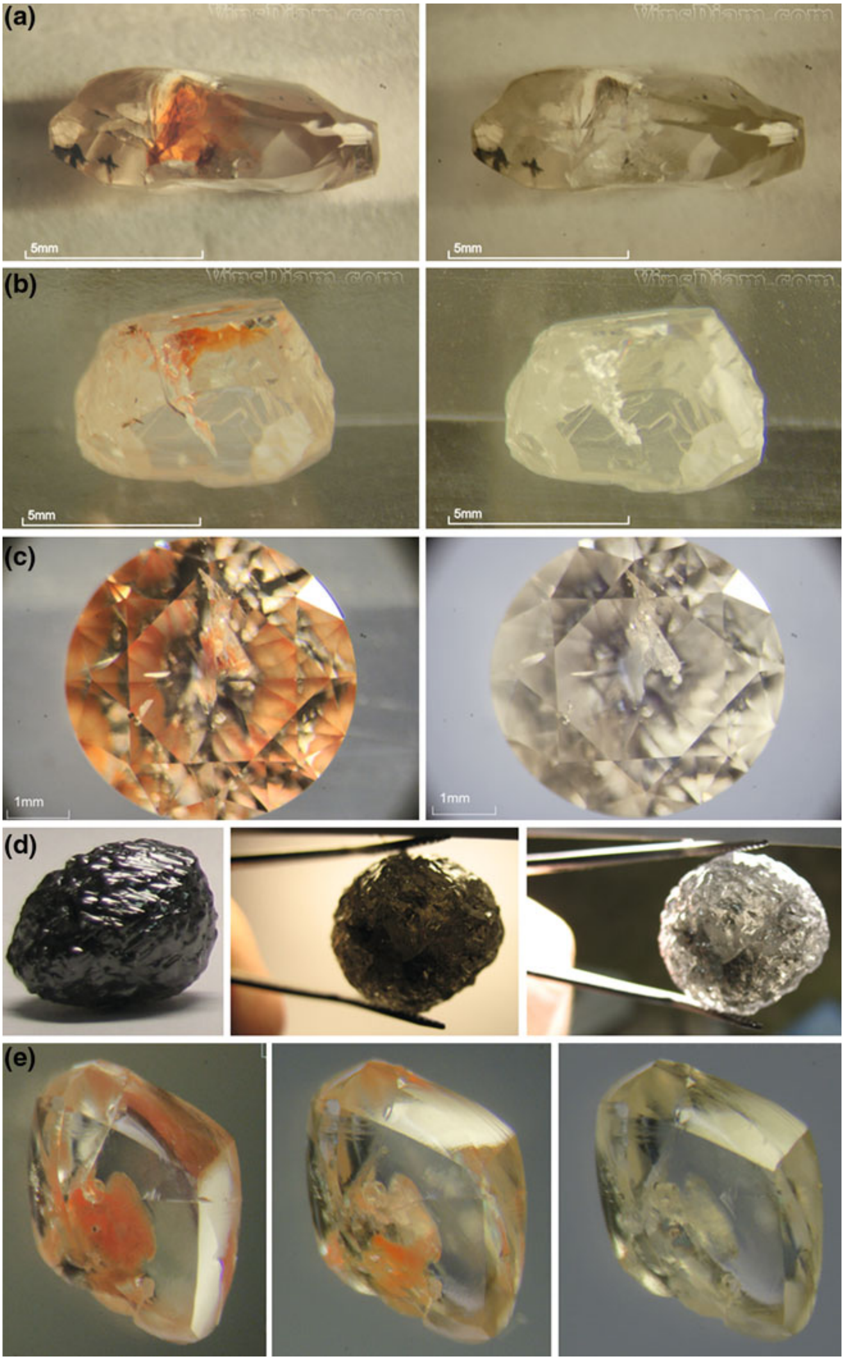
Professional HPHT treatment of diamonds always includes the operation of spectroscopic characterization of initial stones. The aim of this characterization is to determine diamond type, to measure the concentration of the nitrogen-related defects and to evaluate the intensity of the brown/gray color. This data is required for the prediction of the final color of diamond and for choosing optimal temperature–pressure-time parameters of the HPHT annealing.

Based on the results of IR absorption spectroscopy, the diamonds are separated into three major groups: (i) type II diamonds, (ii) diamonds with preferential content of A and B defects, (iii) diamonds of pure types IaA, IaAB′, IaB and IaBB′.

Based on the results of UV–Vis absorption spectroscopy, the diamonds are separated into four groups of brown color: Br1—diamonds of light brown color, Br2—diamonds of medium brown color, Br3—diamonds of intense brown color, Br4—diamonds of dark brown color. Besides, the absorption strength of the 550 nm Pink Band is measured in type IIa diamonds and the strength of the N3-center in type Ia diamonds. After the spectroscopic characterization, the diamonds undergo final cleaning and after that they are ready for HPHT annealing.

8.3 HPHT Annealing

Parameters of HPHT annealing for a particular diamond are dictated by the desired final color, intensity and origin of the initial brown/gray color and the concentration of A- and B defects. Internal structural perfection and shape of the pre-shaped diamond are also taken into account as limiting factors. In most cases, the annealing temperature is set high enough to ensure the color transformation in a time not more than 10 min. However, it must be kept in mind that the risk of


(a)
5mm
5mm
(b)
5mm
5mm
(c)
1mm
1mm
(d)
(e)

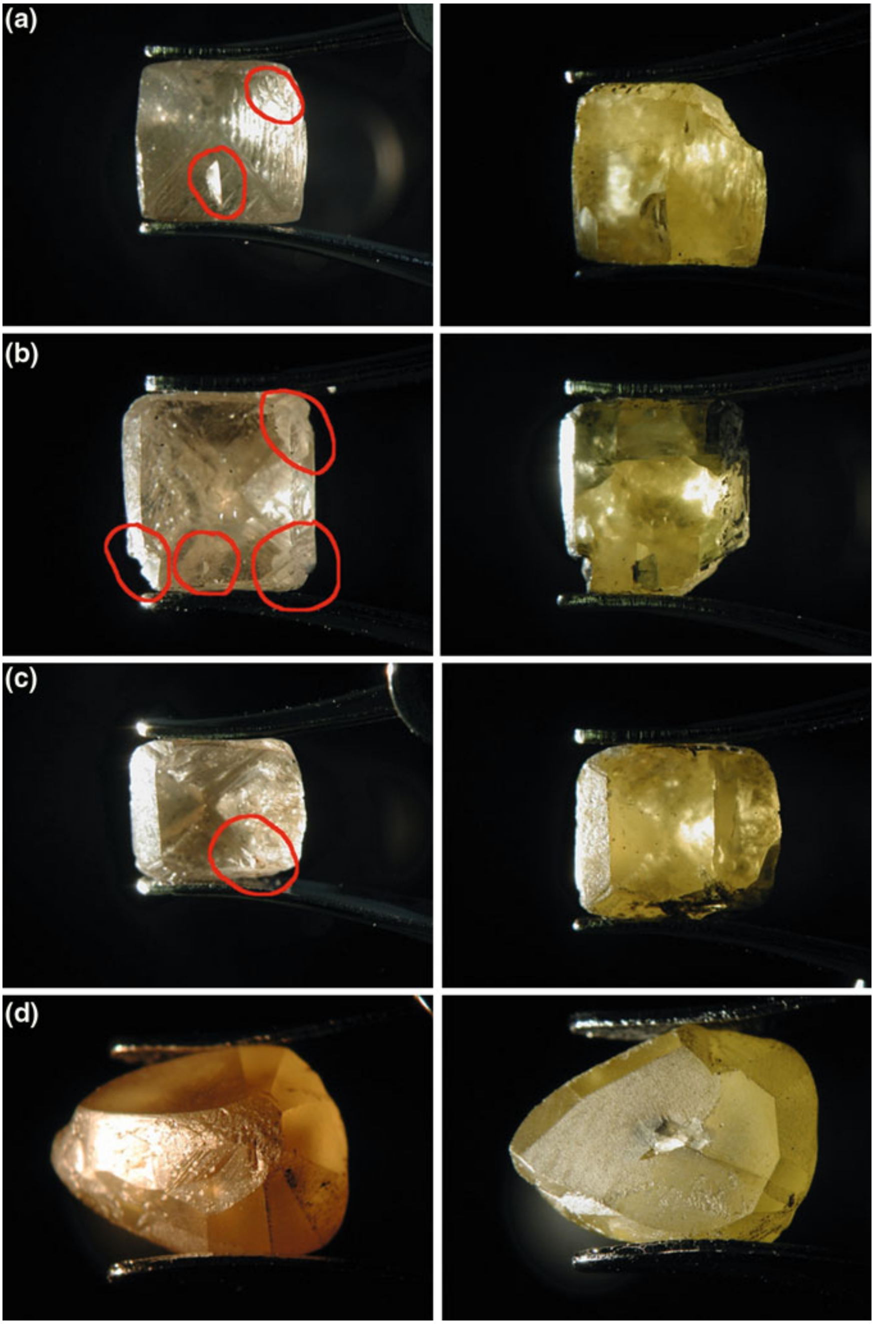
◀ **Fig. 8.4** **a** Before cleaning (*left*), this rough diamond had an iron-containing inclusion inside a crack and three dark mineral inclusions. After deep cleaning (*right*), the iron-containing inclusion is removed completely. One mineral inclusion has almost gone, yet two others remain intact. **b** Before cleaning (*left*), this diamond had mineral contaminants on the surface and an iron-contaminated fracture. After deep cleaning (*right*), all inclusions are completely removed so that one can see the real color of the diamond. **c** Before cleaning (*left*), this diamond had one large orange crack reaching table and crown. *The orange color* is the result of multiple reflections. After deep cleaning (*right*), the diamond is completely free from the colored contaminants. **d** Example of deep cleaning of «resection black» diamonds, which are absolutely non-transparent due to numerous sulphide inclusions (*left*). After deep cleaning (*middle and right*), these diamonds become transparent and light in color. **e** An example of multiple deep cleaning of a rough diamond with multiple colored inclusions (*left*). The first cleaning has removed the inclusions only partially (*middle*). Yet another cleaning has made diamond completely clean (*right*)

failure with total loss of diamond increases with temperature and the probability of the total loss is especially high for the repeated treatment. Pressure is usually set at a value within the range of phase stability of diamond for the chosen temperature. High pressure is especially important for included diamonds, which are prone to graphitization.

For type IIa diamonds, the final color is quite obvious. 80 % of brown type IIa diamonds become colorless or near colorless and 10 % are converted into light-pink. Some rare brown/gray diamonds of type IIb acquire blue color after HPHT annealing. There is an opinion that light-pink color in type IIa diamonds is a transient color and it could be achieved at a certain temperature, e.g., at 2,100 °C. When HPHT annealing is performed at higher temperatures, pink color disappears and diamond becomes colorless. However, in our research experiments and commercial treatments, we have never encountered with the total loss of pink color. Hence, it appears that the HPHT-induced pink color in type IIa diamonds is more stable than it is believed.

Decoloration of type IIa diamonds of initial color Br3—Br4 requires annealing at a temperature of 2,300 °C. The removal of brown color Br1—Br2 can be achieved at lower temperatures. If type IIa diamonds have concentration of A defects at a level of 3 ppm, annealing at a temperature of 2,300 °C makes them light-yellow.

The final color of initially brown type Ia diamonds containing both A- and B defects is determined by the superposition of absorptions of several color centers: the Brown absorption continuum, the N3-, H3-, H2-centers and the C defect absorption continuum. The general way of evolution of these absorptions is the following. The change in color of type Ia diamonds may be seen after annealing at a temperature of 1,800 °C, when the vacancy clusters start to decompose and release vacancies. These vacancies are trapped by A- and B defects and form H3 and H4 defects. The H4 defects are unstable at HPHT conditions and they immediately dissociate and contribute to the formation of H3 defects. Thus the H3-center becomes first dominating optical feature, which contributes to the color changes. Simultaneously with the formation of the H3 defects, the dissociation of A- and B defects into C and N3 defects occures. Though the concentration of these


(a)
(b)
(c)
(d)

◀ **Fig. 8.5** **a** In this pre-shaped diamond, two marked cracks were not removed (*left*). After HPHT annealing, these cracks have resulted in chipping of the right upper corner and development of a large crack propagating from the surface to the center of the stone (*right*). **b** In this pre-shaped stone, four relatively small cracks (*marked*) were not removed completely (*left*). After HPHT annealing (*right*), all these cracks increased, the right bottom corner broke off, the upper right crack has induced a large horizontal crack and graphitization of the top right corner. **c** In this pre-shaped diamond only little crack was left (*marked*). After HPHT treatment, this crack has developed into a large one penetrating in vertical direction through the whole diamond body (*right*). **d** In this pre-shaped diamond, a little inclusion was left close to the surface (*left*). After treatment, this inclusion has resulted in formation of a cavern and development of a *large crack* (*right*)

defects remains minor as compared with that of the H3 defects and they do not contribute noticeably to the color change. The rate of the generation of vacancies increases with intensity of brown color and so does the rate of formation of H3 defects. Hence, the generation of especially high concentration of H3 defects is expected in highly deformed dark brown diamonds. Simultaneously with the H3-center, generation of weak H2-center occurs. The intensity of both centers increases with temperature up to 2,150 °C, the relative intensity of the H2-center growing increasingly faster. At higher temperatures, H3 defects become unstable and their reverse transformation into A defects and vacancies occurs. As a result, the intensity of the H3- and H2-centers decreases and the C defect absorption continuum becomes the dominating absorption. This process of the color center transformation can be interrupted when the desired ratio of the optical center intensities is achieved.

The transformation of the optical centers in type IaA diamonds during HPHT annealing are similar to those occurring in common type IaAB. In contrast, type IaB diamonds behave quite differently. In type IaB diamonds, the generation of H3 defects is a minor process and the formation of the N3 and C defects from the destructed B defects dominates. Since the B defects are the most stable in diamond lattice, they can be destructed in brown diamonds only by moving dislocations, not by temperature. This destruction may become noticeable at temperatures over 1,900 °C. Like in all type Ia diamonds, the removal of brown color of type IaB diamonds occurs at temperatures 2,100–2,300 °C depending on the initial intensity of brown color. If HPHT annealing of type IaB diamonds is performed at temperatures over 2,100 °C, the residual A defects start to dissociate into C defects, what results in formation of the H2 center. At higher temperatures, above 2,200 °C, the A defects aggregate into B defects, the aggregation occurring faster in highly deformed diamonds.

The described defect transformations are responsible for the green-yellow color of type Ia diamonds HPHT-treated at temperatures in the range 1,800–2,300 °C (Fig. 8.7). The resulting color and its intensity is determined by the relative absorption intensities of the N3, H3, H2 centers and the C defect absorption continuum.

Careful calibration and setting of the temperature and pressure parameters during HPHT annealing is characteristic of major companies dealing with color

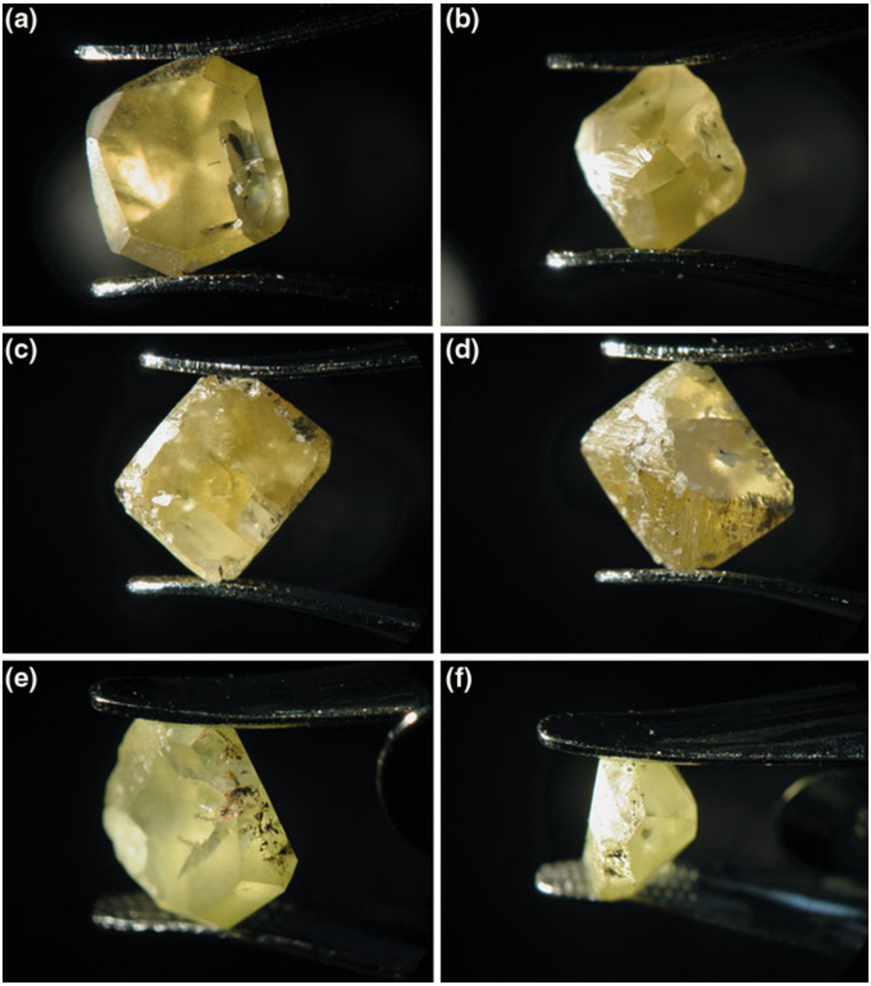


Fig. 8.6 Examples of HPHT-induced damage of the pre-shaped diamonds, on which some areas of rough naturals were not removed. **a** Development of a crack. **b** Chipping. **c** Formation of a crack due to too sharp corners. **d**, **f** Formation of multiple little cracks over the perimeter. **e** Multiple cracks, chipping and graphitization

treatment of diamond. Most small companies do not control the temperature and pressure at all, but follow a “given” recipe, or intuition merely setting the “prescribed” heating power and press force. Hence, many HPHT-treated diamonds on the market have “average” color parameters with noticeable component of the remaining brown color. It is especially characteristic of included and poorly re-polished diamonds.

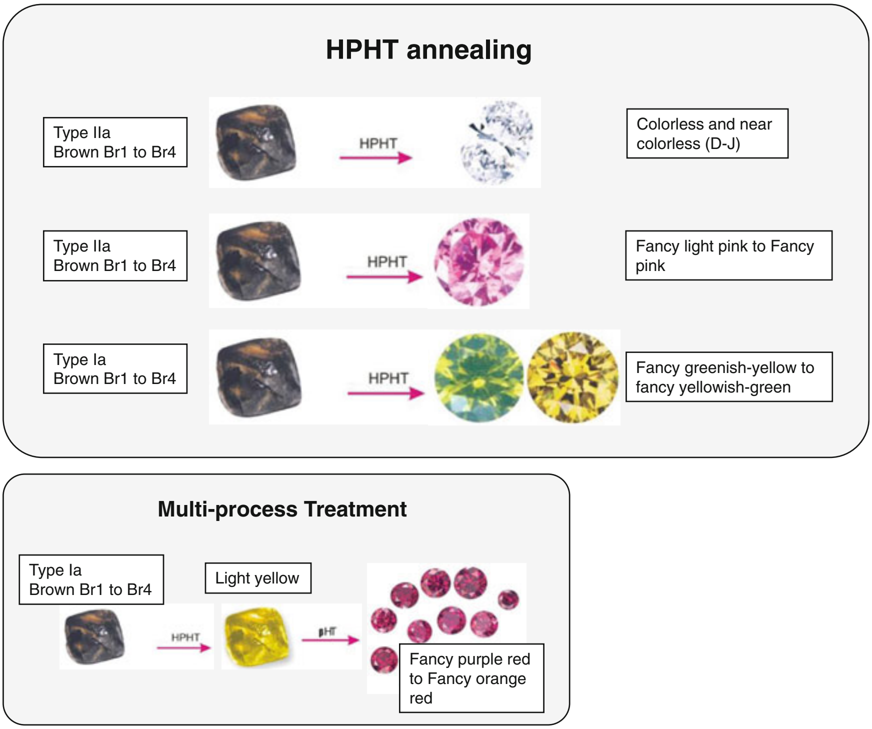


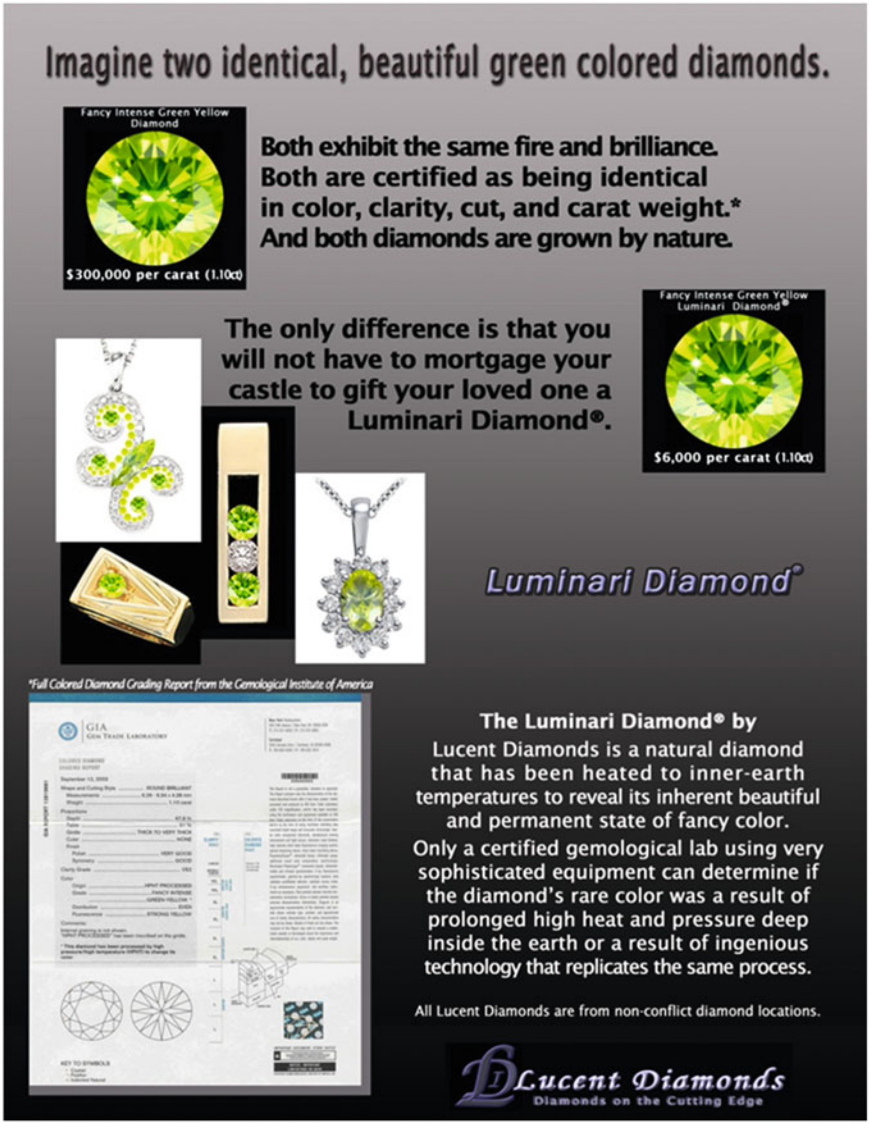
Fig. 8.7 Major color changes of brown diamonds after HPHT treatment

8.4 Commercial Aspects of HPHT Treatment

8.4.1 Price of HPHT-Treated Diamond

The prices of HPHT-treated diamonds gradually go down, whereas the production costs of treatment increase. In year 2000, the price of a yellow-green 1 carat cut stone of VS clarity was about $6,000. A few years later, this price dropped to $3,000 and now it is below $1,500. Correspondingly, the production costs, which include the cost of rough diamond (120–200 $/ct), cost of pre-shaping (40–80 $/ct), cost of HPHT annealing (115–175 $/ct) and the cost of final cut, have increased from $800 to 1,000 in year 2000 to $1,500 today. That is the production costs of yellow-green HPHT-treated diamonds have become comparable with their market price (Grizenko 2011) and, at present in most countries, the commercial production of these diamonds with full disclosure of treatment has no sense (Fig. 8.8).

However, the production of colorless and light-pink type IIa diamonds still remains commercially very attractive. An approximate price of HPHT-treated colorless cut diamonds is determined by a reduction coefficient of 0.3–0.4 applied to the standard Rapaport scale for equivalent natural untreated stones. The prices



Imagine two identical, beautiful green colored diamonds.

Fancy Intense Green Yellow Diamond

$300,000 per carat (1.10ct)

Both exhibit the same fire and brilliance.
Both are certified as being identical
in color, clarity, cut, and carat weight.*
And both diamonds are grown by nature.

Fancy Intense Green Yellow Luminari Diamond®

$6,000 per carat (1.10ct)

The only difference is that you will not have to mortgage your castle to gift your loved one a Luminari Diamond®.

Luminari Diamond®

*Full Colored Diamond Grading Report from the Gemological Institute of America

GIA Gem Trade Laboratory

The Luminari Diamond® by Lucent Diamonds is a natural diamond that has been heated to inner-earth temperatures to reveal its inherent beautiful and permanent state of fancy color.

Only a certified gemological lab using very sophisticated equipment can determine if the diamond's rare color was a result of prolonged high heat and pressure deep inside the earth or a result of ingenious technology that replicates the same process.

All Lucent Diamonds are from non-conflict diamond locations.

Lucent Diamonds
Diamonds on the Cutting Edge

Fig. 8.8 Advertisement flyer of Lucent Diamonds, Inc. for HPHT-treated diamonds of green-yellow color released in 2003

for very rare pink and blue HPHT-treated diamonds are the matter of agreement and remain very high: over $15,000 for a 1 carat stone of VS clarity.

Production of Imperial Red diamonds of rose-red hues (Vins 2004; Wang et al. 2005) also remains profitable. Of these, the most valuable are the diamonds of type IIa with an enhanced A defect content (eventually very low-nitrogen type IaA diamonds). In these diamonds, it is possible to achieve formation of the NV^0 and NV^- centers as the only color centers in the visible spectral range. Absorption of the NV centers without interference from the H3- and N3 centers provides clear "spectral" red color. The actual price of a 1 carat stone of this color and VS clarity ranges from $10,000 to $15,000.

8.4.2 Market of HPHT-Treated Diamonds

Today, disclosed HPHT-treated diamonds cover a tiny fraction of gem diamond market. Percentage of HPHT-treated diamonds of all cut diamonds on the market is below 0.01 %. However, this percentage is much greater for colorless diamonds. Colorless and near colorless type IIa diamonds amount a few percent of all gem diamonds of these colors. Of these, a few tens percent could be HPHT-treated. This percentage is perhaps even higher for high clarity high color type IIa diamonds. Due to their negligible amount, the reported HPHT-treated diamonds do not pose a real commercial threat for diamond market. However, the market potential for HPHT treatment is great. There is a huge amount of diamonds suitable for HPHT treatment. Percentage of high clarity type Ia brown diamonds of all gem quality type Ia diamonds is substantial varying from 1 to 50 % for different deposits. For type IIa brown diamonds, this percentage is less varying from 0.01 to 10 %. There are probably about 5 million polished carats of brown diamonds produced annually. However, only little portion of them is involved in HPHT treatment.

Since the majority of treated stones come to the market undisclosed, it is difficult to evaluate the size of the world market of HPHT-treated diamonds. An estimation of the "civilized" market of yellow-green diamonds would be a few million US dollars in USA and European countries. However, it is difficult to give even a rough assessment of the undisclosed production of HPHT-treated diamonds in Asian countries. This assessment is a particularly challenging task for high color colorless and pink type IIa diamonds, which are very pricy, which might be produced in considerable amounts and for many of which every effort has been taken to conceal the fact of treatment.

Commercial cost of HPHT treatment varies from 100 to 200 $/carat for different companies. An average price for a standard treatment of a 1 carat diamond would be $150. It is important that HPHT annealing is performed not on rough stones and not on finally cut brilliants, but on a specially pre-shaped diamonds.

An example of the prices of HPHT treatment service of one of the companies doing HPHT treatment business in Russia is given in Table 8.1. These prices include spectroscopic characterization of every stone with detailed description of expected final color. The prices do not depend on diamond type and initial diamond color.

Analysis of the structure of the cost of HPHT-treated diamonds produced by this company allows evaluation of the profitability of the HPHT business. The

Table 8.1 Exemplary price chart of HPHT treatment service

Mass in carats	Price in \$/ct (small amount)	Price in \$/ct (large amount)
<0.25	60	40
0.25–0.49	100	65
0.50–0.99	140	95
1.00–1.99	175	115
2.00–3.99	200	135
4.00–10.00	225	150

Table 8.2 Price charts for round brilliants in \$/ct for natural HPHT-treated diamonds of fancy intense yellow, orangey yellow, greenish yellow and yellowish green color

Ct.Wt.	VVS	VS	SI	I1	I2	I3
0.01–0.07	800	700	600	500	250	150
0.08–0.17	952	833	714	595	298	171
0.18–0.29	1,133	991	850	708	354	195
0.30–0.37	1,348	1,180	1,011	843	421	222
0.38–0.49	1,604	1,404	1,203	1,003	501	252
0.50–0.69	1,909	1,670	1,432	1,193	597	288
0.70–0.89	2,272	1,988	1,704	1,420	710	328
0.90–0.99	2,703	2,366	2,028	1,690	845	373
1.00–1.24	3,217	2,815	2,413	2,011	1,005	425
1.25–1.49	3,828	3,350	2,871	2,393	1,196	484
1.50–1.99	4,556	3,986	3,417	2,847	1,424	551
2.00–2.00	5,421	4,744	4,066	3,388	1,694	628
3.00–3.99	6,451	5,645	4,839	4,032	2,016	715

main constituents of the cost are: the price of rough brown diamonds, which is on average \$200/ct, shipping and state tax \$40/ct, pre-shaping and final cut of treated diamonds \$40/ct. An average weight of a pre-shaped diamond is about 50 % of the weight of the initial rough stone. The wholesale price of the pre-shaped diamonds is set at \$150/ct. Taking into account that the average throughput of HPHT treated diamonds is about 30 %, the final production cost of cut treated diamonds is about \$1,100/ct. When this cost is compared with the market prices of colored HPHT-treated diamonds (Table 8.2), it is seen that the production of HPHT-treated diamonds of clarity grade SI becomes profitable starting from the weight 0.38 carat for the final product, or 1.2 carat for initial rough diamonds.

HPHT-treated diamonds of any color can be encountered today on the diamond gem market. However, the majority of HPHT-treated diamonds are colorless and near colorless followed by the stones of yellow-green color. Large HPHT-treated diamonds are rare. Vast majority of HPHT-treated diamonds have weight below 2 carats.

Chapter 9
Concluding Remarks

Concluding this book we would like to make a few comments on some general issues concerning evolution of HPHT treatment technology, HPHT-treated diamonds, methods of their recognition, and the status of HPHT-treated diamond as gem stone.

9.1 Commercial Danger of HPHT Treatment

The potential threat of HPHT treatment lies in the possibility to destroy one of the most valuable properties of high quality natural gem diamond—its rarity. "The essence of gemology—lies in our ability to identify these materials (natural and manmade) and to distinguish any artificially induced change. If rarity ever becomes a meaningless virtue, then the backbone of the trade—the magic of the natural gemstone—will be broken" wrote William Boyajian, President of GIA, (Boyajian 2000a). Indeed, theoretically, a large portion of natural diamonds of inferior colors can be converted into more valuable colorless and fancy color stones. The starting material is piles!

In the first few years after official announcement of HPHT treatment, when there was no reliable information about HPHT-treated diamonds, the diamond market was quite excited and worried and the danger of HPHT treatment to the integrity of the diamond market was talked much about. Soon, however, when the first systematic studies of HPHT-treated diamonds had been performed, it became clear that fortunately this fear is greatly exaggerated. HPHT-treated diamonds could not influence the prices of gem diamonds (Fig. 9.1) for two reasons. Firstly, in most cases, HPHT-treated diamonds could be recognized. Secondly, the color grade of majority of brown natural diamonds could not be considerably improved by HPHT treatment. The latter pertains type Ia brown diamonds which constitute 95 % of all natural diamonds. Since that time, HPHT treatment technology has improved considerably and many companies all over the world have started HPHT treatment business. Yet, all this activity remains a small sector of gem diamond

I. A. Dobrinets et al., *HPHT-Treated Diamonds*, Springer Series in Materials Science 181, DOI: 10.1007/978-3-642-37490-6_9,

trade because a good quality HPHT treatment is a costly technology. It requires a proprietary developed equipment, costly maintenance, costly disposable materials as well as highly trained professionals. HPHT treatment remains a volatile process with certain possibility of loss of diamond (Pope 2006).

The real danger for the diamond market would be the development of a cheap treatment capable of considerable improvement of color grade of type Ia brown diamonds. So far we are not aware of the existence of the methods which could be precursors of such treatment. However, analyzing the available information on HPHT treatment and HPHT-treated diamonds we can try to answer the question whether it is possible to make type Ia brown diamond colorless.

The primary defects determining color of brown type Ia diamonds are vacancy clusters, which produce the Brown absorption continuum. The Brown absorption continuum is present in any natural diamond, suggesting that all natural diamonds were at least slightly plastically deformed in earth. However, in spectra of colorless diamonds, the Brown absorption continuum is negligibly weak, whereas it is strong in brown diamonds. Both, colorless and brown natural untreated diamonds do not contain nitrogen-vacancy defects (NV, H3, H4, N3) in concentrations, which can influence the diamond color. However, type Ia diamonds contain high concentration of A- and B defects, some C defects and Platelets, which are direct building blocks of the nitrogen-vacancy color centers. The straightforward explanation of the absence of the nitrogen-vacancy defects in brown type Ia diamonds would be that they have never experienced high temperature heating,

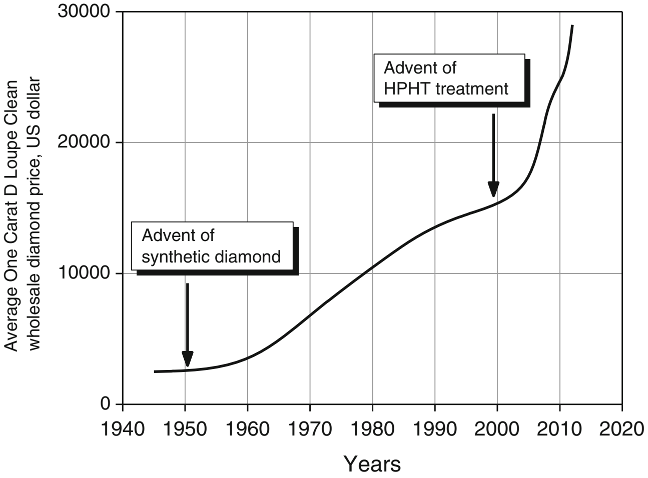


Fig. 9.1 Evolution of average wholesale price for one carat D clarity diamonds from 1945 to 2012. The years of official announcements of commercial technologies of production of synthetic diamonds and HPHT treatment are shown with arrows. Neither the advent of synthetic diamonds, nor the advent of HPHT treatment affected adversely the diamond market. Just the opposite, the diamond price experienced considerable increases after these two events suggesting that the diamond price is driven by major economic trends, but not by the diamond-based technologies

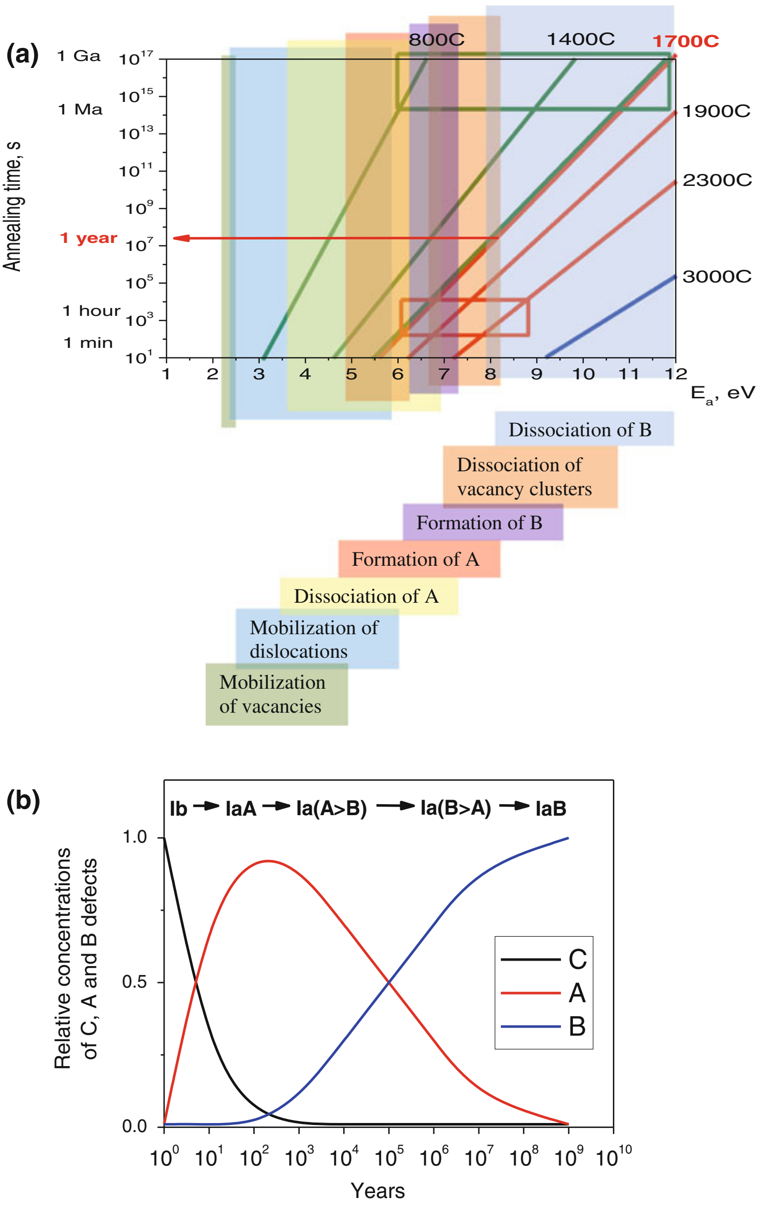
during which the vacancy clusters could be partially dissolved and the released vacancies could form nitrogen-vacancy defects. However, we know that all natural diamonds were heated in the earth interior and some of them to rather high temperatures. This heating must result in formation of nitrogen-vacancy complexes. Even if we assume that the brown type I diamonds were deformed at the end of their geological history close to the earth surface and therefore at low temperatures, the vacancies, produced by plastic deformation, would inevitably form the nitrogen-vacancy complexes. If the temperature were so low that no nitrogen-vacancy centers could form, then the formation of the vacancy clusters would not be possible too. High concentration of vacancies does not produce brown color but dark green color. Thus one has to admit that brown diamonds did experience annealing at rather high temperatures. Then why the nitrogen-vacancy defects have not formed? In order to resolve this contradiction we have to assume that the absence of the nitrogen-vacancy defects is because they simply annealed out. This assumption suggests that the nitrogen-vacancy defects are non-equilibrium defects in diamond at temperatures of 1,200–1,400 °C (average geological temperatures) and they anneal out during the long time natural annealing. Thus, the general picture of formation of impurity-defect structure of natural diamond looks rather simple. Diamonds grow and capture nitrogen during growth. Since nitrogen is omnipresent element in earth, most diamonds are nitrogen-containing. During the growth process and/or thereafter, diamonds experience plastic deformation. From the birth to the expelling to the earth surface, diamonds spend millions of years at rather high temperature. Most point defects in diamond are less stable than multi-atom complexes and therefore point defects tend to form larger clusters. Vacancies combine in vacancy clusters, nitrogen atoms gather in multi-atom defects and interstitial carbon atoms form Platelets. Nitrogen–vacancy point defects may also form clusters or break into single nitrogen atoms and vacancies, which in turn join vacancy and nitrogen clusters. Thus at geological temperatures, the aggregated defects are the equilibrium state of the impurity-defect structure of diamond. The diffusion rates of different defects in diamond at temperatures 1,200–1,400 °C are very different. Vacancies diffuse relatively fast and the formation of vacancy clusters and nitrogen-vacancy defects occurs rapidly. The nitrogen-vacancy defects are more stable than single vacancies and their aggregation requires much longer time. The geological temperatures are not high enough to break the isolated nitrogen-vacancy defects, yet they are sufficient to mobilize them and anneal them out as a whole. Of the discussed point defects, nitrogen atoms have the least mobility in diamond lattice. Thus, even geological times are not long enough to gather all nitrogen atoms in large clusters and most nitrogen in natural diamonds from small few-atom aggregates like A- and B defects. If the above considerations are correct, it becomes clear why majority of natural diamonds are brown and have type Ia. They are just diamonds grown in the presence of nitrogen and undergone long time heating at temperatures 1,200–1,400 °C under high mechanical stress. Colorless type Ia diamonds are those, which, for some rare reason, were not plastically deformed, or those which were originally brown and then got decolorized by heating. The available experimental data on HPHT treatment does not allow us to prove this assumption. However, we are inclined to believe that the vacancy clusters are not absolutely stable at geological temperatures and, given enough time, anneal out. If it is so, then the long-time annealing should convert brown type Ia diamond into colorless. Temperature of such an annealing must not exceed 1,700 °C in order to keep the aggregated nitrogen stable and prevent from generation of C defects, which otherwise would produce yellow color. If the time of this annealing is too long to be practically used (say, over 1 year), one may increase the annealing temperature (standard HPHT treatment) and anneal out the vacancy clusters rapidly. Though in this case, the generated nitrogen-vacancy defects and C defects make diamonds yellow-green. Fortunately, these defects are not as stable as the vacancy clusters and they can be destroyed at a temperature of 1,600 °C in a reasonably short time. In order to reduce the annealing temperature, one could excite the vacancy clusters with intense Vis/UV light during annealing. If the temperature is reduced to 1,600 °C, the annealing process can be performed at normal pressure and then there is no danger of generation of C defects. Thus, we assume that there are ways of artificial decoloration of brown type Ia diamonds. One of them is a conventional HPHT treatment followed by a long-time annealing at a temperature of 1,600 °C (Fig. 9.2a). Another way would be just a long-time annealing at 1,600 °C under Vis/UV excitation. The goal of this treatment is to remove the vacancy clusters and all nitrogen-vacancy defects.

9.2 Fidelity of Identification of HPHT-Treated Diamond

Reliability of identification of HPHT-treated diamonds is the central issue in the HPHT treatment business. It is not the amount of HPHT-treated diamonds, but the uncertain identification, what makes HPHT treatment dangerous for the gem diamond trade. On the other hand, it is the reliable identification, what harness HPHT treatment and segregates HPHT-treated diamonds into a separate sector of the gem diamond market. Today we have to confess that so far we do not have absolutely reliable methods of identification of HPHT-treated diamonds. The main reason for this is the lack of universal features of HPHT-treated diamonds, diversity of natural diamonds, constantly developing technology of HPHT treatment and, last but not least, our incomplete knowledge about impurity-defect structure of natural diamond.

9.2.1 Identification Features

In this book, hundreds of features, used for identification of HPHT treatment, are discussed, yet none of them is 100 % reliable. None of them is also a universal feature, which would be detected in any HPHT-treated diamond. Thus, the


(a)
1 Ga
1 Ma
1 year
1 hour
1 min
Annealing time, s
10^{17}
10^{15}
10^{13}
10^{11}
10^{9}
10^{7}
10^{5}
10^{3}
10^{1}
1
2
3
4
5
6
7
8
9
10
11
12
E_a, eV
800C
1400C
1700C
1900C
2300C
3000C
Dissociation of B
Dissociation of vacancy clusters
Formation of B
Formation of A
Dissociation of A
Mobilization of dislocations
Mobilization of vacancies
(b)
Ib → IaA → Ia(A>B) → Ia(B>A) → IaB
Relative concentrations of C, A and B defects
1.0
0.5
0.0
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
10^{7}
10^{8}
10^{9}
10^{10}
Years
C
A
B

◀ **Fig. 9.2** **a** Annealing time required to achieve an order of magnitude change in concentration of defects with activation energies from 1 to 12 eV. *Red lines* show two most probable temperatures of low temperature HPHT treatment (1,900 °C) and high temperature treatment (2,300 °C). Ultimate HPHT treatment at a temperature of 3,000 °C is shown with *blue line*. *Green lines* show the natural annealing in earth (800 to 1,700 °C). *Green* and *red* boxes show probable time intervals of the natural annealing and HPHT treatment respectively. The horizontal arrow at 1 year represents the hypothetical long-time treatment capable of the natural-like decoloration of brown type Ia diamond at temperatures 1,600–1,700 °C. **b** Schematic diagram showing the transformations of the nitrogen defects in natural diamonds during their annealing in earth at temperatures changing from 1,400 to 800 °C. Diamonds are grown as type Ib. Type Ib rapidly converts into type IaA. Further annealing converts diamonds into type IaAB and then into the final type IaB. Rare type Ib diamonds, ejected from the earth interior at very early stage of their history, represent as-grown natural diamonds. Type IaB diamonds are the most ancient ones

recognition of treatment requires detection, measurement and analysis of many of them. For instance, no spectroscopic feature alone can provide reliable identification of HPHT treatment. Only detection of combinations of the defects not observed in natural stones allows conclusive identification (Smith et al. 2000; Newton 2006).

The standard procedure of recognition of type IIa HPHT-treated diamonds comprises the analysis of the NV^0 and NV^- centers, measurement of intensity of the 270 nm absorption band (if possible, in comparison with the B- and N3-centers) and detection of the GR1 and 576 nm centers. The first step in recognition of HPHT treatment of type Ia diamonds is the measurement and analysis of the relative intensities of the H3-, H2- and C-centers, spectral parameters of the Platelets peak and the detection of the H4 and 491 nm center. If no definite conclusion can be made based on this primary analysis, further detailed spectroscopic and microscopic characterization is needed followed by detailed comparative analysis of all detectable features. Sometimes, a serious scientific investigation has to be performed in order to come to a conclusive decision. Yet even the most comprehensive analysis may give no definite results and then the diamond is reported as "undetermined".

General tendency in the change of PL spectra of type IIa diamonds undergone HPHT treatment is the reduction or complete removal of majority of optical centers (Smith et al. 2000). After the treatment the spectra look "empty". The total absence of luminescence is an important indicator of HPHT treatment of type IIa diamonds (Fisher and Spits 2000). HPHT-treated diamonds, which do not reveal spectroscopic features (empty spectra) may be easily misinterpreted as natural. Unfortunately, so far no distinctive features have been found to be always present (or absent) in the type IIa treated stones. Indicators that clearly establish that a diamond has not been HPHT treated are just as crucial to the characterization process as these that identify the treatment (Smith et al. 2000).

Colorless IIa and IaB diamonds are the most suspicious ones regarding possible HPHT treatment (Deljanin and Fritsch 2001). Gem Labs should pay more attention to near-colorless type IIa and type IaB diamonds (Van Royen et al. 2006). In contrast, colorless type Ia diamonds are most probably non-treated. In particular, colorless and near-colorless diamonds with a defect content over 15 ppm are definitely non-treated. Diamonds of this color and with lower A-nitrogen content (down to 7 ppm) are likely non-treated too (Claus 2005).

All colored diamonds need to be examined for HPHT treatment. Likewise all type IIa colorless or near-colorless diamonds must be checked for possible HPHT treatment (Collins 2006). Besides all type IaB diamonds must be checked too (Van Royen et al. 2006).

"Despite the range of assessment techniques available, it is likely that a few diamonds will be encountered for which it is not possible to say with certainty whether the color is natural or enhanced" said Collins in (Collins 2006) referring to his earlier communication (Collins 2001). Since that time our knowledge in the HPHT processing has been improved, significant improvements have been made in detection methods and this development continues (Fisher 2012).

9.2.2 Non-uniformity of Natural Diamond

A problem with the characterization of natural diamond is its non-homogeneity. This non-homogeneity is of particular concern when using diamond type and the concentration-based parameters as indicators of treatment. Indeed, many natural diamonds consist of zones of very different nitrogen content and hence of different type. These are, for instance, natural diamonds with IaA < B core surrounded by ABC or even Ib envelope. The absorption measurements, performed through the whole body of such diamonds, combined with the supplemental PL measurements performed with a laser beam focused in a few spots on the surface, may provide very contradictory and even misleading data and, consequently, result in a wrong conclusion about treatment. Because of the natural non-uniformity, PL measurements of natural diamond must be performed in several places which look differently and especially in the areas with macro-defects. Internal non-homogeneity of natural diamonds must be always checked before the results obtained by different spectroscopic methods are compared. The simplest and the most reliable method of evaluation of the level of non-homogeneity of a diamond is its fluorescence imaging.

9.2.3 Similarity of Natural and Artificial HPHT

Discussing the identification features of HPHT treatment, we avoid using expressions like "is treated", or "is not treated". Instead, we use the wording like "could be treated/untreated", "is likely untreated/untreated", "is definitely treated/untreated", or "is certainly treated/untreated", yet never just "treated/untreated". It means that there is always room for the opposite. The reason for this uncertainty is the similarity of the processes occurring in diamond during natural

HPHT annealing and HPHT treatment. Of course, HPHT treatment may form defect structures very unusual for natural annealing, but never impossible. Indeed, comparing the degrees of completion of the major defect transformations during natural annealing in earth and during HPHT treatment, one sees that they can be essentially similar (Fig. 9.2).

Considering the formation of diamonds in nature, we assume that majority of natural diamonds grew deep in earth at temperatures about 1,400 °C and pressures ranging from 4 to 6 GPa. Growth time could vary from 70 to 1,750 Ma. At these conditions, the growth medium was soft enough to allow the plastic deformation of the growing diamonds. When the diamonds traveled to the Earth surface, the temperature dropped, yet remaining above the plastic transition threshold of 1,200 °C. During this travel, diamonds were further plastically deformed and they gained brown color. During that heating, all the processes of aggregation and dissociation of the nitrogen defects were completely activated. Therefore, in most nitrogen containing diamonds, the impurity-defect structure came to that of ABC diamonds. The rest of their geological life, diamonds could spend close to the surface at rather low temperatures about 800 °C. This temperature could not affect the stability of the vacancy clusters, but could complete the aggregation of C defects and convert diamonds into the most abundant type brown IaAB (Fig. 9.2b).

Green and red boxes in Fig. 9.2a show that the stages of the major defect transformations are essentially the same for the natural annealing at temperatures from 800 to 1,400 °C for a billion of years and HPHT treatment at temperature from 1,900 to 2,300 °C for 1 h. Hence, one can expect that the content of the major nitrogen C, A and B defects and Platelets in naturally annealed and in HPHT treated diamonds are comparable. Large differences in concentrations can be expected only for the secondary nitrogen-vacancy defects and minor non-nitrogen defects, for their formation might require driving forces other than temperature, pressure and deformation—for instance, irradiation. Yet, since natural annealing and HPHT treatment differ quantitatively, not qualitatively, there are no defects which could form exclusively in nature, or exclusively artificially. In any case, the spectrum of defects generated by multi-process treatment involving irradiation is the same as the one generated naturally. However, the differences in concentrations of many secondary defects are very considerable, and these differences constitute the basis for the recognition of HPHT treatment. For instance, a 100 % natural greenish yellow diamond exhibiting simultaneous presence of the centers A, B, C, B′, H3, N3, N4 to N7, GR1 and H2 has been reported. This is an example of "natural HPHT treatment" and manifestation of the fact that our present knowledge of spectroscopy of HPHT treated diamonds is still limited to ensure the secure identification of treatment (Chalain et al. 2005).

The most challenging situation one has with diamonds, which experienced natural annealing at maximum geological temperatures of 1,700 °C. In this case, the set and the relative concentrations of all defects in treated and untreated diamonds can be very comparable. Thus, the reliable identification of HPHT treatment can be reported only for diamonds processed at temperatures above 1,700 °C. Low-temperature HPHT treatment, and especially low-temperature, long-time treatment performed for several hours cannot be recognized so far based on the present level of our knowledge of HPHT-treated diamonds and available instrumentation. Fortunately, commercial low-temperature HPHT treatment is rarely used and these diamonds remain just curious cases rather than the object of concern of gem diamond trade. In 1999 Moses and co-authors wrote that "although every effort is being made to keep up with these new technologies (treatments), we cannot guarantee that practical means will be found to recognize all of these diamonds" (Moses et al. 1999). By now, in majority of cases the HPHT-treated diamonds can be recognized and, in future, when more data on the treated diamonds will be collected, we believe that an almost absolute recognition will be possible.

9.2.4 Identification Techniques

The most reliable identification of HPHT treatment is based on the measurement and analysis of spectra of optically active defects. As the concentration of many of these defects can be very low, very sensitive spectroscopic equipment is required. So far, the most informative method used for detection of HPHT treatment is low temperature PL spectroscopy with different excitation wavelengths (Smith et al. 2000; Hall and Moses 2000). Optical absorption spectroscopy is very informative too. Yet it is not as sensitive as the photoluminescence spectroscopy. The limitations of the absorption spectroscopy are especially obvious when working with high color diamonds (Collins 2001). In contrast, the sensitivity of PL spectroscopy is high enough for detecting defects in every natural diamond. HPHT-treated diamonds, even those with very low-nitrogen content, exhibit at least traces of the nitrogen-related centers like H3, H4, NV, 389 nm, which can be detected when they are present at a concentration below 1 ppb. There is no natural HPHT-treated diamond, which would not be active in low temperature photoluminescence.

Highly sensitive spectrometers alone are not the solution of the problem of reliable identification of HPHT-treated diamonds. Professionals with experience in spectroscopy and knowledge in physics of diamond are required too. In 2001 Anthony et al., referring to the book of J. Wilks et al. "Properties and Application of Diamond", Buttersworth, London (1991), wrote that "the detection of treated stones is more of an art than a science" with the conclusions like "almost certainly not been treated" (Anthony et al. 2001). At present we know much more about HPHT treatment and today the recognition of the treated diamonds is more of a science than an art.

9.3 Status of HPHT-Treated Diamond

Two decades ago HPHT treatment was presented as a “natural” process, the results of which were believed to be undistinguishable from those of natural annealing in earth. There were proposals to consider the HPHT annealing not as a treatment, but as a “processing” aimed at uncovering all the beauty of natural diamond. In other words, to accept HPHT annealing in the same way as traditional cut, polishing and cleaning. Indeed, why the annealing at a temperature of 2,000 °C is “treatment”, whereas the heating to a temperature of 500 °C during mechanical polishing, or to a temperature of 800 °C under jeweler’s torch is not? In fact, all these temperatures can change the natural color of diamond. Then what is this temperature threshold, which separates the “processing with heating” from the “treatment with heating”? Of course, the reason of this differentiation is not the temperature itself. It is the consequence, which follow the heating. Mechanical cut and polishing increase the value of gem diamond and therefore they are “good”. HPHT annealing destroys the gem diamond rarity, decreases the diamond price and therefore it is “bad”. Due to this commercial reason, HPHT annealing will never be accepted as “processing”, but always as “treatment”. The scientific foundation of this negative attitude to HPHT annealing is our growing knowledge about HPHT-treated diamonds and our potential capability to recognize every treated diamond.

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