# Titanium-bearing synthetic alexandrite and chrysoberyl

Dr Karl Schmetzer, Dr Heinz-Jürgen Bernhardt and Thomas Hainschwang

Abstract: The inclusions, compositions and spectra of synthetic reddish violet titanium-bearing chrysoberyl and synthetic alexandrites grown by the Czochralski method by Kyocera in Japan are described. These samples are compared with titanium-, chromium- and vanadium-bearing synthetic alexandrite cat's-eyes and six-rayed alexandrite stars. It is concluded that reddish violet chrysoberyl is coloured by trivalent titanium; the alexandrites are predominantly coloured by chromium with minor amounts of vanadium being also present. Both groups of samples contain inclusions typical of Czochralski-grown chrysoberyl. The colour and pleochroism of chatoyant and asteriated alexandrites is caused by a combination of some trivalent titanium and chromium with minor traces of vanadium. Three light bands are produced by three series of needle-like, titanium-bearing crystals, most probably rutile needles, which are orientated at about 60° to each other. The production technique of alexandrite cat's-eyes described in numerous patent documents is discussed.

Keywords: asterism, chatoyancy, Czochralski, electron microprobe analysis, rutile, synthetic chrysoberyl, titanium contents, visible range spectra
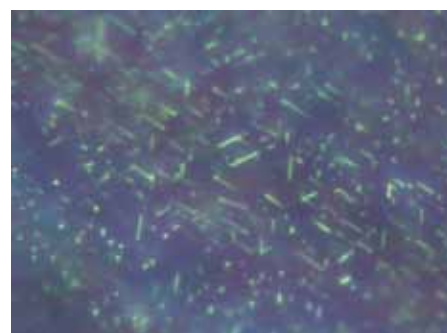
A thin section of a star synthetic alexandrite from Kyocera oriented almost parallel to the **a** *pinacoid shows three series of needles which form angles near 60° to each other. Reflected light, crossed polarizers, field of view 56 x 42 µm. Photo by H.-J. Bernhardt.*

Introduction

Synthetic alexandrite cat's-eyes produced by Kyocera in Japan appeared on the market in the late 1980s with the trade name 'Inamori synthetic alexandrite' or 'Inamori created alexandrite' (Kane, 1987; Scarratt, 1988; Koivula *et al.*, 1988). The material – when cut as cabochon in the proper direction – normally showed a well-centred light band (*Figure 1*), but Kane (1987) mentioned that "when the cabochons were viewed under a strong, single incandescent light source down the long direction, asterism was observed".

When a cabochon is cut with its base perpendicular to that producing a good cat's-eye, a six-rayed asteriated alexandrite can be obtained (*Figure 1*; see also Schmetzer and Hodgkinson, 2011). During the microscopic examinations of the stones mentioned in that paper (*op. cit.*), in immersion it was observed

Figure 1: Synthetic asteriated alexandrite (left, 2.62 ct, diameter 8.0 mm) and synthetic alexandrite cat's-eye (1.55 ct, 7.0 x 6.0 mm) produced by Kyocera in Japan in daylight (above) and incandescent light. Photo by K. Schmetzer.

Titanium-bearing synthetic alexandrite and chrysoberyl

Table I: Trace element contents, colour and spectroscopic properties of titanium-bearing synthetic chrysoberyl and synthetic alexandrite.*

Reddish violet chrysoberyl

Colour and pleochroism

	X ‖ a	Y ‖ b	Z ‖ c
Daylight	light yellow orange	intense orange red	reddish violet
Incandescent light	light yellow orange	intense orange red	reddish purple

Spectroscopic properties, with polarization, absorption maxima (in nm)

Polarization	X ‖ a	Y ‖ b	Z ‖ c
Maxima	565 shoulder	565 shoulder	565
	490	498	495

Chemical properties (average, wt.%)

Sample	RV1 faceted	RV2 faceted	RV3 faceted	RV4 faceted
Technique	microprobe	microprobe	microprobe	microprobe
No. of analyses	10	10	10	10
TiO_2**	0.210	0.228	0.213	0.373
V_2O_3	0.008	0.006	0.019	0.005
Cr_2O_3	0.005	0.008	0.010	0.006
MnO	0.008	0.006	0.010	0.004
Fe_2O_3	0.009	0.006	0.009	0.014

Alexandrite

Colour and pleochroism

	X ‖ a	Y ‖ b	Z ‖ c
Daylight	blue violet	yellow green	blue green
Incandescent light	red purple	yellow orange	blue green

Chemical properties (average, wt.%)

Sample	A1 faceted	A2 faceted	A3 faceted	A4 faceted
Technique	microprobe	microprobe	microprobe	microprobe
No. of analyses	10	10	10	10
TiO_2**	0.014	0.008	0.007	0.007
V_2O_3	0.149	0.158	0.151	0.164
Cr_2O_3	0.393	0.291	0.254	0.308
MnO	0.007	0.009	0.009	0.009
Fe_2O_3	0.007	0.008	0.008	0.010

* Based on a morphological cell with a 4.42, b 9.39, c 5.47   ** total titanium as TiO_2

that the samples did not show the exact pleochroism which has hitherto been observed for synthetic vanadium- and chromium-bearing alexandrite (see, e.g., Schmetzer and Bosshart, 2010; Schmetzer and Malsy, 2011; Schmetzer et al., 2013). In addition, a preliminary spectroscopic examination indicated some differences to the absorption spectra commonly observed for such chromium- and vanadium-bearing, iron-free synthetic samples (with distinctly higher chromium- than vanadium-contents). It was suspected that another colour-causing trace element might be present, but the analytical data had shown only traces of vanadium, chromium and titanium, with the titanium assumed to be present in the form of rutile precipitates, which in turn were responsible for asterism and/or chatoyancy.

Titanium-bearing chrysoberyl with pink coloration was briefly described by Krzemnicki and Kiefert (1999), but no data for pleochroism or spectroscopic properties were given. Titanium-bearing synthetic sapphires as well as titanium-doped synthetic chrysoberyls are grown for technical use as laser crystals. In some of these laser materials, the aim is to create and retain as much as possible of the titanium in its trivalent form. In gemmology, Ti^{3+} was reported as being responsible for the coloration of specifically doped synthetic corundum (Johnson et al., 1995) and titanium-bearing Kashan synthetic ruby in which titanium is present in its trivalent state (Schmetzer and Schwarz, 2007). In the natural environment however, i.e. in most rocks and minerals, titanium is present as Ti^{4+} and trivalent titanium is unstable.

Thus, to explain the colours mentioned above in paragraph two for the phenomenal synthetic alexandrites grown by Kyocera, in this study we investigate the role of Ti in the Kyocera synthetic chrysoberyls and alexandrites, with or without stars or cat's-eyes.

Samples

Stones examined:

a) Reddish-violet chrysoberyl (see samples RV 1–4 in *Table I*): three rough crystals and nine faceted stones *(Figure 2)*. The rough crystals were of somewhat irregular hexagonal cylindrical shape with six side faces and upper and lower bases. Obviously, these cylinders had been sawn from rough Czochralski-grown crystals and the upper and lower bases as well as the side faces had been roughly polished to clean the crystals and give a better visual impression. The faceted gemstones had been cut without specific orientation. All samples had been donated by Kyocera Germany to the Bavarian State Collection for Mineralogy, Munich, Germany.

Titanium-bearing synthetic alexandrite and chrysoberyl

Figure 2: Rough and faceted titanium-bearing synthetic chrysoberyls produced by Kyocera in Japan in daylight (above) and incandescent light; size of the rough crystal above left 16.0 x 15.5 x 10.0 mm, weight 34.12 ct, the faceted sample below left weighs 1.08 ct and measures 7.8 x 5.7 mm. Photo by K. Schmetzer.
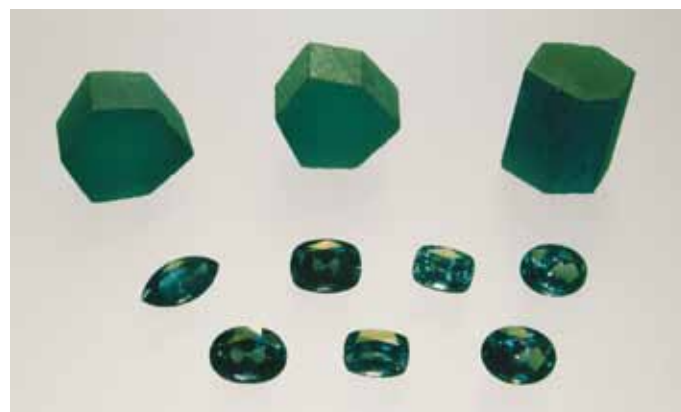
Figure 3: Rough and faceted synthetic alexandrites produced by Kyocera in Japan in daylight (above) and incandescent light; size of the rough crystal above right is 12.2 x 11.2 x 15.6 mm, weight 32.45 ct, the faceted sample below left weighs 1.71 ct and measures 8.0 x 6.0 mm. Photo by K. Schmetzer.

b) Alexandrites from Kyocera (see samples A 1–4 in *Table I*), three pseudohexagonal cylinders and nine faceted samples *(Figure 3)*. The features described in (a) for the rough cylinders of reddish violet chrysoberyl are similar to those shown by these alexandrites.

c) Alexandrite cat's-eyes and stars *(Table II)*: three cabochon-cut samples had been prepared by A. Hodgkinson from a rod-shaped synthetic crystal of 18.84 ct that had been originally purchased in 1988. Two samples showed six-rayed asterism, and the other was a cat's-eye *(Figure 1)*. Two additional cat's-eyes (C2 and C3 in *Table II* and *Figure 4*) were available from the private collection of G. Bosshart.

Results

Titanium-bearing chrysoberyls

The orientation of the edges of the somewhat irregular hexagonal cylinders *(Figure 2)* was more or less parallel to the crystallographic a-axis, which indicates that this was the direction of pulling and growth in the Czochralski process. The overall colour of the samples was reddish violet in daylight with a colour variation to reddish purple in incandescent light.

Figure 4: Synthetic alexandrite cat's-eyes produced by Kyocera in Japan in daylight (above) and incandescent light; sample C2 with lower Ti^{3+} contents weighs 3.29 ct and measures 9.2 x 7.2 mm, sample C3 with higher Ti^{3+} contents weighs 3.19 ct and measures 9.2 x 7.1 mm. Bosshart collection. Photo by K. Schmetzer.

Titanium-bearing synthetic alexandrite and chrysoberyl

Table II: Trace element contents, colour and spectroscopic properties of synthetic alexandrite cat's-eyes and asteriated alexandrite.*

Colour, pleochroism and spectroscopic properties

Cabochon C1 base approx. ‖ **a** (100) weak asterism		X ‖ a	Y ‖ b	Z ‖ c
Incandescent light	view ‖ a-axis, d = 2.5 mm		orange	orange
	view ⊥ a-axis, d = 8.0 mm	intense red orange	non-transparent	non-transparent
Spectroscopic properties, measurement ‖ a-axis			Cr^{3+} spectrum, strong influence of Ti^{3+}	Cr^{3+} spectrum, strong influence of Ti^{3+}

Cabochon C2 base approx. ‖ **b** (010) distinct cat's-eye		X ‖ a	Y ‖ b	Z ‖ c
Incandescent light	view ‖ b-axis, d = 2.8 mm	light purplish red		light green
	view ⊥ b-axis, d = 6.9 or 8.7 mm	intense purplish red	orange	intense green
Spectroscopic properties, measurement ‖ b-axis		Cr^{3+} spectrum, moderate influence of Ti^{3+}		Cr^{3+} spectrum, moderate influence of Ti^{3+}

Cabochon C3 base approx. ‖ **b** (010) weak cat's-eye		X ‖ a	Y ‖ b	Z ‖ c
Incandescent light	view ‖ b-axis, d = 2.6 mm	light yellowish orange		darker orange
	view ⊥ b-axis, d = 6.3 or 8.2 mm	intense red orange	non-transparent	non-transparent
Spectroscopic properties, measurement ‖ b-axis		Cr^{3+} spectrum, strong influence of Ti^{3+}		Cr^{3+} spectrum, strong influence of Ti^{3+}

* based on a morphological cell with a 4.42, b 9.39, c 5.47 and X ‖ a, Y ‖ b, Z ‖ c

d = diameter, representing the maximum path length of light in this orientation of the sample

Chemical properties (average, wt.%)

Sample	Cabochon C1 asteriated**	Cabochon C2 cat's-eye	Cabochon C3 cat's-eye
Technique	LA-ICP-MS	microprobe	microprobe
No. of analyses	2	10	10
TiO_2***	0.58	0.462	0.485
V_2O_3	0.11	0.123	0.119
Cr_2O_3	0.23	0.256	0.257
MnO	bdl	0.006	0.007
Fe_2O_3	bdl	0.007	0.005

** Schmetzer and Hodgkinson, 2011   *** total titanium as TiO_2

bdl = below detection limit

The pleochroism is variable, with similar colours observed for X and Y (yellow orange and orange red), and a more marked difference in the Z direction. The colour for both X and Y is almost identical in daylight and incandescent light, but in the Z direction a colour change from reddish violet in daylight to reddish purple in incandescent light is visible *(Figure 2)*.

The dominant colour-causing trace element of this group of samples is titanium *(Table I)*, the contents ranging from 0.21 to 0.23 wt.% TiO_2 in three samples, to 0.37 wt.% in a somewhat more intensely coloured stone (sample RV4). Other trace elements were only slightly above their respective detection limits in the electron microprobe.

The absorption spectra of the samples show a strong absorption band in the 495 nm range for X, Y and Z, and an additional band in the Z direction located at 565 nm *(Figure 5a, Table I)*. The absorption bands in the visible are assigned provisionally to Ti^{3+} which replaces Al^{3+} in the chrysoberyl structure, which is consistent with literature data (Segawa *et al.,* 1987; Anzai *et al.,* 1987, 1988; Sugimoto *et al.,* 1989). The spectra from the randomly orientated faceted stones *(Figure 5b)* are consistent with these data.

The microscopic examination showed almost plane, only slightly curved growth striations *(Figures 6, 7)* with a predominant orientation more or less parallel to the **a** (100) face, which represent the successive growth surfaces of the chysoberyl. As shown in *Figures 6* and *7*, the distances between these striations are variable. The centres of the rough crystals and the faceted samples were extremely clean with few, if any, inclusions. But in the outer areas of the rough samples, numerous gas bubbles and their migration traces within the growing crystal are present *(Figure 8)*.

Alexandrites

The synthetic alexandrites *(Figure 3)* contain two colour-causing trace elements, chromium and vanadium, with chromium contents always exceeding

Titanium-bearing synthetic alexandrite and chrysoberyl

those of vanadium. In detail, chromium ranges from 0.25 to 0.39 wt.% Cr_2O_3 and vanadium from 0.15 to 0.16 wt.% V_2O_3 *(Table I)*. Other trace elements were only slightly above their detection limits in the electron microprobe.

The orientation of the edges of the somewhat irregular hexagonal cylinders was more or less parallel to the crystallographic a-axis of chrysoberyl, which again indicates growth in this direction in the Czochralski process. Colour, colour change and absorption spectra (see *Table I*) are consistent with data from other iron-free, chromium- and vanadium-bearing synthetic alexandrites grown from the melt, e.g. Czochralski-grown or HOC-grown Russian alexandrites (for further details see Schmetzer and Bosshart, 2010; Schmetzer *et al.*, 2013).

The microscopic examination showed almost plane, only slightly curved growth striations *(Figure 9)* with an orientation parallel to the **a** (100) face, which again reflects the growth surfaces. Some samples showed extremely strong growth zoning which revealed a characteristic interference pattern under crossed polarizers *(Figure 10 a,b)*. Mostly rounded, occasionally also somewhat elongated gas bubbles were seen in some samples *(Figure 11)*, and there are a few
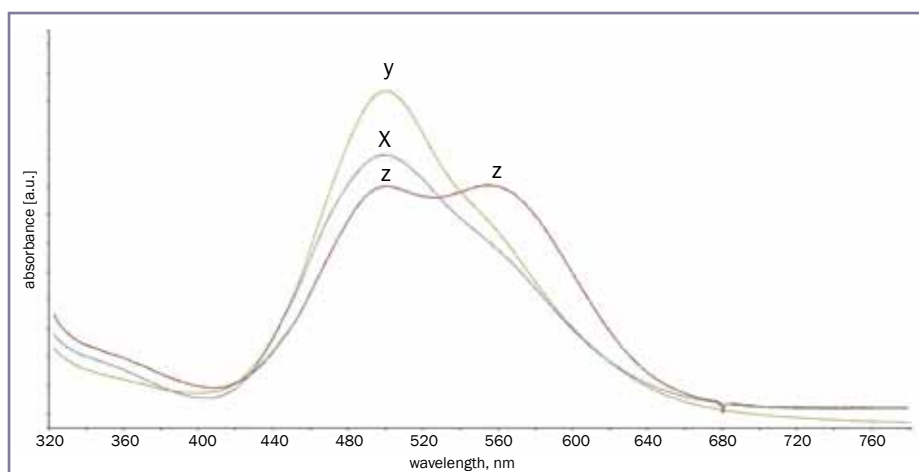
Figure 5a: Absorption spectra of a titanium-bearing synthetic chrysoberyl crystal in polarized light (with X ∥ a, Y ∥ b and Z ∥ c).
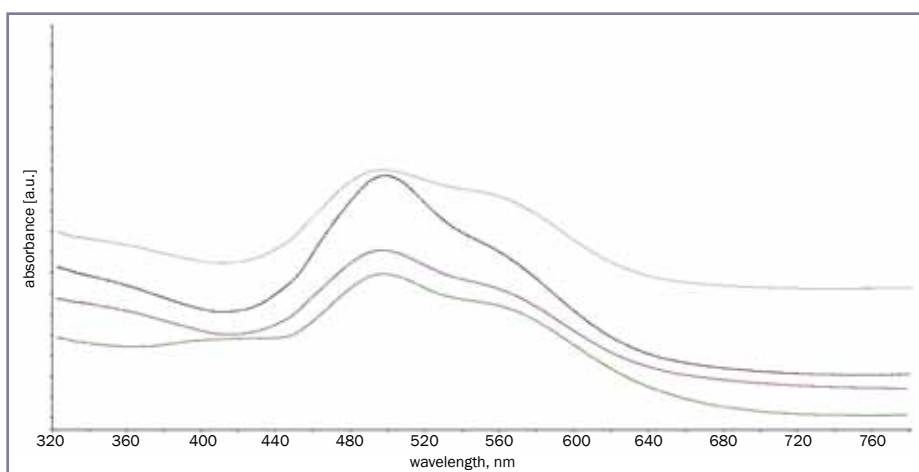
Figure 5b: Absorption spectra of four faceted titanium-bearing synthetic chrysoberyls in random orientation; the spectra of three chrysoberyls are vertically displaced for clarity.
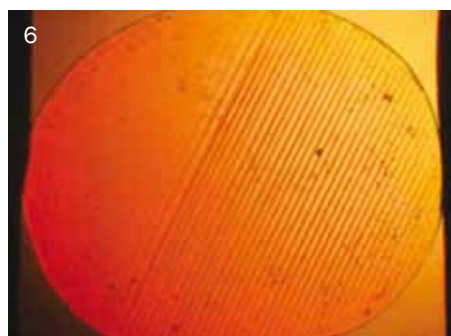
Figure 6: Slightly curved and quite coarse growth striations in reddish violet, titanium-bearing synthetic chrysoberyl produced by Kyocera in Japan. Immersion, field of view 6.9 x 5.2 mm. Photo by K. Schmetzer.

Figure 7: A sample of reddish violet, titanium-bearing synthetic chrysoberyl produced by Kyocera in Japan, is different from that in Figure 6, in which slightly curved growth striations show a much finer structure. Immersion, field of view 3.4 x 2.5 mm. Photo by K. Schmetzer.

Figure 8: Gas bubbles and the traces left as they migrated during growth of the crystal of reddish violet, titanium-bearing synthetic chrysoberyl. Immersion, field of view 2.4 x 1.8 mm. Photo by K. Schmetzer.
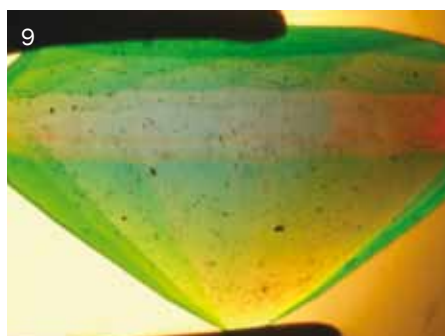
Figure 9: Slightly curved growth striations in synthetic alexandrite. Immersion, field of view 6.5 x 4.6 mm. Photo by K. Schmetzer.

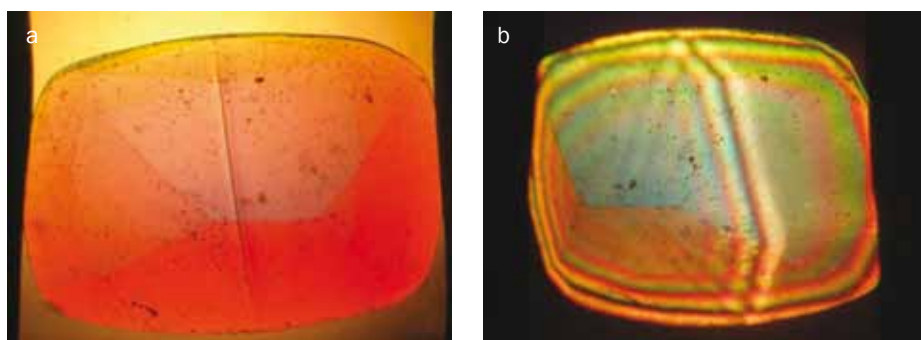## Titanium-bearing synthetic alexandrite and chrysoberyl

Figure 10: (a) Very distinct growth boundary in Kyocera synthetic alexandrite viewed in plane-polarized light. (b) Under crossed polarizers, a characteristic interference pattern is visible. Immersion, field of view 7.5 x 5.7 mm. Photos by K. Schmetzer.

Figure 11: Mostly rounded, occasionally also somewhat elongated gas bubbles in synthetic alexandrite. Immersion, field of view 3.7 x 2.7 mm. Photo by K. Schmetzer.
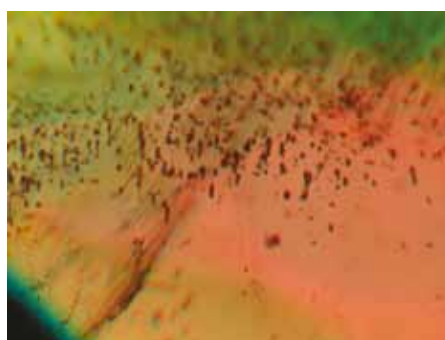
Figure 12: Gas bubbles and their migration traces within the growing crystal in Kyocera synthetic alexandrite. Immersion, field of view 2.1 x 1.6 mm. Photo by K. Schmetzer.
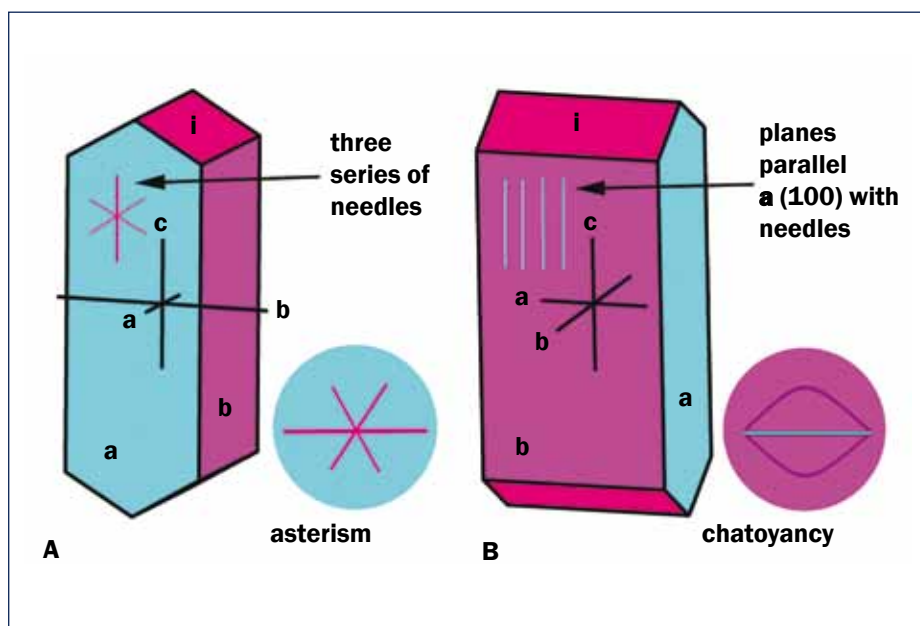

Figure 13: Schematic drawings of asteriated or chatoyant synthetic alexandrite crystals in views parallel to the a-axis (A) and parallel to the b-axis (B). The light effect is due to three series of needles which are all located in planes parallel to the **a** (100) pinacoid; the orientations of the needles are parallel to the c-axis and the two **i** (011) faces. In a view parallel to the a-axis (A) the orientations of the needles reflect light to form a regular six-rayed star; in a view parallel to the b-axis (B), only one strong light band is seen in the centre of the chatoyant cabochon.

gas bubbles with migration traces (*Figure 12*, see also *Figure 8*).

In summary, both varieties — the titanium-bearing chrysoberyl and the chromium- and vanadium-bearing, iron-free alexandrite — showed the typical structural features and inclusions which are common in synthetic chrysoberyl grown by the Czochralski technique. Colour, colour change, pleochroism and absorption spectra of the alexandrites are comparable to other synthetic samples with similar trace element contents. The spectra of the pink titanium-bearing samples are consistent with literature data.

Alexandrites showing chatoyancy and/or asterism

All the Kyocera alexandrite cat's-eyes or star stones seen by the authors show three different light bands. With an orientation of the base of the cabochon parallel to the **a** (100) pinacoid, a star will be visible, but with the base of the cabochon parallel to the **b** (010) pinacoid, only one dominant light band will be seen through the centre of the cabochon's dome, and the other two light bands at the girdle are almost invisible (*Figure 13 A,B,* see also *Figures 1, 4*).

From the orientation of these light bands it was concluded that three series of elongated particles are present which cause the reflections. These particles are located in layers parallel to the **a** (100) pinacoid, with one series of particles oriented parallel to the c-axis and the other two forming angles of 60° and -60° with the c-axis (i.e. particles elongated along the **i** and **–i** {011} prism faces of chrysoberyl). These minute particles, however, were too small to be identifiable with the gemmological microscope.

Chemical properties: The samples revealed distinct chromium and vanadium contents, with chromium contents always exceeding the amounts of vanadium measured. In detail, chromium contents were found between 0.23 and 0.26 wt.% Cr_2O_3 with vanadium contents ranging from 0.11 to 0.12 wt.% V_2O_3 *(Table II)*. The titanium contents range from 0.46 to 0.58 wt.% TiO_2, distinctly higher than the values found in

Titanium-bearing synthetic alexandrite and chrysoberyl

the reddish violet titanium-bearing samples (see *Table I*). Also, consistent with these small ranges, the microprobe scans across polished windows at the bases of the two cabochons indicate the absence of any distinct chemical zoning.

Examination of dark layers: The two asteriated alexandrite cabochons and the three cat's-eyes examined contain darker, non-transparent layers within a matrix of transparent alexandrite (*Figure 14*). Careful optical orientation of the samples (for the method see Schmetzer 2010, 2011) indicate that these layers are oriented parallel to the **a** (100) pinacoid. To evaluate the nature of these dark layers, we cut thin slices parallel to the slightly curved base of two of the chatoyant cabochons and of one asteriated alexandrite and prepared petrographic thin sections approximately 60 µm thick. According to the orientation of these dark layers, the thin section cut from the asteriated alexandrite was parallel to, and the two thin sections prepared from the cat's-eyes were perpendicular to these layers.

The thin section of the asteriated alexandrite, i.e. the section parallel to the **a** (100) pinacoid, showed a dense pattern of small reflecting needles. These needles have three preferred orientations of their long axes and intersect with angles of approximately 60° (*Figure 15,* see also Figure with the Abstract). The other two sections perpendicular to the b-axis, i.e. perpendicular to the dark layers, showed a clear zoning consisting of layers with high concentrations of needles alternating with areas which are more or less free of any needles (*Figure 16 a,b*). The needles are sometimes visible in the form of parallel strings (*Figure 16a),* but occasionally also thicker layers containing needles were seen (*Figure 16b*).

The individual needles in the Kyocera samples were too small either for microprobe or for Raman analysis, but visually similar, somewhat larger needles with identical orientation in natural alexandrite crystals were proven by microprobe analysis to be rutile single crystals and twins (Schmetzer and Bernhardt, unpublished research). Thus,
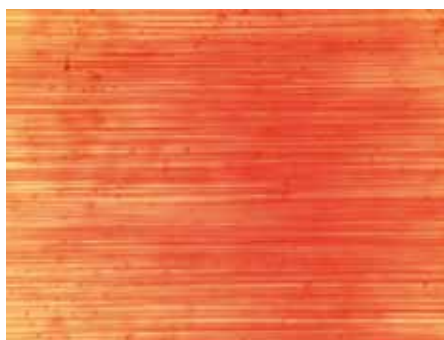

Figure 14: In a view perpendicular to the a-axis of a cat's-eye or star Kyocera alexandrite, numerous dark planes within a transparent matrix are visible using an immersion microscope; these layers parallel to the **a** (100) pinacoid contain numerous tiny titanium-bearing needles which are the cause of the three light bands observed. The a-axis runs vertically, field of view 3.6 x 2.7 mm. Photo by K. Schmetzer.

Figure 15: A thin section of a star synthetic alexandrite from Kyocera oriented almost parallel to the **a** pinacoid shows three series of needles which form angles near 60° to each other. Reflected light, crossed polarizers, field of view 112 x 84 µm. Photo by H.-J. Bernhardt.

Figure 16a,b: Thin sections of Kyocera chatoyant synthetic alexandrites oriented almost perpendicular to the **b** pinacoid show layers parallel to the **a** plane with numerous tiny needles alternating with layers of transparent alexandrite. The layers are thicker in b. Reflected light, crossed polarizers, field of view 112 x 84 µm. Photos by H.-J. Bernhardt.

by analogy, these needles in the Kyocera titanium-doped synthetic alexandrites are most probably rutile. This probability is consistent with the information in various patent documents mentioned in Box A.

Colour and pleochroism: After careful orientation of the available cabochons using optical methods in the immersion microscope it was observed that the pleochroism of these samples was not always consistent with the pleochroism that had been and is commonly observed in natural and synthetic alexandrite. Although the slightly curved bases of the cabochons showed only minor deviations (< 15°) to the **a** (100) and **b** (010) pinacoids of the crystals, we found it difficult to obtain the exact position of all three crystallographic axes if not in immersion. This matters

because we observed that only a slight deviation from a precise orientation (say, in a view exactly parallel to one of the three axes) causes quite large differences in the observed colours and pleochroism. We also noted that there are significant differences in colour, in different directions, which relate to the path lengths of the light through the stones.

Consequently, at this stage in the investigation, we confined our observations to the immersed stones in incandescent light. The presence of the dark layers in combination with the position of the optic axes obtained under crossed polarizers enabled an exact orientation of each cabochon in the immersion microscope. However, in assessing colour, one must keep in mind path length differences, and it is evident

Titanium-bearing synthetic alexandrite and chrysoberyl

Table A. Production of alexandrite cat's-eyes

Author(s)/applicant	Patent documents in Japanese/date*	Patent documents in English/date*	Method for crystal growth	Annealing step/atmosphere	Dopant for cause of colour	Dopant/cause for asterism
Kawachi (Kochi) Suwa Seikosha KK (Seiko Epson Corporation), Tokyo	JP 54-006900 A (1979)	US 4,218,282 (1980)	Floating zone	Not mentioned	Chromium oxide	Titanium oxide
Kawachi and Kojima Miyasaka Kunugi Saito all assigned to Seiko Epson Corporation, Tokyo	JP 55-062884 A (1980) JP 58-130197 A (1983) JP 59-152291 A (1984) JP 59-152292 A (1984)		Floating zone	oxidising	Chromium oxide, iron oxide	Titanium oxide
Shindo *et al.*, National Institute for Research in Inorganic Materials, Tsukuba	JP 57-191297 A (1982) JP 57-191298 A (1982)		Floating zone	oxidising		Titanium oxide
Oguri and Hirota, Sumitomo Cement Co., Ltd., Tokyo	JP 58-120597 A (1983) WO 85/00392 A1 (1985)	EP 0148946 A1 (1985) US 4,634,492 (1987)	Floating zone	oxidising	Chromium oxide, vanadium oxide, iron oxide	Titanium oxide
Saito, Seiko Epson Corporation, Tokyo	JP 59-162196 (1984)		Floating zone, starting material is aluminium hydroxide	Not mentioned	Chromium oxide, iron oxide	Development of tubular fluid inclusions
Isokami and Nagata (Isogami and Nakata), Kyocera Corporation, Kyoto	JP 60-071598 A (1985)	US 4,621,065 (1986)	Czochralski; flux (lithium molybdate)	Not mentioned	Oxides of iron, cerium, vanadium, cobalt, tungsten, chromium, nickel, manganese	Oxides of titanium, tin, zirconium, germanium
Miyasaka, Seiko Epson Corporation, Tokyo	JP 61-256998 A (1986)			Diffusion treatment		Titanium oxide powder

* abbreviations: JP Japan; WO World Intellectual Property Organization; EP Europe; US United States of America
patent family members in other languages, e.g. German, were omitted

■ annealing at high temperatures not mentioned

■ annealing at high temperatures in oxidising atmospheres

■ growth from aluminium hydroxide, no annealing step

■ diffusion treatment

Titanium-bearing synthetic alexandrite and chrysoberyl

Box A

Production of synthetic alexandrite cat's-eyes in the patent literature

The production of synthetic chrysoberyl and alexandrite cat's-eyes is described in numerous Japanese and international patent applications, most of them published in the 1980s (*Table A*). A first short note is found in two patent documents published in 1979 and 1980, assigned to Seiko Epson Corporation (Suwa Seikosha KK, see *Table A*). Later, two different processes were described in more detail, the first one published in various applications by Seiko Epson Corporation, by the National Institute for Research in Inorganic Materials and by Sumitomo Cement Co. The second process is assigned to Kyocera Corporation.

The first method for the production of alexandrite cat's-eyes involves a two-step growth and annealing process (see, e.g., the patent documents by Oguri and Hirota, 1983, 1985 a,b, 1987, assigned to Sumitomo Cement Co.). The first step includes the production of homogeneous single crystals containing titanium oxide as dopant. It is claimed that such specifically-doped crystals can be grown by any known technique suitable for the crystal growth of chrysoberyl, but the floating zone method is described in detail (the floating zone technique was described in a gemmological journal by Schmetzer, 2012). Crystal growth is performed under neutral (e.g. argon or nitrogen) or reducing atmospheres and most titanium is present in its trivalent state. In the second step, the crystal is annealed at elevated temperatures in an oxidizing atmosphere when the titanium is oxidized and elongated particles, most probably rutile needles, are precipitated. These exsolved particles are responsible for the chatoyant effect of the material when cut as a cabochon.

A process assigned to Kyocera Corporation describes the production of chrysoberyl cat's-eyes with a similar first step growth process using a specific dopant. But, there is no mention of a subsequent heat treatment step (Isogami and Nakata, 1985, 1986). Unfortunately, the authors were unable to obtain any conclusive information from the Kyocera Company to throw light on this omission. The following substances are listed by Kyocera as possible dopants: titanium oxide (TiO_2), germanium oxide (GeO_2), zirconium oxide (ZrO_2), and tin oxide (SnO_2). In addition to introducing a dopant to cause chatoyancy, the oxides of vanadium and/or chromium and/or nickel and/or cobalt and/or iron are added for colour. As examples, crystal growth by the Czochralski technique and the flux method are described, but there is no information about the orientation of the precipitates which are responsible for the cat's-eye.

Two further ways of producing cat's-eyes should be mentioned briefly. In a patent document assigned to Seiko Epson Corporation (Saito, 1984b), the production of alexandrite cat's-eyes by the floating zone technique is described. Due to the use of aluminium hydroxide as starting material and a special growth atmosphere, tubular fluid inclusions were developed, which are responsible for chatoyancy. Secondly, the production of alexandrite cat's-eyes by diffusion treatment of synthetic alexandrite crystals in titanium oxide powder was described by Miyasaka (1986).

---

that observations perpendicular to the bases of the cabochons (viewing only two of the three pleochroic colours X, Y or Z) are along much shorter path lengths than the two directions of view parallel to the bases of the cabochons. These latter paths of light range from 6.3 to 8.7 mm, while across the cabochons, the paths are 2.5 to 2.8 mm long. A summary of observations is given in *Table II*.

In detail, we observed that in one of the cabochons examined, the pleochroism shows only minor deviations from the pleochroism of chromium- and vanadium-bearing alexandrite (cabochon C2 in *Table II*). In contrast, the other cabochons (samples C1 and C3 in *Table II*) showed a yellowish orange or orange coloration for smaller paths of light. For observations

in directions parallel to the bases of the cabochons (i.e. with longer paths of light) X was intense red orange, and Y and Z were dark (not transparent, see *Figure 17 A,B*).

Absorption spectra were recorded perpendicular to the bases of the cabochons. Cabochon C2 has a pleochroism almost identical to that of normal alexandrite but showed a chromium spectrum with somewhat less transparency around 500 nm, i.e. in the area between the two strong chromium absorption bands (*Figure 18*, sample C2). In contrast, the transparency in the same area was very much reduced within the spectra of cabochons C1 and C3 (*Figure 18*). This means that, in addition to the chromium-vanadium absorption bands,

there is also a stronger absorption in the 500 nm range.

From the pure spectra of chromium (Cr^{3+}) and titanium (Ti^{3+}) in chrysoberyl shown in *Figure 19,* it is evident that the maximum titanium absorption around 500 nm is more or less at the position of the absorption minimum between the two strong chromium bands. Consequently the absorption spectra of the asteriated and chatoyant Kyocera alexandrites can be understood if we postulate the presence of Ti^{3+} in the structure in addition to the Ti within the rutile needles. Sample C2 shows a smaller influence of Ti in the spectrum. This indicates that a higher percentage of the titanium is present in the form of rutile needles causing a stronger cat's-eye in this sample (see

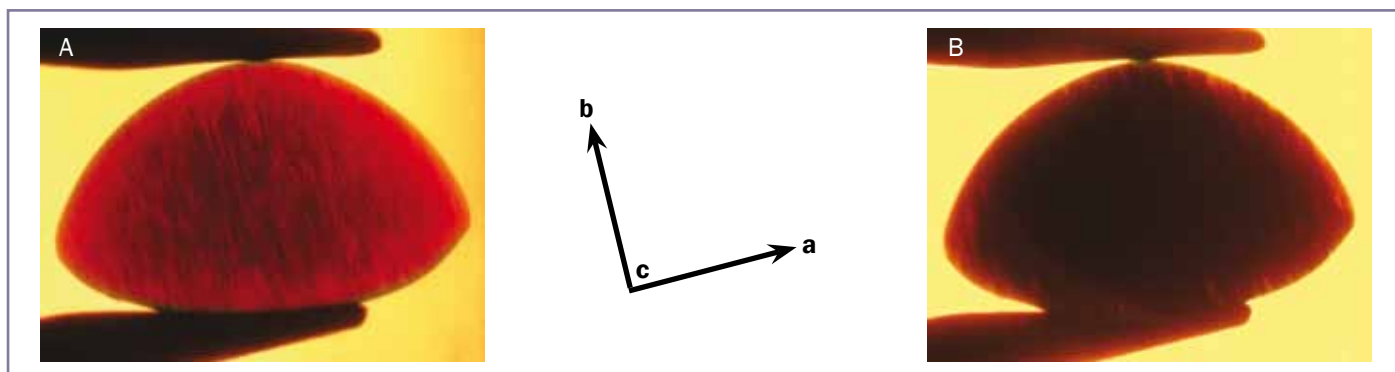## Titanium-bearing synthetic alexandrite and chrysoberyl

*Figure 17A,B: A view parallel to the c-axis of a Kyocera chatoyant synthetic alexandrite; the orientations of the three axes are indicated. The base of the cabochon is almost perpendicular to the b-axis (parallel to the **b** plane); dark layers with titanium-bearing needles are oriented perpendicular to the a-axis (parallel to the **a** plane). In this orientation in immersion and plane polarized light, with rotation of the polarizer (Figures A and B, respectively) the two pleochroic colours X and Y can be observed; X ‖ a is intense red orange (A) and Y ‖ b is non-transparent (B). Field of view 9.1 x 6.8 mm. Photos by K. Schmetzer.*
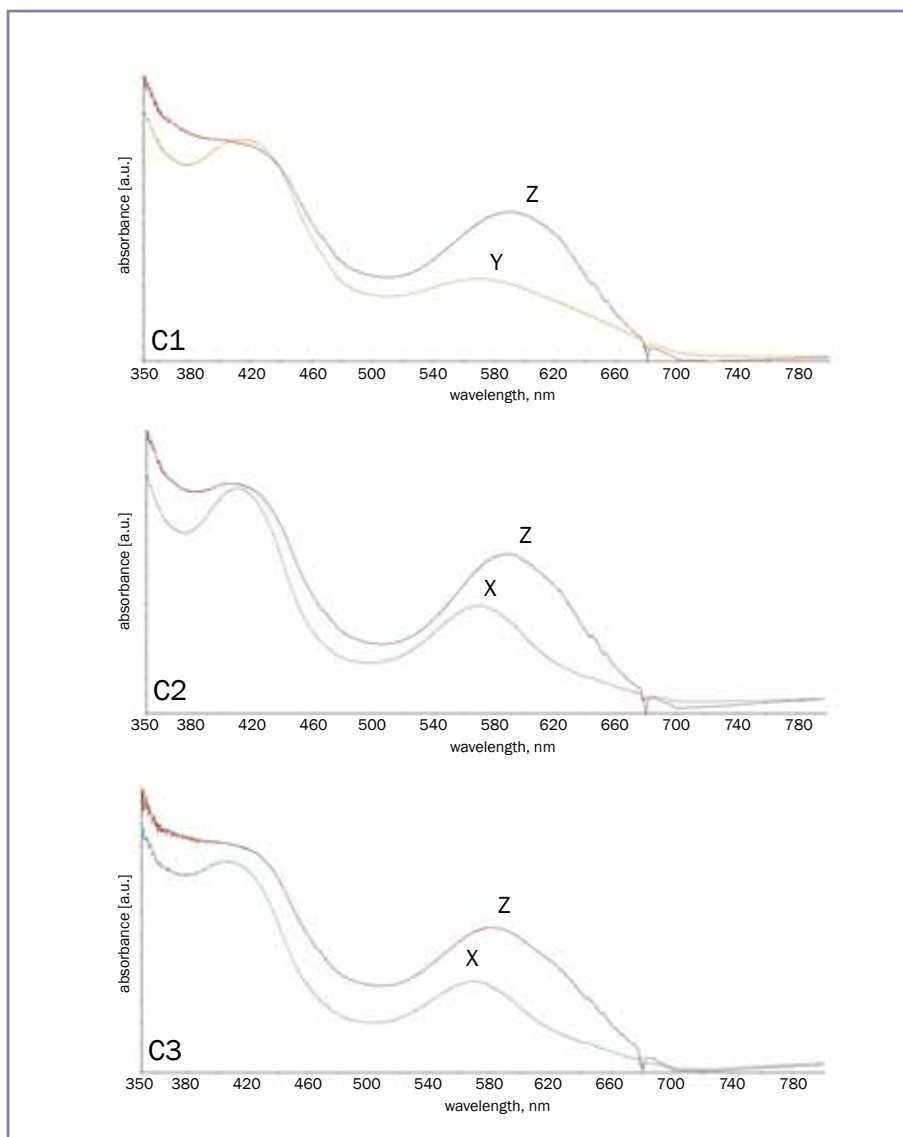

Figure 18: Absorption spectra for star synthetic alexandrite cabochon C1 (see Table II) and cat's-eye cabochons C2 and C3 for polarized light with X ‖ a, Y ‖ b and Z ‖ c; the spectra were recorded perpendicular to the bases of the cabochons with maximum sample thickness from 2.5 to 2.8 mm; for each sample, only two polarized spectra were taken, i.e. Y,Z for sample C1 (beam parallel to the a-axis) and X,Z for samples C2 and C3 (beam parallel to the b-axis).

Figure 4). The two other cabochons C1 and C3 show a distinctly higher absorption in the 500 nm range probably caused by an elevated percentage of titanium in the trivalent state. Thus, the main light bands in these samples are somewhat weaker due to fewer rutile needles being present *(Figures 1,4)*.

Discussion

The average chromium and vanadium contents of Kyocera synthetic alexandrites showing asterism or chatoyancy are slightly lower than those measured in the 'normal' synthetic alexandrites from that producer. But their total titanium contents are higher and at least twice those of the reddish-violet chrysoberyls which are coloured by trivalent titanium.

The spectra indicate that titanium in asteriated or chatoyant alexandrites is present in the structure in its trivalent state on aluminium lattice sites (and so contributes to the colour). The titanium is present in its tetravalent state in the needle inclusions, probably as rutile, and is responsible for the light bands in the cabochons. Three series of needles are oriented parallel to the c-axis, to the **i** and to the **–i** {011} prism faces in layers parallel to the **a** (100) pinacoid. Although various amounts of titanium might also be present as Ti^{4+} within the chrysoberyl structure, Ti^{4+} does not cause absorption in the visible range. Therefore, most probably, the absorption spectra in our stones are due to a superimposition of the absorption bands of trivalent chromium,

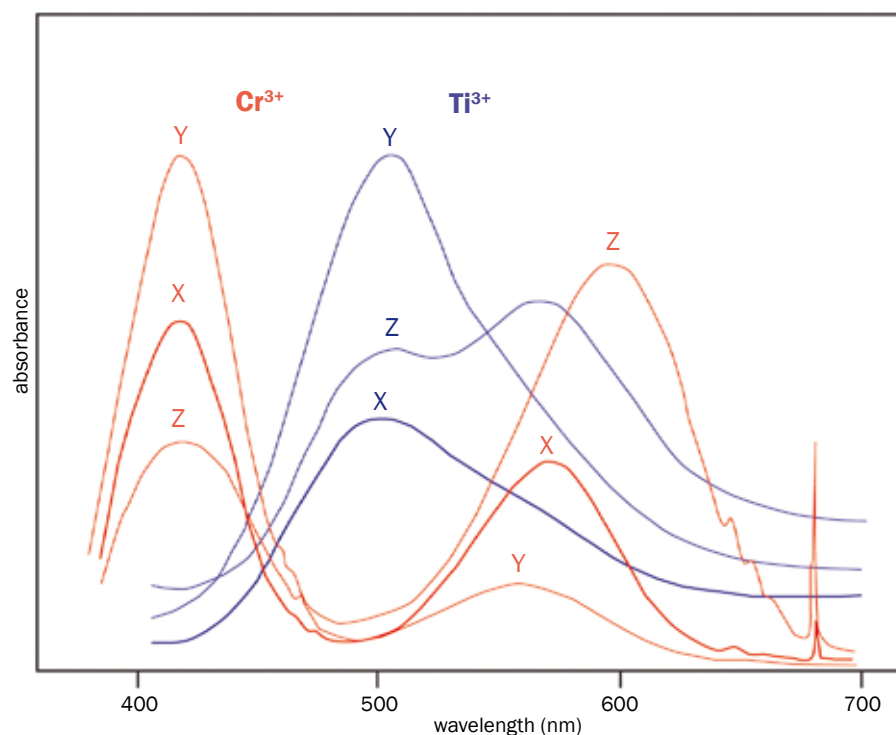Titanium-bearing synthetic alexandrite and chrysoberyl

Figure 19: Plot of the polarized absorption spectra of chromium (Cr³⁺, taken from Heller et al., 1999) and titanium (Ti³⁺, taken from Anzai et al., 1987) in chrysoberyl; for all three directions (X, Y and Z) the absorption maxima for titanium are located between the two strong chromium absorption bands; for samples which contain distinct amounts of chromium together with titanium in its trivalent state, only X is intense red orange, and Y and Z become very dark, almost non-transparent.

vanadium and titanium — with variable intensity of the titanium absorption bands. This situation is similar to the presence of trivalent chromium and trivalent titanium in some Kashan synthetic rubies as described by Schmetzer and Schwarz (2007).

The formation of needle-like titanium-bearing precipitates in synthetic chrysoberyl by annealing the grown crystal is described in numerous patent documents (see Box A, *Table A*), but the mechanism of this process is not explained in them. It is not known whether titanium in its tetravalent state is first produced from Ti³⁺ before the exsolution of titanium oxide and formation of titanium-bearing precipitates. Neither do they contain the reason why there are bands or zones of needle-like inclusions in the stones. In synthetic titanium-bearing star corundum, a similar zoning of needle-like precipitates has been described. This zoning is present in crystals which were grown under fluctuating thermal conditions (Burdick and Jones, 1954) with zones with varying concentrations of needle-like precipitates only becoming visible after a subsequent annealing step. So it is possible that similar fluctuating temperatures during crystal growth might be responsible for the zoning of rutile precipitates in the Kyocera synthetic alexandrites, zones which are invisible until highlighted by the treatment.

Acknowledgements

References

Anzai, Y., Yamagishi, K., Yamaguchi, Y., and Moriya, K., 1987. Solid state laser hosts. EP 0 238 142 A2, assigned to Mitsui Mining & Smelting Co. Ltd, 23.9.1987

Anzai, Y., Yamagishi, K., Yamaguchi, Y., and Moriya, K., 1988. Solid state laser hosts. US 4,765,925, assigned to Mitsui Mining and Smelting Co. Ltd, 23.8.1988

Burdick, J.N., and Jones, R.A., 1954. Synthetic corundum crystals and process for making same. US 2,690,062, assigned to Union Carbide and Carbon Corporation, 28.9.1954

Heller, D.F., Chin, T.C.-K., and Krasinski, J.S., 1999. Method and apparatus for pumping of transition metal ion containing solid state lasers using diode laser sources. US 6,009,114, assigned to Light Age Inc., 28.12.1999

Isokami, M., and Nagata, R., 1985. Synthetic chrysoberyl cat's-eye single crystal. JP 60-071598 A, assigned to Kyocera Corporation, 23.4.1985 [in Japanese]

Isogami, M., and Nakata, R., 1986. Chrysoberyl cat's-eye synthetic single crystal. US 4,621,065, assigned to Kyocera Corporation, 4.11.1986

Johnson, M.L., Mercer, M.E., Fritsch, E., Maddison, P., and Shigley, J.E., 1995. "Ti-sapphire": Czochralski-pulled synthetic pink sapphire from Union Carbide. *Gems & Gemology,* **31**(3), 188–95

Kane, R.E., 1987. Inamori synthetic cat's-eye alexandrite. *Gems & Gemology,* **23**(3), 158–62

Kawachi, A., 1979. Production of clean chrysoberyl single crystal. JP 54-006900 A, assigned to Suwa Seikosha KK (Seiko Epson Corporation), 19.1.1979 [in Japanese]

Kawachi, A., and Kojima, H., 1980. Chrysoberyl single crystal showing cat's-eye effect and production thereof. JP 55-062884 A, assigned to Seiko Epson Corporation, 12.5.1980 [in Japanese]

Koivula, J.I., Fritsch, E., and Fryer, C., 1988. The gemmological characteristics

of Inamori synthetic cat's-eye alexandrite chrysoberyl. *Journal of Gemmology,* **21**(4), 232–6

Kochi, A., 1980. Method of preparation of chrysoberyl and beryl single crystals. US 4,218,282, assigned to Suwa Seikoska KK (Seiko Epson Corporation), 19.8.1980

Krzemnicki, M.S., and Kiefert, L., 1999. Bluish green, light green and pink synthetic chrysoberyl. *Gems & Gemology,* **35**(3), 175

Kunugi, M., 1984. Synthesis of chrysoberyl cat's-eye. JP 59-152291, assigned to Seiko Epson Corporation, 30.8.1984 [in Japanese]

Miyasaka, H., 1983. Manufacture of artificial alexandrite cat's-eye. JP 58-130197 A, assigned to Seiko Epson Corporation, 3.8.1983 [in Japanese]

Miyasaka, H., 1986. Production of alexandrite cat's-eye. JP 61-256998 A, assigned to Seiko Epson Corporation, 14.11.1986 [in Japanese]

Oguri, H., and Hirota, M., 1983. Chrysoberyl single crystal showing luster effect and its production. JP 58-120597 A, assigned to Sumitomo Cement Co. Ltd., 18.7.1983 [in Japanese]

Oguri, H., and Hirota, M., 1985a. Chrysoberyl single crystal showing iridescent effect and process for its preparation. WO 85/00392 A1, assigned to Sumitomo Cement Co. Ltd., 31.1.1985 [in Japanese]

Oguri, H., and Hirota, M., 1985b. Chrysoberyl single crystal showing iridescent effect and process for its preparation. EP 0 148 946 A1, assigned to Sumitomo Cement Co. Ltd., 24.7.1985

Oguri, H., and Hirota, M., 1987. Chrysoberyl single crystal and method for producing the same. US 4,634,492, assigned to Sumitomo Cement Co. Ltd., 6.1.1987

Saito, M., 1984a. Synthesis of alexandrite cat's eye crystal by floating zone method. JP 59-152292 A, assigned to Seiko Epson Corporation, 30.8.1984 [in Japanese]

Saito, M., 1984b. Production of artificial crystal of alexandrite cat's-eye by floating zone process. JP 59-162196 A, assigned to Seiko Epson Corporation, 13.9.1984 [in Japanese]

Scarratt, K., 1988. Kyocera synthetics. *Journal of Gemmology,* **21**(3), 136–9

Schmetzer, K., 2010. *Russian alexandrites.* Schweizerbart Science Publishers, Stuttgart, 141 pp.

Schmetzer, K., 2011. Measurement and interpretation of growth patterns in chrysoberyl, including alexandrite. *Journal of Gemmology,* **32**(5–8), 129-44

Schmetzer, K., 2012. Natural alexandrites and chrysoberyls from Madagascar with irregular and regular growth patterns. *Australian Gemmologist,* **24**(10), 243–8

Schmetzer, K., Bernhardt, H.-J., Balmer, W.A., and Hainschwang, T., 2013. Synthetic alexandrites grown by the HOC method in Russia: internal features related to the growth technique and colorimetric investigation. *Journal of Gemmology,* **33**(5/6), 113–29

Schmetzer, K., and Bosshart, G., 2010. Colorimetric data of Russian alexandrite and yellowish green to green chrysoberyl. In: Schmetzer, K. *Russian alexandrites.* Schweizerbart Science Publishers, Stuttgart, 107–20

Schmetzer, K., and Hodgkinson, A., 2011. Synthetic star alexandrite. *Gems & Jewellery,* **20**(3), 9–11

Schmetzer, K., and Malsy, A.-K., 2011. Alexandrite and colour-change chrysoberyl from the Lake Manyara alexandrite-emerald deposit in northern Tanzania. *Journal of Gemmology,* **32**(5–8), 179–209

Schmetzer, K., and Schwarz, D., 2007. The causes of colour variation in Kashan synthetic rubies and pink sapphires. *Journal of Gemmology,* **30**(5/6), 331–7

Segawa, Y., Sugimoto, A., Kim, P.H., Namba, S., Yamagishi, K., Anzai, Y., and Yamaguchi, Y., 1987. Optical properties and lasing of Ti^{3+} doped $BeAl_2O_4$. *Japanese Journal of Applied Physics,* **26**(4), L291–2

Shindo, I., Sakauchi, H., and Takegawa, S., 1982a. Preparation of single crystal of chrysoberyl shedding luster. JP 57-191297 A, assigned to National Institute for Research in Inorganic Materials, 25.11.1982 [in Japanese]

Shindo, I., Sakauchi, H., and Takegawa, S., 1982b. Preparation of single crystal of chrysoberyl shedding luster. JP 57-191298 A, assigned to National Institute for Research in Inorganic Materials, 25.11.1982 [in Japanese]

Sugimoto, A., Segawa, Y., Kim, P.H., Namba, S., Yamagishi, K., Anzai, Y., and Yamaguchi, Y., 1989. Spectroscopic properties of Ti^{3+}-doped $BeAl_2O_4$. *Journal of the Optical Society of America B,* **6**(12), 2334–7

The Authors

Dr Karl Schmetzer
D 85238 Petershausen, Germany
email: SchmetzerKarl@hotmail.com

Dr Heinz-Jürgen Bernhardt
ZEM, Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität, D 44780 Bochum, Germany
email: Heinz-Juergen.Bernhardt@rub.de

Thomas Hainschwang
GGTL Laboratories, Gemlab (Liechtenstein)/GemTechLab, FL-9496 Balzers, Liechtenstein/CH-1227 Geneva, Switzerland
email: thomas.hainschwang@ggtl-lab.org