The gemmological properties and infrared spectra of brucite, an imitation of nephrite and Shoushan stone

Li Jianjun, Yu Xiaoyan, Cai Jia, Liu Xiaowei, Fan Chengxing and Cheng Youfa

Abstract: Nephrite and Shoushan stones have a long history of use as ornamental gem material for jewellery and carving in China. However, the reserves of the stones have dramatically decreased recently and a growing number of their imitations, such as brucite, have entered the Chinese market. Microscope examination, testing with dilute hydrochloric acid, Fourier Transform Infrared (FTIR) spectra and energy-dispersive X-ray fluorescence (EDXRF) spectra have proved to be useful techniques to distinguish nephrite or Shoushan stones from brucite.

Keywords: brucite, gemmological properties, infrared spectra, nephrite, Shoushan stone,

Introduction

In China over the past 5000 years, high quality nephrite has been carved as royal seals, the emblem of power of emperors (Yang *et al*., 1986; Chen et al., 2004; Tang *et al*., 2002). Shoushan stone has also been carved as seals, and is named from its source in Shoushan in the northern suburbs of Fuzhou, Fujian province, P.R. China (Wu and Cui, 1999). Shoushan stone comprises around one hundred varieties, among which 'Tianhuang stone' is the most precious and enjoys a reputation as 'the emperor of stones'. Ever since Tianhuang stone became the favourite of Qianlong, an emperor of the Qing Dynasty, its price has been high. It is said that one Liang (a unit of mass equivalent to 50 g used in ancient China) of Tianhuang stone is worth ten Liang of gold.

However, because of scarce reserves, the trade price of Tianhuang stone has been up to a hundred times that of gold. In turn, this helps raise the price of other varieties of Shoushan stone.

In recent years the most sought-after gem materials mentioned above have become more available and have sold for very high prices. This in turn has led to a wider range of material being considered as gemstones. Hitherto, most Shoushan stone has consisted of the kaolin group minerals dickite and nacrite, or of pyrophyllite, rarely of illite (see Box A). This paper aims to characterize a recent imitation of nephrite and Shoushan stone which consists of brucite.

Materials and methods

The Laboratory of the National Gold and Diamond Testing Center (NGDTC) of P.R. China recently received a sample (numbered B1) that was described as Shoushan stone from the Shanbowei deposit by the retailer. Its diaphaneity, lustre and colour (greyish green and reddish brown) *(Figure 1)* are indeed similar to some varieties of Shoushan stone. In addition, two strands of beads (B2 and B3) *(Figure 2)* were submitted by a client who stated that they were sold to him as nephrite. However, both strands showed an unusually dim lustre compared to nephrite. B1, B2 and B3 are actually all the same material, brucite, although they show considerable differences in appearance. For the purposes of this investigation, a glass imitation of nephrite (B4) and a strand of nephrite beads with relatively strong lustre numbered B5, are characterized for comparison.

The samples were tested by

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Table I: Gemmological properties of samples B1 to B5, and Shoushan stone of the dickite and/or nacrite type and Shoushan stone of the pyrophyllite type.

Property	Carving	Strands of beads				Shoushan stone of the dickite and/or nacrite type†	Shoushan stone of the pyrophyllite type†
	B1	B2	B3	B4	B5		
Size (mm)	130×100×85	8	12	8	8		
Colour	greyish-green and reddish brown	white	white	white	white	greyish white, greyish yellow, brownish red	white, yellowish green, dark purple, yellow, brownish red, grey
diaphaneity	translucent to semitranslucent	translucent	translucent	translucent	semitransparent to translucent	semitranslucent to opaque	semitranslucent to opaque
Lustre	greasy	waxy	waxy	vitreous	vitreous	subvitreous to waxy	waxy
SG	2.39	*	*	*	*	2.57~2.68‡	2.65~2.90‡
Mohs' hardness	2.5	2.5~3	2.5~3	6	3~6.5	2.5~3	2~3
RI distant vision	1.55	1.56	1.56	1.52	1.57~1.62	1.56~1.57	1.56~1.57
UV fluorescence							
short-wave	inert	inert	very weak	weak to faint white	very weak	inert-strong white	inert-strong white
long-wave	inert	inert	parts faint white	strong bluish white	parts faint white	inert-strong white	inert-strong white
Internal features	resemble veins in radishes	wispy inclusions resembling cotton	fine-grained wispy inclusions	radial microcracks	fine-grained texture resembling 'glutinous rice'	fine pyrite inclusions, red spots, resemble veins in radishes	most common were red or yellow spots, red healed fractures
Reaction to hydrochloric acid (HCl)	no gas bubbles, but etch pits were observed	none to few gas bubbles with etch pits	none to few gas bubbles with etch pits	inert	abundant gas bubbles to no gas bubbles	inert	inert

* SGs of beads not measured

† Data from Sun *et al.* (2003) and Feng *et al.* (2008)

‡ SG data is a very important feature in distinguishing the two types of Shoushan stone, while advanced instruments should be applied to identify them with accuracy

Figure 1: Carving of a Chinese traditional pattern in brucite (sample B1); it is 130 mm tall and 100 mm wide. This imitates high quality Shoushan stone. Photo by Li Jianjun.

routine gemmological methods. Mohs' hardnesses were obtained using standard minerals and the 2.5 values in *Table I* refer to comparisons with fingernails. Refractive indices (RIs) using the distant vision method were measured with a gemmological refractometer; specific gravity (SG) values were obtained using an electronic balance with deionized water as a measuring medium. Fluorescence was tested using standard long-wave (365 nm) and short-wave (254 nm) UV lamps. Internal features were examined with a binocular gemmological microscope using darkfield and brightfield illumination at 10× to 70× magnification.

In addition, dilute hydrochloric acid was used to test inconspicuous areas on the five samples to see if there was any effervescence.

A Thermo Nicolet NexusTM 470 Fourier Transform Infrared (FTIR) spectrometer equipped with a specular reflection accessory and a CentaurμsTM Infrared (IR) Microscope was used to obtain IR spectra. The range between 6000–400 cm^{-1} at a standard resolution of 4 cm^{-1} with 16 scans (per spectrum), was recorded for each sample using two methods. Powdered samples were compressed into KBr pellets for measurement in transmission mode; and the specular reflection method was used on the solid sample. The IR spectra of five samples were obtained before the backgrounds were scanned at room temperature. The IR spectra of B1 were recorded using the specular reflection accessory because its size exceeds the sample stage of the IR microscope. Other samples were examined by using the IR microscope.

X-ray fluorescence spectra of B2 and B3 were recorded using a Thermo Noran QuanX EC EDXRF spectrometer at 20 kV with a Rh target and no filter. The data acquisition time was 100 seconds for each sample spectrum at vacuum.

Results and discussion

Gemmological properties

Samples B1–B5 were subject to routine gemmological examination and the results are presented in *Table I*; the properties of Shoushan stone of the dickite and/or nacrite type as well as Shoushan stone of the pyrophyllite type are also given for comparative purposes.

No obvious absorption spectra were observed in samples B1–B5 when viewed with a hand-held spectroscope examined at NGDTC. The gemmological properties of B4 *(Table I)* indicate that the beads are glass and those of B5 suggest that the beads are nephrite, but the SG, hardness and RIs of B1, B2 and B3 are not diagnostic for identification.

FTIR spectroscopy

Two beads from B2 and three beads from B3 were selected at random and IR spectra obtained using the FTIR microscope. Also, spectra from B1 were obtained using the specular reflection accessory. Infrared spectra typical of the different kinds of Shoushan stone are given in *Box A*

In the range 1200–400 cm^{-1}, the IR reflectance spectra of B1, B2 and B3 showed strong and broad reflection bands below 800 cm^{-1} *(Figure 3)* indicating the presence of a metal oxide or hydroxide; this is consistent with the results of the IR transmission spectra of B3 (see *Figure 5*).

In the range 2000–800 cm^{-1}, B1, two beads from B2 (see *Figure 4,* B2a and B2b) and one bead from B3 (see *Figure 4,* B3a) exhibited broad reflection bands positioned at ~1550–1400 cm^{-1}. These are due to the stretching vibrations of the CO_3^{2-} group. Bands centred at 890 cm^{-1} detected in B1 (see *Figure 4,* B1) and B2 (B2a and B2b) can be assigned to the bending vibrations caused by the CO_3^{2-} group which are consistent with magnesite ($MgCO_3$) (Santillan *et al.*, 2005). Therefore both B1 and B2 contain a metal oxide or hydroxide as the main component and a small amount of magnesite.

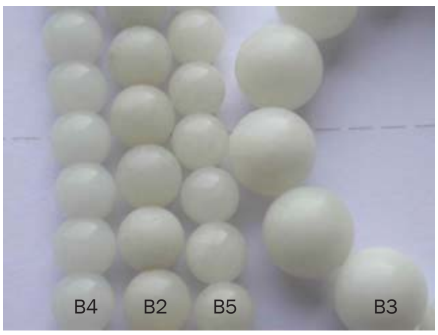

Figure 2: Sections of four strands of beads (of diameters between 8 and 12 mm) sample numbers B2, B3, B4 and B5. They are all pale grey and have a vitreous to waxy lustre that could easily be confused with white nephrite or some varieties of Shoushan stone. These strands of beads are identified as brucite (B2 and B3), glass (B4) and nephrite (B5). Photo by Li Jianjun.

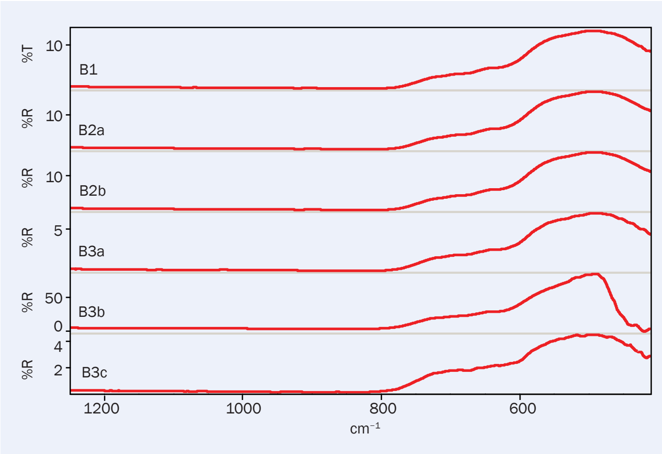

Figure 3: Reflectance IR spectra of sample B1 and five beads randomly selected from samples B2 and B3 show similar broad reflection peaks, centred below 800 cm^{-1}, indicating that all three materials are the same.

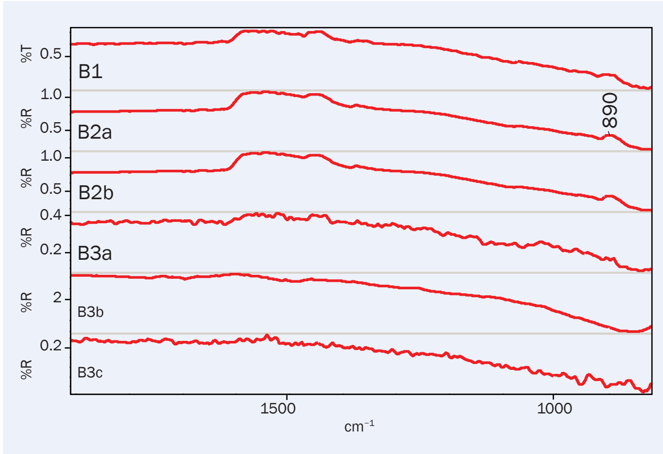

Figure 4: Reflectance spectra of the samples in Figure 3 in a different IR range, showing similar reflection bands between ~1550 and 1400 cm^{-1} due to the stretching vibration of the CO_3^{2-} group. B1, B2a and B2b show reflection bands centred at 890 cm^{-1} caused by bending vibrations of the CO_3^{2-} group, indicating that magnesite ($MgCO_3$) is present.

Transmission IR spectra from a mineral mixed with KBr commonly give results which are more accurate than spectra from the reflection mode. Therefore one bead of B3 was selected and powder scraped from an inconspicuous area. *Figure 5* shows the transmission spectrum of B3. In the 4000–3000 cm^{-1} region, a sharp band centred at 3698 cm^{-1} along with a broad band at 3420 cm^{-1} correspond to vibrations and stretching of OH bonds (Braterman and Cygan, 2006). Comparing the IR spectra of B1, B2 and B3 with those published by Peng and Liu (1982), the carving and beads can be identified as brucite ($Mg(OH)_2$).

The reflection IR spectra recorded from each bead of B4 were almost the same; the broad peak between 1200 and 800 cm^{-1} is assigned to Si-O vibrations in the $[SiO_4]$ group. No split peaks caused by silicate minerals were observed, indicating that the beads are amorphous (see *Figure 6*).

However, the reflection IR spectra of beads of B5 showed obvious variation *(Figure 6)*. The main mineral component of B5 is tremolite and in some beads there are small amounts of ferroan dolomite (ankerite) which is indicated by reflection peaks in the 1600–1400 cm^{-1} region; these are due to stretching vibrations of the CO_3^{2-} group; also a peak at 877 cm^{-1} is assigned to a CO_3^{2-} group bending vibration. The presence of ferroan dolomite in B5 (nephrite) is in

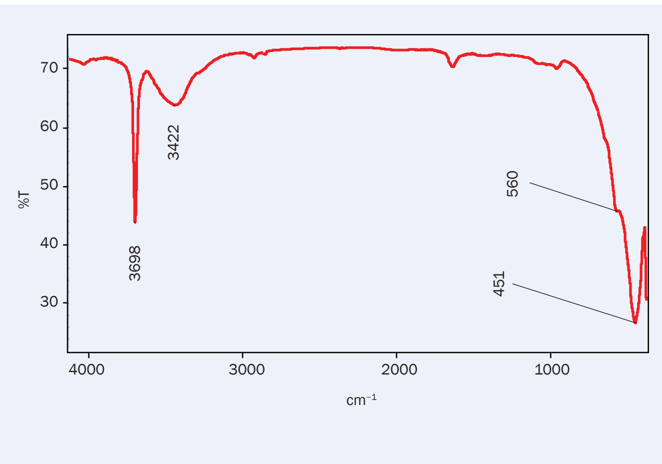

Figure 5: Transmittance IR spectrum obtained from powder from the drill hole of a B3 bead mixed with KBr and pelletized. The bands positioned at 3698 and 3422 cm^{-1} can be assigned to OH stretching vibrations (Braterman and Cygan, 2006). The bands at 451 and 560 cm^{-1} are consistent with brucite ($Mg(OH)_2$) (Peng and Liu, 1982).

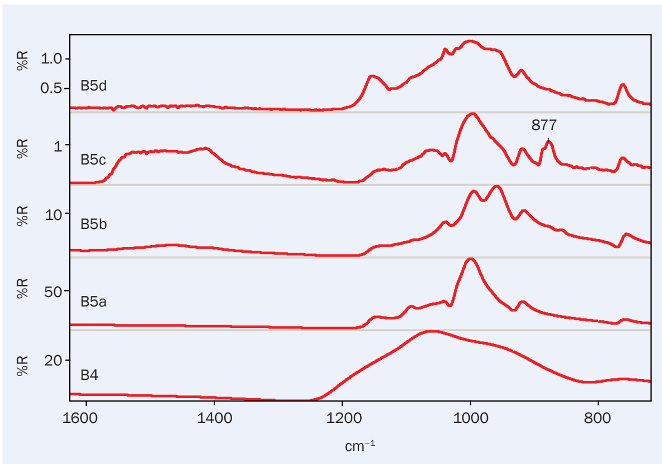

Figure 6: The reflectance IR spectrum of B4 shows only one broad band positioned at 1100–800 cm^{-1} due to Si-O vibrations, suggesting that it is amorphous. The reflectance spectra of the nephrite beads B5 show obvious variation. Note particularly that in the 1600–1400 cm^{-1} range, there are peaks in B5c which can be assigned to stretching vibrations of the CO_3^{2-} group, and a peak at 877 cm^{-1} due to bending vibrations in the CO_3^{2-} group, both indicating the presence in the nephrite of a carbonate mineral.

Box A

Almost all Shoushan stone is composed either of dickite and/or nacrite, or of pyrophyllite; rare specimens consist of illite and sericite. Typical IR spectra of the main Shoushan stone constituents are given below with comments.

Figure A1

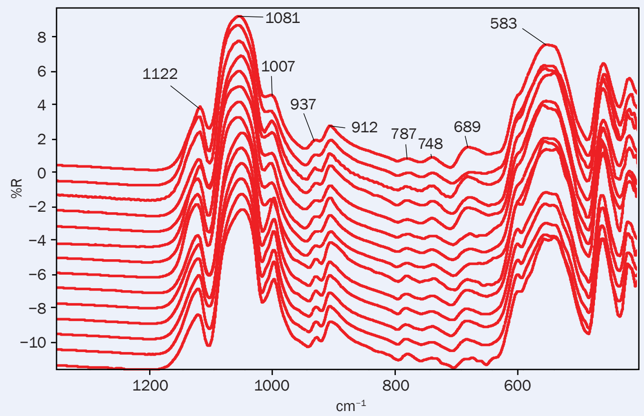

Figure A2

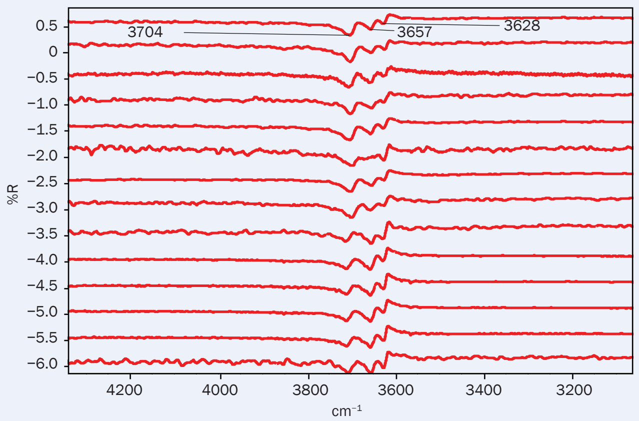

Figure A3

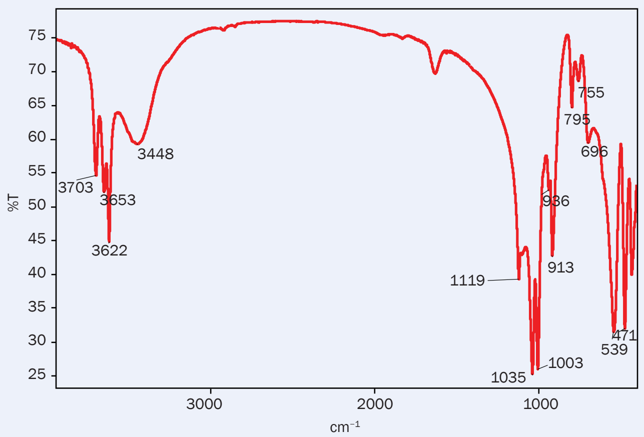

Figure A4

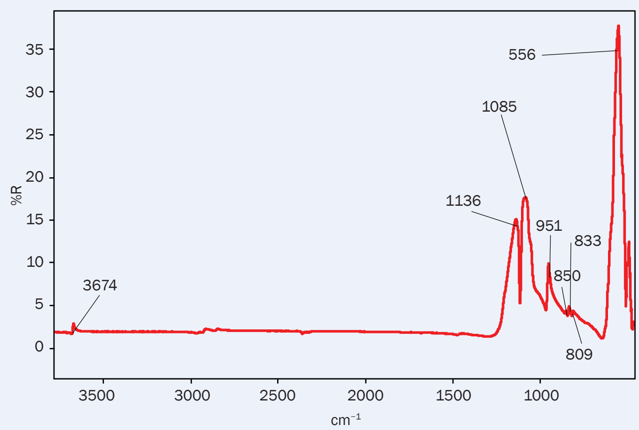

Figure A5

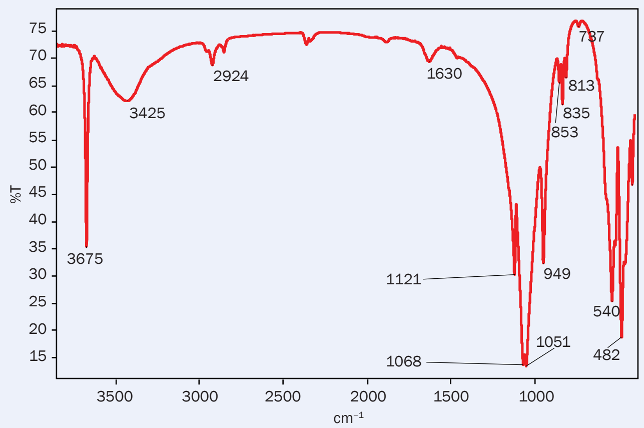

Figure A1: Reflectance spectra of Shoushan stone of the dickite and/or nacrite type showing peaks in the 1200–1000 cm⁻¹ range arising from stretching vibrations of Si-O bonds (Shoval et al.*, 2002), 912 and 1007 cm⁻¹ caused by bending vibrations of OH bonds (Fang* et al.*, 2005).*

Figure A2: Reflectance spectra of Shoushan stone of the dickite and/or nacrite type showing bands centred at 3704, 3657 and 3628 cm⁻¹, which are assigned to O-H stretching bonds (Franco et al.*, 2006).*

Figure A3: Transmission IR spectrum of dickite showing peaks at 3703, 3653 and 3622 cm⁻¹ corresponding to OH stretching bonds (Balan et al.*, 2002).*

Figure A4: The IR reflection spectrum of Shoushan stone of the pyrophyllite type showing a weak band at 3674 cm⁻¹ which arises from the u(OH) vibration (Wang et al.*, 2002); the peaks at 850 and 809 cm⁻¹ show the presence of quartz and kaolinite (Amritphale* et al.*, 1992).*

Figure A5: Transmission spectrum of Shoushan stone of the pyrophyllite type showing a sharp band at 3675 cm⁻¹ due to the u(OH) vibration (Ignacio Sainz-Diaz et al.*, 2004).*

agreement with the fact that the nephrites occur in dolomitic marbles associated with metasomatic alteration (Wang *et al*., 1990; Yui and Kwon, 2002).

EDXRF

Samples B2 and B3 were quantitatively analysed using an EDXRF spectrometer and the results indicate major Mg along with Si, Ca and Fe as trace elements in both samples (Li *et al*., 2008).

Conclusions

Brucite, a layered magnesium hydroxide, is extracted on an industrial scale along with dolomite, dolomite marble and serpentinite and refined to produce magnesium. Most is white but some is multicoloured when traces of iron or manganese are present. Some of the more attractive material is now being used as an imitation of nephrite jade and Shoushan stone, both of which are highly valued by the Chinese people.

As the price of high-quality nephrite increased by virtue of its rarity, lower quality nephrite came onto the market to meet the demand for 'jade'. This lower quality nephrite can contain impurities of calcite and dolomite — which lower the RI, SG and hardness of the stone and, at the same time, provide the opportunity for materials of similar properties to come onto the market. Brucite is a good example.

It is not easy to identify brucite by using standard gemmological techniques although its unusually dim lustre would suggest that the material being examined is an imitation. EDXRF may provide clues to determine the material by analysing the major and minor elements it contains, but further work is necessary to confirm the applicability of this testing procedure. When examining samples like brucite which have gemmological properties such as a Mohs' hardness of 2–4 and are translucent to opaque, routine gemmological examinations are not sufficient to determine their identity. However, FTIR spectroscopy using both KBr pellets in transmission mode and the solid sample in reflection mode can provide conclusive evidence that the imitation is actually brucite.

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The Authors

Li Jianjun (geoli@vip.sina.com) and **Cheng Youfa**
National Gold & Diamond Testing Center of China (NGDTC), Jinan, Shandong Province, P.R. China

Dr Yu Xiaoyan
The professor in Gemological College at the China University of Geosciences, Beijing, P.R. China

Cai Jia
China University of Geosciences, Beijing, P.R. China

Liu Xiaowei
Shandong Institute of Metrology (SDIM), Jinan, P.R. China

Fan Chengxing
Shenzhen laboratory of the National Jewellery Quality Supervision and Inspection Center of China (NJQSIC)