INFRARED SPECTROSCOPIC STUDY OF FILLED MOONSTONE

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The laboratory of the National Gold & Diamond Testing Center (NGDTC) encountered some plagioclase (moonstone) beads with blue adularescence. Fifteen of the 22 moonstones fluoresced moderate to strong bluish white to long-wave UV, with the fluorescence visible in fissures. Electron microprobe analysis of one bead and micro-infrared reflectance spectra of all 22 samples indicated a composition nearly identical to albite. The specimens with strong fluorescence exhibited 3053 and 3038 cm^{-1} peaks in their direct transmission infrared spectra, confirming impregnation by a material with benzene structure. This treatment can be detected with a standard gemological microscope by observing characteristics such as relief lines.

In identifying gemstones from the Chinese market over the last five years, the National Gold & Diamond Testing Center (NGDTC) found that some treatments usually applied to top-grade colored stones such as emerald (Johnson et al., 1999) or jadeite jade (Fritsch et al., 1992) had also been used to enhance other materials. Impregnated aquamarine, tourmaline, and kyanite have all been encountered. Li et al. (2008) examined the characteristics and identifying features of filled aquamarine. Wang and Yang (2008) reported on a filling technology applied to carvings, beads, and faceted gems from the jewelry market of Guangdong Province. They also researched the identification of these filled gemstones.

A few months ago, the NGDTC laboratory received from a client six bracelets of plagioclase (moonstone) beads with blue adularescence. The bracelets were reportedly from Donghai County in Jiangsu Province, the trading center for crystal quartz. They displayed moderate to strong bluish white fluorescence in an irregular curvilinear pattern, which caused suspicion. Observing the beads from different directions showed that the fluorescence was confined to the fractures, and the authors deduced the presence of some foreign material. In addition to determining the mineral composition of the samples, we collected infrared spectra to confirm the existence of the filling material and examine its composition.

MATERIALS AND METHODS

The samples came from a strand of 22 moonstone beads (table 1) that showed beautiful blue adularescence (figure 1). We examined the samples' standard gemological properties using an Abbe refractometer, an ultraviolet fluorescence lamp, and a microscope.

The chemical composition of sample 1 was first determined by electron microprobe analysis at the Chinese Academy of Geological Sciences (CAGS). The sample was removed from the strand, and a flat surface was polished oblique to the lamellae of polysynthetic twinning. After the electron microprobe analysis we could still see the strongest adularescence of this sample and collect its infrared spectra for further tests. CAGS used a JXA-8230 electron microprobe with an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam diameter of 5 μm. Jadeite was used as the Na standard, and Na was run before the other elements to avoid undercounting sodium. The standard materials for this test were natural minerals and synthetic oxides, and the detection limit was about 100 ppm.

The 22 samples, including sample 1, were also tested at NGDTC with a Nicolet Nexus 470 Fourier transfer infrared spectrometer. To collect the microscopic reflective infrared spectra, we used an MCT/B detector. A total of 32 sample scans were taken at a resolution of 8.0 cm^{-1} and a background gain of 4.0. The Omnic 6.1a software recommends a scanning wavenumber range of 4000–650 cm^{-1}, and the infrared
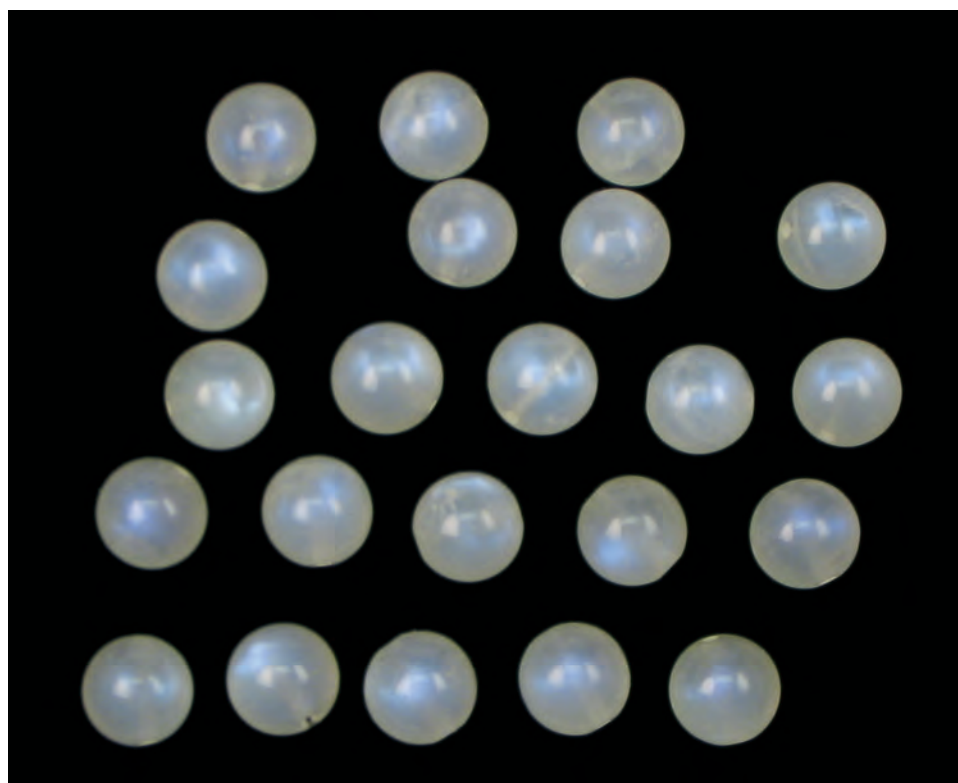
Figure 1. These 22 moonstone beads (4.01–4.31 ct) show blue adularescence. Testing showed that they were impregnated by a material with benzene structure. Photo by Jianjun Li.

spectrometer extended that range to 7800–400 cm⁻¹. Given the test requirements of the functional group (4000–2000 cm⁻¹) and the fingerprint region of silicate minerals in reflective infrared spectroscopy, the scanning wavenumber range was set at 1300–500 cm⁻¹.

Thompson and Wadsworth (1957) used infrared spectroscopy to determine albite and anorthite proportions in plagioclase. Li Jianjun et al. (2007) showed

In Brief

- A strand of 22 moonstone beads with blue adularescence displayed an irregular pattern of bluish white fluorescence, arousing suspicion of treatment.

- A combination of standard gemological testing and infrared spectral analysis showed that the moonstone had been impregnated by a material with benzene structure.

- While UV fluorescence can indicate the possibility of impregnation, infrared spectroscopy provides more conclusive evidence.

that the infrared spectra will vary when the samples are tested in different orientations. Thus the authors sought to obtain infrared spectra from a consistent crystal orientation to determine whether the samples

had the same composition. We used a simple orientation method: With the light source directed from the viewpoint, we looked for the area where the blue adularescence was the strongest and recorded the micro-infrared reflective spectra of each sample from the same orientation. Because the chemical composition of sample 1 was determined by both EPMA and microscopic reflective infrared spectroscopy, comparing the spectra of all other samples to that of sample 1 allowed us to determine whether they had the same composition.

Direct transmission was then applied to each whole bead to test the existence of the filling material using a DTGS KBr detector. A total of 32 sample scans were taken at a resolution of 8.0 cm⁻¹, a background gain of 1.0, and a scanning range of 7000–400 cm⁻¹. With air as the background, we collected the spectra of infrared rays through each whole bead.

RESULTS AND DISCUSSION

Gemological Properties. The samples' spot refractive index (RI) was approximately 1.53. The RI of the polished surface on sample 1 was 1.530–1.535. Because each sample contained a hole for stringing, specific gravity was not measured due to the possible complication caused by the holes. Most samples fluoresced weak to moderate blue-white to long-wave UV (table

TABLE 1. Data for the 22 moonstone samples.

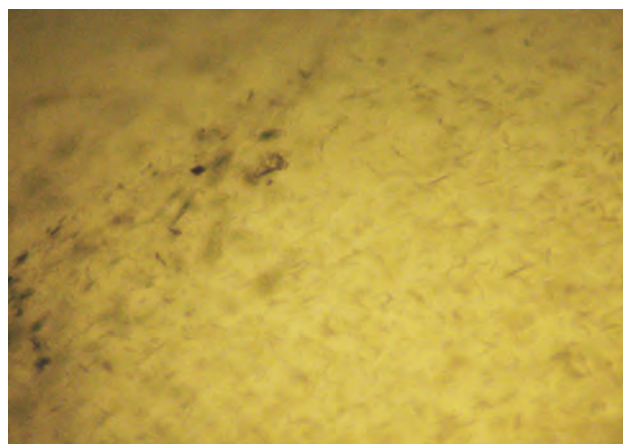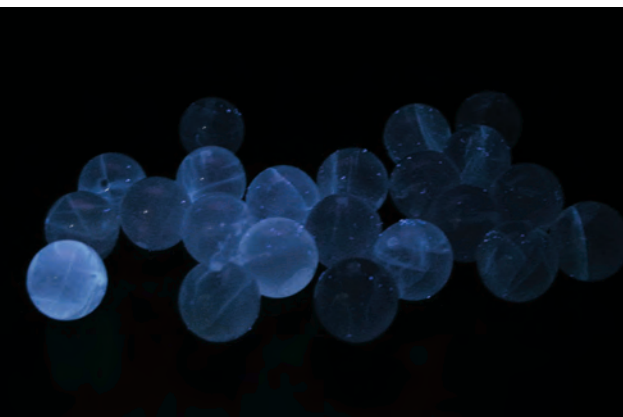| Sample number	Weight (ct)	Diameter (mm)	Long-wave UV reaction
1	4.21	8.55	Moderate
2–6			Moderate
7			Weak
8			Strong
9			Moderate
10, 11			Very weak
12			Moderate
13	4.01–4.31	8.41–8.63	Inert
14			Moderate
15			Weak
16			Strong
17, 18, 19			Moderate
20, 21			Very weak
22			Strong
1 (polished section)	3.75	8.55 x 6.36	Moderate

Figure 3. Brightfield illumination revealed fine, closely woven needle-shaped and schistose inclusions in this 4.18 ct moonstone. Photomicrograph by Jian-jun Li; magnified 70×.

1; figure 2 left). Only one sample was inert to long-wave, while three displayed strong fluorescence. Under short-wave UV their fluorescence was weaker or inert (figure 2, right). Because the fluorescence was visible along the fissures, we deduced that there might be some foreign material within them. Large fissures would contain more foreign substance, producing stronger fluorescence while the beads with no fissures were inert under UV fluorescence lamp.

Microscopic observation with brightfield illumination revealed a fine, closely woven needle-shaped schistose structure (or inclusions) in all samples (figure 3), while parallel twin layers were visible from certain directions (figure 4). There was a clear relationship between twinning planes and adularescence intensity: Adularescence was the strongest when the lighting and viewing directions were approximately perpendicular to the twinning planes. To keep a constant viewing direction, we collected micro-infrared reflectance spectra of all samples with the incident infrared rays perpendicular to the twinning planes.

Figure 2. Most of the moonstones fluoresced moderate to strong blue-white to long-wave UV, with the fluorescence visible in the fissures (left). Under short-wave UV (right), most of them either fluoresced weak bluish white (seen in the fissures) or were inert. Photo by Jianjun Li.
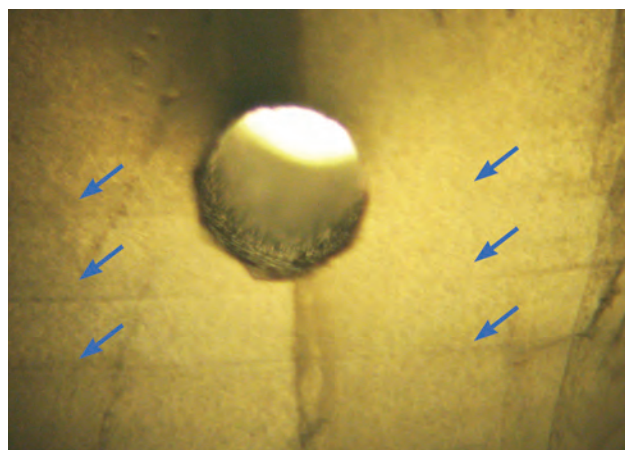
Figure 4. Fine internal parallel layers (polysynthetic twins) were observed with brightfield illumination. The circular feature near the center is a hole for stringing. Photomicrograph by Jianjun Li; magnified 30×.
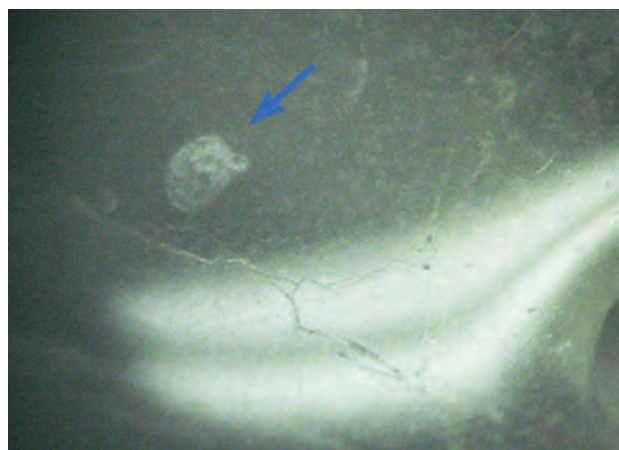

Figure 5. Veins were observed on the surface of the moonstones. Only one sample displayed residual flat, high-relief areas (holes or gas bubbles, indicated by the blue arrow). Photomicrograph by Jianjun Li; magnified 40×.

Observing these samples under the microscope with overhead illumination, we saw many veins on their surfaces, which appeared similar to the relief lines on filled aquamarine described by Li et al. (2009). Nevertheless, it was difficult to find the fractured reflective surfaces we would expect to accompany such veins; cracks were visible on the surface but barely penetrated the moonstone (figure 5). Meanwhile, an unusual residual flat high-relief area (again, see figure 5) was observed in sample 2, but not in any other moonstone. Similar high-relief areas are common microscopic features in filled aquamarine (Li et al., 2008) and thought to be products of incomplete filling. In other words, they were holes or gas bubbles.

Electron Microprobe Analysis. Complete electron microprobe data from six analytical points on sample 1 are listed in table 2. Based on the calculation method of Brandelik (2009), the three components of sample 1 are albite (Ab), orthoclase (Or), and anorthosite (An). The calculated composition of sample 1 was $Ab_{91.01}Or_{1.92}An_{7.07}$.

Infrared Spectroscopy Analysis. As figure 6 demonstrates, the 22 samples had very similar micro-infrared reflection spectra when they were collected at the strongest iridescence area (perpendicular to the polysynthetic twinning plane). This means the samples had identical mineral composition.

TABLE 2. Electron microprobe data of sample 1, calculated as $Ab_{91.01}Or_{1.92}An_{7.07}$.

No.	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	NiO	K_2O	Na_2O	P_2O_5	SO_3	Total
LJJ-1-1	66.796	0.008	20.704	0.008	0.044	0.011	1.513	0.008	nd	0.358	10.559	nd	nd	100.009
LJJ-1-2	66.572	nd	20.771	0.002	0.056	nd	1.472	nd	0.003	0.357	10.376	0.022	nd	99.631
LJJ-1-3	66.524	0.025	20.844	0.015	0.066	0.002	1.501	nd	nd	0.344	10.497	0.003	nd	99.821
LJJ-1-4	66.609	0.005	20.68	0.023	0.075	nd	1.46	nd	nd	0.312	10.567	nd	nd	99.731
LJJ-1-5	66.772	0.014	20.752	0.011	0.059	nd	1.521	nd	0.009	0.351	10.84	nd	nd	100.329
LJJ-1-6	66.573	nd	20.747	0.015	0.036	0.02	1.474	0.021	nd	0.317	10.749	nd	nd	99.952

nd = Not detected
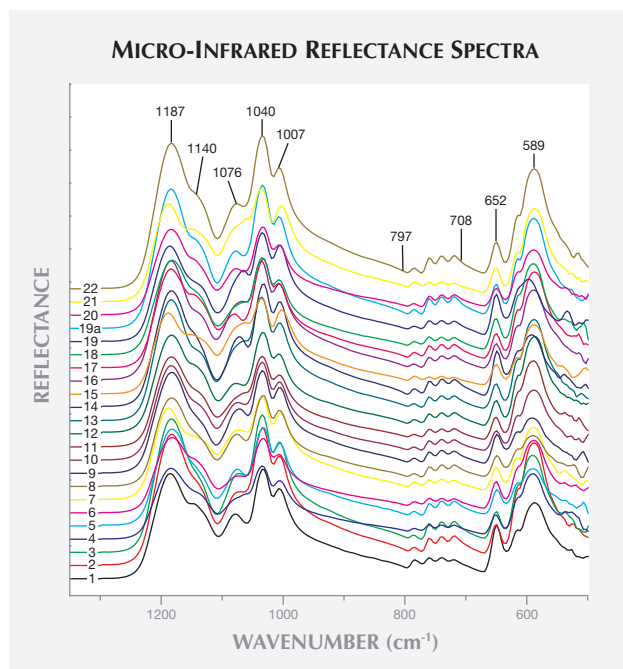
MICRO-INFRARED REFLECTANCE SPECTRA

Figure 6. Micro-infrared reflectance spectra of the moonstone samples were collected at the area of strongest adularescence (with incident infrared rays perpendicular to the polysynthetic twinning plane). The similar patterns indicate a nearly identical composition.

1200–900 cm^{-1}: This region shows the Si-O stretching vibration bands in SiO$_4$ tetrahedral polymers (Zhang et al., 1986). The 22 samples generally shared the same peaks or shoulders: 1187, 1040, and 1007 cm^{-1} peaks; a 1140 cm^{-1} shoulder; and a shoulder developing to a peak in the 1076 cm^{-1} region.

800–700 cm^{-1}: This region shows the Si-O bending vibration bands in SiO$_4$ tetrahedral polymers, as well as the Al-O stretching vibration bands in polyhedral polymers (Zhang et al., 1986). There were four peaks in all 22 samples.

Below 700 cm^{-1}: These are the stretching vibration bands of Al-O (and/or Si-O) and the bending vibration bands of O-Si-O (and/or O-Al-O), producing sharp peaks at 652 and 589 cm^{-1} and the shoulders between them (Zhang et al., 1986).

As figure 7 shows, the direct transmission infrared spectra of the beads with moderate or strong fluorescence collected from three orthogonal directions presented absorption peaks at 3053 and 3038 cm^{-1}, which is due to the cumulative frequency involved in the stretching vibration of C-H in benzene

and the bending vibration of the benzene ring (Johnson et al., 1999a,b). The 4344 cm^{-1} peak was due to the combined frequencies of the stretching and bending vibrations of C-H in CH$_3$ and CH$_2$ (Zhang et al., 1999), but the peak at about 4065 cm^{-1} was associated with the combined frequencies of the stretching vibrations of C-H and C-C bands from organic material. Interestingly, an earlier study of filled jadeite jade found a 4060 cm^{-1} absorption peak, confirming the filler material as epoxy or a similar substance (Zhang et al., 1999). Meanwhile, the infrared spectra of untreated moonstones from NGDTC's database

Figure 7. These direct transmission infrared spectra are from a filled moonstone with moderate fluorescence (sample 12) and untreated moonstones from NGDTC's database (a, b, and c). Top: The spectra of two white moonstones (a and b) and an orange moonstone (c) do not present peaks at 4344, 4065, 3053, and 3038 cm^{-1}. Bottom: The spectra of the filled moonstone, collected from three orthogonal directions, do show these four peaks. The 4344 cm^{-1} peak is from the combined frequency related to the stretching and bending vibration of C-H in the structure of CH$_2$, and the 4065 cm^{-1} peak is due to the combined frequencies of the C-H and C-C stretching vibrations. The 3053 and 3038 cm^{-1} peaks are associated with the combined frequencies of the C-H stretching vibration and the bending vibration of the benzene ring.

DIRECT TRANSMISSION INFRARED SPECTRA
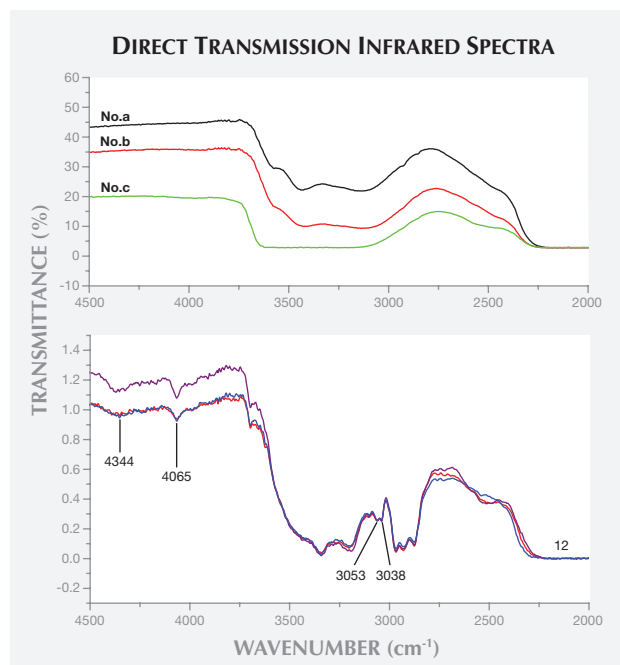
showed no peaks at 4344, 4065, 3053, or 3038 cm^{-1} (again, see figure 7).

Most of the beads showed absorption peaks at 2969, 2927, and 2869 cm^{-1}, associated with the stretching vibration of CH_2. Three strong absorption peaks at 2962, 2926, and 2872 cm^{-1} were frequently found by Johnson et al. (1999a) in a study of emerald filled by epoxy. The untreated moonstones did not present these three peaks (again, see figure 7).

From the above tests, we confirmed that all the beads were filled by a material with the structure of benzene.

There was a clear difference in the 2927–2869 cm^{-1} range between the strongly and weakly fluorescent samples. The strongly fluorescent moonstone had a strong absorption band, and the weakly fluorescent samples showed weak absorption (figure 8). This suggests that samples with stronger fluorescence contain more filling.

CONCLUSION

From standard gemological testing, electron microprobe analysis, and infrared spectral analysis of the fluorescent moonstone samples, we reached several conclusions. The sample tested by electron microprobe had a composition of $Ab_{91.01}Or_{1.92}An_{7.07}$, or albite. Micro-infrared reflectance spectroscopy showed that all 22 samples had a nearly identical composition. Microscopic examination revealed curved veins without the fractured, reflective surfaces expected to accompany them. These surface features plus the patterned fluorescence indicated that the samples were filled. 3053 and 3038 cm^{-1} peaks in their direct transmission infrared spectra confirmed that the beads were impregnated by a material with benzene structure. In terms of identification, UV fluorescence
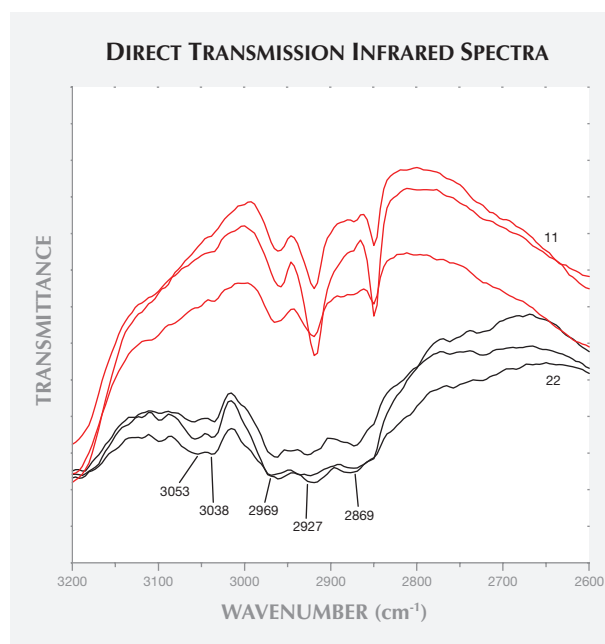

DIRECT TRANSMISSION INFRARED SPECTRA

Figure 8. Direct transmission infrared spectra are shown for samples with very weak fluorescence (sample 11) and strong fluorescence (sample 22). Each sample was examined from three orthogonal directions. The difference between the strongly fluorescent and weakly fluorescent samples at 3053, 3038, 2969, 2927, and 2869 cm^{-1} is associated with CH_2. Strong fluorescence is associated with a strong absorption band, and weak fluorescence with weak absorption.

could indicate the need for further testing, while the infrared spectra could provide more conclusive evidence of impregnation.

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REFERENCES

Brandelik A. (2009) CALCMIN—An EXCELTM Visual Basic application for calculating mineral structural formulae from electron microprobe analyses. *Computers & Geosciences*, No. 35, pp. 1540–1551.

Fritsch E., Wu S.-T, Moses T., McClure S.F., Moon M. (1992) Identification of bleached and polymer-impregnated jadeite. *G&G*, Vol. 28, No. 3, pp. 176–187, http://dx.doi.org/10.5741/GEMS.28.3.176.

Johnson M.L., Elen S., Muhlmeister S. (1999a) On the identification of various emerald filling substances. *G&G*, Vol. 35, No. 2, pp. 82–107, http://dx.doi.org/10.5741/GEMS.35.2.82.

——— (1999b) Characterization of some emerald filling substances. *G&G*, Vol. 35, No. 3, pp. 149–151.

Li J.J., Luo Y.P., Chen Zh., Meng L.J. (2007) Usefulness and limitations of using routine FTIR spectra for identifying gemstones compared with the use of classical FTIR spectra using KBr pellets. *Australian Gemmologist*, Vol. 23, No. 2, pp. 64–70.

Li J.J., Liu X.W., Chen Y.F. et al. (2008) Characteristics and identity of filled aquamarine. *China Gems*, Vol. 17, No. 1, pp. 187–189 (in Chinese).

Li J.J., Sun Y., Hao W.J., Luo H., Cheng Y.F., Liu H.F., Liu Y., Ye H., Fan Ch. X. (2009) Polymer-filled aquamarine. *G&G*, Vol. 45, No. 3, pp. 197–199.

Li J.J., Liu X.W., Li G.H. (2011) Methods for identifying the polymer-filled peristerite. *Journal of Gems and Gemmology*, Vol. 13, No. 4, pp. 43–46 (Chinese article with English abstract).

Thompson C.S., Wadsworth M.E. (1957) Determination of the composition of plagioclase feldspars by means of infrared spectroscopy. *American Mineralogist*, Vol. 42, Nos. 5–6, pp. 334–341.

Wang P., Pan Zh.L., Weng L.B. (1984) *Systematic Mineralogy* (in Chinese). Publishing House of Geoscience, pp. 402–403.

Wang Y.M., Yang M.X. (2008) The filling treatment of semi-precious gemstones. *Journal of Gems and Gemmology*, Vol. 10, No. 4, pp. 23–27 (Chinese article with English abstract).

Zhang B.L., Gao Y. (1999) Identification of B jade by FTIR spectrometer with near-IR fibre-optic probe accessory. *Journal of Gems and Gemmology*, Vol. 1, No. 2, pp. 25–28 (Chinese article with English abstract).

Zhang B.M., Yuan Y.M., Shen Sh.Y. (1986) The variation of infrared spectra of plagioclases from basic-ultrabasic intrusions in Yanbian and Panzhihua, Sichuan Province. *Earth Science*, Vol. 11, No. 6, pp. 616–623 (Chinese article with English abstract).