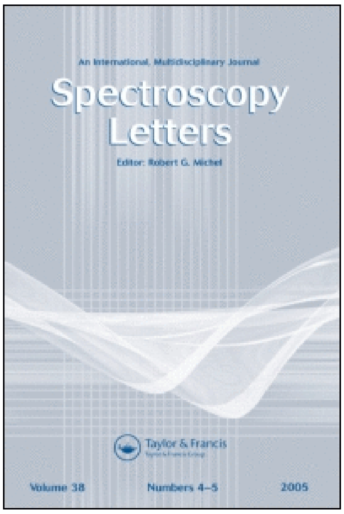

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The Application of Confocal Micro-Raman Spectrometer to Nondestructive Identification of Filled Gemstones

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The Application of Confocal Micro-Raman Spectrometer to Nondestructive Identification of Filled Gemstones

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ABSTRACT The technique of micro-Raman spectroscopy has the advantages of being nondestructive, high speed, high accuracy and also can be used for finite-precision analysis in combination with microscopy. In this paper, bleached and filled jadeite-jade and filled ruby were selected as the analysis objects, and then micro-Raman spectroscopy in combination with XRF and IR was carried out for detection and analyses. There were many microcracks observed in the micrograph of jadeite-jade, which is the result of bleaching with strong acid, and it was proved that these cracks were filled with epoxy resin by the diagnostic Raman shifts near 777, 1123, 1611, 2930, and 3065 cm^{-1}. Many cracks and white floccules were observed in the micrograph of filled ruby; This was the result of filling with lead glass and organic material. In addition, the broad and strong Raman shift near 1563 cm^{-1} was attributed to lead glass, and Raman shifts near 2331, 2874, and 3285 cm^{-1} were attributed to organic filler. This analysis method also can be applied for identification of other varieties of filled gemstones.

KEYWORDS bleached and filled jadeite-jade, filled ruby, identification, micro-Raman

INTRODUCTION

Although observed for the first time in 1928, the Raman effect has recently attracted attention in industry and in academic research. When a monochromatic light interacts with a sample, which acts as a scattering center, the light will be scattered as shown in Fig. 1, producing both inelastic scattering (Stokes scattering and anti-Stokes scattering) and elastic scattering (Rayleigh scattering) signals. The scattering signal carries abundant information about the molecular structure of the sample. The inelastic scattering is called Raman scattering. When the scattered photon loses energy to the molecule, its frequency will be lower than that of the incident photon. This kind of scattering is called Stokes Raman scattering. When the scattered photon absorbs energy from the molecule, its frequency will be higher than that of the incident photon. This kind of scattering is called anti-Stokes Raman scattering. The frequency shift of the Raman scattering signal is a

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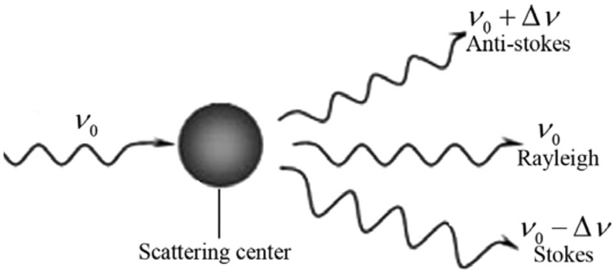

FIGURE 1 Scattering of light by a scattering center has elastic and inelastic components.

reflection of the vibration and rotational modes of the molecule. Featuring the advantages of noninvasiveness, high speed, and high accuracy, the Raman spectroscopic technique can be used for qualitative or even quantitative sample analysis.[1,2]

The study of gemstones, including their identification and examination, is one of the fields that require a nondestructive and effective analysis method due to the preciousness of the material. So, Raman technology was quickly introduced into the gemology field in the late 1900s, and it is becoming more and more important in gemstone or gem mineral research, and many related applications have been reported.[2–9] However, there are few reports about identifying natural, synthetic, and treated gemstones,[10–13] so that further application of Raman spectroscopy in the gemology field is restricted to some extent.

Nowadays, there are many artificial treated and synthetic gemstones in the market, such as treated diamond,[14] bleached and/or colorated jadeite-jade,[13] dyed pearl, filled or colored ruby, and so further; which has enormous impact on the jewelry industry. Generally, gemstone identification is mainly based on observation and tests performed by conventional instruments (microscopy, fluorescent lamp, refractometer), and a few large-scale instruments (FT-IR, XRF, UV-VIS-NIR, SEM-EDS, XRD, ICP-AES) were introduced and used for aiding identification. Filling is a type of treatment process in which a foreign substance is filled into surface-reaching cleavage or internal cracks of stone to enhance its appearance, strength, or apparent clarity. When the crack is extremely small or the concentration of filler is low, it is difficult to determine filled stones by general instruments. So, it is evident that confocal micro-Raman spectroscopy with high resolution is an ideal analysis method for identifying these filled stones.

MATERIALS AND METHODS

In this study, samples involving bleached and filled jadeite-jade and filled ruby were selected as the analysis objects; These types of filled stones were occasionally submitted to a gemstones testing center at East China university of science and technology for identification in the past 2 years. In addition, the corresponding natural stones were selected as comparative objects.

Collection of Raman spectra was performed on the condition of dark background and room temperature with a Renishaw inVia+Reflex Raman spectrometer. It exhibits two switchable excitation lasers (center wavelengths are 785 nm and 514 nm, respectively) and optical resolution of 1 cm^{-1}. The testing parameters are as follows: output power is 300 mW, and attenuation is set at 10% (jadeite) and 50% (ruby); exposure time is 10 s, and accumulation is 3; grating is 1200; calibration material is single crystalline silicon; eyepiece is 10× lens, and objective is optional fixing with 5×, 10×, 20×, and 50× lens; the diameter of confocal incidence light spot is about 1–2 μm; the traced spectral range is 4000–100 cm^{-1}, and the ordinate intensities are expressed in intensity (a.u.). Additionally, the micrographs are obtained at the same time in the analysis process.

Other nondestructive analysis methods, such as XRF and FT-IR, were used for analysis in this study. Quantitative analysis was performed with a XRF-1800 sequential X-ray fluorescence spectrometer, with the testing parameters Rh target, 40 KV power, 95 mA current, and 8°/min scanning speed. The element traced range is ^{8}O–^{92}U, the results of elements are expressed as their oxides, and the detection limit is >0.01% in concentration. The collection of IR spectrum was performed with a Magna-IR 550 Fourier transform infrared spectrometer, in which the optical resolution is 0.5 cm^{-1}. Transmission spectrum is traced in the range 4000–400 cm^{-1}, and the line intensities are expressed in transmittance (%).

RESULTS AND ANALYSES

Bleached and Filled Jadeite-Jade

The samples involving natural and treated jadeite-jades are shown in Fig. 2. The treated jadeite-jade has no obvious cracks under magnifier 10× and a natural green color, and the owner bought it at a price of

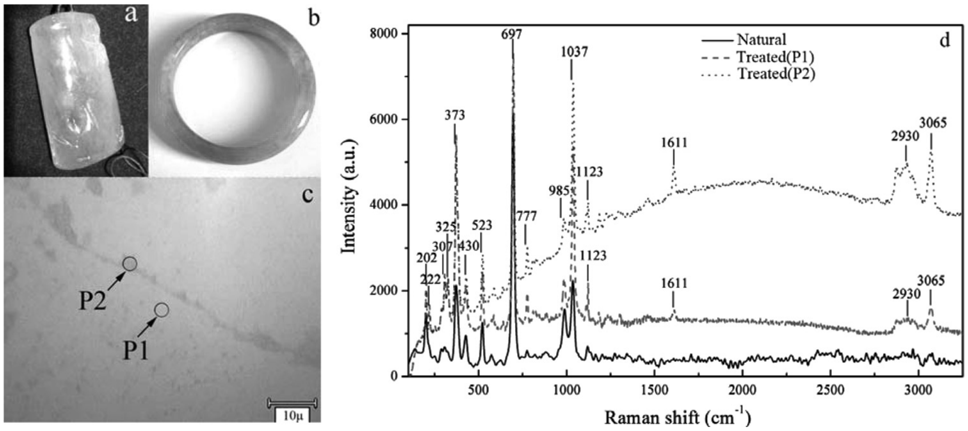

FIGURE 2 Jadeite-jade samples, microscopic testing graph, and corresponding Raman spectra; (a) natural jadeite-jade; (b) treated jadeite-jade; (c) micrographs (500×). In (c), there is a long and narrow crack, P_1 is far away from this crack, and P_2 is a position of this crack; (d) Raman spectra of natural and treated jadeite-jades.

more than $30,000 in Hong Kong. However, it presents many micro-cracks and filling evidence under optical microscopy with higher magnification. The micrographs (objective 50× lens, magnification 500×) were obtained by Raman spectrometer, and Raman spectra at different position (P_1 and P_2, shown in Fig. 2c) were subsequently collected. Additionally, Raman spectrum of natural jadeite-jade was also collected, and all the spectra are shown in Fig. 2d.

The jadeite-jade could be expressed as the structural formula $NaA1Si_2O_6$ for its main composition; the crystal structure is shown in Fig. 3. It is evident that the jadeite structure is composed of $[SiO_4]$ tetrahedron, $[M_1O_8]$ octahedron, and $[M_2O_6]$ octahedron, and the Raman shifts of primary mineral $NaA1Si_2O_6$ are constantly located in the range 1200–100 cm^{-1}, in which stretching modes ($Si–O_{str}$) of Si–O are located in the range 800–1200 cm^{-1}; bending modes ($Si–O_{bend}$) of Si–O are located in the range 400–800 cm^{-1}; rotary vibrations ($R([SiO_4])$) of $[SiO_4]$ groups are located in the range 200–400 cm^{-1}; and translatory vibrations ($T([SiO_4]^{4-})$) of $[SiO_4]$ groups and relative vibration modes of metallic ions (M_1 or M_2) are located in the range 100–200 cm^{-1}.[11] Additionally, the stretching modes attributed to inorganic groups are generally located in the range 1500–4000 cm^{-1}, such as $C–C_{str}$, $C{=}C_{str}$, $C–H_{str}$, and $O–H_{str}$. Comparing Raman spectra of natural and treated jadeite-jades in combination with assignments of Raman shifts, the analytic results and spectral features are concluded in Table 1.

According to the analytic results in Table 1, it is well konwn that Raman shifts near 305, 325, 373, 433, 523, 697, 985, and 1037 cm^{-1} are attributed to jadeite mineral, whether it is natural or treated; among them, Raman shifts near 374, 696, and 1037 cm^{-1} are considered as the diagnostic spectral lines of jadeite-jades owing to their strong spectral features.[6] In addition, several Raman shifts are observed near at 777, 1123, 1611, 2930, and

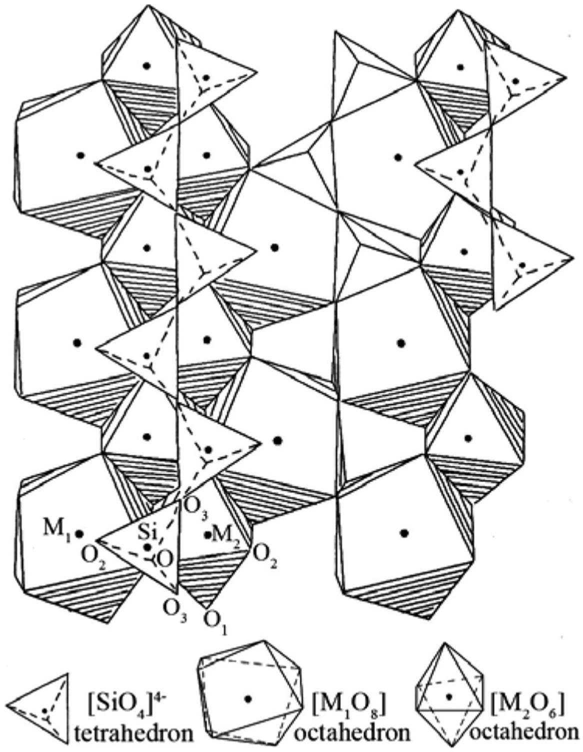

FIGURE 3 Crystal structure of jadeite. M_1 site is mainly occupied by monovalent cation, most commonly Na^+; $[M_2O_8]$ octahedron is relatively small, and M_2 site is mainly occupied by Al^{3+} in jadeite.

TABLE 1 **Raman Shifts of Natural and Treated Jadeite-Jades, Spectral Features, and Assignments**

Raman shifts (cm^{-1}) of jadeite-jade			
Natural (a)	Treated (P_1)	Treated (P_2)	Assignments
305 m	307 m	307 m	R[SiO_4]
325 m	325 m	325 m	
373 s	373 s	373 s	
433 m	430 m	430 m	Si–O_{bend} in [SiO_4] groups
523 m	523 m	523 m	
697 s	697 s	697 s	
	777 m	777 m	Out-of-plane bending of C–H in phenyl
985 m	985 m	985 m	Si–O_{str} in [SiO_4] groups
1037 s	1037 s	1037 s	
	1123 m	1123 m	C–O_{str} in epoxy group
	1611 w	1611 m	C=C_{str} in phenyl
	2930 m	2930 s	C–H_{str} in –CH_2 or –CH_3 group
	3065 m	3065 s	C–H_{str} in phenyl

3065 cm^{-1} in the spectra of treated jadeite-jade. They might be attributed to vibration modes of organic groups involving phenyl, C=C, and C–H. In general, there is no organic material in raw jadeite-jade, so the jadeite-jade might be treated by filling with organic material, most commonly epoxy resin or olefin.[11] In the bleaching and filling process, which is not widely accepted, epoxy resin is filled into the microcracks of jadeite-jade, so as to improve its strength and apparent clarity. In the waxing process, which is widely accepted, olefin is used for improving the transparency and luster of jadeite-jade. Because the main composition of olefin is a type of straight-chain alkane, it is doubtless that there is no apparent Raman shift in the range 2000–1500 cm^{-1} and 4000–3000 cm^{-1}. Thus, it is evident that the jadeite-jade has been treated by filling with epoxy resin, whose Raman shifts are observed at 777, 1123, 1611, 2930, and 3065 cm^{-1}. Furthermore, 1123, 1611, 2930, and 3065 cm^{-1} originate from strectching modes of C–O in epoxy groups, C=C in phenyls, C–H in alkyl groups, and C–H in phenyls respectively.

Microcracks are observed in the *micrographs* (Fig. 2c), which might be the result of acid bleaching. As for the Raman shifts related to epoxy resin, the spectral features of P_2 are commonly stronger than those of P_1. It is evident that epoxy resin is mainly concentrated in these microcracks.

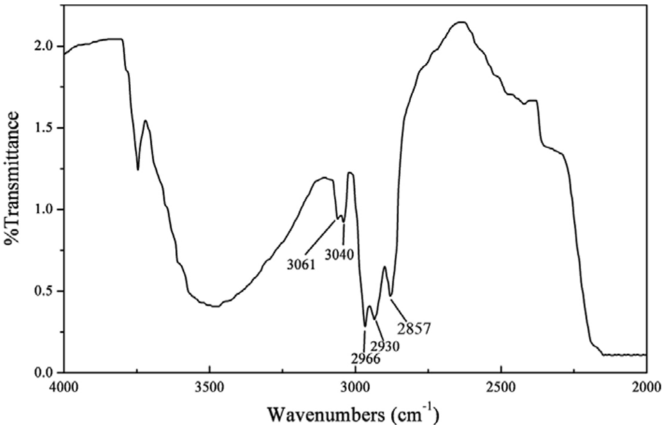

FIGURE 4 **Infrared spectrum of treated jadeite-jade in the range 4000–2000 cm^{-1}.**

The IR spectrum of treated jadeite-jade was collected *in addition to* Raman spectroscopy. However, the sample was so thick that optical transmittance in the range 2000–400 cm^{-1} is low. Thus, its IR spectrum in the range 4000–2000 cm^{-1} is shown in Fig. 4. There are five absorption bands observed at 3061, 3040, 2966, 2930, and 2857 cm^{-1} that are worth notice. The applicaton of *the* infrared spectrometer to identification of bleached and filled jadeite-jades has been reported by Chen et al.[16] It is evident that bands 3061 and 3040 cm^{-1} are attributed to stretching modes of C–H in phenyls, bands 2966, 2930, and 2857 cm^{-1} are attributed to stretching modes of C–H in alkyl groups of epoxy resin. As for olefin, it does not have apparent band in the range 4000–3000 cm^{-1}, which is obviously different from epoxy resin. Therefore, it is also confirmed that the jadeite-jade has been filled with epoxy resin; this analytic result equates with the result obtained by Raman spectroscopy.

Filled Ruby

The ruby samples involving natural and treated stones are shown in Fig. 5. By testing and researching, it was approved that ruby in Fig. 5b has been treated by filling with inorganic and organic material. It is a new and advanced treating process, so that this type of filled ruby, which could be frequently encountered in the market in the past 2 years, presents a bigger potential for deception. According to the micrographs in Fig. 5c (objective 5× lens, magnification 50×), the Raman spectra of treated ruby focusing on different position (P_1 and P_2) were

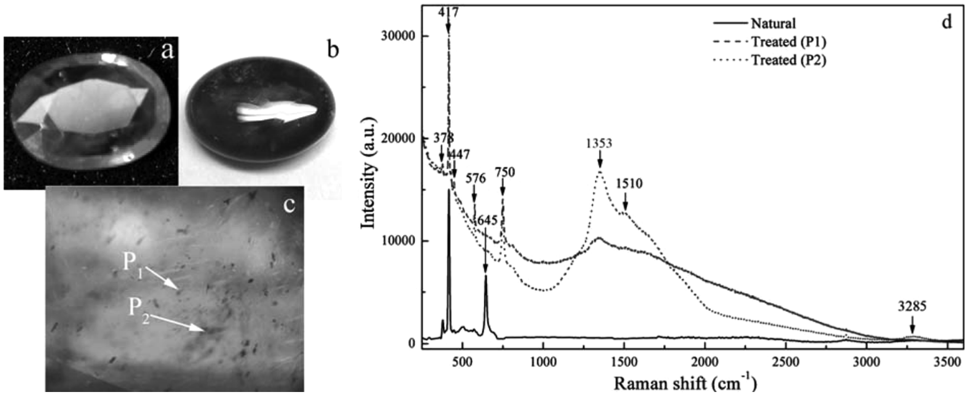

FIGURE 5 Ruby samples, microscopic testing graph, and corresponding Raman spectra; (a) natural ruby; (b) treated ruby, which presents many macroscopic white floccules (c) microscopic testing graph (50×), in which there are many floccules and a few of spherical bubble; floccules in the area of P_2 are much more common than in the area of P_1; (d) Raman spectra of natural and treated rubies.

collected with incident light polarized perpendicular to the globoidal center. In addition, Raman spectrum of natural ruby was also collected with incident light polarized perpendicular to the table facet; all the Raman spectra are shown in Fig. 5d.

Ruby is a type of corundum gemstone that belongs to the D_{3d} space group with two formula units of Al_2O_3 per unit primitive cell of the trigonal system; $[AlO_6]$ octahedron is the main structural cell. According to the D_{3d}^6 symmetry and $2A_{1g} + 5E_g$ active phonon modes, the Raman spectrum of ruby is expected to have seven Raman shifts with maxima at 378, 418, 432, 451, 578, 645, and 751 cm^{-1}.[5,15] Therefore, Raman shifts near 378, 417, 447, 576, 645, and 750 cm^{-1} in this paper originated from bending and stretching modes of $[AlO_6]$ groups in ruby, and 417 cm^{-1} presents the strongest spectral feature. It is known that Raman shift 645 cm^{-1} is at full strength when incident light is parallel to the *c*-axis, but it would vanish and two new Raman shifts appear at 576 and 749 cm^{-1} when incident light was polarized perpendicular to the *c*-axis.[17] Therefore, it is evident that the table facet of natural ruby is polarized perpendicular to the *c*-axis, whereas the globoidal center of treated ruby is parallel to the *c*-axis; the latter phenomenon is rarely encountered in natural stone but usually could be found in synthetic or treated stone.

Obviously, Raman shift attributed to $[AlO_6]$ groups in ruby is located in the range 350–800 nm, so other Raman shifts exceeding this range might be attributed to filler or natural inclusion, that is there are two or more Raman shifts in the range 800–2000 cm^{-1}, such as 1353 and 1510 cm^{-1}, and there are many Raman shifts in the range 2000–3500 cm^{-1}, such as 3285 cm^{-1}.

The spectral characteristic of treated ruby in the range 800–2000 cm^{-1} with focusing on the area of P_2 is extremely similar to that of lead glass reported by Vandenabeele and Moens,[2] so it is assumed that this ruby has been treated by filling with lead glass. The Raman spectrum of lead glass counterfeited as ruby was also collected and is shown in Fig. 6. It is evident that the Raman spectra of lead glass (Fig. 6b) and ruby (Fig. 6a) in the range 800–2000 cm^{-1} present similar spectral feature, that is the maxima of Raman shift is near 1356 cm^{-1}, and its FWHM is about 500 cm^{-1}. Thus it could be considered that the ruby has been treated by filling with lead glass under high temperature.

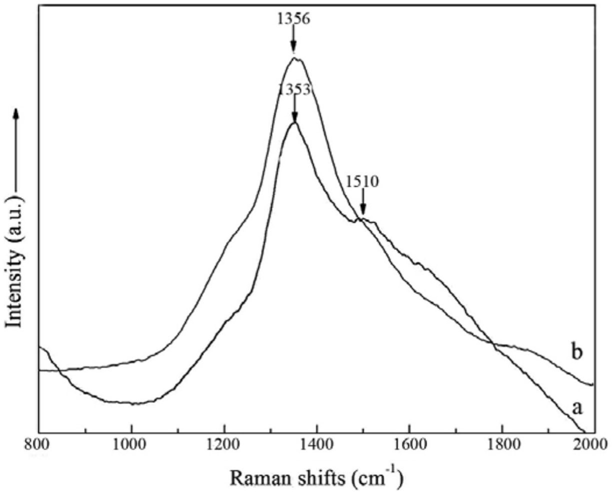

FIGURE 6 Raman spectra of treated ruby (P_2) and lead glass in the range 800–2000 cm^{-1}; (a) treated ruby; (b) lead glass.

TABLE 2 **Analytic Result of Treated Ruby (b) Tested by XRF**

Analytes	Al_2O_3	SiO_2	PbO	Fe_2O_3	Cr_2O_3	K_2O
Results (%)	93.82	4.40	1.16	0.44	0.16	0.02

The quantitative analysis on treated ruby was carried out by XRF, and the result is shown in Table 2. It is evident that treated ruby has huge amounts of elements Si (SiO_2 4.40%) and Pb (PbO 1.16%). Generally, the concentrations of compositions SiO_2 and PbO in natural ruby are respectively lower than 1% and 0.1%; Pb cannot even be detected by XRF. Therefore, it is approved that lead glass (the main compositions are PbO and SiO_2) has been filled into this ruby; it is well matched with the analytic result provided by micro-Raman spectrum.

Figure 7 shows the Raman spectral range 2200–3500 cm^{-1} of treated ruby (P_2), in which two sharp Raman shifts at 2331, 2874 cm^{-1} and one broad Raman shift at approximately 3285 cm^{-1} are observed. However, these Raman shifts have not been reported in previous references related to ruby. It could be considered that 3285 cm^{-1} originates from the stretching modes of O–H (O–H_{str}) in hydroxyl groups, 2874 cm^{-1} is attributed to stretching modes of C–H (C–H_{str}) in alkyl groups, and 2331 cm^{-1} may be related to stretching modes of C≡C (C≡C_{str}) in alkynyl groups or cumulated double bond. Thus, it is proved that treated ruby also has been filled with organic material, which might be a type of oil.

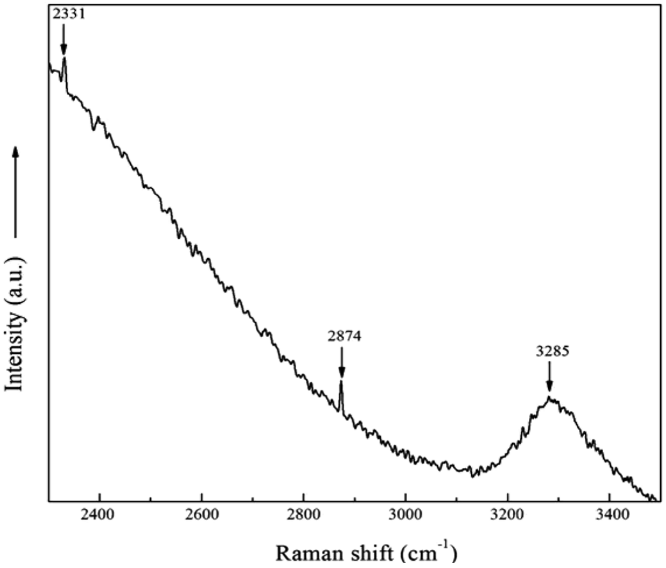

FIGURE 7 **Raman spectrum of treated ruby (P_2) in the range 2300–3500 cm^{-1}.**

According to Raman spectral analysis in combination with quantitative analysis performed by XRF, it is proved that the ruby was treated by a filling process with both inorganic (lead glass) and organic (possibly oil) materials. Therefore, it is speculated that the treated ruby was first heat treated at high temperature (1300–1500°C), so as to improve its color and clear up internal impurity, filling with lead glass was performed at the same time, so as to cover up cracks and enhance its apparent clarity; and filling with organic oil was then performed at lower temperature, so as to further cover up cracks and enhance its apparent clarity. Although the treatment process is not quite sophisticated, this type of treated ruby has greater fraudulence than any treated ruby previously encountered. Owing to the difficulty in identifying treated ruby and the limitation of analysis methods, many testing stations in China refuse to identify ruby for trade companies and consumers.

DISCUSSION

There are many varieties of filled gemstones that could be encountered in the market, such as diamond treated by laser drilling and glass filling,[14] ruby treated by filling with inorganic (lead glass) and/or organic (oil) material, jadeite-jade treated by acid bleaching and epoxy resin filling, opal treated by filling with colored oil, emerald treated by filling with colored oil or polymer, turquoise treated by polymer filling, and so forth. As the treatment technology advances and treaters become more experienced, detection of these filled stones becomes a serious challenge. Additionally, it also requires jewelers to discover treated stones in market transactions.

Although use of confocal micro-Raman spectrometer for identification in the gemology field is not a new approach, its application is limited *to a* few reports about gemstone identification and by high price of spectrometer. However, it is doubtless that micro-Raman could play a much more important role in this field. As for filled stones, the filler is mainly concentrated in the cracks, thus, the detection process carried out by confocal micro-Raman spectrometer is as follows: first, select proper objective lens and obtain a clear *micrograph* at proper position of *the* stone; second, focus light spot to a diameter of

1–2 μm and collect Raman spectra at different positions with crack or not; finally, compare and analyze Raman spectra, and point out the Raman shifts attributed to filler, which is commonly organic material and glass. Because of the scant data published and its own application limitation, micro-Raman spectrometer for gemstone identification should be used in combination with other auxiliary equipment, such as XRF, SEM-EDS, IR, UV-VIS, and NIR.

CONCLUSION

Micro-Raman spectroscopy has the advantages of being nondestructive, high speed, and high accuracy, and also can be used for finite-precision analysis in combination with *micrograph*. In this study, bleached and filled jadeite-jade and filled ruby were selected as the analysis objects, and micro-Raman spectroscopy in combination with XRF and IR was carried out for detection and analyses. There ware many microcracks observed in *micrograph* of jadeite-jade, which is the result of bleaching with strong acid, and it was proved that these cracks were filled with epoxy resin by the diagnostic Raman shifts near 777, 1123, 1611, 2930, and 3065 cm^{-1}. Many cracks and white floccules were observed in the *micrograph* of filled ruby; This was the result of filling with lead glass and organic material. In addition, the broad and strong Raman shift near 1563 cm^{-1} was attributed to lead glass, and Raman shifts near 2331, 2874, and 3285 cm^{-1} were attributed to organic filler. The analysis method also can be applied for identification of other varieties of filled gemstones, such as diamond treated by laser drilling and glass filling, or emerald treated by filling with colored oil or polymer. Thus, it is doubtless that micro-Raman spectroscopy could play a much more important role in the gemology field.

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