The Application of a Mini-Raman Spectrometer on Gemstones Identification and Examination

FAN Jian-Liang, LIU Xue-Liang, and GUO Shou-Guo
Gemstone Testing Center, East China University of
Science and Technology, Shanghai, 200237 China, P.R.C.
Translated and prepared by
Ken Li and Kevin Carr
B&W Tek Inc., Newark, DE 19713 USA

Fig. 3 MiniRam™ II Raman spectrometer is completely field portable.

Abstract: Offering comparable performance as scientific-grade Raman spectrometers, a portable mini-Raman spectrometer can realize none-invasive sample analysis with high speed and accuracy. This article gives a brief introduction of Raman spectroscopic technology and its application in the field of gemstone identification and examination. Several examples are provided, including: identification of diamond from zircon through Raman spectra difference; identification of unknown gemstone through characteristic Raman band; identification of isomorph or subspecies of gemstone through shift in characteristic Raman band; identification of gemstone origin through Raman analysis of gemstone inclusion.

Keywords: Mini-Raman spectrometer, Gemstone, Identification

Introduction

The Raman Effect was discovered in 1928. However, it was only recently that the Raman Effect was utilized as an analytical technique [1]. Featuring the advantages of non-invasiveness, high speed, and high accuracy, the Raman spectroscopic technique can be used for qualitative or quantitative sample analysis [2, 3]. According to the ScienceDirect® database (Elsevier B.V.), published scientific papers relating to Raman technology have increased with dramatic speed from 1990 to 2007 (see Fig. 1). Apparently, this indicates that Raman spectroscopic technology is becoming more and more important in both industrial and research fields. The study of gemstones, including their identification and examination, is one of the fields that requires a non-invasive and effective analytical method due to the preciousness of the material. However, conventional scientific-grade Raman spectroscopic systems are both cumbersome in size and expensive in cost, which limits their application in the gemstone research field. Recently, B&W Tek, Inc. of Newark, DE, USA developed several types of portable, lightweight Raman spectrometers (MiniRam™) to fill the niche. Through cooperation with the East China University of Science and Technology, a standard Raman spectroscopic database of commonly know gemstones has been established. It is expected that the mini-Raman spectrometer will play an important role in the identification and examination of gemstones.

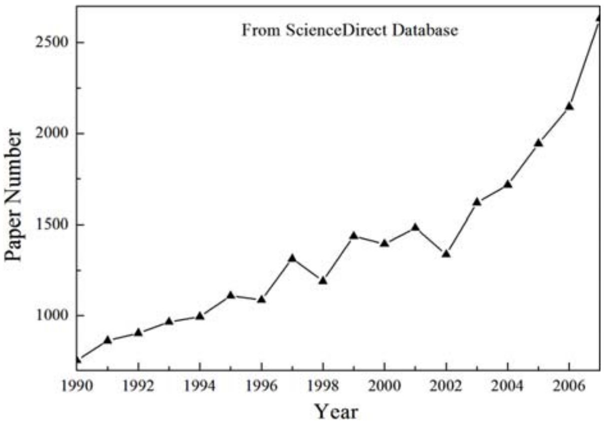

Fig. 1 Published scientific papers relating to Raman technology (data from ScienceDirect database).

1. Operating principle and specifications of the Mini-Raman spectrometer

When a monochromatic light interacts with a sample, which acts as a scattering center, the light will be scattered as shown in Fig. 2, 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 reflection of the vibration and rotational modes of the molecule. Consequently the Raman spectrum (a relation of Raman scattering intensity vs. frequency shift) can be utilized to analyze the molecular structure of the material.

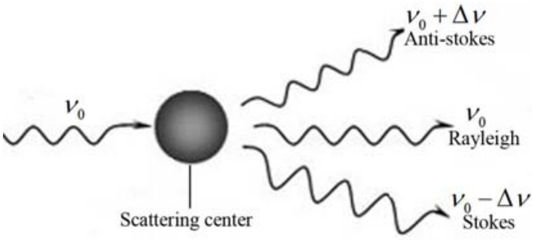

Fig. 2 Scattering of light by a scattering center has elastic and inelastic components.

The Mini-Raman spectrometer may be supplied with either of two excitation wavelengths, i.e. 785 nm or 532 nm. The following spectra were measured with a MiniRam II spectrometer from B&W Tek (see Fig. 3), which has a spectral coverage from 175 cm^{-1} to 3100 cm^{-1} and a spectral resolution of 10 cm^{-1}. The excitation laser in the MiniRam II used in this study is a high power (>300 mW), spectrum stabilized 785 nm laser diode. The integration time of the spectrometer can be adjusted from 9 ms to 65535 ms to adapt for different Raman signal levels.

2. Gemstone identification and examination

Gemstone identification

Diamond, ruby, sapphire, emerald, and chrysoberyl are the five ‘most precious’ gemstones in the world, while jadeite and nephrite are also very popular gemstones in the Chinese market. The natural gemstones are very rare and often highly priced. To cater to the demand of average consumers, certain substitutes for natural gemstone are distributed in the market. These substitutes bear similar appearance (such as color, gloss, etc.) to the natural gemstone. When they are made into jewelry, it becomes extremely difficult to identify these substitutes since typical gemstone testing can no longer be performed. However, the Raman spectra can reveal the composition of the gemstone and differentiate natural gemstone from their substitutes.

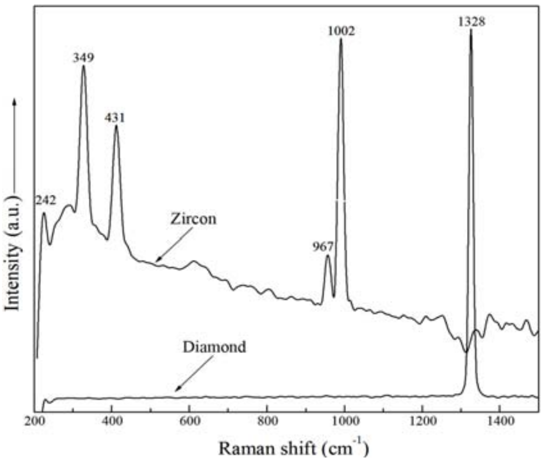

Fig.4 Raman spectra of diamond and zircon are distinctly different.

Zircon and cubic zirconia are often used in the market as substitutes for diamonds. Many customers have been cheated by these ‘fake’ diamonds. A Raman spectrum analysis can easily differentiate diamond from zircon as shown in Fig. 4. Apparently, the spectrum of diamond shows only one very strong and sharp Raman band at around 1328 cm^{-1}, which corresponds to the C-C stretching mode. This Raman signal is so strong that the spectrometer requires an integration time of only 100 ms to obtain a clear Raman spectrum. In contrast, the spectrum of zircon shows multiple Raman bands at around 349, 431, 967 and 1002 cm^{-1}, in which the 349 and 431 cm^{-1} bands correspond to the Si-O bending mode whereas the 967 and 1002 cm^{-1} bands correspond to the Si-O stretching mode. Thus the Raman spectrum analysis can help to easily identify diamond from its substitutes.

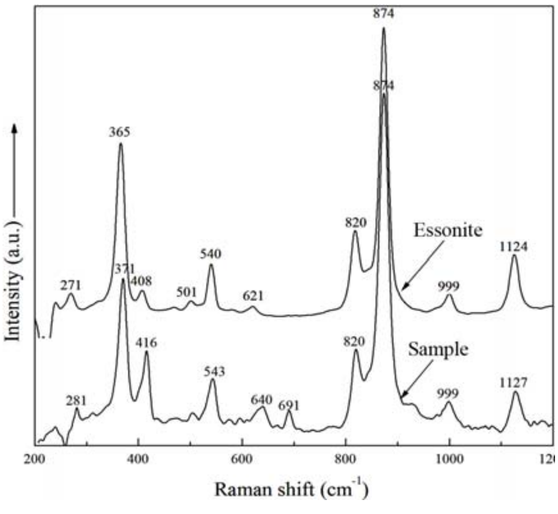

Fig.5 Raman spectra of an unknown sample and Grossular show distinct similarities.

Identification of an unknown gemstone sample

Sometimes it is hard to identify an unknown gemstone sample using its physical properties such as refractive index, density, or other optical properties. For example, a kind of yellow colored jade was introduced into the gemstone market in 2006. This yellow colored jade was misjudged as yellow jadeite due to a similar appearance. However, the refractive index (1.73), density (3.50g/cm^3), and other physical properties of this yellow colored jade is significantly different from that of jadeite. The Raman spectrum of this jade sample was measured and compared with the standard Raman spectra of gemstones in our database. The results show that its Raman spectrum matches well with that of Grossular as shown in Fig. 5. So this kind of ‘jade’ is likely a polymorphic form of Grossular. The Raman bands at 820, 874, 999 and 1127 cm^{-1} correspond to Si-O stretching mode in $[S_iO_4]^{4-}$; the 543 and 640 cm^{-1} band corresponds to Si-O bending mode; and the 281, 371 and 416 cm^{-1} band corresponds to rotational mode of $[S_iO_4]^{4-}$ [5].

Study on isomorphism in gemstone

Isomorphism is an important phenomenon for gemstones since the color of most gemstones is caused by impurities in the form of an isomorph. The inclusion of isomorphic impurities also causes changes in the physical (density, refractive index, gloss) and optical property (Raman spectrum, absorption spectrum) of the gemstone.

One example is garnets, which are nesosilicates having the general formula of $X_3Y_2\,[SiO4]_3$, where the X site is generally occupied by Mg^{2+}、Fe^{2+}、Mn^{2+}、Ca^{2+} and the Y site by Al^{3+}、Fe^{3+}、Cr^{3+}、Ti^{3+}、V^{3+}. According to the type and content of the metallic cations in X, Y site, the garnets can be categorized into pyralspite garnets (general formula $(Mg，Fe，Mn)_3Al_2[SiO_4]_3$, including Pyrope, Almandine, and Spessartine) and ugrandite garnets (general formula $Ca_3(Al, Fe, Cr)_2[SiO_4]_3$, including Grossular, Andradite, and Ugrandite). Fig. 6 shows the Raman spectra of Pyrope, Almandine, Spessartine, and Grossular garnets, in which the Y site is occupied by Al^{3+}. The Raman bands and the corresponding vibration modes of these garnets are listed in Table 1 [6]. The Raman bands in the 800-1200 cm^{-1} region are related to the Si-O stretching mode ($Si\text{-}O_{Str}$); the Raman bands in the 400-650 cm^{-1} region are related to the Si-O bending mode ($Si\text{-}O_{Bend}$); and those in the 200-400 cm^{-1} region are related to the rotational ($R(SiO_4)^{4-}$) and translation ($T(SiO_4)^{4-}$) vibration mode of $(S_iO_4)^{4-}$.

	$Si\text{-}O_{Str}$		$Si\text{-}O_{Bend}$	$R(SiO_4)^{4-}$	
	A_{1g}	E_g+F_{2g}	A_{1g}	A_{1g}	E_g+F_{2g}
(Pyrope)	912	1047、854	552	355	/
(Almandine)	904	1025、850	547	340	365
(Spessartine)	900	1022、844	543	341	365
(Grossular)	874	999、820	540	365	408

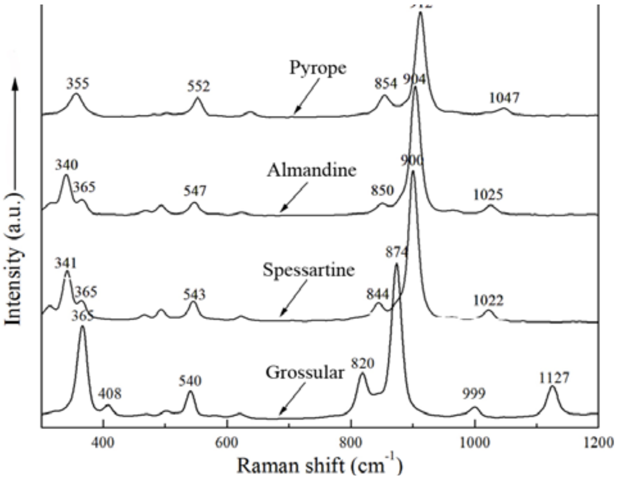

Table 1 & Fig. 6 Raman spectra of different garnets correspond to the mode assignments of Si-O and SiO_4.

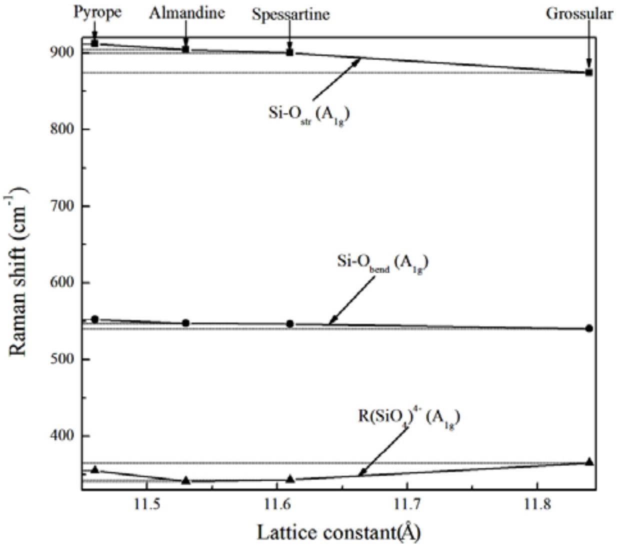

Fig. 6 Raman shifts of garnets decrease with increased lattice constant.

Fig. 6 shows the value of Raman shift for the $Si\text{-}O_{Str}$、$Si\text{-}O_{Bend}$ and $R(SiO_4)^{4-}$ band in relation to the lattice constant for different types of garnets. It is apparent that the Raman shift of $Si\text{-}O_{Str}$ mode decreases with increased lattice constant. For example, the Raman shift of $Si\text{-}O_{Str}$ mode decreases from 912 cm^{-1} in Pyrope by 38 cm^{-1} to 874 cm^{-1} in Grossular. The Raman shift of $Si\text{-}O_{Bend}$ mode also decreases with increased lattice constant, such as from 552 cm^{-1} in Pyrope to 540 cm^{-1} in Grossular. This decrease in Raman shift is caused by the decrease of Si-O bond energy. Since the divalent cations in the X site have different diameters ($Ca^{2+}>Mn^{2+}>Fe^{2+}>Mg^{2+}$), the corresponding $[XO_8]$ hexahedrons thus have different lattice constants. A larger lattice constant results in lower Si-O bond energy, thus a reduction in the Raman shift of $Si\text{-}O_{Str}$、$Si\text{-}O_{Bend}$ modes, whose energy are proportional to the Si-O bond energy. In contrast, the variation of the $R(SiO_4)^{4-}$ band Raman shift does not show apparent trend with lattice constant. This relation of Raman shift with metallic cation type and content provides important evidence for the identification of isomorph or subspecies of gemstones.

Examination of inclusions in a mineral [7]

Study of the inclusions is an important method used in mineralogy, geology, and gemstone examination [8-11]. Raman spectroscopic analysis of the inclusion can provide important information regarding the origin, quality, and mineragenetic condition of the gemstone. Shown in Fig. 7a is the measured Raman spectrum of a ruby sample when the excitation laser light is focused in the vicinity of one of its inclusions. It is worth to note that this Raman spectrum shows two Raman bands at 710 and 1085 cm^{-1} in addition to the Raman bands at 378, 417, 430, 447, 576 and 750 cm^{-1}, which are known to be related to the $[AlO_6]$ vibration modes. This two additional Raman bands are produced by the substance in the inclusion. By comparing this Raman spectrum with that of calcite crystal (Fig. 7b), it is clear that these two Raman bands match well with the Raman bands of calcite. Thus the inclusion substance of the ruby is calcite and the 710 and 1085 cm^{-1} Raman bands are related to the bending and stretching modes of $[CO_3]^{2-}$, respectively. It can also be concluded that this ruby sample is natural without undergoing heat treatment.

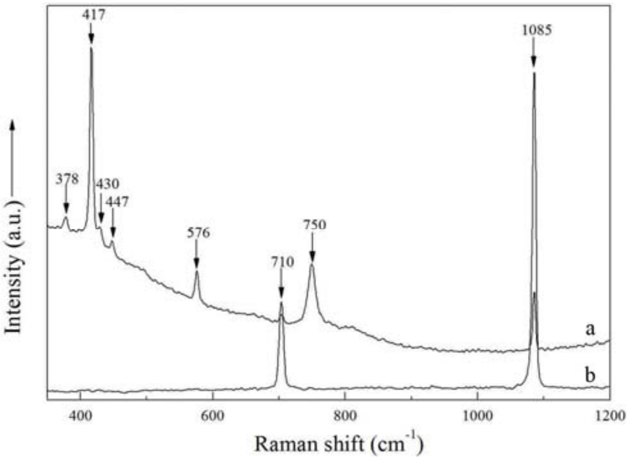

Fig.7 Raman spectra of "a-Ruby" and "b-calcite crystal" reveal that the inclusion substance in the ruby is calcite.

3. Some limitations of the miniature Raman spectrometer

The current version of miniature Raman spectrometer suffers from the following drawbacks, which limit its application in gemstone identification and examination.

(1) Resolution: The resolution of the miniature Raman spectrometer (5-10 cm^{-1}) is relatively lower that that of scientific grade Raman spectrometers (<1 cm^{-1}). Thus some weak and narrow Raman bands can not be effectively detected. The low resolution also prohibits quantitative measurement of the FWHM bandwidth of a specific Raman band.

(2) Spectral coverage range: The miniature Raman spectrometer provides a spectral coverage from 200 to 2000 cm^{-1}, whereas the Raman bands of most vibration modes of organic molecules fall around 3000 cm^{-1}. Thus the miniature Raman spectrometer can not be used to identify those fake gemstones filled with organic substances, such as those epoxy filled jadeite, ruby, emerald, etc.

(3) Fluorescence: Some samples, such as those containing rare earth elements, transit metal elements, and organic substance, exhibit strong fluorescence background under laser excitation. When the fluorescence background is too strong, the Raman signal cannot be detected.

(4) Probe: The current version of miniature Raman spectrometer lacks a microscope probe. Thus the laser light can not be accurately focused to examine a specific point in the sample, such as those inclusions, fillings, and cracks in the gemstone.

4. Conclusion

Raman spectroscopy technology can be used for qualitative or quantitative sample analysis. It features the advantage of non-invasiveness, high speed and high accuracy. The portable miniature Raman spectrometer offers comparable performance as the scientific grade Raman spectrometer. With advances in the basic research of Raman spectroscopic technology and the enrichment of gemstone Raman spectra database, it will play an even more important role in the identification and examination of gemstones.

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