Raman Spectroscopic Inspection and Analysis of Zircon Inclusion in Corundum
-Effect of Heat Treatment on Zircon Inclusion

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1. Introduction

In the field of gemology, the research on inclusions in gemstone is considered as one of the very important topics. Whether a gemstone has been heat treated or the origin of a gemstone can be inferred from its inclusion. Since Raman spectrometer is a nondestructive quantitative analytical tool, with its penetrative nature, it has long been an ideal instrumentation for the study of inclusions in gemstones.

It is inevitable that ruby and sapphire contain inclusions, the existence of which normally affects the transparency and hardness, and hence the value and price of the hosting gemstone. One of the most commonly seen inclusions of corundum is zircon. Heat treatment tends to result in the decomposition of zircon to its component oxides. The sub-solidus decomposition reaction of zircon takes place at about 1400˚C, i.e., zircon decomposes to form baddeleyite and a amorphous glassy SiO_2-rich phase. Inspected and analyzed by nondestructive 785 nm micro-Raman spectrometer, we found that the position, FWHM (full width at half maxima) and intensity of the characteristic peak of included zircon have changed after heat treatment. In addition, the amorphous glassy SiO_2-rich phase was excited to produce high background fluorescence in the spectral range 200~600 cm^{-1}, accompanied by PL spectrum.

The effect and variation of zircon Raman peaks with respect to different temperature during heat treatment and the excited PL peaks can be used as a criterion for the justification of whether these ruby and sapphire have been heat treated at high temperature. Moreover, from their intensity and FWHM in Raman and PL peaks, with also can estimate the temperature of heat treatment.

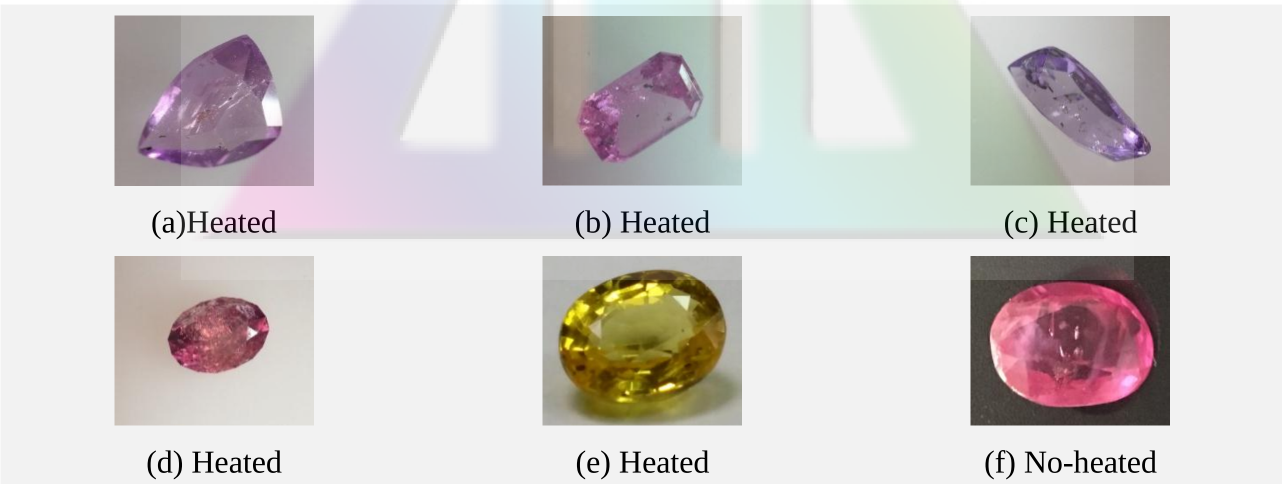
2. Instrumentation

Throughout the experiment, the Raman spectrometer UID-A2 Micro-Raman System (UID Analysis)(**Pic.1, Table I**) was used. The wavelength of the laser beam and the power used for the experiment are 785 nm and 450 mw, respectively. Using multi-mode laser specification, our laser spot covers a large area of spatial resolution exceeding 30 *u*m on samples, which allows a homogeneous sampling of the Raman signal. The spectral range of the spectrometer used for data acquisition was 250~2350 cm^{-1}. The tested samples of Corundum were provided by Taiwan Central Gem Laboratory, Wu Chao-Ming Gemological Institute and Laboratory, and Lai Tai-An Gem Laboratory .

Pic.1 UID-A2+Micro

Table I Micro-Raman system specifications

Spatial resolution : >25 μm (Multi-Mode, 10x Objective)	
CMOS Resolution : ~0.3 um / pixel	Objectives : 4 x, 10x, 40x ,100x
Laser Spot On Target	Illumination & Camera



Pic.2 Sample photos in this article

3. Inspection and Analysis

3.1 Spectral Analysis of Non-Heat Treated Zircon Inclusion

By eyeball observation, the non-heat treated inclusion of zircon looks crystal clear in appearance (see Photos 1a, 1b). By means of 785 nm model micro-Raman spectrometer, the spectrum of zircon inclusion is collected and shown in Figure 1. Since the inclusion lies in about 3 mm underneath the ruby crystal, it is inevitable that in addition to Raman signals, the spectrum also contains signals from ruby. The characteristic Raman peaks of zircon are the ν_3 mode (anti-symmetric stretching) and ν_1 mode (symmetric stretching), which show up at 1011 cm^{-1} and 977 cm^{-1}, respectively. There is some deviation in the peak position of Raman peaks under high pressure compared with pure zircon in free state under atmosphere pressure (1007 cm^{-1}/974 cm^{-1}). It is attributed to the crystal deformation as a result of metamictization or high pressure effect.

Except for the Raman peaks of zircon, there is no sign of spectrum that indicates the presence of amorphous glassy SiO_2.

Photo.1a

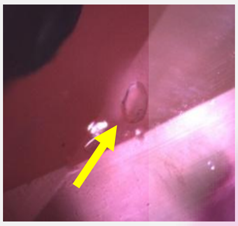


Photo.1b

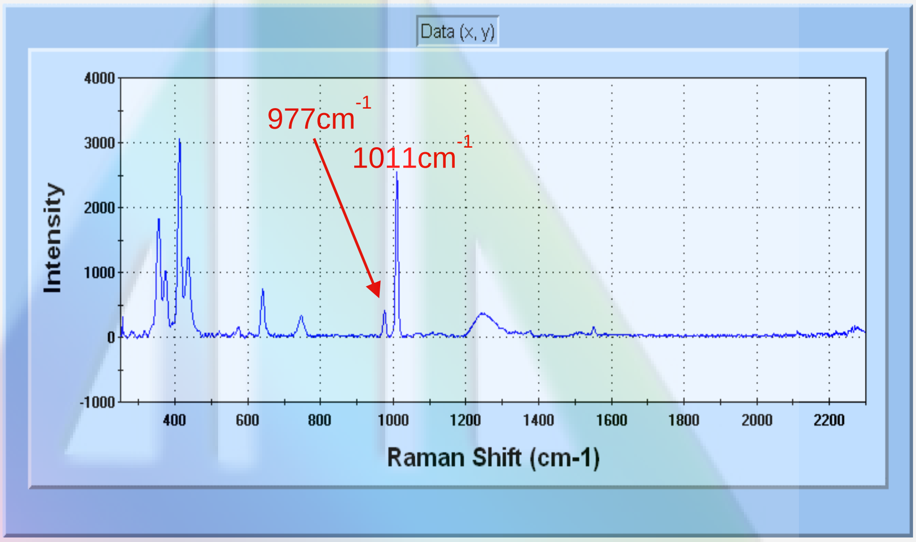


Fig.1 Raman and PL spectrum of non-heat treated zircon inclusion.

3.2 Spectral Analysis of Heat Treated Zircon Inclusion

By eyeball observation, the heat treated inclusion of zircon always shows dull mist on the surface or rim of the crystal (see Photos 2b). Raman inspection on this crystal shows both Raman and PL spectra (Figure 2-1). The Raman main peaks of zircon under more pressure, the ν_3 mode and ν_1 mode show up at 1015 cm^{-1} and 980 cm^{-1}, respectively. In comparison with synthetic zircon crystal, the position of these peaks shifts more to the right, with lower intensity and smaller FWHM (Figure 2.2).

In addition to the Raman peaks of zircon, there exists also PL spectrum of SiO related in the spectral range 1300~2000 cm^{-1}, with main PL peak at around 1378 cm^{-1}.

Photo.2a

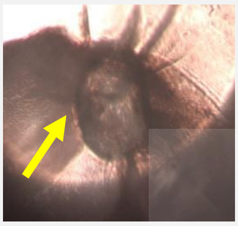


Photo.2b

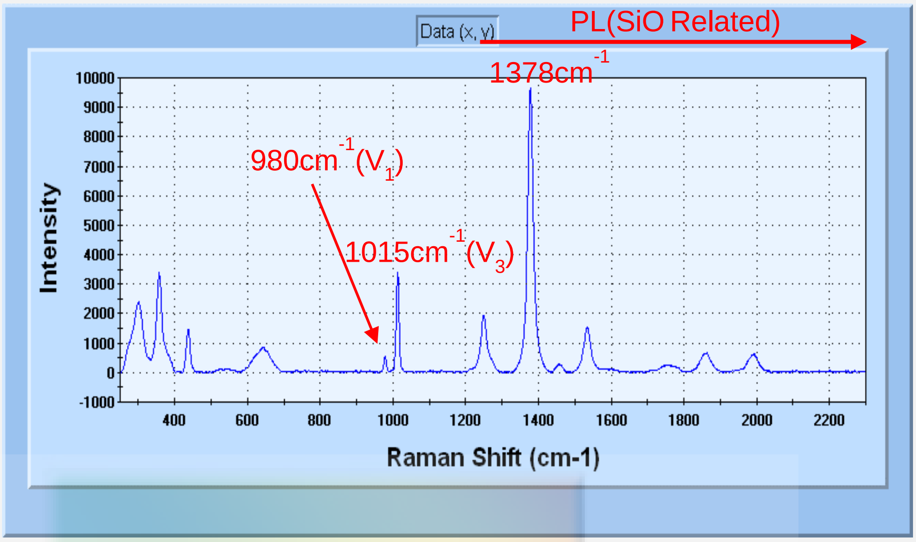


Fig.2.1 Raman and PL spectrum of slightly heat treated inclusion of zircon.

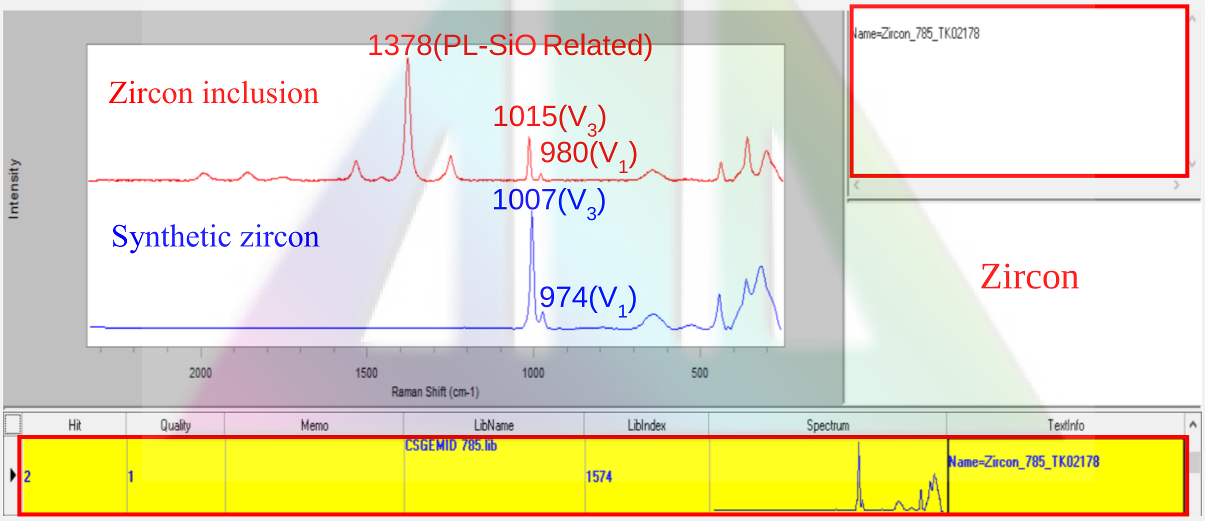


Fig.2.2 Staked spectra in comaprison with synthetic pure zircon.

3.3 Effect of Heat Treated on the Position, FWHM and Intensity of Zircon Raman Peaks

As analyzed in Section 3.1 and 3.2, an increase in temperature may cause an increase in confining pressure under close system, the main Raman peaks of zircon in corundum will shift even more right to 1014~1022 cm^{-1} with a lower intensity gradually. As the temperature and duration of heat treatment increase, the effect on the intensity of the Raman peaks gets more obvious, and the FWHM of these peaks is gradually lowered (see Figure 3).

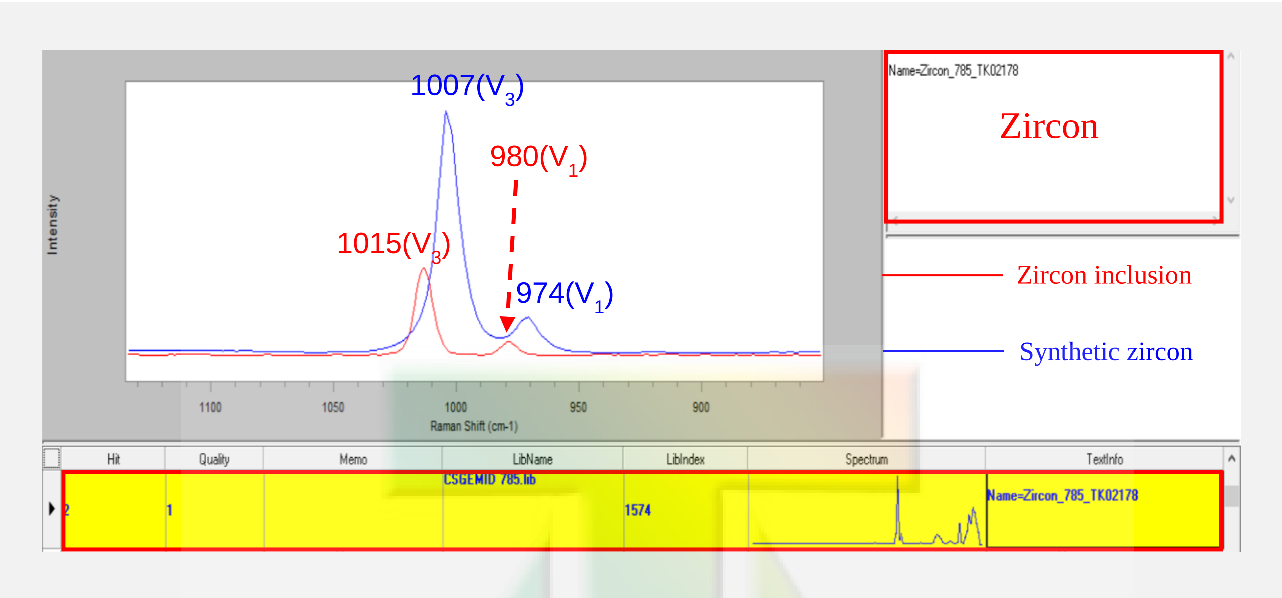


Fig.3 Overlain spectra showing the change of zircon after heat treatment.

3.4 Comparative Analysis on Zircon Inclusion with Different Degree of Heat Treatment

In short, when suffered heat treatment of different degree, the zircon inclusion in ruby not only changes its appearance and shape, but also shows different extent of change in its Raman spectrum (Figure 4). When zircon inclusion is heavily heated or prolonged heated, Raman peaks of baddeleyite will be observed in the Raman spectrum. In addition, the PL strong background fluorescence and Raman spectra induced from amorphous glassy SiO_2, also observed in the spectral range 200~600 cm^{-1}, will be more intense (see Figure 4.1). The FWHM of PL peak of SiO related at 1378 cm^{-1} will also get broader (see Figures 4.2 and 4.3).

Photo.3a

Photo.3b

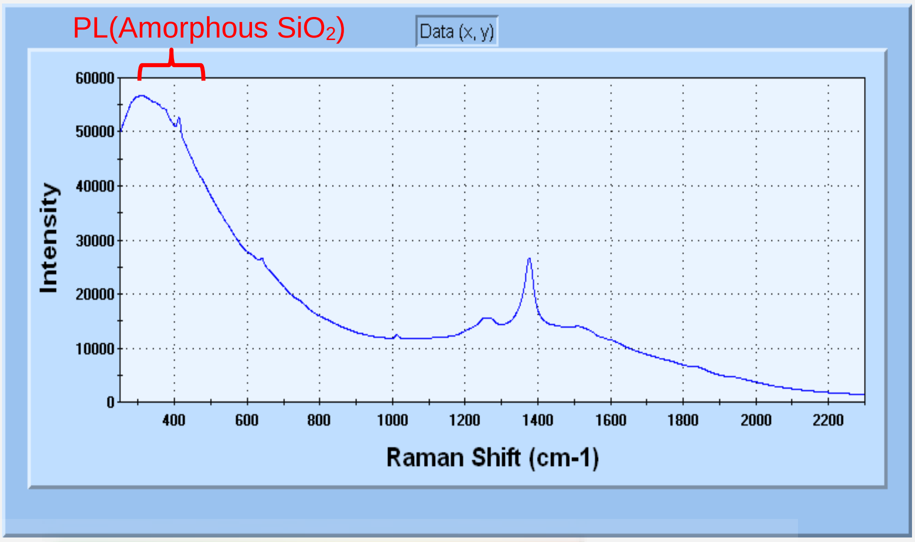


Fig.4.1 Raman and PL spectrum of heavily heat treated inclusion of zircon (raw spectrum)

Photo.3a

Photo.3b

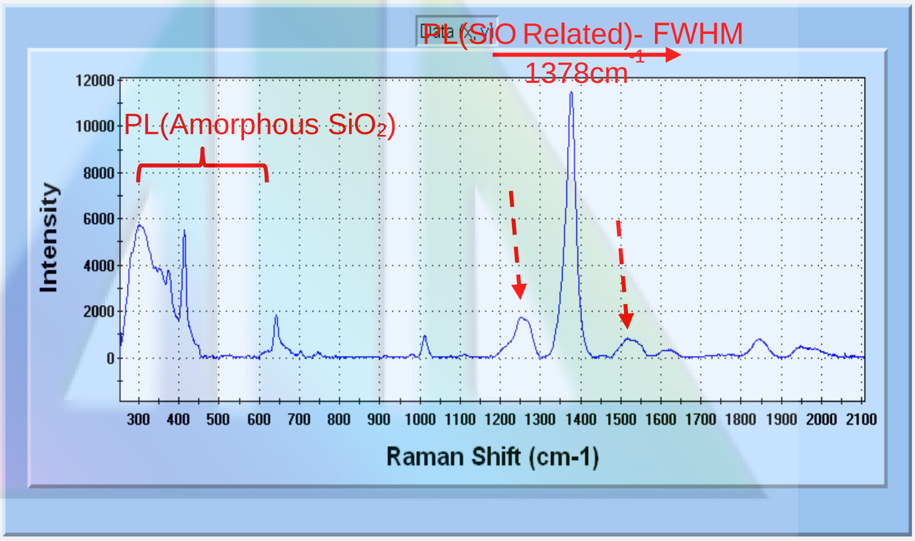


Fig.4.2 Raman and PL spectrum of heavily heat treated inclusion of zircon (baseline corrected).

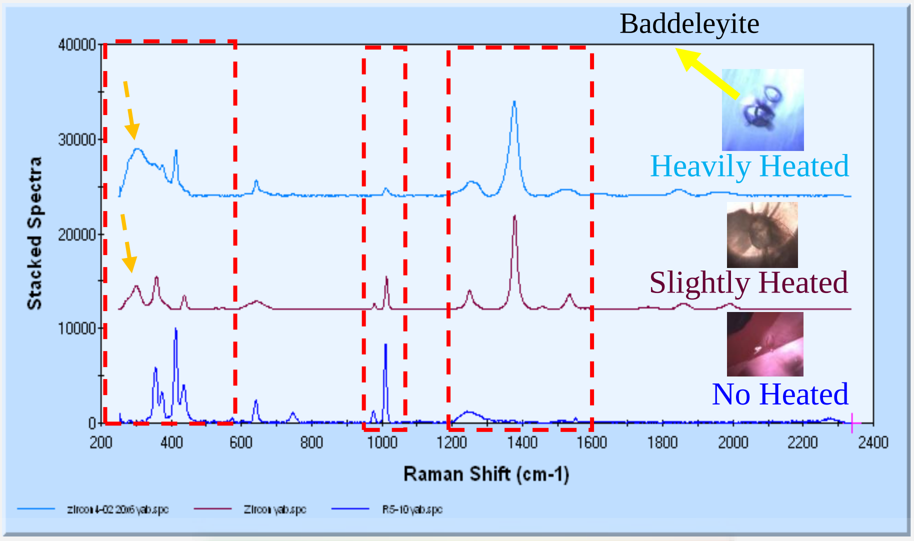


Fig.4.3 Staked spectra showing zircon inclusion under different degree of heat treatment. The matching and comparison indicates that obvious change takes place in peak position, intensity and MWHM.

4. Discussion and Conclusion

The zircon inclusion in ruby and sapphire gradually heated and decomposed to baddeleyite and amorphous glassy SiO_2 during the thermal treatment procedure. The position of ν_3 mode and ν_1 mode, FWHM and intensity of Raman peaks are affected and show variation. In addition, when excited by 785 nm laser beam, the fluorescence background of amorphous glassy SiO_2 will be excited and the spectrum will show up in the spectral range 200-600 cm^{-1} (795~825 nm). The main PL peaks of excited SiO related shows up its major peak at around 1380 cm^{-1}. If 532 nm laser is used in the Raman spectrometer, the PL peaks of SiO related will show up in the spectral range 300-600 cm^{-1} (542~552 nm). The Raman and PL spectra of amorphous glassy SiO_2 or SiO related excited by different laser sources is in good agreement with the spectra of ordinary SiO_2 glass, though the crystal structure of these silica may not be the same under different temperature.

The crystal structure of zircon inclusion may be damaged due to metamictization or pressurization in their hosting minerals. Basically, thermal treatment at 1400˚C will cause zircon inclusion to decompose, while melting of zircon takes place at1600˚C. The decomposition temperature and melting temperature are lower than zircon in its free state. It is reported that zircon in corundum is confined at a pressure up to 25 kbar. In a close system, an increase in temperature may cause an increase in the confining pressure, therefore, when corundum is heated up to 1400°C, the zircon inclusion may actually suffer a pressure much greater than 25 kbar. The excess stress tends to cause the decomposition and melting of zircon at a temperature lower than zircon in the air. This is in principle similar to the heating of substances in an autoclave. The series of change in crystal structure of zircon inclusion under different thermal treatment can be monitored by the inspection of Raman spectrometer. Careful examination of Raman spectra of zircon inclusion can reveal whether the hosting corundum has been heat treated, and the temperature at which the treatment is conducted can even be estimated. This kind of identification method is of scientific significance.

The sensitivity (S/N ratio) of a Raman spectrometer is crucial for the judgment of whether a corundum specimen has been thermally treated, or for the estimation of the temperature of the treatment. The quality of the Raman spectra relies highly on S/N ratio which may affect the detection of characteristic peaks and fluorescence, especially, the PL peaks. This is a very important note that has to be keep in mind by researchers or appraisals.

The results reported in this study are far from completion due to the lack of sufficient specimens from different localities, as well as the limited systematic experiments on thermal treatment of the specimens. The analytical results on the Raman and PL spectra of zircon inclusion reported here have provided a direction for the research of the effect of thermal treatment on inclusions. It can be applied to the study of the effect of temperature (particularly at low temperature) on various inclusions in corundum. With the advantage of being non-destructive, Raman and PL spectrometers will be the best tools to be selected for this field of study.

5. Acknowledgment

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6. Reference

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