



Confocal Raman Imaging: A Different View of Diamond Inclusions

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Introduction

Confocal Raman imaging is a widely used spectroscopic technique to visualize the spatial distribution of components, morphological differences, or physical phenomena that affect chemical structure at various depths within a sample. Two-dimensional (2-D) Raman imaging involves using a motorized stage to move the sample so as to collect Raman spectra at positions across a defined area at a set focal plane (x- and y-directions). Key features of the collected spectra—including peak areas, peak heights, peak widths, correlation to a reference spectrum, MCR (multivariate curve resolution), etc.—are then used to produce a 2-D image. The image is displayed using colors to represent varying values (intensity, correlation values, component classifications, peak position, etc.) generated from these spectral profiles. These images represent spatial distributions of different aspects of the sample, including chemical components and molecular structures. By collecting a series of these 2-D areas at different focal planes (different z positions), a three-dimensional (3-D) chemical map can be generated. This expands upon the unique views of 2-D Raman imaging to deliver a more complete view of the sample and even better understanding of spatial distributions.

Confocal Raman imaging can be used to investigate mineral inclusions while they are encapsulated in a surrounding matrix. This alleviates the need to expose the contents of the inclusion and thereby prevents any possible loss of materials, contamination of the inclusion, or chemical changes due to exposure to ambient conditions. Also, polishing down particularly hard materials such as diamonds to expose inclusions is time-consuming and costly as well as destructive and irrevocable. Confocal depth analysis thus provides an advantageous method for studying intact inclusions in minerals including diamonds.

The investigation of inclusions within diamonds provides valuable snapshots of information about their formation, preserved within the diamond matrix. Analyzing the contents of these inclusions can reveal the conditions (pressure and temperature) during the diamond's formation and the surrounding materials present at that time. Such details offer crucial clues to the origins of the diamonds. Additional important information can be gleaned from the diamond itself, such as shifts of the diamond peaks, which are often associated with residual stress.

In this application note, the use of confocal Raman imaging to investigate inclusions in diamonds is illustrated using a natural diamond sample. While the whole breadth of different types of inclusions and defects in diamonds is beyond the scope of this note, the results from the analysis of this sample demonstrate the concepts that can be applied in similar analyses.

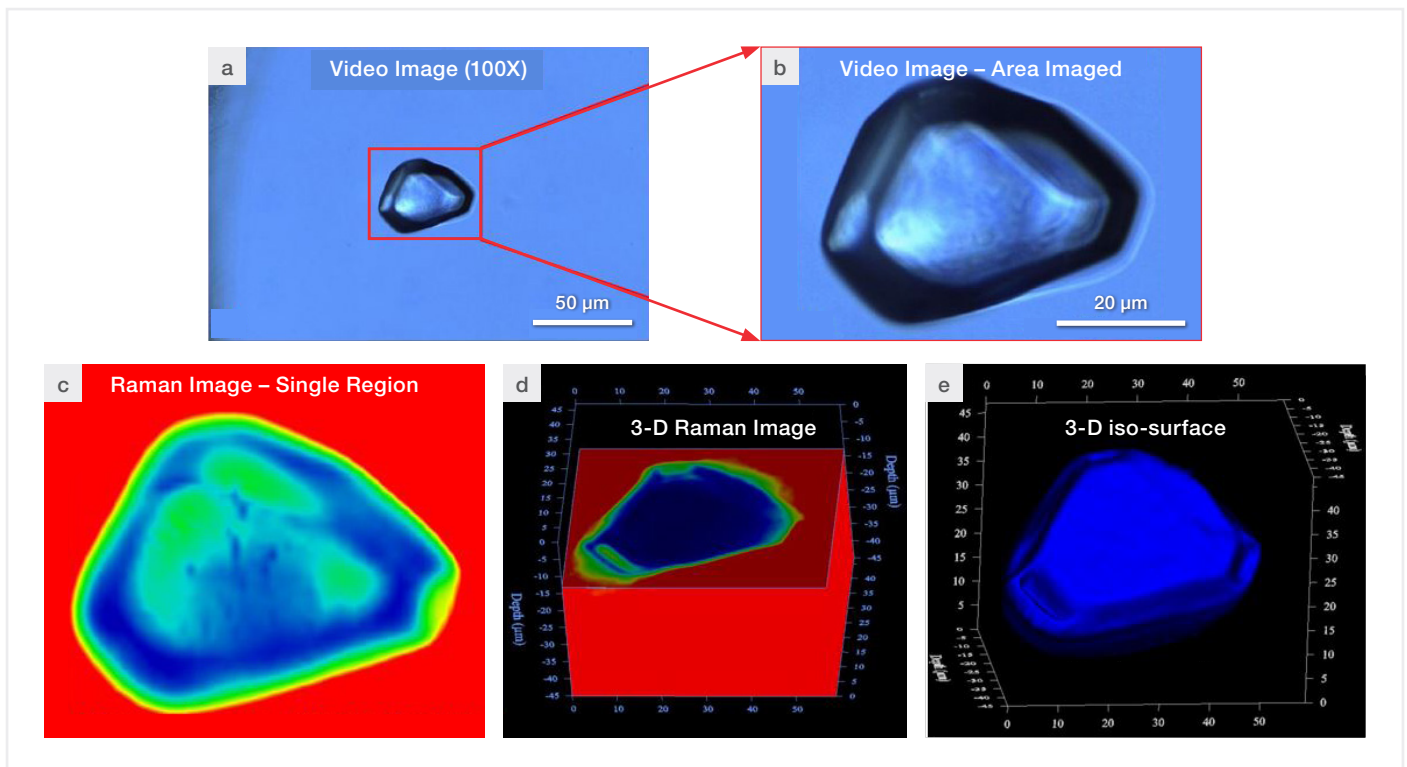


Figure 1. (a) Full field of view of the visual image of the inclusion using a 100X objective; (b) visual image of the x-y region on the sample used for Raman imaging ($59\ \mu\text{m} \times 47\ \mu\text{m}$); (c) Single x-y region Raman image based on the diamond peak at $1,334\ \text{cm}^{-1}$ —the red indicates higher peak intensity and blue lower diamond peak intensity due to the presence of the inclusion; (d) 3-D Raman image based on the $1,334\ \text{cm}^{-1}$ diamond peak sliced down along the z axis to show the blue color indicating a decrease in intensity caused by the inclusion; (e) 3-D Raman image shown as an iso-surface.

Experimental

The confocal Raman imaging data was collected using a Thermo Scientific™ DXR3xi Raman Imaging Microscope configured with a 532 nm laser. The video images and Raman imaging data were collected using a 100X objective. The image pixel size used in the x-y planes was 1 micron and different x-y slices were collected by varying the focal position in 1-micron steps. The 3-D images were generated from the series of x-y regions using the 3-D visualization feature in the Thermo Scientific™ OMNICxi 3D Visualization Software.

Results

Figure 1 shows visual images (a-b) of the inclusion and the Raman images (c-e) generated based on the intensity of the $1,334\ \text{cm}^{-1}$ diamond peak, which corresponds to the optical phonon mode at the Brillouin zone center of the diamond's face-centered cubic crystal structure. The inclusion has a reduced diamond content, represented by the blue and green color in the chemical map, whereas the diamond itself shows up as red (Figure 1c). This 2-D image is a single slice out of the series of x-y regions collected at different z values. Figure 1d shows the 3-D image of the diamond with the inclusion. The 3-D imaging software allows the user to slice into the image along any axis. In this case it is used to remove the top diamond layers (red) along the z axis that would otherwise block the view of the inclusion within the surrounding diamond in the interior of the image. Figure 1e provides an iso-surface image where only the inclusion is displayed. While these images provide the dimensions and contour of the inclusion, they do not give insight to the material inside the inclusion.

Figure 2 shows the Raman spectrum of the material inside the inclusion (full spectrum, shown at top), with an expanded view of the 1,200-50 cm^{-1} spectral region (middle spectrum) where the inclusion peaks reside. The pattern of the peaks in the spectrum matches well with those of a reference spectrum of omphacite (bottom spectrum), but the Raman shifts are noticeably different. For instance, the main peak at 678 cm^{-1} in the reference spectrum is shifted to 684 cm^{-1} in the inclusion spectrum. Both compositional variance and residual stress are known to cause peak shifts, although a 6- cm^{-1} shift is unusually large for stress-induced shifts. Omphacite, a silicate mineral $((\text{Ca},\text{Na})(\text{Mg},\text{Fe}^{2+},\text{Al})\text{Si}_2\text{O}_6)$, is a major constituent of eclogite that can be found in kimberlite pipes. Kimberlite is a common host matrix for diamonds. Omphacite inclusions in diamonds have been reported¹ so it is reasonable to infer that that the inclusion in this sample is omphacite. The spectrum of the inclusion (1,200-50 cm^{-1}) was then used as a correlation reference to produce the 3-D images of the inclusion shown in Figure 3. The inclusion is near the top surface of the diamond but still fully enclosed by the diamond matrix.

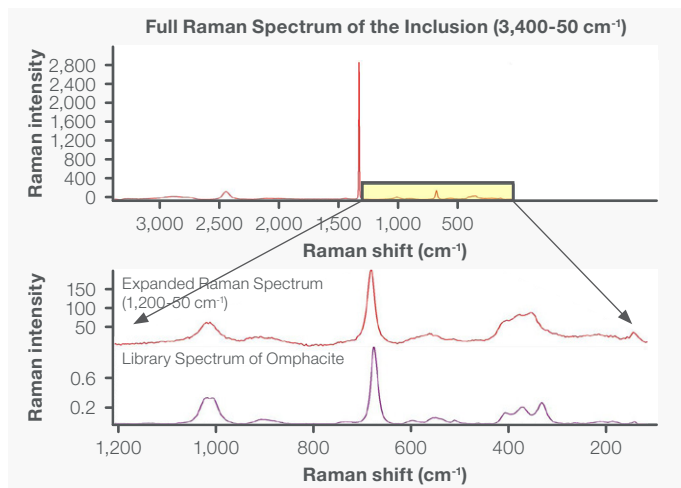


Figure 2. A representative Raman spectrum from inside the inclusion. The 1,200-50 cm^{-1} region of the spectrum is expanded to show the spectral features of the inclusion better. The library spectrum of Omphacite $((\text{Ca},\text{Na})(\text{Mg},\text{Fe}^{2+},\text{Al})\text{Si}_2\text{O}_6)$ is shown as a likely match to the inclusion material.

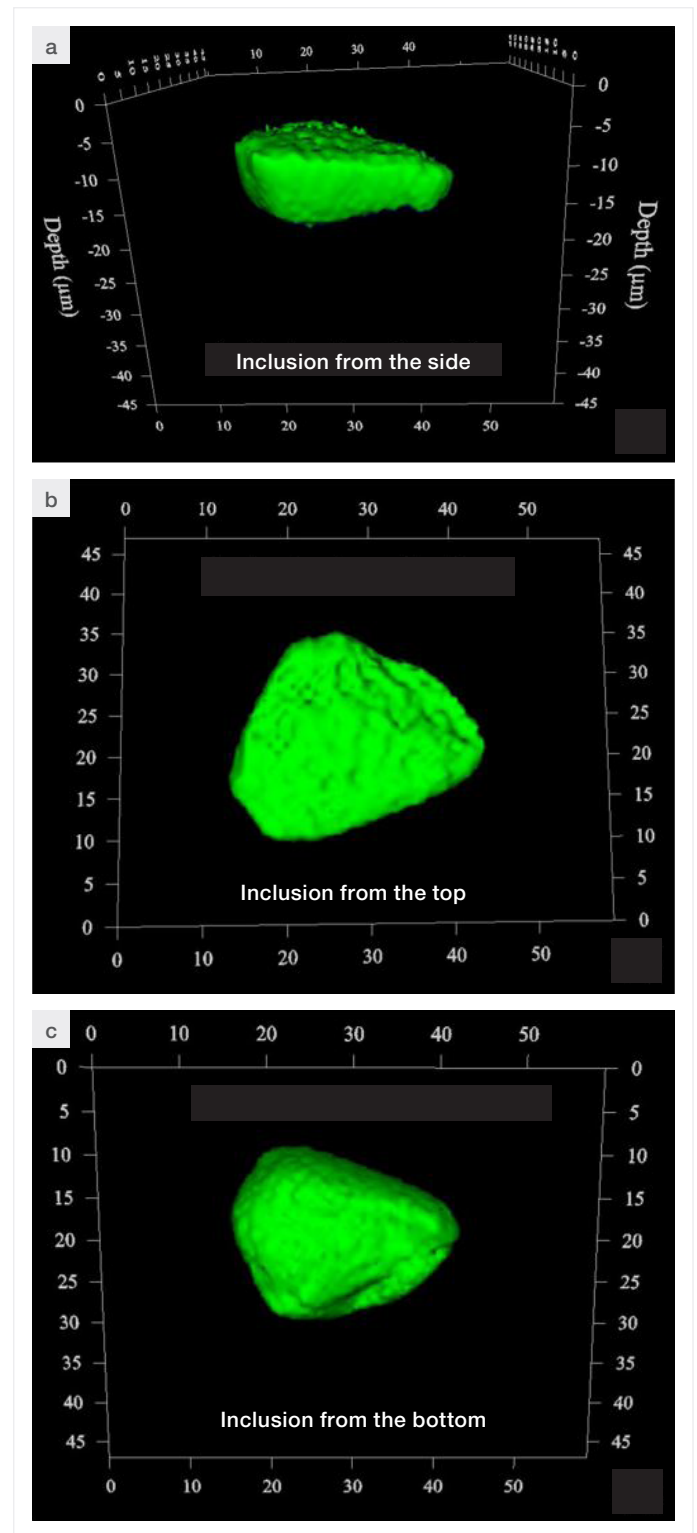


Figure 3. 3-D Raman images of the inclusion generated by correlation to the 1,200-50 cm^{-1} spectral region shown in Figure 2. Side, top, and bottom views of the inclusion are shown. The inclusion is approximately 49 μm x 38 μm .

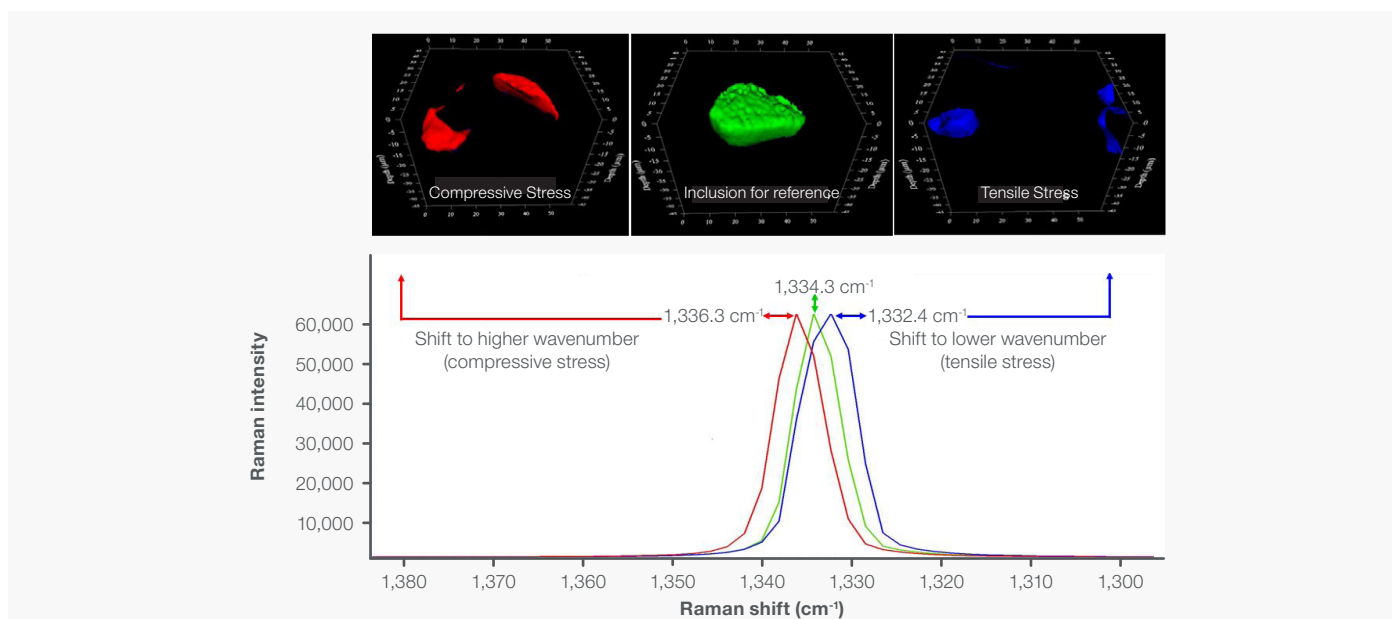


Figure 4. Raman stress images based on the shift of the diamond peak. The red areas indicate compressive stress (higher wavenumber shift) and the blue areas indicate tensile stress (lower wavenumber shift). The green spectrum is the unstressed diamond peak position. The image of the inclusion is shown as a positional reference.

Raman imaging of the diamond matrix around the inclusion can also provide important information. The diamond peak ($1,334\text{ cm}^{-1}$) is known to shift position when the diamond is under stress. In Figure 4, the green spectrum represents the diamond not under stress. Peak shifts to higher wavenumbers signify compressive stress (the red trace) and peak shifts to lower wavenumbers indicate tensile (stretching) stress (the blue trace). The shifts in the peaks can be used as profiles to generate Raman images showing the spatial distribution of the stress in the diamond. The 3-D images in Figure 4 were generated using peak position profiles, where the profile of the compressive stress is shown in red, and the profile of the tensile stress is shown in blue. The image of the inclusion is shown as a positional reference. It appears that the compressive stress is located at the edges of the inclusion. However, the position of the tensile stress does not seem to be spatially related to the inclusion. It is worth mentioning that compressive stress around inclusions in diamonds could arise from mismatches in thermal expansion coefficients, volume changes during phase transitions, the presence of high-pressure phases trapped within the inclusions, or mechanical constraints imposed by the rigid diamond lattice. A rigorous understanding of the chemical nature of the inclusions and compressive stress around inclusions can provide valuable insights into the history and formation processes of the diamonds.

Conclusion

Raman spectroscopy has been used previously for the analysis of inclusions in minerals² and diamonds³. The DXR3xi Raman imaging microscope can extend that approach to 3-D confocal Raman imaging that allows for the identification of inclusion materials and also the depth profiling of the inclusion based on spectral features. The resulting 3-D images provides a clear visualization of the chemical compositions, the spatial distributions, and the dimensions and contours of the samples. This significantly enhances the understanding of the 3-D spatial relationships of features within the diamond. In addition to the inclusion itself, the Raman spectrum of the diamond can provide information on residual stress, both compressive and tensile. In this study, the 3-D visualization revealed a strong spatial correlation between the inclusion and the compressive stress, which contrasted with the lack of spatial correlation between the inclusions and the tensile stress. These types of spatial relationships may provide additional information about the formation of the diamonds.

References

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3. Antony Burnham, David James, Application Note 52568, *Raman Mapping of Mineral Inclusions in Diamonds and other Mineral Samples*, Thermo Scientific 2014.

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