Imaging of internal stress around a mineral inclusion in a sapphire crystal: application of micro-Raman and photoluminescence spectroscopy

Naoki Noguchi, Ahmadjan Abduriyim, Ichiko Shimizu, Nanako Kamegata, Shoko Odake and Hiroyuki Kagi

We developed a micro-Raman and photoluminescence imaging technique for visualizing the internal stress fields in a sapphire crystal. The technique was applied to an Australian sapphire gemstone with a zircon inclusion. Considering piezospectroscopic effects on Raman and photoluminescence spectra, the Raman shifts of sapphire around the zircon inclusion were converted to hydrostatic pressure and deviatoric components of stress tensor. The internal stress was highly concentrated at the tips of the zircon crystal, where the deviatoric stress and the hydrostatic pressure component reached 700 and 470 MPa, respectively. Generation of compressive stress on the crystal surface of zircon can be explained by the difference in thermal expansion coefficients and elastic constants between sapphire and zircon. In general, internal stress fields induced by mineral inclusions reflect the pressure and temperature conditions at which the host sapphire gemstones were crystallized. Thus, the present technique can be utilized to identify the origin of gemstones. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: micro-Raman spectroscopy; photoluminescence spectroscopy; sapphire; inclusion; internal stress

Introduction

Sapphire and ruby are precious and popular colored gemstone varieties. The main chemical component of these gemstones is Al₂O₃. Sapphire also contains Ti, Fe, and Cr as impurities. The location where these gemstones are mined is an important factor in determining their value. At present, the location can be identified by quasi-destructive geochemical analyses, such as laser ablation–inductively coupled plasma mass spectroscopy and particle-induced X-ray emission (PIXE). The development of a nondestructive method to identify the geological origin of a sapphire gemstone is a current objective in gemology. Gemstones of sapphire often contain other mineral species as inclusions. Such inclusions become trapped inside the sapphire, which is referred to as the ‘host’, during its formation. Because the mineral inclusion species depend on the geophysical and geochemical conditions where the inclusion was formed, the identification of inclusions in sapphire can provide information regarding its origin. Micro-Raman spectroscopy is a promising method for the identification of inclusions in sapphire. Previous studies have undoubtedly characterized sapphires by the identification of their inclusions using micro-Raman spectroscopy. However, if geological conditions at different sapphire mines are similar, the mineral inclusion species overlap. For example, the inclusion species in sapphires that originate from the alkali basalt regions of Australia, Thailand, China, Cambodia, Laos, Vietnam, and Nigeria overlap. Thus, for a more precise classification, the inclusions need to be characterized by additional factors that reflect the geological conditions of the source region.

Here, our attention is focused on the internal stress retained in the sapphire gemstone. Internal stress is induced around an inclusion in a sapphire after its ascent to the surface from the deep crust where it originally formed. The internal stress around an inclusion is caused by differences in the elasticity and thermal expansivity between the host and inclusion minerals. Because both these physical constants are anisotropic, the internal stress field around an inclusion depends on the relative crystallographic orientations of the host and the inclusion mineral and the shape of the inclusion. Therefore, the internal stress field is expected to be isotropic. The internal stress field around the inclusion reflects the pressure–temperature (P–T) conditions at the locus of the formation of the inclusion during the ascent of the sapphire. Thus, the determination of the stress field around an inclusion in a sapphire may help to locate the depth of its point even for identical mineral inclusion species. Previous studies reported...
internal pressure data for various host minerals (except sapphire) or their inclusions using micro-Raman spectroscopy.\textsuperscript{[15–18]} Raman mapping was also applied to image the internal pressure field around an inclusion.\textsuperscript{[19–22]} However, no spectroscopic studies on the determination of the components of a stress tensor around an inclusion in a host mineral have been published.

In this study, we report a new spectroscopic method for measuring an internal stress field around an inclusion in a sapphire by two-dimensional (2D) Raman and three-dimensional (3D) photoluminescence (PL) mapping measurements. This study is the first step toward the establishment of a new method for identifying the location in which a sapphire gemstone originated.

Sample characterization

The sapphire gemstone examined in this study was obtained from the Swamp Oak mine, Inverell district, New South Wales, Australia (Fig. 1). With geochemical and petrological observations, several models have been proposed for the formation process of sapphire-bearing rocks in this region.\textsuperscript{[6,23,24]} Two representative models suggest that the sapphire gemstones were formed either in the middle crust by a hybrid reaction between carbonatite melts and silicic magma\textsuperscript{[19–22]} or in the lower crust by a contact metamorphic process of aluminous rocks.\textsuperscript{[25]} The $P$–$T$ conditions for the formation of sapphire suggested in these models are $\sim 0.5$ GPa and $\sim 400^\circ$C and $0.7$–$1.1$ GPa and $700$–$900^\circ$C, respectively.

The trace element contents in the sample were measured by laser ablation–inductively coupled plasma mass spectroscopy as follows: Fe, 4198.7 $\pm$ 97.1 ppm; Ti, 226.9 $\pm$ 41.7 ppm; Ga, 89.3 $\pm$ 1.4 ppm; Mg, 17.7 $\pm$ 3.2 ppm; V, 8.6 $\pm$ 0.3 ppm; and Cr, 4.1 $\pm$ 1.3 ppm. The sapphire grain contains several zircon ($\text{ZrSiO}_4$), rutile ($\text{TiO}_2$), and albite ($\text{NaAlSi}_3\text{O}_8$) inclusions. Most of the zircon and albite inclusions are accompanied by radial cracks in the host sapphire crystal. Table 1 lists the thermoelastic constants of these minerals. Internal pressure estimates based on the isotropic elastic inclusion model\textsuperscript{[33]} (Fig. S1) demonstrated that the large difference in the thermoelastic constants could induce high internal stress around the zircon inclusions. Thus, we selected a zircon inclusion with the dimensions of $30 \times 30 \times 65$ $\mu$m$^3$ for the spectroscopic analysis (Fig. 1). A sapphire slab in the thickness of 2.2 mm was prepared so that the zircon inclusion was not exposed to the surface. Considering the selection rule for sapphire with the $D_{3d}$ space group\textsuperscript{[34]}, the slab was cut almost parallel to the $(2 \bar{1} 1 \bar{1})$ plane so that sufficient signals can be obtained for the six Raman bands, i.e. two $A_{1g}$ modes (418.5 and 645.2 $\text{cm}^{-1}$) and four $E_g$ modes (378.4, 430.6, 576.4, and 750.6 $\text{cm}^{-1}$). The precise crystallographic orientation was determined by the electron back-scattering diffraction technique using a scanning electron microscope (JSM-7000F, JEOL Co. Ltd.) equipped with an electron back-scattering diffraction detector. The difference in crystallographic orientations between the host sapphire grain and the zircon inclusion was determined by a micro-X-ray diffractometer equipped with a multilayer confocal mirror (Micro Max 007HF X-ray generator with an R-AXIS IV imaging plate, Rigaku Co. Ltd.). The crystallographic orientations of these minerals are illustrated in Fig. 1 by using the VESTA program.\textsuperscript{[35]} The $c$ axis of zircon is almost parallel to that of sapphire; the angle between them is $3.0^\circ$.

### Experimental methods

Outlines of stress measurements

The internal stress, $\sigma_{ij}(i,j=x,y,z)$, of sapphire can be divided into a hydrostatic pressure component, $P$, and deviatoric stress components, $\sigma_{ij}'(i,j=x,y,z)$, as

$$\sigma_{ij} = \sigma_{ij}' - P \delta_{ij}$$

where $\delta_{ij}$ is the Kronecker’s delta. Positive values of the axial stresses ($\sigma_{xx}$, $\sigma_{yy}$, and $\sigma_{zz}$) represent tensile stresses. In high-pressure experiments using diamond anvil cells, photoluminescence of sapphire with wavelengths of 694.3 (R1) and 692.9 nm (R2), which are excited at $\text{Cr}^{3+}$ impurities, has been widely used for

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**Table 1.** Comparative crystal chemistry of sapphire and inclusions

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Crystal system</th>
<th>Bulk modulus/GPa</th>
<th>Linear thermal expansion coeff./10$^{-6}$/K</th>
<th>Volume thermal expansion coeff./10$^{-6}$/K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapphire (α-$\text{Al}_2\text{O}_3$)</td>
<td>Trigonal</td>
<td>257</td>
<td>a: 7.3 b: 8.3</td>
<td>23.0</td>
<td>[25,26]</td>
</tr>
<tr>
<td>Zircon (ZrSiO$_4$)</td>
<td>Tetragonal</td>
<td>227</td>
<td>a: 4.4 b: 7.6</td>
<td>9.1</td>
<td>[27,28]</td>
</tr>
<tr>
<td>Rutile (TiO$_2$)</td>
<td>Tetragonal</td>
<td>216</td>
<td>a:8.9 b: 11.1</td>
<td>29.1</td>
<td>[29,30]</td>
</tr>
<tr>
<td>Albite (NaAlSi$_3$O$_8$)</td>
<td>Triclinic</td>
<td>70</td>
<td>a: 15.3 b: 5.7 c: 2.0</td>
<td>28.9</td>
<td>[31,32]</td>
</tr>
</tbody>
</table>
evaluation of $P$ \cite{36}. The R2-line is especially useful because it is insensitive to differential stress.\cite{37–39} Pressure dependence of Raman shifts was also quantified in diamond anvil cells at quasi-hydrostatic conditions (Table 2 \cite{40}). However, full components of stress tensor have not been determined.

Recently, Kimachi et al.\cite{41} conducted bending tests of a synthetic sapphire crystal at atmospheric pressure and determined the relationship between Raman shifts and strain tensor, $\varepsilon_{ij}$ ($i, j = x, y, z$), on the basis of the deformation potential theory (see the Appendix). Given the elastic stiffness constants,\cite{42} $\sigma_{ij}$ can be derived from the strain tensor. However, Kimachi’s equation cannot accurately describe the hydrostatic pressure dependence of the Raman shifts given in Table 2. This fact suggests that influence of nonhydrostatic stress on Raman shifts is different from that of hydrostatic pressure; in the former case, relative distances of the atoms and the bond angles are changed, whereas only isotropic changes occur in the latter case. Hence, we applied Kimachi’s method to determine the deviatoric components of stress tensor. Accordingly, the sapphire crystal under hydrostatic pressure $P$ was chosen as a reference state of $\varepsilon_{ij}$. $P$ in the aforementioned equation was independently determined by the R2-line of sapphire. Before applying Kimachi’s equation, the pressure-induced shift of the Raman bands corresponding to the internal pressure $P$ was calculated with the coefficients given in Table 2\cite{40} and was subtracted from the raw data of the Raman shifts.

### Micro-Raman and photoluminescence measurements

The micro-Raman measurement system is composed of an optical microscope (BX60, Olympus Optical Co. Ltd.) equipped with a motor-driven X–Y–Z sample stage (FC-101G, Sigma Koki Co. Ltd.; AF/$\alpha$, Flovel Co. Ltd.), an Ar$^+$ laser oscillator (IMA, Melles Griot Co. Ltd.), a holographic notch filter (HIPF-514.5-1.0, Kaiser Optical Systems, Inc.), and a polychromator (500IS, CHROMEX Co. Ltd.) with the focal length of 50 cm. The polychromator is equipped with a back-illuminated charge-coupled device with 128 $\times$ 1024 pixels (DU-401-IR-DD, Andor Technology Co. Ltd.). Diffractive gratings of 2400 and 1200 grooves/mm were selected for the Raman and PL measurements, respectively. The entrance slit width of the spectrometer was fixed at 80 $\mu$m. Spectral resolutions per pixel are 0.6 $\text{cm}^{-1}$ and 0.04 $\text{nm}$ for Raman and PL measurements, respectively. The laser emission line of 514.5 nm was used to excite Raman scattering and PL. The laser power at the focal point was 17 mW for the Raman measurements and 0.28 nW for the PL measurements. The theoretical spot size of the laser beam, which was focused through an objective lens of magnification $\times 50$ (Olympus MPlan FL N50, N.A. = 0.80) is 2 $\mu$m. The energy axes of the Raman and PL spectra were calibrated by neon emission lines, as described later.

The 3D PL mapping was carried out to visualize the residual pressure distribution around the zircon inclusion and identify the horizontal (X–Y) plane where the maximum pressure is retained. Mapping of the PL spectra was conducted in a $140 \times 160 \times 110$ $\mu$m$^3$ region with the grid size of $5 \times 5 \times 22$ $\mu$m$^3$ by using point-by-point illumination through the sequential translation of the sample stage. The exposure time for each measurement point was 3 s, and the total time for acquiring all spectra was 5 h.

Considering the selection rule of Raman bands, 2D Raman mapping measurements were carried out in two optical configurations. First, the $c$ axis of the sapphire was set parallel to the polarization plane of the laser light to detect the $E_g$ bands (Fig. 2(a)). Second, to detect the $A_{1g}$ bands, the polarization of the laser beam was rotated 90° by inserting a half-wavelength retardation plate (Fig. 2(b)). At each configuration, the sample stage was moved in the X–Y direction with a step size of 5 $\mu$m, and an area of $140 \times 160$ $\mu$m$^2$ (Fig. 1) was scanned by the laser beam. The exposure time was 60 s for each point, and the total time to scan the entire area was 16 h.

### Calibration of the energy axis

The stress-induced Raman shift of crystalline solids is generally very small; for example, in sapphire, it is approximately 1.0 $\text{cm}^{-1}$ even when the elastic strain of the sapphire exceeds $10^{-3}$\cite{41}. Thus, precise spectroscopic measurements are needed to detect the stress-induced shifts of Raman bands. The long-term stability of the spectrometer must be considered, especially with mapping measurements. Fukura et al.\cite{43} reported that room
temperature fluctuations induced the thermal expansion and contraction of a spectrometer, and as a result, the deviation of the energy axis occurred in the spectra. For instance, a room temperature fluctuation with the amplitude of 0.8°C induced a 0.15 cm⁻¹ deviation in the Raman shift. To overcome this problem, a real-time calibration system using a neon lamp was constructed. In this system, the Raman scattering light from a sample and the neon emission light were simultaneously detected at the upper and lower columns of the charge-coupled device array, respectively. The previous calibration method was dedicated to the measurement of a single Raman band of diamond, which is attributable to the $F_{2g}$ mode (1332 cm⁻¹). Odake et al.[21] applied a neon emission line at 918.5 cm⁻¹ or 540.1 nm for correcting the deviation of the energy axis. In the present case of sapphire, subtle peak shifts of the six Raman bands, observed in the 350–750 cm⁻¹ range, should be determined within the accuracy of 0.1 cm⁻¹. Eight intense emission lines of neon, which appeared in the 250–920 cm⁻¹ range (Fig. 3(a)), were chosen as standard wavenumbers. These emission lines were monitored during the Raman mapping analysis. Figure 3(b) plots the differences ($\delta\omega$) between the raw and the ideal wavenumbers of the neon emission lines. It shows that the change in deviation over time is different for each neon emission line, suggesting that the deviation depended on both the wavenumber and the length of time. The deviation of each neon spectrum was expressed as a quadratic function of the wavenumber. The fitted curves, as shown in Fig. 3(c), were used to calibrate the Raman spectra.
Results

Estimate of internal pressure

In general, a peak fitting technique can improve the wavenumber resolution of a peak position within an accuracy of one-tenth of the resolution per pixel. Using the Igor software package (WaveMetrix Co. Ltd.), the R1-line and R2-line in the PL spectra (Fig. 4) were fitted by Lorentzian functions after subtracting the background by a baseline correction.

The X–Y section of the 3D map of the R2 wavenumbers in which the highest wavenumber was detected is shown in Fig. 5(a). The section is 370 μm beneath the surface of the sample. Internal pressures (estimated from the pressure-induced shift of the R2-line) concentrate around the zircon inclusion. The highest pressure (470 MPa) was observed at the tip of the zircon inclusion. The difference in wavelength between the R1-line and R2-line (Fig. 5(b)) is sensitive to differential stress, i.e. difference between the maximum and minimum compressional stresses of sapphire. In contrast to the internal pressure fields estimated in Fig. 5(a), Fig. 5(b) suggests that the differential stress is concentrated at the top and bottom of the zircon inclusion.

Figure 5. (a) Map showing the wavelength of the R2-line (λ_R2) around the zircon inclusion shown in Fig. 1. Scales for internal pressure and pressure-induced shift of the Raman band at 418.5 cm⁻¹ (A_{1g}) are also shown. The pressure-induced shift was determined from the pressure and the rate of the shift of the 418.5 cm⁻¹ band to pressure, 1.7 cm⁻¹/GPa (Table 2). The mapped area is 140 × 160 μm². (b) Map showing the difference in wavelength between the R1-line and R2-line (Δλ = λ_R1 − λ_R2).

Figure 6. Maps of the shifts of the six Raman bands – two A_{1g} modes (a, b) and four E_g modes (c–f) – around the zircon inclusion. The peak position of the E_g bands cannot be determined because the Raman bands of zircon overlap. Therefore, the values for the E_g field in the inclusion area have no physical meanings.
Estimate of deviatoric stress

The peak positions of the Raman bands were determined by fitting Lorentzian functions in a manner similar to that used in the analysis of the PL spectra. To avoid a systematic error resulting from a nonlinear background curve because of luminescence from impurities (Fig. 2(a)), each spectrum was divided into six segments such that each segment included one of the six Raman bands. Peak fitting was then performed on each segment. The deviations of the Raman bands from those observed on the sample surface were mapped on a horizontal section (Fig. 6). The Raman bands are shifted up to 2 cm\(^{-1}\), and the maps of the shifts show anisotropic patterns and vary with the Raman band. For the maps of the \(E_g\) modes (Fig. 6(c-f)), the pair comprising the 378.4 and 430.6 cm\(^{-1}\) modes attributable to the external normal vibration\(^{[44]}\) and the pair comprising the 576.4 and 750.6 cm\(^{-1}\) modes attributable to the internal normal vibration\(^{[44]}\) show a similar distribution, whereas the distributions of the positive and negative signs in each pair were inverted. It is noteworthy that all maps include the regions of negative shifts. This fact cannot be explained solely by the pressure effect because the pressure-induced shifts of these Raman bands are blue shifts.\(^{[40]}\) Thus, contributions of nonhydrostatic stress components induced by the zircon inclusion should be considered.

The stress field around the zircon inclusion was estimated as follows. First, the pressure-induced shifts of each Raman band were calculated from the pressure determined by the R2-line (Fig. 5(a)) and the calibration data for the pressure dependence of the Raman shifts given in Table 2. Figure 5(a) shows an example for the 418.5 cm\(^{-1}\) band (\(A_{1g}\)). The shifts induced by the deviatoric stress were then estimated by subtracting the pressure-induced shifts from the raw shift in the Raman spectra (Fig. 6). Substituting these values into the left sides of Eqs 4 and 5 (Appendix), \(\sigma_{ij}\) was determined at each measurement point. Here, the spatial coordinates \(x\) and \(z\) are set parallel to one of the \(a\) axes and the \(c\) axis of the sapphire, respectively (Fig. 7). The stress field estimated from the spectroscopic data is shown in Fig. 8.

Discussion

The PL spectra of sapphire revealed increased pressure around the inclusion surface (Fig. 5 (a)). The principal deviatoric stress parallel to the \(z\) axis is compressive (\(\sigma_{zz}\) < 0) at both ends of the zircon inclusion (Fig. 8(c)) and that in the \(x\) and \(y\) directions is compressive (\(\sigma_{xx}\) < 0 and \(\sigma_{yy}\) < 0, respectively) on both sides of the inclusion (Fig. 8(a, b)). These 2D observations and the
crystal symmetries indicate that the crystal surfaces of zircon are compressed in all directions. Generation of compressive internal stress can be primarily explained by the difference in thermal expansion coefficients and elastic constants between sapphire and zircon; in the present case, the thermal expansion coefficient of sapphire is higher than those of zircon in all directions (Table 1), and the diagonal components of the stiffness tensor of the former\(^{[42]}\) are larger than those of the latter\(^{[45]}\). Thus, the zircon inclusion expands more rapidly than the sapphire crystal during cooling and decomposition of the host rock, resulting in extraneous stress at the wall of the inclusion.\(^{[33]}\) The deviatoric stress is very high (\(-\sigma_{zz} \approx 700\) MPa), and the hydrostatic pressure component is also high (\(P \approx 470\) MPa) at both ends of the zircon crystal (Figs 5(a) and 8(c)). The anisotropic stress field described here is possibly due to stress concentration at the tips of the crystal.

Whereas the deviatoric stress fields for the axial components (\(\sigma_{xx}, \sigma_{yy}, \) and \(\sigma_{zz}\)) are symmetric around the long axes of the inclusion (Fig. 8(a–c)), the shear components (\(\sigma_{xy}, \sigma_{yz}, \) and \(\sigma_{zx}\)) show asymmetric patterns (Fig. 8(d–f)); for example, there exists local concentrations at the top–right and bottom–left of the zircon inclusion (denoted by dashed lines in Fig. 8(d–f)). However, the axial components of deviatoric stress are almost neutral at these sites. The stress tensor in this region could be explained by distortion of the crystalline lattice in the diagonal direction (Fig. 9). On the other hand, \(\sigma_{xy}, \sigma_{yz}, \) and \(\sigma_{zx}\) are close to zero at the top–left and bottom–right of the inclusion. It is possible that the large cracks observed under a microscope (Fig. 1) have relaxed the internal stress around them.

The normal stress on the crystal surface of zircon takes the maximum value around 1.2 GPa (\(-\sigma_{zz} + P\)) at the top and bottom, whereas normal compression on the side surfaces of zircon (\(-\sigma_{yy} + P\)) is 0.3–0.4 GPa (Figs 5(a) and 8(b)). On the other hand, the thermoelastic calculation of a spherical zircon inclusion (Fig. S1) gives internal stresses of 1.4 GPa for the lower crust origin models,\(^{[6]}\) respectively. Relatively smaller values obtained in the present spectroscopic analysis may be due to the development of the radial cracks. For accurate determination of the \(P-T\) condition of sapphire crystallization, influences of crystal shapes, cracking, and anisotropy in thermoelastic constants must be taken into account in the inclusion model. Results of the present spectroscopic method would be fully utilized to improved inclusion models in future.

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**Appendix**

Piezospectroscopic effects on Raman bands are formulated by the deformation potential theory\(^{[46,47]}\) The stress-induced wavenumber shift and splitting of Raman bands due to a reduction in symmetry are described by the deformation potential \(V_i\). The effect of stress is introduced as a perturbation to a Hamiltonian. The change in the vibrational energy \(\Delta \omega\) can be calculated by solving an eigenvalue problem describing the perturbing potential \(V\), which is defined as

\[
V = \sum_{ij} V_{ij} \epsilon_{ij} \quad i, j = x, y, \text{ or } z
\]  

(1)

where \(\epsilon_{ij}\) is the strain tensor. It is considered that the symmetry of the sapphire demands that \(V\) is invariant under the \(D_{3d}\) symmetry operation, as expressed by the following equation:

\[
V = \sum_{ij} V_{ij} \epsilon_{ij} = \frac{1}{2} \left[ (V_{xx} + V_{yy}) (\epsilon_{xx} + \epsilon_{yy}) + V_{zz} \epsilon_{zz} \right] + \frac{1}{2} \left[ (V_{xx} - V_{yy}) (\epsilon_{xx} - \epsilon_{yy}) + 2 V_{yz} \epsilon_{yz} \right] + \frac{1}{2} \left[ (-V_{xy}) (\epsilon_{xy}) + 2(-V_{xz}) (\epsilon_{xz}) \right]
\]  

(2)

In Eq. 2, \((V_{xx} + V_{yy})\) and \(V_{zz}\) belong to \(A_{1g}\), \((V_{xx} - V_{yy})\) and \(V_{yz}\) belong to \(E_g\) \((x), \) and \(V_{xy}\) and \(V_{xz}\) belong to \(E_g\) \((y). \) By using the orthogonality theorem, \(\Delta \omega\) is expressed for the \(A_{1g}\) mode as

\[
\Delta \omega = \frac{1}{2} \left( A_{1g, f} | V_{xx} + V_{yy} | A_{1g, f} \right) \epsilon_{xx} + \epsilon_{yy} + \left( A_{1g, f} | V_{zz} | A_{1g, f} \right) \epsilon_{zz}
\]  

(3)

where \(A_{1g, f}\) is a vibrational wave function. The aforementioned can be rewritten as

\[
\Delta \omega_{A_{1g}} = c_0 (\epsilon_{xx} + \epsilon_{yy}) + c_1 \epsilon_{zz}
\]  

(4)

where

\[
c_0 = \frac{1}{2} \left( A_{1g, f} | V_{xx} + V_{yy} | A_{1g, f} \right) \text{ and } c_1 = \left( A_{1g, f} | V_{zz} | A_{1g, f} \right)
\]  

are deformation potential constants. Similarly, the stress-induced shifts are written for the \(E_g\) modes as

![Figure 9. Schematic illustration of the strain field around the zircon inclusion inferred from the deviatoric stress field in Fig. 8. The lattice strain is represented by the deformation of the grid pattern.](image-url)
The latter was ignored in the experimental calibration by Kimachi this article.

Deformation potential constants for \( A_{1g} \) and \( E_g \) modes are listed in Table 3. If the stress-induced Raman shifts are measured for these six bands, the stress tensor can be derived from Eqs 4 and 5.

Supporting information

Supporting information may be found in the online version of this article.

References


Table 3. Deformation potential constants for \( A_{1g} \) and \( E_g \) modes

<table>
<thead>
<tr>
<th>Mode</th>
<th>( c_0/\text{cm}^{-1} )</th>
<th>( c_1/\text{cm}^{-1} )</th>
<th>( c_2/\text{cm}^{-1} )</th>
<th>( c_3/\text{cm}^{-1} )</th>
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<tr>
<td>( A_{1g} )</td>
<td>418.5</td>
<td>-415.8</td>
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<td></td>
<td>645.2</td>
<td>-1311.2</td>
<td>-378.4</td>
<td>378.4</td>
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<tr>
<td>( E_g )</td>
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<td></td>
<td>450.6</td>
<td>-3210.01</td>
<td>-2020.55</td>
<td>979.30</td>
</tr>
</tbody>
</table>

\[
\Delta \omega_{E_g} = d_0 (\omega_{xx} + \omega_{yy}) + d_1 \omega_{zz} + \Delta
\]

where \( d_0 \), \( d_1 \), \( d_2 \), and \( d_3 \) are deformation potential constants. The reduction in symmetry from \( D_{3d} \) to \( C_2 \) by lattice deformation induces the splitting of the \( E_g \) band into the \( A \) and \( B \) bands; which correspond to the ‘+’ and ‘-’ signs in Eq. 5, respectively. The latter was ignored in the experimental calibration by Kimachi et al. because \( B \) band is relatively insensitive to stress. The deformation potential constants of the \( A_{1g} \) and \( E_g \) bands determined by Kimachi et al. is listed in Table 3. If the stress-induced Raman shifts are measured for these six bands, the stress tensor can be derived from Eqs 4 and 5.