Raman and X-ray investigations of LiFeSi$_2$O$_6$ pyroxene under pressure

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In situ Raman spectroscopy at high pressure was utilized to follow the phase transition of a synthetic sample of Li-aegerine pyroxene (LiFeSi$_2$O$_6$) from its low-pressure (C2/c) phase to its high-pressure (P2$_1$/c) phase. The phase change occurred between 0.7 and 1 GPa and was accompanied by a change in coordination of the Li atom from 4 to 5, which was confirmed by single-crystal X-ray diffraction. This is the first report of the Raman spectrum of Li-aegerine in the P2$_1$/c phase. As was previously observed with other pyroxenes, additional changes in the Raman spectra were observed at pressures higher than the phase transition, including the splitting of the peak near 700 cm$^{-1}$, which has traditionally been utilized to indicate the phase transition. Comparisons with the Raman spectra of spodumene in both symmetries are utilized for a discussion of modes.

KEYWORDS: pyroxene; phase transition; pressure

INTRODUCTION

Li-aegerine (LiFeSi$_2$O$_6$) is a monoclinic, optically biaxial synthetic member of the pyroxene group of minerals. Pyroxenes (general formula M$_2$M$_1$Si$_2$O$_6$) comprise ~25% of the Earth's volume to a depth of 400 km. There are a variety of symmetries exhibited by pyroxenes, most notably C2/c, P2$_1$/c, Pbcn and Pbcn, and most pyroxenes appear to undergo phase transitions between these various symmetries as a function of pressure, temperature and composition. Exposing a sample to low temperature often induces the same or similar phase transitions as high pressure because both are associated with a decrease in cell volume. The atomic scale mechanisms for these changes has been the subject of much study. A recently discovered phase transition in Mg–Fe-rich pyroxenes, accompanied by a volume change, is now accepted as an origin of deep-focus earthquakes that cluster at a depth of about 225 km.

In Li-aegerine, chains of FeO$_6$ (M1) octahedra separate chains of SiO$_4$ tetrahedra (Fig. 1). Li occupies the M2 site. Generally, in pyroxenes the M2 site is observed to be 4-, 5-, 6- or 8- coordinated, depending on pressure, temperature and composition of the pyroxene. In C2/c symmetry there are three symmetrically non-equivalent oxygens, designated O1, O2, and O3. O1 oxygens are at the apices of the SiO$_4$ tetrahedra, O2 are on the base of the tetrahedra and O3 are on the base of the tetrahedra bridging the silicon atoms.

Recently, a vibrational study utilizing infrared spectroscopy was performed on Li-aegerine (LiFeSi$_2$O$_6$) through the low-temperature-induced phase transition from C2/c to P2$_1$/c. While no Raman spectra were reported for the P2$_1$/c phase, an increase in the number of infrared modes was observed at 220 K. At room temperature, the mineral displays space group symmetry of C$_{2h}$ (C2/c). In this phase, both Li and Fe occupy positions of C$_2$ site symmetries. The Si and three types of oxygen display C$_1$ site symmetry. According to factor group analysis, there are 14 $A_l$ and 16 $B_l$ Raman-active modes associated with the C2/c phase. X-ray data providing structural information on the C2/c phase were first reported by Clarke et al.

The detailed crystallographic structure of the low-temperature LT-P2$_1$/c phase was given by Redhammer et al. An analysis of the procrystal electron density distribution using the X-ray data indicates an increase in coordination for the Li atom from four to five at the phase transition as a new bond to one of the Si—O bridging oxygens (O3) is formed (Fig. 1). In this coordination, the bonding is similar to spodumene in the P2$_1$/c phase, which is also 5-coordinated. The coordination change destroys the C$_2$ symmetry displayed by the M2 cations, and all atoms occupy...
The first Raman study of accompanying changes in the Raman spectra. To date, this is pressure-induced bonding changes of LiFeSi$_2$O$_6$ and the a
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EXPERIMENTAL
Synthesis
The sample was a 60 × 70 × 100 μm green crystal of LiFeSi$_2$O$_6$ as described previously. Single crystals of LiFeSi$_2$O$_6$ (LiHP4a) were synthesized at 1523 K and a pressure of 3 GPa over a period of 78 h in a piston–cylinder apparatus at the Institute of Crystallography, RWTH Aachen. About 25 mg of a carefully ground stoichiometric mixture of LiCO$_3$, Fe$_2$O$_3$, and SiO$_2$ were placed in a small platinum tube, welded shut, and, in turn, placed in a graphite–pyrophyllite furnace. This synthesis resulted in green, short, prismatic crystals up to 100 μm in length, associated with minor amounts of greenish black glass.

High-pressure Raman spectroscopy
The crystal was loaded into a four pin Merrill–Basset-type diamond cell with reciprocal vector (110) parallel to the cell axis. Diamond anvil culet size was 600 μm. A stainless-steel gasket was used. The gasket was 250 μm thick, pre-indented to 70 μm, with a 250 μm diameter sample chamber. The cell was loaded with a LiFeSi$_2$O$_6$ crystal and a small ruby fragment, and filled with 4:1 methanol–ethanol pressure medium. Pressures were determined from fitted positions of the R$_1$ and R$_2$ ruby fluorescence spectra using the calibration of Mao et al. The estimated error in pressure was 0.05 GPa. Pressure was measured before and after each spectrum acquisition and the reported value is an average of these two. Both ruby fluorescence and Raman spectra were excited with radiation of 514.5 nm from an argon ion laser. Utilizing an 1800 grooves mm$^{-1}$ grating centered at 529.5 nm, the region from 82 to 992 cm$^{-1}$ was acquired using WinSpec software. The region from 401 to 1276 cm$^{-1}$ was acquired with the spectrometer’s grating centered at 538 nm.

There was no specific polarization alignment along the crystal axes. Raman scattering was collected in the backscattered geometry. Data were imported into GRAMS 32 software and peak positions were found using the peak fitting utility. The average error in peak position was 0.9 cm$^{-1}$. Spectra shown are background corrected and normalized for peak height comparison.

RESULTS AND DISCUSSION
There are several changes apparent in the spectra over the pressure range studied. One occurs between 0.23 and 0.74 GPa, one occurs between 2 and 3 GPa, several occur between 6 and 7 GPa and another change occurs at 8.71 GPa. The changes that occur at 0.74 GPa include the appearance of the sample with no medium, and they appear in the same place in other high-pressure experiments but not in Raman experiments performed on other LiFeSi$_2$O$_6$ crystals. Additionally, a peak appears in the Raman spectrum of spodumene (LiAlSi$_2$O$_6$). The mode at 883 cm$^{-1}$ is due to the symmetric CCO stretch for methanol, which comprises four times the amount of pressure medium. The mode at 884 cm$^{-1}$ is one of several changes that occur at 8.71 GPa.

Additionally, a peak appears in the Raman spectrum of ethanol at 884 cm$^{-1}$, which is due to the symmetric CCO stretch. Unfortunately, this peak is very close to a mode due to the pyroxene ($v_{39}$). The CCO stretch for methanol, which comprises four times the amount of pressure medium, appears at 1033 cm$^{-1}$. This is probably the broad peak assigned as $v_{37}$. Also occurring at this pressure are the disappearances of the shoulders at $v_{9}$ and $v_{12}$, while $v_{15}$ becomes stronger and better resolved.
Figure 2. Low-wavenumber region of the Raman spectra of Li-aegirine as pressure is increased. X-ray data indicate that the phase transition from C2/c to P21/c occurs between 0.7 and 1.22 GPa. There are changes in the Raman spectra in this pressure region, but changes that are more readily apparent occur in the pressure region near 6 GPa. Other changes occur between 8 and 10 GPa. No X-ray data were collected at these pressures.

Between 0.70 and 1.00 GPa, a phase transition from C2/c to P21/c was confirmed by X-ray diffraction. When the sample changed symmetry, the Li atom went from 4- to 5-coordinated with the formation of a bond between Li and the O3a atom. There are several changes in the Raman spectra near 2 GPa. First, there is a change in slope (wavenumber/pressure) (see Figs 6–8). More significant is the apparent splitting of peaks near 600 and 675 cm⁻¹. The peaks in this region have previously been assigned as Si—O chain stretches, and used as benchmarks for the phase transition from C2/c to P21/c. According to crystallographic evidence, the phase transition occurs at least 1 GPa below the appearance of the splitting of the peak at 675 cm⁻¹. As first pointed out in Ref. 9, this is additional evidence suggesting that the splitting of this peak is not a good indicator of the phase transition in Li-pyroxenes. There is, however, no crystallographic or diffraction evidence of a phase transition near 2 GPa.

Figure 3. High-wavenumber region of the Raman spectra as pressure is increased. This region of the Raman spectra display changes in the same pressure regions as described for Fig. 2. Note the soft mode, ν².

Figure 4 shows Raman spectra of LiAlSi₂O₆ and LiFeSi₂O₆ in both the C2/c phase and the P21/c phase. The difference in peak intensities between the two phases is probably due to different orientations of the crystals when the spectra were acquired and different polarizabilities of the modes due to the change in chemical composition of the materials. Interestingly, in C2/c, even though the two materials do not have the same number of Li—O3 bonds (none for LiFeSi₂O₆ and two for LiAlSi₂O₆), the Raman spectra are very similar. Arrows indicate peaks or groups of peaks that appear to have the same assignments. At 0 GPa, the peaks for LiFeSi₂O₆ are shifted to lower wavenumbers than the same peaks in spodumene. The substitution of iron for aluminum atom changes the M—O bonds and probably also the Si—O bonds.

Table 1 shows the Li—O3 bond lengths for spodumene in both symmetries and LiFeSi₂O₆ in the P21/c phase. Although the P21/c data for the LiFeSi₂O₆ were acquired through a T-induced phase transition rather than a P-induced phase.
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Figure 4. Raman spectra of spodumene (LiAlSi₂O₆) and Li-aegirine (LiFeSi₂O₆) in low-pressure C₂/c phase and high-pressure P₂₁/c phase. These plots display the similarities between the spectra of the two pyroxenes, which allows a possible assignment of Raman bands of LiFeSi₂O₆ by analogy with the spectra of spodumene.

Table 1. Bond length and electron density data at the bond critical (saddle) point between Li and O₃ for LiAlSi₂O₆ and LiFeSi₂O₆ (data from Downs,² except for LiFeSi₂O₆ at 1.08 GPa)²

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Space group</th>
<th>Conditions</th>
<th>Li—O₃ bond length/Å</th>
<th>Electron density/e Å⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAlSi₂O₆</td>
<td>C₂/c</td>
<td>0 GPa</td>
<td>2.249</td>
<td>0.08843</td>
</tr>
<tr>
<td>LiAlSi₂O₆</td>
<td>P₂₁/c</td>
<td>3.34 GPa</td>
<td>2.150</td>
<td>0.10733</td>
</tr>
<tr>
<td>LiAlSi₂O₆</td>
<td>P₂₁/c</td>
<td>8.84 GPa</td>
<td>2.085</td>
<td>0.12429</td>
</tr>
<tr>
<td>LiFeSi₂O₆</td>
<td>C₂/c</td>
<td>298 K</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>LiFeSi₂O₆</td>
<td>P₂₁/c</td>
<td>200 K</td>
<td>2.381</td>
<td>0.05262</td>
</tr>
<tr>
<td>LiFeSi₂O₆</td>
<td>P₂₁/c</td>
<td>100 K</td>
<td>2.358</td>
<td>0.05510</td>
</tr>
<tr>
<td>LiFeSi₂O₆</td>
<td>P₂₁/c</td>
<td>1.08 GPa</td>
<td>2.411</td>
<td>0.05364</td>
</tr>
</tbody>
</table>

² This table demonstrates the increase in electron density in the Li—O₃ bonds as pressure is increased for spodumene. Similarly, the electron density increases in LiFeSi₂O₆ as the temperature decreases. There is no Li—O₃ bond in the C₂/c symmetry, so no electron density is recorded.

transition, the data acquired at 200 K are comparable to those acquired at 3.34 GPa, as both sets of data are very close to the phase transition in both materials. The O₃ bond radius along the Li—O₃ bond (distance from the center of the atom to the bond critical point) is smaller and the electron density is larger in LiAlSi₂O₆ than in LiFeSi₂O₆. The smaller electron density is reflected by the shift of the Raman peaks to lower wavenumbers. As expected, with increase in pressure or decrease in temperature, the electron density of the Li—O₃ bonds increases along with the Raman shift.

The P₂₁/c spectra of the two different compounds at 3.47 and 3.54 GPa are not as comparable as the data acquired for the compounds at 0 GPa, as the phase transition occurs in LiAlSi₂O₆ near 3.3 GPa and in LiFeSi₂O₆ between 0.7 and 1.0 GPa so the LiFeSi₂O₆ spectrum is much further from its transition than the LiAlSi₂O₆ spectrum. This difference accounts for the shift to higher wavenumbers of some peaks in the LiFeSi₂O₆ spectrum compared with the same peaks in the LiAlSi₂O₆ spectrum.

The absence of the peaks near 442 and 418 cm⁻¹ in the LiFeSi₂O₆ spectra is an argument for assigning these bands in spodumene to modes associated with vibrations of the Li—O₃ bonds, as LiFeSi₂O₆ has no bonds from Li to O₃ in the C₂/c phase. Even stronger evidence is the appearance of a peak at 432 cm⁻¹ (ν₁₈) in the P₂₁/c spectrum of LiFeSi₂O₆. The smaller peak at lower wavenumbers, which would correspond to the peak at 418 cm⁻¹ in C₂/c spodumene, is not readily evident owing to the proximity of the higher intensity bands in the approximate location where that mode would appear. The Raman data indicate that modes at ν₃, ν₆, ν₉, ν₁₂, ν₁₃ and ν₁₈ display the most dramatic changes in slope between 1 and 3 GPa.

Comparison of the C₂/c Li-aegirine Raman modes with the peaks assigned to the C₂/c phase of spodumene leads to the following peak assignments based only on the visual
The changes in the Raman spectrum near 6 GPa are characterized by the splitting of $v_{27}$ into $v_{26}$ and $v_{27}$, in addition to the appearance of $v_{11}$, $v_{12}$ and $v_{16}$. The following peaks become much stronger at 5.65 GPa: $v_{18}$, $v_{36}$ and $v_{39}$. Peaks disappearing at 5.65 GPa include $v_{14}$, $v_{15}$, $v_{24}$, $v_{29}$ and the broad peak due to the pressure medium. The splitting of one unpaired electron in the energy state. Though the iron center in LiFeSi$_2$O$_6$ is not technically in an $O_h$ symmetry (it is $C_2$), the local symmetry of the cation is $O_h$, or very close to $O_h$, so the use of the energy level model is appropriate.

In a spin–spin crossover, some Fe sites within the crystal could change spin states, inducing site non-equivalence. Increasing the pressure would change more of the iron sites to the low-spin state, and so forth until all of the iron sites had transformed to the low-spin state from the high-spin state. König et al. put forth the idea that spin state transitions occur in domains, with cooperative interactions carrying neighboring sites across the energy barrier to spin state transition, thereby creating domains in the crystal where all sites have changed spin states. These domains are large enough to display crystallographic differences and, as such, two separate phases are observable by X-ray crystallography.

Spodumene was observed to undergo a phase change which began at one side of the crystal and continued through the rest of the crystal, so phase changes originating in one location of the crystal and continuing throughout as pressure is increased are not unprecedented. Haddad and co-workers identified a cooperative spin-crossover mechanism leading to domain formations in a solid iron(III) compound. König et al. also put forth the theory that all first-order (discontinuous) spin state transitions are associated with hysteresis, as an effect of the formation of domains. Observation of hysteresis in LiFeSi$_2$O$_6$ would then further support the argument that a spin state transition occurs in the material. However, on examination of the peak positions versus pressure, no significant hysteresis is observable (Fig. 5). In fact, the Raman shift measured as the pressure was decreased shows a slight decrease over the shift measured as the pressure was increased – exactly the opposite of what is expected with hysteresis. Additionally,
visual inspection of the crystal showed no discontinuous color change such as would be expected with a large change in the ligand field energy. From 0 to 6 GPa the crystal remained dark green. There has been a report of a crystal also in the $P2_1/c$ space group [tris($\alpha$-picolylamine)iron(II) chloride–ethanol] that displayed abrupt changes in the lattice parameters, $a$ and $c$, without changing space groups but with anomalies in the Mössbauer and magnetic susceptibility data of the compound. Therefore, similar behavior in LiFeSi$_2$O$_6$ is not inconsistent with previous literature. The absence of hysteresis and the absence of a crystallographic phase change seems to suggest that the spin transition, if it occurs, is of a continuous nature and is likely due to the formation of domains within the crystal. However, absence of evidence is a poor way to prove a hypothesis and more study is required.

The Raman peak at $\nu^*$ displays anomalous peak shift with pressure (Fig. 3). Most of the other peaks increase in wavenumber as the pressure is increased, but $\nu^*$ appears to be a soft mode, decreasing in wavenumber with increasing pressure. Soft modes are modes that show a weakening of the bond associated with displacive phase transitions. Interestingly, the soft mode appearing in LiFeSi$_2$O$_6$ disappears by 7 GPa. The shift of all peaks with pressure is illustrated in Figs 6–8. Soft modes are frequently associated with instability in the structure and frequently disappear at phase transitions, which is further evidence of a second structural transition of LiFeSi$_2$O$_6$ at high pressures.

The final observed changes in the spectra occur at 8.71 GPa. Spectroscopic changes noted at this pressure are the

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**Figure 6.** Variation of peak positions with pressure, all data collected as pressure was increased. Error bars were from the peak-fitting program and represent the error in peak position after fitting a mixed Gaussian–Lorentzian peak to either a convergence or a local minimum of the chi-squared value. The error in pressure is estimated as 0.05 GPa. The peak at 1127 cm$^{-1}$ is emission from the LCD monitors in the laboratory and as such does not shift with pressure. This fact was utilized to ensure the uniformity of calibration in the spectra in which the peak appeared. Lines connecting the data points serve as guides to the eye, they should not be taken to imply the modes are necessarily related.

**Figure 7.** Variation of peak positions with pressure, mid-wavenumber region of spectra. The same pressure conditions as in Fig. 6 are displayed here. Note the appearance of several peaks at the phase transformation, near 1 GPa, and the disappearance of peaks at higher pressures, near 10 GPa.

**Figure 8.** Variation of peak positions with pressure, low-wavenumber portion of spectra. The same pressure region as in Figs 6 and 7 is displayed. Note the many changes in the spectra at the phase transformation, near 6 GPa, and near 10 GPa. The use of holographic notch filters allows data to be collected close to the Rayleigh line. There is much information in the region from 100 to 200 cm$^{-1}$ that would be lost if this region were not studied.
disappearance of $v_4$, $v_{13}$, $v_{17}$, $v_{29}$, $v_{36}$ and $v_{39}$, the strengthening of $v_1$ and $v_2$ and the reappearance of $v_{14}$. Spodumene also displays changes in the Raman spectra at pressures above the phase transition (from 8 to 10 GPa). The second change in spodumene is also characterized by a decrease in the number of peaks present, just as is observed in LiFeSi$_2$O$_6$. This change was attributed to a secondary change in the structure of spodumene that retained the symmetry – possibly a change in coordination number of the Li atom from 5 to 6. The same change in coordination of the Li atom is possible for LiFeSi$_2$O$_6$. Further investigations by X-ray diffraction are being carried out to determine if this is the case.

Raman spectra were not acquired above 11.87 GPa. The pressure medium was examined visually to ensure that no freezing occurred and, as such, the pressure applied was hydrostatic through all pressures reported here. No band broadening, such as that detected under non-hydrostatic conditions, was observed.

There are several peaks that remain apparent throughout the entire pressure range. These include $v_3$, $v_9$, $v_{16}$, $v_{21}$, $v_{23}$, $v_{27}$ and $v_{34}$. The Raman modes at 284 and 519 cm$^{-1}$ reported in previous Raman spectra of the C$_2$/c phase of Li-aegirine were not apparent in this study; however, peaks at 246 and 529 cm$^{-1}$ are observed. Raman modes previously reported at 1012 or 1038 cm$^{-1}$ are also not apparent in this study. These modes may not be apparent in the crystal orientation studied because of the previously discussed dependence of Raman peak intensity on orientation. Additionally, this study assigns the longest wavenumber band at atmospheric pressure at 1079 cm$^{-1}$, whereas previously it was reported at 1084 cm$^{-1}$.

Spectra were also acquired while decreasing pressure in small increments from 5.89 to 0.27 GPa. The crystal shattered during the process, but still gave high-quality spectra that display the first and second changes in the spectra. As discussed above, no significant hysteresis was apparent.

The peak designated as $v_2$ splits to form a doublet at pressures above 2.30 GPa. The formation of a doublet from a singlet is indicative of the removal of the degeneracy of this mode with the symmetry change. That is, the loss of the $C_2$ symmetry element makes vibrations that were formerly of equal energy unequal. A doublet in this region of the spectrum has previously been utilized as a benchmark for the P2$_1$/c phase in pyroxenes. However, this study shows that the doublet does not appear at the phase change, but at pressures about 1.3 GPa above the phase change. That is, the decrease in symmetry is not manifested in the Raman spectra until 1.3 GPa above the pressure where X-ray diffraction indicates the bonding change occurs. It may be that the doublet does not appear in this material until the Si—O3—Si angles in the A and B chains are different by more than 2° or the O3—O3—O3 angles in the A and B chains are different by more than 30°. The Si—O3—Si angles in LiFeSi$_2$O$_6$ at 3.1 GPa, are different by 2.3° and the difference is 2.5° at 3.9 GPa. However, in spodumene, the Si—O3—Si angles are different by 2.9° at 8.8 GPa. No doublet is apparent in spodumene, so the difference in chain angles is not responsible for the doublet in the Raman spectrum near 700 cm$^{-1}$.

CONCLUSIONS

This work is the first report of the Raman spectra of the pressure-induced phase transition from C2/c to P2$_1$/c in LiFeSi$_2$O$_6$. The spectra appear to be similar to the spectra for spodumene (LiAlSi$_2$O$_6$), especially in the P2$_1$/c phase, where both have 5-coordinated Li atoms. The similarity between the spectra allows some comparison between them and tentative mode assignments based on previous work. The changes in the Raman spectra near 6 GPa may be indicative of spin crossovers brought about by the increase in lattice energy. Finally, the Raman spectrum displays an additional change above 8 GPa, characterized by the disappearance of several peaks, which is similar to what occurs in spodumene. These changes may also be due to a phase transition that retains the P2$_1$/c symmetry but changes the bonding around the Li atom. Current X-ray studies are under way to determine if this is indeed the case. Determination of the origins of the secondary change in the spectrum can give additional information about the mechanism of the high-pressure phase changes in Li-pyroxenes.

REFERENCES