

Raman spectroscopic study of spodumene ($\text{LiAlSi}_2\text{O}_6$) through the pressure-induced phase change from $C2/c$ to $P2_1/c$

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High-pressure Raman spectroscopy was used to follow the effects of a phase transition on the Raman spectrum of a natural specimen of the pyroxene spodumene, from its low-pressure ($C2/c$) to its high-pressure ($P2_1/c$) phases. The transition occurred at 3.2 GPa and was accompanied by an increase from 15 to 23 observed peaks, owing to a decrease in symmetry. Comparisons were made with other pyroxenes with the same space groups. The change in Raman shift with pressure of all peaks observed is reported. An additional change in the spectrum is observed between 7.7 and 8.9 GPa, possibly due to the formation of an additional bond between Li and O3 or some other transition that retained the mineral's $P2_1/c$ space group. Splitting of the peak appearing at $\sim 700\text{ cm}^{-1}$, used to characterize the $P2_1/c$ phase in other studies, was not observed. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: spodumene; pyroxene; pressure-induced phase change; high-pressure Raman spectroscopy

INTRODUCTION

Spodumene ($\text{LiAlSi}_2\text{O}_6$) is a monoclinic, optically biaxial member of the pyroxene group of minerals. Pyroxenes (general formula $\text{M}_2\text{M}_1\text{Si}_2\text{O}_6$) comprise approximately 25% of the Earth's volume to a depth of 400 km.¹ There are a variety of symmetries exhibited by pyroxenes, most notably $C2/c$, $P2_1/c$, $Pbca$ and $Pbcn$, and all pyroxenes appear to undergo phase transitions between these various symmetries as a function of pressure and temperature. The atomic scale mechanisms for these changes have been the subject of much study.² A recently discovered phase transition in pyroxenes, accompanied by a volume change, is now accepted as an origin of deep-focus earthquakes at a depth of about 225 km.^{3–5} Spodumene is a principle source of lithium and has uses in the glass and ceramics industries. In spodumene, chains of AlO_6 (M1) octahedra separate chains of SiO_4 tetrahedra (Fig. 1). Li occupies the M2 site. In general, the M2 site is observed to be 4-, 5-, 6- or 8-coordinated, depending on pressure, temperature and composition. 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. Sharma and Simons have already reported the Raman spectra of three high-temperature polymorphs of spodumene and glasses of spodumene composition.⁶ A recently discovered high-pressure phase of spodumene⁷ was not one of the polymorphs studied.

Depending on temperature and pressure, spodumene has been observed in either $C2/c$ or $P2_1/c$ symmetry.⁷ At pressures below 3.2 GPa, the mineral displays space group symmetry C_{2h}^6 ($C2/c$). In this phase, both Li and Al occupy positions of C_2 site symmetries. The Si and all three types of oxygens display C_1 site symmetry. According to factor group analysis, there are 14 A_g and 16 B_g Raman-active modes associated with the $C2/c$ phase.

Near 3.2 GPa, the mineral undergoes a reversible phase transition to the C_{2h}^5 space group ($P2_1/c$).⁷ At the transition, the coordination of the Li atom changes from 6 to 5 when the bond to the O3 oxygen atom in the 3-position breaks (see Fig. 1).² The loss of this bond destroys the C_2 symmetry of the mineral. In the $P2_1/c$ phase, all atoms in spodumene display C_1 site symmetries. There should be 30 Raman-active A_g modes and 30 B_g modes. The phase transition is accompanied by a 1.4% decrease in volume. This phase transition has been documented by x-ray diffraction studies.⁷

The Raman spectrum of spodumene in the $P2_1/c$ phase has not yet been reported. It is the purpose of this paper

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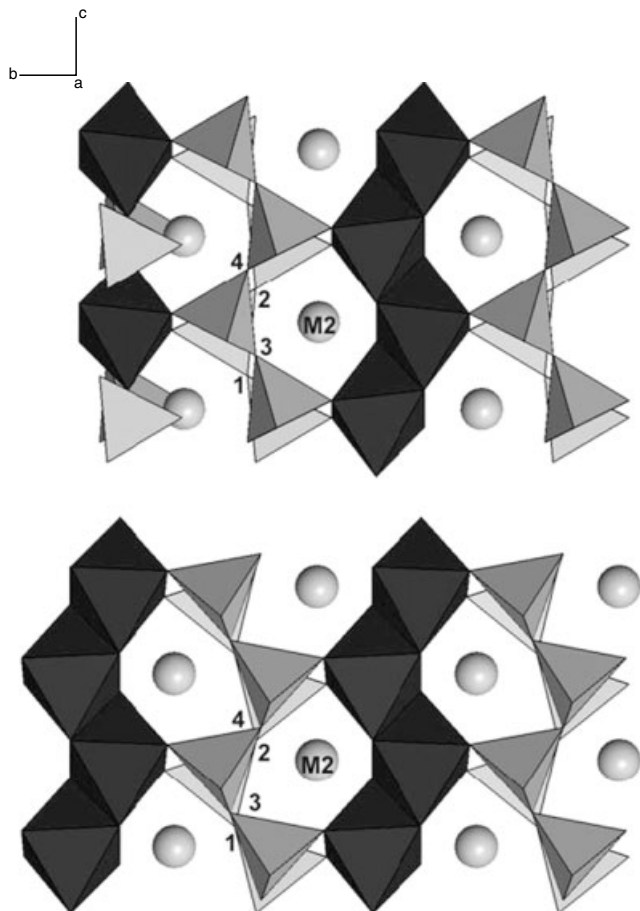


Figure 1. Top, $C2/c$ spodumene structure, and bottom, $P2_1/c$ spodumene structure. Solid lines illustrate Li–O bonds. The dotted line illustrates the bond that appeared at 8.84 GPa in Ref. 7.

to demonstrate the changes in the Raman spectrum of spodumene that are indicative of the phase transition from $C2/c$ to $P2_1/c$ and to compare the Raman spectra of these phases with similar phases in other pyroxenes. It is becoming apparent that the transformations between pyroxenes that display $C2/c$, $P2_1/c$, $Pbca$, $Pbcn$ and $P2_1cn$ (C_{2h}^6 , C_{2h}^5 , D_{2h}^{14} , D_{2h}^{15} , C_{2v}^9) symmetries are much more common than previously thought. As such, an additional purpose of this paper is to establish a method to characterize the different symmetries using Raman spectroscopy.

EXPERIMENTAL

The sample was a fragment of a large, pale pink gem crystal from Pala, San Diego County, CA, USA. The $200 \times 200 \times 25 \mu\text{m}$ fragment was loaded into a four-pin Merrill Basset-type diamond cell with (110) parallel to the cell axis. The diamond anvil culet size was $600 \mu\text{m}$. A stainless-steel gasket, $250 \mu\text{m}$ thick, pre-indented to $50 \mu\text{m}$, with a hole diameter of $300 \mu\text{m}$ was used. The cell was loaded

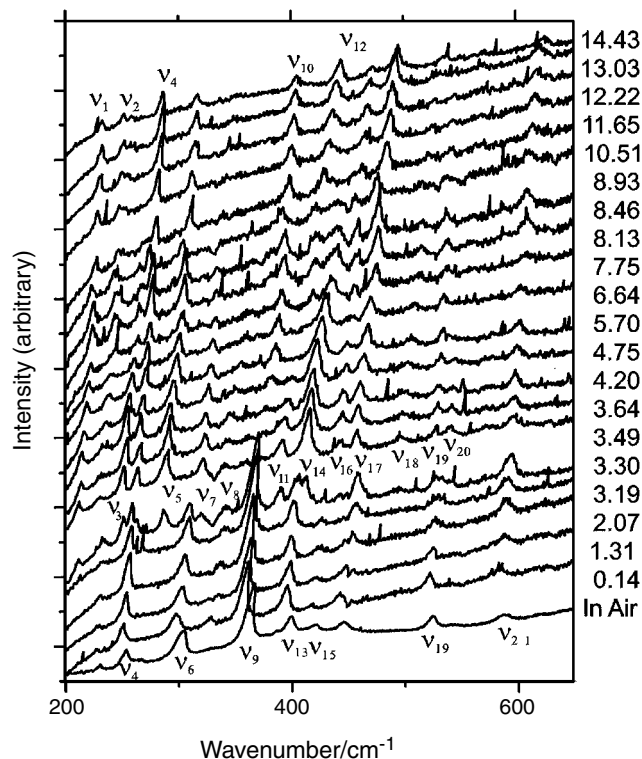


Figure 2. Low-wavenumber region of spectra as the pressure is varied. Note the spectrum at 3.30 GPa where both phases are evident and the change in spectra between 7.75 and 10.51 GPa.

with the spodumene crystal and a small ruby fragment, and filled with 15:4:1 methanol–ethanol–water 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.*⁸ The error in pressure is estimated to be 0.05 GPa. Pressure was measured before and after each spectrum acquisition and the reported value is the average of these two measurements. Both ruby fluorescence and Raman spectra were excited with a 514.5 nm argon ion laser.

There was no specific polarization alignment along the crystal the axes. Raman scattering was collected in the backscattered geometry. Rayleigh scattering was filtered out using two Kaiser Optics holographic filters. Spectra were acquired using a Jobin Yvon Spex HR 460 spectrometer and a liquid nitrogen-cooled 1152×256 pixel Princeton Instruments charge-coupled device (CCD) detector. Utilizing an $1800 \text{ grooves mm}^{-1}$ grating centered at 530 nm, the region from 104 to 1010 cm^{-1} was acquired using WinSpec software. However, owing to interference from the filters, only the region above 200 cm^{-1} was analyzed. Data were imported into GRAMS 32 software and peak positions were found using the peak fitting utility. Errors averaged less than 1 cm^{-1} for all peak positions with the errors for most peaks falling well below 1 cm^{-1} .

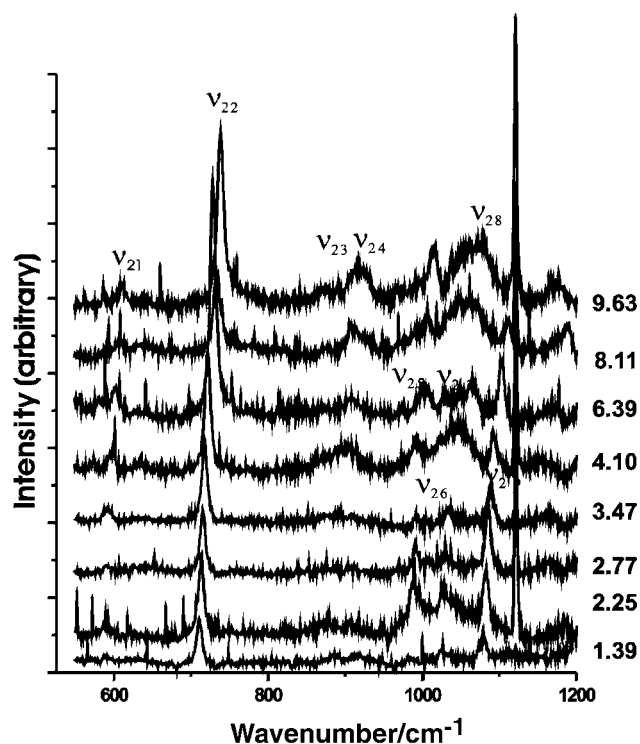


Figure 3. High-wavenumber region of spectra as pressure is decreased. The peak at 1119 cm^{-1} represents interference from monitors in the room, not Raman scattering.

Data for the region from 200 to 1000 cm^{-1} were acquired as the pressure was increased to 16.18 GPa , where conditions were no longer hydrostatic (see Fig. 2). The pressure was then decreased to 9.63 GPa . Data for the region from 1000 to 1210 cm^{-1} were acquired as the pressure was decreased to 1.39 GPa (see Fig. 3). Appearing in many of the spectra is a peak at 1115 cm^{-1} that is attributable to an emission line of flat-screen monitors utilized in the laboratory, not a genuine Raman peak. No data were acquired above 1210 cm^{-1} since earlier studies have shown that there are no peaks apparent at higher wavenumbers, and because of interference due to Raman scattering from the diamond line at $\sim 1330\text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Near 3.2 GPa , spodumene undergoes a phase transition from $C2/c$ to $P2_1/c$. This is evidenced by the dramatic change in the Raman spectrum. Although it is difficult to say definitely, it appears that some peaks split into two, some disappear altogether and several peaks appear at the transition (Figs 4 and 5).

Peaks ν_8 , ν_{21} , ν_{22} , ν_{24} and ν_{29} appear through all pressures, although their positions shift with increasing pressure. Peaks ν_6 , ν_9 , ν_{15} and ν_{28} are not present above the transition. Peak ν_4 appears to split into ν_3 and ν_4 , ν_{13} into ν_{11} and ν_{14} , ν_{17} into ν_{16} and ν_{17} , ν_{19} into ν_{19} and ν_{20} and ν_{26} into ν_{25} and ν_{27} . The following peaks appear at the phase transition: ν_1 ,

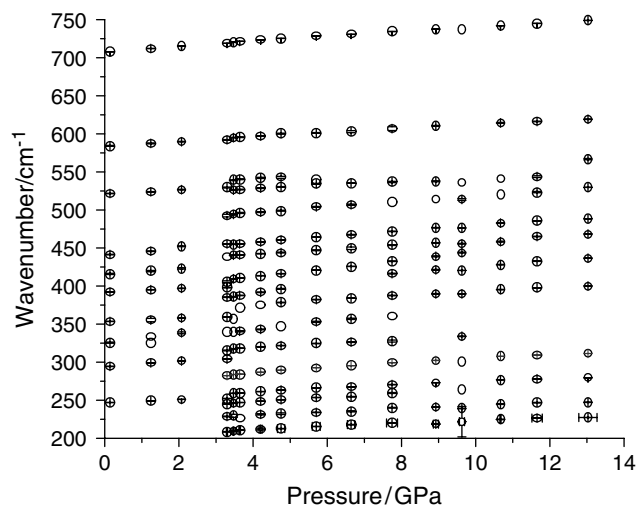


Figure 4. Plots of peak position as a function of pressure.

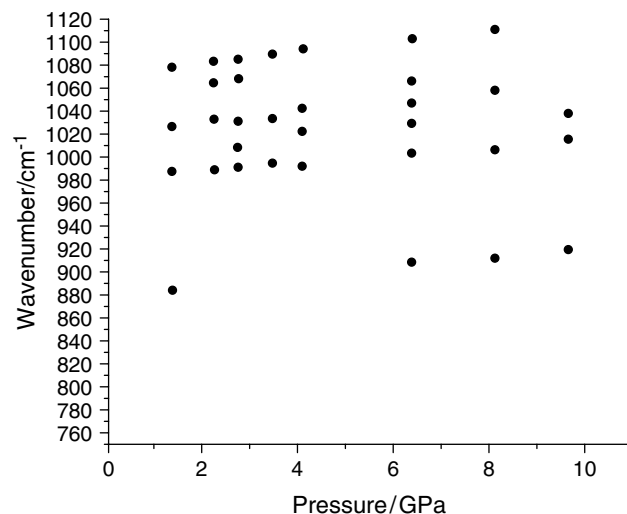


Figure 5. Plot of high-wavenumber peak positions as a function of pressure. Data acquired as pressure was decreased.

ν_2 , ν_5 , ν_7 , ν_{10} and ν_{18} . Peak ν_{12} only appears after 7.7 GPa . Peaks ν_3 , ν_7 , ν_8 , ν_{11} , ν_{14} and ν_{20} do not appear through the highest pressures. The disappearance of these peaks might be evidence for a change in spodumene that may be associated with a second transition that retains the $P2_1/c$ symmetry. Peak ν_{24} is a very weak and broad peak. It is difficult to determine if this peak is constantly present, if it appears at the transition or if it is a Raman peak at all associated with the mineral. The wavenumber at which the peak appears shifts linearly with pressure, indicating that it may be a Raman peak. The authors suggest that this peak is due to the methanol–ethanol pressure medium, as there is a peak appearing in the ethanol spectrum at 883 cm^{-1} and none appearing in the spectrum of spodumene at atmospheric pressure.

Prior to the phase transition, there were only 15 peaks apparent in the spectrum. According to factor group analysis, there should be a total of 30 peaks, 14 of A_g symmetry and 16 of B_g symmetry. Although no attempt was made in this experiment to discern the symmetries of the peaks, it is evident that too few appear. There are many reasons why the expected peaks may not be apparent, including accidental degeneracy (two peaks having the same energy, thereby appearing at the same wavenumber), two peaks having very close to the same energy with the resolution of the instrument being inadequate to distinguish between them, or the peaks could have too low an intensity to be above the noise of the measurement. Huang *et al.*⁹ proposed that in a natural sample, disorder created by cation substitution might broaden the peaks, making them indistinct. This natural sample also exhibited fluorescence, which increased the noise of the measurement such that several peaks, known from previous studies to be present (especially in the 900–1200 cm^{-1} region), are not apparent. The sample was investigated with excitation at 785 nm, and was found to fluoresce at this wavelength also.

With the destruction of the C_2 site symmetry at the M1 and M2 positions, modes appear that were degenerate before the phase transition, especially in the low-wavenumber region of the spectrum. It is logical to assume that some of these

modes are directly related to vibrations involving the M2 atom. In this experiment, ν_3 , ν_{13} , ν_{17} , ν_{19} and ν_{26} all appear to split, though ν_{26} may actually be an appearance of a peak, not a splitting. In addition, the following modes appear, indicating that they also are related to M1 or M2 vibrations: ν_1 , ν_2 , ν_5 , ν_7 , ν_{10} and ν_{18} . This is not inconsistent with previous studies, which have assigned pyroxene bands appearing below 550 cm^{-1} to cation translation, bending and stretching of bonds related to M1 and M2, and longer wavelength lattice modes.^{9,10–13} Note that in the $P2_1/c$ symmetry, there are two distinct silicate chains, which should contribute to an increase in number of modes observed as well, although most likely in the higher wavenumber region.

The spectrum of spodumene in the low-pressure phase can be compared with the Raman spectra of diopside, $\text{CaMgSi}_2\text{O}_6$, which is another pyroxene with $C2/c$ symmetry.^{13,14} At atmospheric pressure, diopside has eight bonds associated with the M2 site, whereas spodumene has six. Chopelas and Serghiou¹³ report that at high pressure, however, diopside may also have six bonds to the M2 site, although this is unconfirmed. Also note that in diopside, M2 is bonded to O_{31} , O_{32} , O_{33} and O_{34} , whereas in spodumene, M2 is bonded to O_{32} and O_{33} .

Figure 6 compares the spectra of diopside (bottom) and spodumene (top) in the $C2/c$ phase at 1 atm. Both spectra

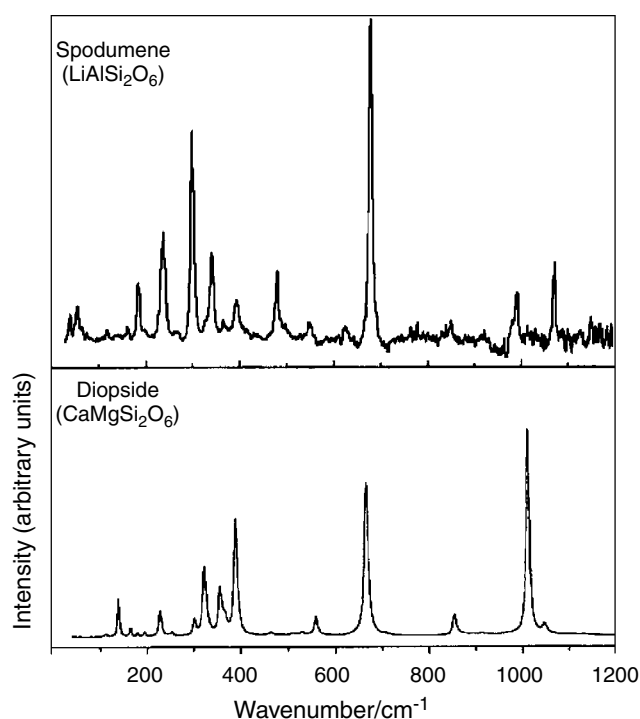


Figure 6. Top, $C2/c$ spodumene on (110) face, and bottom, $C2/c$ diopside on (110) face. Reference 19 assigns the vibrational regions in pyroxenes as follows: 800–1200 cm^{-1} Si– O_{nb} stretch, 650–800 cm^{-1} Si– O_{b} stretch, 425–650 cm^{-1} Si–O bend and 50–425 cm^{-1} complex lattice vibrations due to Si–O bend and M–O interactions.

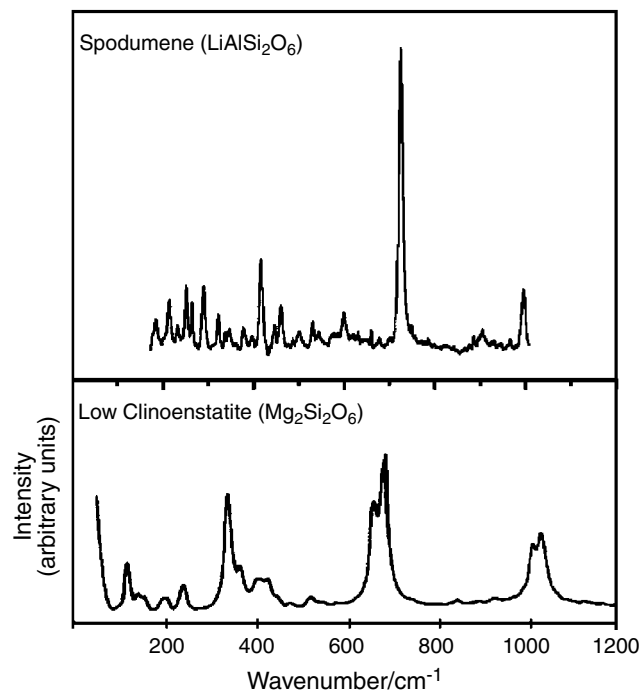


Figure 7. $P2_1/c$ spodumene at 4.70 GPa (top) and $P2_1/c$ low clinoenstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$) at 0 GPa (bottom, from reference 16 used with permission). Reference 19 assigns the vibrational regions in pyroxenes as follows: 800–1200 cm^{-1} Si– O_{nb} stretch, 650–800 cm^{-1} Si– O_{b} stretch, 425–650 cm^{-1} Si–O bend and 50–425 cm^{-1} complex lattice vibrations due to Si–O bend and M–O interactions.

have a singlet between 600 and 800 cm^{-1} that is indicative of the $C2/c$ phase in pyroxenes.^{9–11,15} Both spectra have strong peaks near 140 cm^{-1} and also have similar peaks in the 500–600 cm^{-1} range, the Si—O chain bending region. Between 200 and 500 cm^{-1} there is little similarity between the two spectra. The region above 1000 cm^{-1} , where SiO stretching is found, is different in the two spectra, even though both spectra were acquired with laser light incident on the (110) face of the minerals. Peak intensities in this region have shown a strong dependence on crystal orientation. However, since the two minerals are oriented identically, this is not the explanation for the different number of peaks.

Above the transition, 23 peaks were observed. The following peaks appear to be indicative of a $P2_1/c$ phase in spodumene: $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_7, \nu_{10}, \nu_{12}, \nu_{14}, \nu_{16}$ and ν_{18} . Although there are again too few peaks, there is a definite increase in the number of peaks, which indicates a decrease in symmetry of the crystal. Because the only change in bonding in this mineral is related to the Li—O3 bonds, any change in the spectrum should be attributable to those vibrations involving the M2 atom (Li) or the O3 atoms. Additionally, the peaks above 1000 cm^{-1} were often difficult to discern after the transition because a broad peak appeared from 1050

to 1100 cm^{-1} , which obscured any lower intensity peaks present (see Fig. 3).

Figure 7 shows a comparison between two pyroxenes of $P2_1/c$ symmetry, spodumene (top) and low clinoenstatite (MgSiO_3) (bottom).¹⁶ In the 600–800 cm^{-1} region for clinoenstatite a doublet appears, indicating two symmetrically distinct Si—O chains.^{9,15–17} For spodumene, a singlet appears in this region throughout all pressures. In all other spectra of $P2_1/c$ pyroxenes, there is a doublet in this region. It is difficult to compare the Si—O stretching region (above 800 cm^{-1}) because of the broad, indistinct peak that appeared in this region during our experiment. There appear to be similarities between 180 and 250 cm^{-1} , but few other parallels between these two spectra are apparent.

Tables 1 and 2 show the observed change in wavenumbers with pressure (referred to as slope). Compression of the pyroxenes occurs primarily by the geometry change of M1 and M2 octahedra because the silica tetrahedra are relatively incompressible.^{17,18} The M2 octahedra are more affected by this distortion than are the M1 octahedra,¹⁷ hence a larger change in wavenumber with pressure indicates that the peak is likely to be associated with M2—O bonds. The peak that showed the largest change with pressure after the transition, peak ν_{11} , was also one that disappeared near 8 GPa. The

Table 1. Peak positions (in cm^{-1}) listed with pressure^a

| | 0.141 | 1.243 | 2.071 | 3.295 | 3.47 | 3.638 | 4.203 | 4.754 | 5.702 | 6.640 | 7.745 | 8.927 | 9.630 | 10.668 | 11.654 | 13.026 | Slope (pre-/post-) |
|------------|-------|-------|-------|-------|------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------|--------|-----------------------|
| ν_1 | | | | 209 | 209 | 211 | 212 | 213 | 216 | 218 | 220 | 219 | 222 | 225 | 227 | 227 | 1.86 |
| ν_2 | | | | 229 | 230 | 227 | 232 | 232 | 234 | 235 | 240 | 241 | 239 | 245 | 247 | 247 | 2.01 |
| ν_3 | | | | 245 | 246 | 247 | 249 | 251 | 254 | 255 | 260 | | 264 | | | | 2.90 |
| ν_4 | 247 | 249 | 251 | 252 | 259 | 260 | 261 | 263 | 266 | 267 | 271 | 273 | | 277 | 278 | 279 | 1.63/2.20 |
| ν_5 | | | | 282 | 284 | 284 | 287 | 290 | 293 | 295 | 299 | 302 | 301 | 308 | 309 | 311 | 2.90 |
| ν_6 | 295 | 299 | 302 | 304 | | | | | | | | | | | | | 2.89 |
| ν_7 | | | | 315 | 317 | 318 | 320 | 322 | 325 | 326 | 328 | | | | | | 2.56 |
| ν_8 | 326 | 334 | 339 | 340 | 340 | 341 | 343 | 347 | 352 | 357 | 360 | | | | | | 4.50/4.92 |
| ν_9 | 354 | 355 | 358 | 359 | | | | | | | | | | | | | 1.92 |
| ν_{10} | | | | | 357 | 371 | 375 | 378 | 382 | 384 | 388 | 390 | 390 | 395 | 398 | 400 | 3.50 |
| ν_{11} | | | | 385 | 386 | 388 | 392 | 396 | | | | | | | | | 7.59 |
| ν_{12} | | | | | | | | | | | 416 | 421 | 421 | 428 | 433 | 437 | 4.16 |
| ν_{13} | 392 | 395 | 397 | 398 | | | | | | | | | | | | | 1.92 |
| ν_{14} | | | | 406 | 410 | 411 | 414 | 416 | 421 | 426 | 433 | 439 | 444 | | | | 5.44 |
| ν_{15} | 416 | 420 | 423 | | | | | | | | | | | | | | 3.63 |
| ν_{16} | | | | 439 | 441 | 441 | 443 | 444 | 447 | 450 | 454 | 457 | 456 | 458 | 465 | 468 | 2.77 |
| ν_{17} | 441 | 446 | 452 | 455 | 455 | 455 | 458 | 461 | 464 | 467 | 472 | 477 | 476 | 483 | 485 | 488 | 4.61/3.58 |
| ν_{18} | | | | 493 | 494 | 496 | 497 | 499 | 504 | 507 | 510 | 514 | 514 | 521 | 523 | 530 | 3.55 |
| ν_{19} | 522 | 524 | 527 | 530 | 526 | 527 | 529 | 530 | 534 | 535 | 537 | 538 | 536 | 541 | 544 | 567 | 2.61/2.90 |
| ν_{20} | | | | | 539 | 540 | 542 | 543 | 540 | | | | | | | | 0.54 |
| ν_{21} | 584 | 587 | 590 | 592 | 595 | 596 | 597 | 600 | 601 | 603 | 607 | 611 | | 614 | 616 | 619 | 2.60/2.52 |
| ν_{22} | 708 | 712 | 715 | 719 | 721 | 722 | 723 | 725 | 729 | 731 | 734 | 738 | 738 | 742 | 745 | 749 | 3.49/2.88 |

^a Error in peak position is $<2 \text{ cm}^{-1}$. Slope is change in Raman shift with pressure in $\text{cm}^{-1} \text{ GPa}^{-1}$. First number is pre-transition (0–3.47 GPa), second is post-transition (3.47–13.03 GPa).

Table 2. Long-wavenumber (in cm^{-1}) peak position data

| | 1.386 | 2.254 | 2.78 | 3.467 | 4.1 | 6.388 | 8.107 | 9.63 | Slope (pre-/post-) |
|------------|-------|-------|------|-------|------|-------|-------|------|-----------------------|
| ν_{23} | 885 | | | | | 908 | 911 | 918 | 3.11 |
| ν_{24} | 987 | 989 | 991 | 995 | 992 | 1003 | 1007 | 1014 | 3.44/3.41 |
| ν_{25} | | | 1008 | | 1022 | 1029 | | 1038 | 2.95 |
| ν_{26} | 1027 | 1033 | 1031 | 1033 | | | | | 2.85 |
| ν_{27} | | | | | 1043 | 1046 | 1058 | | 4.62 |
| ν_{28} | | 1064 | 1068 | | | 1066 | | | 7.16 |
| ν_{29} | 1079 | 1083 | 1085 | 1089 | 1094 | 1103 | 1112 | | 5.00/4.68 |

fact that its position changed so dramatically with pressure and that ν_{11} disappeared indicate that this peak is closely associated with an M2—O3 bond.

Between 8 and 10 GPa there is another change to the Raman spectrum of spodumene. Peaks ν_3 , ν_7 , ν_{10} and ν_{18} are no longer apparent above 10 GPa and a peak at 416 cm^{-1} appears. It is possible that these changes in the spectrum can be attributed to the formation of a new Li—O3 bond to O3₄, while retaining the $P2_1/c$ symmetry. This possibility must be investigated further. Chopelas and Serghiou¹³ recently reported a similar change in the Raman spectrum of diopside ($\text{CaMgSi}_2\text{O}_6$), which they attribute to a $C2/c$ to $C2/c$ change. The disappearance of some peaks and the appearance of others demonstrate this change. It is therefore likely that at high pressures other pyroxenes undergo similar changes that are apparent in the Raman spectrum but do not necessarily change the symmetry of the mineral.

CONCLUSIONS

The $C2/c$ to $P2_1/c$ phase transition in spodumene is clearly demonstrated by several distinctive spectral changes. Of

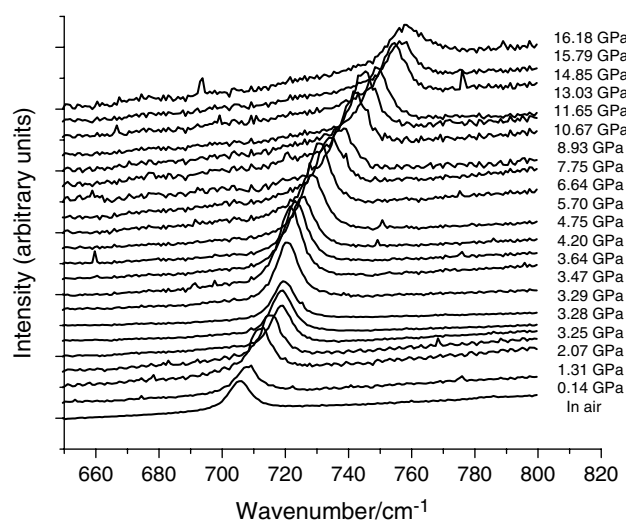


Figure 8. Silicate chain stretching peak through all pressures. No splitting or significant broadening, which would indicate a $P2_1/c$ phase, is apparent above the transition.

particular note is the splitting of the 250 cm^{-1} peak into a doublet. Also, the appearance of a singlet instead of a doublet between 600 and 800 cm^{-1} in the $P2_1/c$ phase appears to be unique to spodumene, as other $P2_1/c$ pyroxenes display a doublet. The existence of the 700 cm^{-1} doublet has been attributed to two symmetrically distinct silicate chains and a singlet to two symmetrically equivalent chains.^{9,15–17} If we accept this argument, then there is no Raman spectroscopic evidence that the transition creates symmetrically non-equivalent Si—O chains in spodumene. However, x-ray evidence indicates that there is a symmetry change to $P2_1/c$, so the interpretation must be incorrect. Other variations in the spectrum are consistent with a model of M2—O3 bond changes that leave M1—O and Si—O bonds intact. It could be argued that there are in fact two peaks present, but they are accidentally degenerate. X-ray diffraction studies show that the two silicate chains are symmetrically distinct, but geometrically similar at the transition, while other $P2_1/c$ pyroxenes have geometrically very different silicate chains near their transitions. Spodumene's Si—O3—Si bond angles are very similar in both silicate chains near the transition, $\sim 134^\circ$.⁷ We can contrast this with clinoenstatite's bond angles of 133 and 127° . Other $P2_1/c$ pyroxenes display Si—O3—Si bond angles of 141 and 139° in $\text{LiScSi}_2\text{O}_6$, 140° in both chains for $\text{LiGeSi}_2\text{O}_6$, 129 and 138° in $\text{Fe}_2\text{Si}_2\text{O}_6$ and 138 and 129° in $\text{Zn}_2\text{Si}_2\text{O}_6$. The argument could be made that because of their geometric similarity, the two silicate chains' vibrational bands would lie on top of one another. However, as the pressure is increased in spodumene, the similarity of the chains decreases. At 8.8 GPa , the bond angles are 131 and 128° and above this pressure they should continue to decrease in similarity.⁷ A broadening of the Raman peak should have occurred because of this difference, but no evidence of such broadening appears (Fig. 8). In addition, previous studies which assign the doublet to singlet change in the spectrum to the Si—O chains utilized samples containing iron,^{9–11} except for studies on enstatite ($\text{MgCaSi}_2\text{O}_6$).¹⁵ Spodumene ($\text{LiAlSi}_2\text{O}_6$) and jadeite ($\text{NaAlSi}_2\text{O}_6$) both display singlets whereas Li-aegirine ($\text{LiFeSi}_2\text{O}_6$) and aegirine ($\text{NaFe}^{2+}\text{Si}_2\text{O}_6$) both display doublets at low pressures, even though all of these are in the $C2/c$ phase (Fig. 9). Clearly, the presence of a doublet is not indicative of the $P2_1/c$ phase in all pyroxenes.

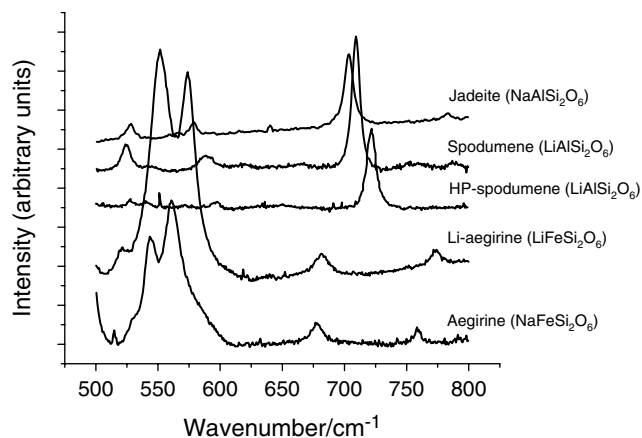


Figure 9. Strong doublets appear in the spectra of $C2/c$ aegirine ($\text{NaFeSi}_2\text{O}_6$) and $C2/c$ Li-aegirine ($\text{LiFeSi}_2\text{O}_6$), but not in $P2_1/c$ spodumene (high-pressure $\text{LiAlSi}_2\text{O}_6$), $C2/c$ spodumene (low-pressure $\text{LiAlSi}_2\text{O}_6$), or $C2/c$ jadeite ($\text{NaAlSi}_2\text{O}_6$).

Furthermore, another set of spectral changes appearing around 7.7 GPa might be indicative of a second transition. A recent study by Downs² shows that a transition to $C2/c$, but with M2 bonded to $\text{O}3_1$ and $\text{O}3_4$ instead of $\text{O}3_2$ and $\text{O}3_3$, is expected upon continued increase in pressure following a $P2_1/c$ to $P2_1/c$ bonding change. The second set of changes in the Raman spectrum of spodumene observed in this study may be indicative of the first step ($P2_1/c$ to $P2_1/c$) of the phase transition back to $C2/c$.

Future investigations into the bonding characteristics of spodumene will include the calculation of force constants and utilizing this information to calculate the wavenumbers of all Raman modes in spodumene. A Raman study on an oriented crystal has been conducted to elucidate further the assignment of peaks, especially in the region below 600 cm^{-1} .

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