Raman study of crystalline polymorphs and glasses of spodumene composition quenched from various pressures

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Abstract

Raman spectra are reported for the three known polymorphs of LiAlSi2O6, for glasses of LiAlSi2O6 composition synthesized at 1500° and 1750°C and over the pressure range 0.001-20 kbar, and for a glass of LiAlSi2O6 composition synthesized at 1 atm and 1500°C. A comparison of the spectra of LiAlSi2O6-I, -II, and -III indicates that the change in the coordination of Al from four-fold (LiAlSi2O6-II and -III) to six-fold (LiAlSi2O6-I) results in major changes in the spectra. The observed number of Raman bands are compared with those predicted on the basis of factor group analysis, and we propose that little or no deviation of the structure of α-spodumene from the C2/c space group occurs.

The spectra of the glasses of LiAlSi2O6 composition synthesized over the pressure range 0.001-20 kbar resemble those of LiAlSi2O6-I and -III, which indicates that Al is tetrahedrally coordinated in the glasses over the pressure range investigated. The major spectral differences between the 1 atm and high-pressure glasses are explained in terms of differences in the symmetry of the local ordering of the network structure and a systematic decrease in the T-O-T bond angle with increasing pressure. The overall effect of pressure on the structure of LiAlSi2O6 melts is to increase the degree of local ordering and to change the local network structure from phase II- and phase III-like arrangements to a coesite-type structure.

Introduction

Sharma et al. (1979) recently investigated the structure of melts of jadeite composition as a function of pressure by measuring the Raman spectra of the jadeite melt quenched from pressures up to 40 kbar, and demonstrated that Al remains tetrahedrally coordinated throughout the pressure range investigated. The results of that study led to a rejection of a previous hypothesis (Waff, 1975) that a pressure-induced coordination change of Al from four- to six-fold is responsible for the observed decrease in viscosity of melt of jadeite composition at elevated pressures (Kushiro, 1976, 1978; Kushiro et al., 1976). To aid in understanding the structure of aluminosilicate melts at ambient and high pressures, the Raman spectra of LiAlSi2O6 in both crystalline and glassy states have been measured. Spodumene composition was selected because it can be crystallized, by varying pressure and temperature, in three crystalline polymorphs (Munoz, 1967), which have aluminum in four-fold (LiAlSi2O6-II and -III) and six-fold (LiAlSi2O6-I) coordination. In the literature, the polymorphs LiAlSi2O6-I, -II, and -III are also referred to as α-spodumene, β-spodumene, and γ-spodumene (or β-eucryptite), respectively. The latter convention is not structurally appropriate for naming high-pressure-related polymorphs; therefore, the nomenclature introduced by Li (1968) is used in this paper. By comparing the Raman spectra of different polymorphs of LiAlSi2O6, the effect of Al in four- and six-fold coordination on the spectra can be evaluated. Furthermore, a direct comparison of the Raman spectra of glasses of spodumene composition prepared over the pressure range 0.001-20 kbar with the spectra of crystalline polymorphs can provide a better understanding of the local structure of these glasses.

Infrared spectra of LiAlSi2O6-I and -II were studied by Ignat'eva (1959). Murthy and Kirby (1962) reported the infrared spectra of solid solutions of
LiAlSi$_2$O$_4$-II—silica and LiAlSi$_2$O$_4$—III (β-eucryptite)—silica.

Measurements of the Raman spectra of different polymorphs of LiAlSi$_2$O$_4$, of glasses of the composition LiAlSi$_2$O$_4$ synthesized at 1500° and 1750°C over the pressure range 0.001–20 kbar, and of a glass of Li$_3$AlSi$_2$O$_5$ composition (LiAlSi$_2$O$_6$ + 0.25 Li$_2$O) synthesized at 1 atm are reported here for the first time. The glass of Li$_3$AlSi$_2$O$_5$ composition was investigated to evaluate the effect of nonbridging oxygen on the Raman spectrum.

**Experimental methods**

Glass of Li$_3$AlSi$_2$O$_5$ composition was prepared from oxide mixes of high-purity SiO$_2$, Al$_2$O$_3$, and reagent-grade Li$_2$CO$_3$. A method analogous to the preparation of K$_2$O–Al$_2$O$_3$–SiO$_2$ glasses (Schairer and Bowen, 1955) was used. Glass of spodumene composition was kindly provided by Dr. D. B. Stewart of the U.S. Geological Survey.

A sample of LiAlSi$_2$O$_4$-I was crystallized from glass of LiAlSi$_2$O$_4$ composition in a sealed Pt$_{95}$Au capsule at 30 kbar and 1350°C (Munoz, 1967) in a solid-media, high-pressure apparatus (Boyd and England, 1960) for 6 hr. Similarly, phase III was crystallized from the glass over a period of 3 hr in a sealed Pt$_{95}$Au capsule at 10 kbar and 1000°C in a gas-media, high-pressure apparatus (Yoder, 1950). A sample of LiAlSi$_2$O$_4$-II was prepared by crystallizing glass of spodumene composition for 48 hr in a sealed Pt$_{95}$Au capsule at 1350°C and ambient pressure. The glasses at high pressures (10 and 20 kbar) were synthesized from glass of spodumene composition prepared at 1 atm by quenching the melt of LiAlSi$_2$O$_4$ composition from 1750°C under pressure in a solid-media, high-pressure apparatus. The samples were sealed in Pt$_{95}$Au capsules 3 mm in diameter and 4 mm long.

Raman spectra were recorded with a Jobin-Yvon Raman spectrometer. Samples were excited with the 488.0 nm line of an Ar$^+$ ion laser with a laser power of 300–400 mW at the sample. Scattered radiation was collected at 90° to the exciting beam. Details of the Raman apparatus are given elsewhere (Sharma, 1978).

The refractive indices of the glasses were measured by the immersion method. The refractive index of the oil that matched that of the glass was determined with a microrefractometer and monochromatic sodium light. The density of the glasses was measured in toluene with a Berman torsion microbalance. Both refractive indices and densities were corrected for thermal expansion to 25°C.

**Results**

Raman spectra of the different polymorphs of LiAlSi$_2$O$_4$ are given in Figure 1. The positions and other spectral characteristics of the bands are summarized in Table 1.

Raman spectra of glasses of the compositions LiAlSi$_2$O$_4$ and Li$_3$AlSi$_2$O$_5$ and the spectrum of LiAlSi$_2$O$_4$-III are shown in Figure 2. The spectra of glasses of spodumene composition synthesized at 10 and 20 kbar are shown in Figure 3. The observed vibrational frequencies, the refractive indices, and the densities are tabulated in Table 2.

**Discussion**

**Raman spectra of crystalline polymorphs**

LiAlSi$_2$O$_4$-III (γ-spodumene). This phase belongs to the hexagonal space group P6$_3$22, Z = 1, and has a stuffed β-quartz type structure in which Li atoms occupy interstitial positions and an equipoint of rank 3, and Si$^{4+}$ is replaced randomly by Al$^{3+}$ (Li, 1968). Phase III therefore has, in addition to Si–Al disorder, three-fold cationic disorder. Disorder in the structure is reflected in the Raman spectrum of phase III, which shows a strong Rayleigh tail and broad Raman bands (Fig. 1). Because of the disordered structure it is not possible to apply rigorously the methods of group theoretical analysis to the spectrum. A reasonable assignment of the prominent bands can, however, be proposed by comparing the spectrum of LiAlSi$_2$O$_4$-III with the spectrum previously reported for β-quartz (Bates, 1972) that is isotypical to phase III. The strongest band at 480 cm$^{-1}$ in the spodumene is assigned to the A$_1$ mode and corresponds to the 462 cm$^{-1}$ band observed in β-quartz. The shoulders at 102 and 440 cm$^{-1}$ are assigned to the E$_1$ mode and correspond to the E$_1$ modes of β-quartz observed at 99 and 428 cm$^{-1}$. The weak band at 742 cm$^{-1}$ is assigned to the E$_2$ mode and corresponds to the E$_2$ of β-quartz at 788 cm$^{-1}$. The weak and broad bands at 1044 and 1088 cm$^{-1}$ are assigned to the E$_1$ and E$_2$ modes, respectively, and the corresponding bands in β-quartz were observed at 1067 (E$_1$) and 1173 (E$_2$) cm$^{-1}$. In the spectrum of LiAlSi$_2$O$_4$-III the vibrational bands that may be attributed to the corresponding E$_2$ mode of β-quartz at 688, 409, and 245 cm$^{-1}$ were not detected. Similarly, bands that may be attributed to LiO$_4$ tetrahedra were not detected.
give rise to weak Raman bands but strong infrared bands in the 1000–1200 cm\(^{-1}\) region, are associated with the motion of bridging oxygen atoms along a line parallel to Si–Si. This motion can be called antisymmetric stretch because it results in opposite distortion of the two neighboring Si–O bonds. By analogy, the strongest Raman band at 480 cm\(^{-1}\) in the spectrum of spodumene is assigned to the symmetric T–O–T stretching (\(\nu_s\)) mode, where T = Si or Al in the network, and the bands at 1044 and 1088 cm\(^{-1}\) are assigned to antisymmetric T–O–T stretch modes.

The T–O–T bond angle in LiAlSi\(_4\)O\(_{12}\)-III is smaller (151.6\(^{\circ}\)) than the Si–O–Si bond angle in \(\beta\)-quartz (Li, 1968; Taylor, 1972). It seems that the smaller value of the T–O–T angle in LiAlSi\(_4\)O\(_{12}\)-III causes the \(\nu_s\) (T–O–T) band to appear at higher frequency (480 cm\(^{-1}\)) than the \(\nu_s\) (Si–O–Si) band (462 cm\(^{-1}\)) in \(\beta\)-quartz. The lowering of the \(\nu_s\) (T–O–T) frequencies

<table>
<thead>
<tr>
<th>Polymorphs of Spodumene</th>
<th>Raman Frequencies (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma)-spodumene</td>
<td>(\beta)-spodumene</td>
</tr>
<tr>
<td>1095 (sh)†</td>
<td>...</td>
</tr>
<tr>
<td>1044 (sh)</td>
<td>...</td>
</tr>
<tr>
<td>1044 (sh)</td>
<td>...</td>
</tr>
<tr>
<td>103 (sh)†</td>
<td>742 (sh)</td>
</tr>
<tr>
<td>440 (sh)</td>
<td>492 s</td>
</tr>
<tr>
<td>480 s</td>
<td>...</td>
</tr>
<tr>
<td>770 w,bd</td>
<td>742 w</td>
</tr>
<tr>
<td>770 w,bd</td>
<td>...</td>
</tr>
<tr>
<td>864 vw,bd</td>
<td>...</td>
</tr>
<tr>
<td>990 (sh)</td>
<td>...</td>
</tr>
<tr>
<td>1095 (sh)†</td>
<td>...</td>
</tr>
<tr>
<td>1044 (sh)</td>
<td>...</td>
</tr>
<tr>
<td>1088 w,bd</td>
<td>1044 w,bd</td>
</tr>
<tr>
<td>1094 w,bd</td>
<td>...</td>
</tr>
</tbody>
</table>

*Measurement accuracy is ±2 cm\(^{-1}\).
† Abbreviations: v, very; w, weak; m, medium; s, strong; bd, broad; sh, shoulder.
Fig. 2. Raman spectra of LiAlSi₂O₆-III (A), and of glasses of the compositions LiAlSi₂O₆ (B) and Li₁₋₅AlSi₂O₆₁₂₅ (C). I₁ and I₁ on the glass spectra, respectively, refer to the spectra recorded with the electrical vector of the scattered light parallel to and perpendicular to the electrical vector of the laser beam (laser 488.0 nm, Ar⁺ ion, 200 mW, slit 6 cm⁻¹).

in LiAlSi₂O₆-III compared with νₘ (Si–O–Si) in β-quartz is due to elongation of the T–O bonds and isomorphous substitution of Al for Si in the network. The modes of vibration of SiO₄ and AlO₄ tetrahedra interact strongly and produce coupled modes (Iishi et al., 1971; Moenke, 1974). Milkey (1960) investigated the infrared spectra of 57 tectosilicate crystals and found that the νₘ (T–O–T) absorption peaks show an irregular but systematic shift to lower frequencies as Al/Si is increased.

LiAlSi₂O₆-II (β-spodumene). According to X-ray diffraction data, LiAlSi₂O₆-II belongs to the tetragonal space group P4₁2₁2 with four molecules (Z = 4) in the unit cell (Li and Peacor, 1968). The structure is isotypical with keatite, and it consists of a three-dimensional alumino silicate network. The distribution of Si and Al in the tetrahedra is random. Li atoms are four-fold coordinated and occupy interstitial positions. The four Li atoms per unit cell are distributed among four sets of paired sites of eight-fold coordination. Phase II thus has Si–Al disorder and also two-fold cationic disorder.

The Raman spectrum of LiAlSi₂O₆-II is composed of broad bands (Fig. 1). Eleven Raman bands are observed (Table 1), much fewer than the expected number of Raman bands from the large unit cell of LiAlSi₂O₆-II. The presence of disorder in phase II will make the bands weak and broad. Some of the bands might be accidentally degenerate. It is also possible that the principal features of the vibrational spectrum of LiAlSi₂O₆-II are determined by a much smaller pseudo cell. White (1975) has pointed out that in complex silicate structures with large unit cells the long-range forces within the unit cell are not sufficiently strong in most silicates to separate all the motion into discrete spectral bands.

Fig. 3. Polarized Raman spectra of LiAlSi₂O₆ glasses formed from the liquid quenched at 10 and 20 kbar (laser 488.0 nm, Ar⁺ ion, 200 mW, slit 6 cm⁻¹).
Table 2. Raman frequencies* (cm⁻¹), densities, and refractive indices of glasses prepared at different pressures

<table>
<thead>
<tr>
<th>Composition:</th>
<th>LiAlSi₂O₆</th>
<th>Li₁.₅Al₁.₂5Si₂O₆₂5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (kbar):</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Density (g/cm³):</td>
<td>2.340</td>
<td>2.375</td>
</tr>
<tr>
<td>Refractive index:</td>
<td>2.435</td>
<td>2.485</td>
</tr>
</tbody>
</table>

Frequencies* |

| 476 s, p | 480 s, p | 476 s, p |
| 588 (sh), p | 588 (sh), p | 588 (sh), p |
| 760 w, bd | 756 w, bd | 764 w, bd |
| 980 w, bd, wp | 964 w, p | 964 w, bd, p |
| 1032 w, bd, wp | 1048 w, bd, p | 1048 w, bd, p |

*Measurement accuracy is ±10 cm⁻¹ for weak and broad bands and ±4 cm⁻¹ for strong bands.
†Abbreviations: w, weak; s, strong; bd, broad; sh, shoulder; p, polarized; dp, depolarized; wp, weakly polarized.

The Raman spectrum of keatite is not known. Comparison of the spectra of LiAlSi₂O₆-II and -III (Fig. 1) reveals that in the 400-1200 cm⁻¹ region the spectra of these polymorphs are very similar. This resemblance indicates that both these phases have three-dimensional network structures in which Al³⁺ is present in four-fold coordination. In LiAlSi₂O₆-II the strong band due to the ν₁ (T-O-T) mode appears at 492 cm⁻¹, and the ν₃ (T-O-T) modes appear at 990 and 1094 cm⁻¹. The differences in the T-O-T bond angles and T-O bond lengths in LiAlSi₂O₆-II and -III are responsible for the differences in the positions of the bands in these polymorphs.

LiAlSi₂O₆-I (α-spodumene). This phase has a monoclinic structure of pyroxene chains, and Al³⁺ is present in six-fold coordination. Change in the coordination of Al³⁺ from four- to six-fold has a drastic effect on the Raman spectrum of spodumene (Fig. 1). In the spectrum of LiAlSi₂O₆-I, the bands are much sharper and the intensities of the bands in the 900-1200 cm⁻¹ region are enhanced owing to creation of nonbridging oxygen (see below).

Many clinopyroxenes belong to space group C2/c with Z = 4 (Clark et al., 1969). The number of formula units in the primitive cell is two, and therefore the expected 57 (= 3N - 3) optic modes will be distributed among the following symmetry species (Etchepare, 1972):

\[ \Gamma = 14A_g(R) + 16B_g(R) + 13A_u(IR) + 14B_u(IR) \]

where R and IR refer to Raman and infrared active modes, respectively.

Etchepare (1972) studied Raman spectra of an oriented single crystal of diopside (CaMgSi₂O₆) and detected 13 A₄ and 15 B₄ modes. In polycrystalline diopside samples, however, only 23 Raman modes were detected because some of the bands overlap. In LiAlSi₂O₆-I only 21 bands were observed (Fig. 1, Table 1). On the basis of X-ray diffraction studies it has been proposed that spodumene belongs to space group C2 rather than to space group C2/c (Clark et al., 1969). For space group C2 all the 57 optic modes should be both Raman- and infrared-active. If the deviation of the structure from the C2/c space group is small, the A₄ and B₄ modes in the Raman spectrum are expected to be very weak. Because only 21 Raman bands are observed and the previously reported infrared bands (Ignat’eva, 1959) do not coincide with the positions of the Raman bands, we can conclude that distortion of the structure of spodumene from the C2/c space group is small, if present. Graham (1975) has pointed out that spodumene belongs to the C2/c space group, and the extra reflections observed by Clark et al. (1969) are probably due to microscopic inclusions in the sample. Infrared reflectance and Raman measurements on oriented single crystals of LiAlSi₂O₆-I are needed to resolve the question of the space group of spodumene.

The strong band at 707 cm⁻¹ in the spectrum of LiAlSi₂O₆-I is a characteristic band of pyroxene chains and is due to symmetric stretch of the bridging oxygen ν₁ (Si-O-Si) in the chain (White, 1975). In the Raman spectra of other pyroxene minerals, e.g., diopside (CaMgSi₂O₆), clinoenstatite (MgSiO₃), and enstatite (MgSiO₃), one or two intense bands in the 650-680 cm⁻¹ range were also observed and were as-
signed to the motion of bridging oxygen in the chains (White, 1975). In the 1000–1200 cm\(^{-1}\) region a band of medium intensity at 1066 cm\(^{-1}\) is due to symmetric stretching of the terminal nonbridging oxygen \([\nu_2(Si-O^-)]\) in the chain. In diopside and other pyroxenes, which do not contain Al\(^{3+}\) ions, the \(\nu_1\) (Si–O–Si) mode appears near 1000 cm\(^{-1}\) and is very intense (White, 1975). In the LiAl\(_2\)Si\(_2\)O\(_6\)–I spectrum the medium intensity of this band compared with the \(\nu_2\) (Si–O–Si) band is probably due to the more covalent character of some of the Al–O bonds. In fact, the X-ray diffraction study (Clark \textit{et al.}, 1969) has indicated that in LiAl\(_2\)Si\(_2\)O\(_6\)–I the Al–O bond lengths in Al\(_6\) octahedra vary (two Al–O distances of 1.818, two of 1.943, and two of 1.997 ± 0.002\(\AA\)).

Raman bands due to the AIO\(_6\) group are usually weak in intensity, and their positions depend upon coupling with the neighboring groups (Tarte, 1966; Adams, 1975). The bands attributed to the Al–O stretching mode of the AIO\(_6\) group are 520, 474, and 438 cm\(^{-1}\) (Adams, 1975). In the spectra of LiAl\(_2\)Si\(_2\)O\(_6\)–I, the AIO\(_6\) groups, which have strong interactions with pyroxene chains, may be contributing to the weak bands at 435 and 518 cm\(^{-1}\).

**Effect of Al\(^{3+}\) coordination change on the Raman spectra of LiAl\(_2\)Si\(_2\)O\(_6\) polymorphs**

The change in the coordination of aluminum from four- to six-fold modifies the structure of the silicate framework from a three-dimensional aluminosilicate network without nonbridging oxygens to a pyroxene structure with two nonbridging oxygens per silicon atoms. As pointed out above, the vibrational modes of AIO\(_4\) and SiO\(_4\) tetrahedra are coupled, and the vibrational modes due to AIO\(_6\) octahedral groups are expected to be weak and may also be coupled to other vibrational modes. It is not possible, therefore, to evaluate directly the effect of the coordination change in terms of vibrational modes of the AIO\(_4\) and AIO\(_6\) groups. The effect of the coordination change can, however, be evaluated indirectly by considering changes in the frequencies and intensities of the bands associated with the motion of bridging and nonbridging oxygen atoms. A comparison of the Raman spectra of three polymorphs of LiAl\(_2\)Si\(_2\)O\(_6\) (Fig. 1) in the spectral range 400–1200 cm\(^{-1}\) indicates that the change of coordination of Al\(^{3+}\) from four- to six-fold coordination causes a large shift in the position of the strong band associated with the motion of bridging oxygen. The \(\nu_1\) (Si–O–Si) stretching mode in LiAl\(_2\)Si\(_2\)O\(_6\)–I appears at 707 cm\(^{-1}\), whereas the \(\nu_2\) (T–O–T) stretching modes in phases II and III appear at 492 and 480 cm\(^{-1}\), respectively. The change of coordination of Al\(^{3+}\) from four- to six-fold also causes an increase in the intensities of the bands in the 1000–1200 cm\(^{-1}\) region relative to the band associated with the motion of bridging oxygen. The band at 1066 cm\(^{-1}\) in the spectrum of LiAl\(_2\)Si\(_2\)O\(_6\)–I is due to a symmetric stretching motion of the terminal nonbridging oxygen in the chain. The antisymmetric stretching motion of the bridging oxygen in the chain, which gives rise to the characteristic infrared spectrum, is subdued in the Raman spectrum because of its weak intensity.

**Raman spectra of glasses**

Glasses of LiAlSi\(_4\)O\(_8\) and Li\(_2\)AlSi\(_2\)O\(_6\), composition quenched at 1 atm. The prominent features in the Raman spectrum of glass of LiAl\(_2\)Si\(_2\)O\(_6\) composition quenched at 1 atm are the strong band at 476 cm\(^{-1}\) and the broad, weakly polarized bands in the 900–1200 cm\(^{-1}\) region (Fig. 2). The positions and the intensities of the Raman bands in the spectrum of glass of spodumene composition are closely related to the positions and intensities of the most prominent bands in the spectra of crystalline LiAl\(_2\)Si\(_2\)O\(_6\)–II and -III, both of which have a three-dimensional network structure with Al\(^{3+}\) in four-fold coordination. The bands in the glass spectrum are, however, much broader than their counterparts in the spectra of LiAl\(_2\)Si\(_2\)O\(_6\)–II and -III polymorphs. The broadening of the Raman bands in the spectrum of the glass is due to additional disorder in the glass structure.

The close resemblance of the relative intensities and positions of the Raman bands in the spectrum of glass of LiAl\(_2\)Si\(_2\)O\(_6\) composition to their counterparts in the spectra of LiAl\(_2\)Si\(_2\)O\(_6\)–II and -III indicates that in the glass Al\(^{3+}\) is present in four-fold coordination and acts as a network former.

A qualitative description of the local structure in the three-dimensional network of LiAl\(_2\)Si\(_2\)O\(_6\) glass can be made by taking into account the positions and polarization behavior of the Raman bands. It is known that the intertetrahedral angle (T–O–T, where T = Si or Al) in real glasses is not everywhere the same but is distributed about the most likely value, estimated by X-ray diffraction to be 144° in SiO\(_2\) and 133° in GeO\(_2\) glass (Wong and Angell, 1976, p. 409–507). In fact, the glass probably has an ensemble of local environment with a statistical distribution of the intertetrahedral angle. The variation of the T–O–T angle in the glass is the basis of the disorder and is responsible for the broadening of the Raman bands. In this situation, the peak position of the nondegenerate \(\nu_1\)
[Si(Al)–O–Si(Al)] mode would be related to the most probable T–O–T angle in the glass structure (Galeener, 1979). The peak position of the strongest Raman band in the glass spectrum is close to that of the ν_{2} [Si(Al)–O–Si(Al)] band in the spectrum of LiAlSi_{2}O_{5}–III. It seems, therefore, that the most probable T–O–T angle in the glass of LiAlSi_{2}O_{5} composition is close to that of LiAlSi_{2}O_{5}–III. In SiO_{2} glass, which has a β-quartz-like arrangement (3Si at the D_{2} site), the Raman bands in the 900–1200 cm\(^{-1}\) region are depolarized (Wong and Angell, 1976, p. 409–507). In the spectrum of the glass of LiAlSi_{2}O_{5} composition, the bands in the 900–1200 cm\(^{-1}\) region are, however, weakly polarized. The weakly polarized nature of the bands in this region can be explained as due to the lower site symmetry of Si(Al) in LiAlSi_{2}O_{5}–II [4Si(Al) at the C_{3} site and 8 at the C_{4} site]. The glass may, therefore, have LiAlSi_{2}O_{5}–II-like and –III-like arrangements in which clusters having LiAlSi_{2}O_{5}–II-like arrangements dominate. The above structural model of the glass of spodumene composition is also consistent with the observed crystallization behavior of the glass at 1 atm. The LiAlSi_{2}O_{5}–II crystals grow rapidly when the temperature of the melt is lowered 25°C below the liquidus, 1429°C ± 1°C (Munoz, 1967; Li and Peacor, 1968), whereas the crystallization of LiAlSi_{2}O_{5}–III at 1 atm has to be carried out at lower temperature (977°C) for at least 1/2 hr (Li, 1968).

In order to evaluate the effect of nonbridging oxygen in the glass on the Raman spectrum, 0.25 M Li_{2}O was added to the melt of LiAlSi_{2}O_{5} composition. The presence of excess Li\(^+\) in the glasses causes an increase in the intensity of the bands in the 900–1200 cm\(^{-1}\) region relative to that of the ν_{2} [Si(Al)–O–Si(Al)] band, which shifts toward higher frequency (Fig. 2). Similar changes are observed when alkali metal oxides are added to SiO_{2} melt (Simon, 1960). These changes are caused by the creation of nonbridging oxygen in the network structure. In the glass of Li_{1.5}AlSi_{2}O_{6.25} composition the ratio r, corresponding to the integrated intensity of the contour from 900 to 1250 cm\(^{-1}\) to the integrated intensity of the band from 200 to 650 cm\(^{-1}\) is 0.7, whereas in the glass of LiAlSi_{2}O_{5} composition this ratio is 0.52. The presence of 0.08 nonbridging oxygen per network-forming cation [Si(Al)] on the average thus results in a 35 percent increase in the relative intensity of the bands in the 900–1200 cm\(^{-1}\) region. Raman spectroscopy is, therefore, a sensitive tool for detecting the presence of nonbridging oxygen in the silicate network.

In the spectrum of glass of Li_{1.5}AlSi_{2}O_{6.25} composi-
prepared at 10 and 20 kbar (Fig. 3), are estimated to be 0.34 and 0.32, respectively. For the 20-kbar glass the value of \( r \) is 34 percent less than the value of \( r \), (0.52) for the 1-atm glass and is in contrast to the observed 35 percent increase in the value of \( r \) in the spectrum of glass of LiAlSiO\(_6\) composition due to the contribution of the nonbridging oxygen to the contour in the 900–1200 cm\(^{-1}\) region. The decrease in the value of \( r \) in the spectra of high-pressure glasses further reinforces the conclusion that Al\(^{3+}\) remains predominantly in tetrahedral coordination, and defect structures involving nonbridging oxygen are minimized in the high-pressure LiAlSiO\(_6\) glasses.

In the spectra of high-pressure glasses of LiAlSiO\(_6\) composition a strong band at 80 cm\(^{-1}\) is observed (Fig. 3). This band, as pointed out before, is due to disorder-induced phonon density of states arising from low-lying optic modes as well as the high-lying acoustic modes. In the 1-atm glass of LiAlSiO\(_6\) composition a similar low-frequency band is not resolved. The presence of a well-defined low-frequency band in the high-pressure glasses is probably related to more ordered and less open structure of these glasses.

In the case of high-pressure jadeite glasses, Sharma et al. (1979) have proposed that local short-range ordering in high-pressure glasses may in part resemble that in coesite. The changes observed in the spectra of high-pressure glasses are similar to those observed in the spectra of high-pressure glasses of jadeite composition. The observed decrease in the frequency of the \( v_\text{as} (T-O-T) \) in the spectra of high-pressure LiAlSiO\(_6\) glasses can be attributed to a decrease in the average T-O-T angle, which may be associated with a slight increase in the average T-O bond length. It can be concluded, therefore, that the high-pressure LiAlSiO\(_6\) glasses may also have, in part, a coesite-like arrangement. A coesite model of the structure of high-pressure LiAlSiO\(_6\) glasses is consistent with the observed increase in density and refractive index of the LiAlSiO\(_6\) glasses with increasing pressure.

It should be pointed out that within the accessible pressure range in the apparatus used for the present work \( \alpha \)-spodumene (LiAlSiO\(_6\)-I) does not melt congruently (Munoz, 1967). It will be interesting to see whether or not Al\(^{3+}\) remains six-coordinated in the melt at higher pressures (65 kbar), where LiAlSiO\(_6\)-I melts congruently.

**Conclusions**

The spectra of LiAlSiO\(_6\)-II and -III polymorphs show a close resemblance but differ greatly from the spectrum of LiAlSiO\(_6\)-I (\( \alpha \)-spodumene), owing to Al\(^{3+}\) coordination and Si-Al ordering. The positions and number of Raman bands in the spectrum of \( \alpha \)-spodumene are compatible with the pyroxene structure having the \( \text{C}2/c \) space group.

This study of different polymorphs of LiAlSiO\(_6\) shows that change in the coordination of Al\(^{3+}\) from four- to six-fold produces large changes in the frequencies and relative intensities of the Raman bands associated with the motion of bridging and non-bridging oxygen atoms. The bands associated with these motions give well-defined Raman bands even in the spectra of silicate glasses, and therefore can be used to determine the role of Al\(^{3+}\) in aluminosilicate crystals and glasses.

On the basis of similarity in the Raman spectra of LiAlSiO\(_6\) glasses, prepared by quenching up to 20 kbar pressure, and that of LiAlSiO\(_6\)-II and -III, we conclude that Al\(^{3+}\) is predominantly tetrahedrally coordinated in these glasses. On the basis of the polarization characteristics of the Raman bands and the position of the \( v_\text{as} (T-O-T) \) mode, we propose that the 1-atm glass has LiAlSiO\(_6\)-II-like and -III-like arrangements in which the clusters having LiAlSiO\(_6\)-II-like arrangements dominate. With increasing pressure the local symmetry of Si,Al in the network is lowered compared with that of LiAlSiO\(_6\)-III, and the glass structure at high pressures may in part resemble that of coesite.

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**References**


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