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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 $LiAlSi_2O_6$, for glasses of $LiAlSi_2O_6$ composition synthesized at 1500° and 1750°C and over the pressure range 0.001–20 kbar, and for a glass of $Li_{1.5}AlSi_2O_{6.25}$ composition synthesized at 1 atm and 1500°C. A comparison of the spectra of $LiAlSi_2O_6$-I, -II, and -III indicates that the change in the coordination of Al from four-fold ($LiAlSi_2O_6$-II and -III) to six-fold ($LiAlSi_2O_6$-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 $LiAlSi_2O_6$ composition synthesized over the pressure range 0.001–20 kbar resemble those of $LiAlSi_2O_6$ -II and -III, which indicates that Al^{3+} is four-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 $LiAlSi_2O_6$ 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^{3+} 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^{3+} 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 $LiAlSi_2O_6$ 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 ($LiAlSi_2O_6$-II and -III) and six-fold ($LiAlSi_2O_6$-I) coordination. In the literature, the polymorphs $LiAlSi_2O_6$-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 $LiAlSi_2O_6$ 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 $LiAlSi_2O_6$-I and -II were studied by Ignat'eva (1959). Murthy and Kirby (1962) reported the infrared spectra of solid solutions of

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$LiAlSi_2O_6$-II–silica and $LiAlSi_2O_6$-III (β-eucryptite)–silica.

Measurements of the Raman spectra of different polymorphs of $LiAlSi_2O_6$, of glasses of the composition $LiAlSi_2O_6$ synthesized at 1500° and 1750°C over the pressure range 0.001–20 kbar, and of a glass of $Li_{1.5}AlSi_2O_{6.25}$ composition ($LiAlSi_2O_6$ + 0.25 Li_2O) synthesized at 1 atm are reported here for the first time. The glass of $Li_{1.5}AlSi_2O_{6.25}$ composition was investigated to evaluate the effect of nonbridging oxygen on the Raman spectrum.

Experimental methods

Glass of $Li_{1.5}AlSi_2O_{6.25}$ composition was prepared from oxide mixes of high-purity SiO_2, Al_2O_3, and reagent-grade Li_2CO_3. A method analogous to the preparation of K_2O–Al_2O_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 $LiAlSi_2O_6$-I was crystallized from glass of $LiAlSi_2O_6$ composition in a sealed $Pt_{95}Au_5$ 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 $Pt_{95}Au_5$ capsule at 10 kbar and 1000°C in a gas-media, high-pressure apparatus (Yoder, 1950). A sample of $LiAlSi_2O_6$-II was prepared by crystallizing glass of spodumene composition for 48 hr in a sealed $Pt_{95}Au_5$ 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 $LiAlSi_2O_6$ composition from 1750°C under pressure in a solid-media, high-pressure apparatus. The samples were sealed in $Pt_{95}Au_5$ 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 $LiAlSi_2O_6$ 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 $LiAlSi_2O_6$ and $Li_{1.5}AlSi_2O_{6.25}$ and the spectrum of $LiAlSi_2O_6$-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

$LiAlSi_2O_6$-III (γ-spodumene). This phase belongs to the hexagonal space group $P6_322$, $Z = 1$, 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 $LiAlSi_2O_6$-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_1 mode and corresponds to the E_1 mode 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 $LiAlSi_2O_6$-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,

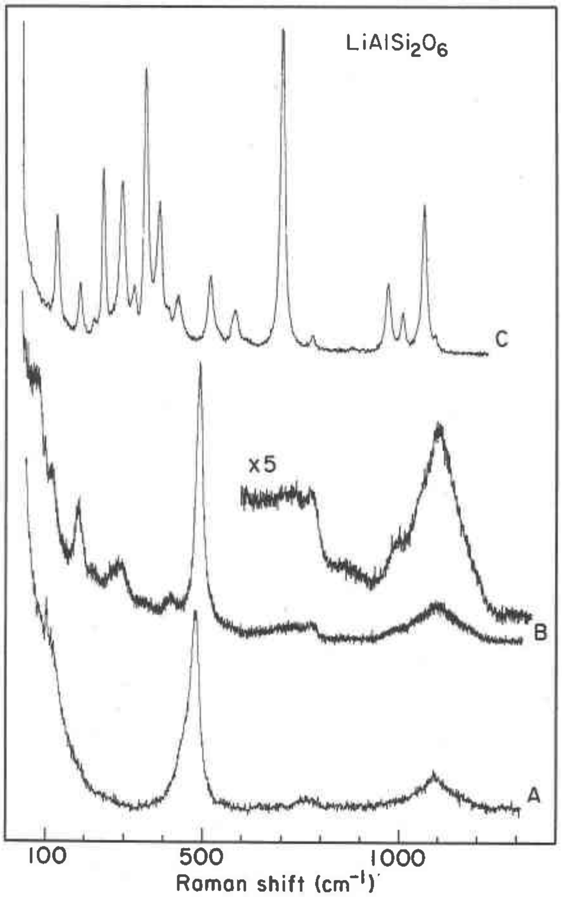

Fig. 1. Raman spectra of (A) $LiAlSi_2O_6$-III, (B) $LiAlSi_2O_6$-II, and (C) $LiAlSi_2O_6$-I (α-spodumene) (laser 488.0 nm, Ar^+ ion, 300 mW, slit 3 cm^{-1}).

probably because they are too weak. Hase and Yoshida (1979) have recently identified Raman bands due to Li–O vibrational modes of the LiO_4 tetrahedron in Li_2CO_3. These bands are weak. In $LiAlSi_2O_6$-III, the presence of disorder at the Li site will make the Li–O vibration too weak to detect.

The strongest band at 480 cm^{-1} and the weak bands in the 1000–1200 cm^{-1} region are characteristic of $Si(Al)O_4$ tetrahedra with four bridging oxygens. According to theoretical studies on SiO_2 glass (Bell and Dean, 1972; Sen and Thorpe, 1977; Laughlin and Joannopoulos, 1977), the strongest Raman band in the spectrum is associated with the motion of bridging oxygen along a line bisecting the Si–O–Si angle. Galeener (1979) suggested that this motion may be described as Si–O–Si symmetric stretch because, when acting along, the motion of oxygen results in identical distortion of two neighboring Si–O bonds. Similarly, the highest frequency modes, which 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 (ν_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 $LiAlSi_2O_6$-III is smaller (151.6°) than the Si–O–Si bond angle in β-quartz (Li, 1968; Taylor, 1972). It seems that the smaller value of the T–O–T angle in $LiAlSi_2O_6$-III causes the ν_s (T–O–T) band to appear at higher frequency (480 cm^{-1}) than the ν_s (Si–O–Si) band (462 cm^{-1}) in β-quartz. The lowering of the ν_{as} (T–O–T) frequencies

Table 1. Raman frequencies* (cm^{-1}) of different polymorphs of spodumene

γ-spodumene	β-spodumene	α-spodumene
...	∿75 (sh)	...
102 (sh)†	116 (sh)	129 m
...	184 m	189 w
...	...	225 vw
...	...	247 m
...	288 w	...
...	...	296 m
...	...	326 w
...	...	356 s
...	...	389 m
...	412 w	412 vw(sh)
440 (sh)	...	436 w
480 s	492 s	...
...	...	512 w
...	...	542 vw,bd
...	...	583 w
...	...	614 vw
...	...	707 s
742 vw,bd	∿720 vw,bd	...
...	770 w,bd	782 w
...	864 vw,bd	...
...	...	884 vw
...	...	973 w
...	990 (sh)	...
...	...	1012
1044 (sh)	...	...
...	...	1066 m
1088 w,bd	...	...
...	1094 w,bd	1095 vw(sh)

*Measurement accuracy is ±2 cm^{-1}.

†Abbreviations: v, very; w, weak; m, medium; s, strong; bd, broad; sh, shoulder.

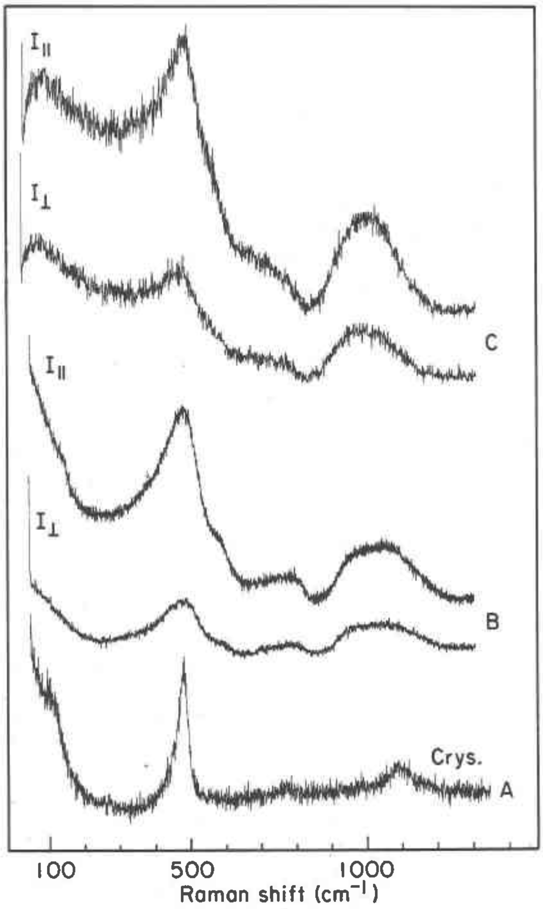

Fig. 2. Raman spectra of LiAlSi$_2$O$_6$-III (A), and of galsses of the compositions LiAlSi$_2$O$_6$ (B) and Li$_{1.5}$AlSi$_2$O$_{6.25}$ (C). $I_{\parallel}$ and $I_{\perp}$ on the glass spectra, respectively, refer to the spectra recorded with the electrical vector of the scattered light parallel to and perpendicular to the electrical vector of the laser beam (laser 488.0 nm, Ar$^+$ ion, 200 mW, slit 6 cm^{-1}).

in LiAlSi$_2$O$_6$-III compared with ν_{as} (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 SiO$_4$ and AlO$_4$ 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 ν_{as} (T–O–T) absorption peaks show an irregular but systematic shift to lower frequencies as Al/Si is increased.

LiAlSi$_2$O$_6$-II (β-spodumene). According to X-ray diffraction data, LiAlSi$_2$O$_6$-II belongs to the tetragonal space group $P4_32_12$ 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 LiAlSi$_2$O$_6$-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 LiAlSi$_2$O$_6$-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 LiAlSi$_2$O$_6$-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.

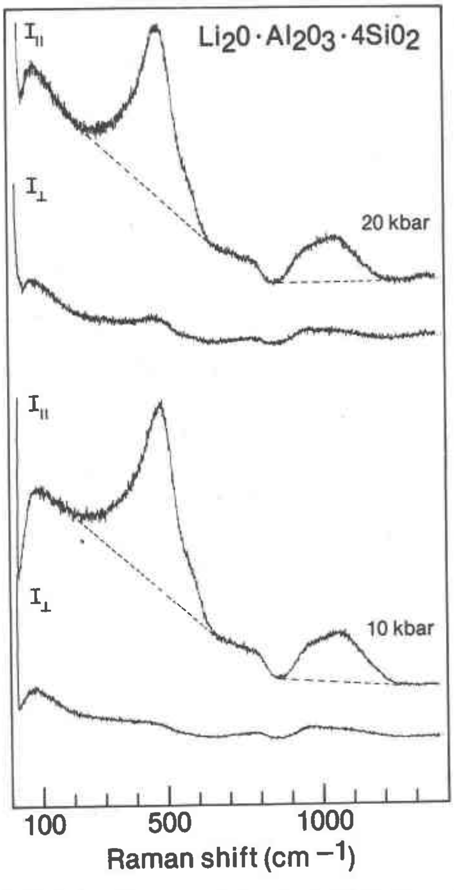

Fig. 3. Polarized Raman spectra of LiAlSi$_2$O$_6$ glasses formed from the liquid quenched at 10 and 20 kbar (laser 488.0 nm, Ar$^+$ ion, 200 mW, slit 6 cm^{-1}).

Table 2. Raman frequencies* (cm^{-1}), densities, and refractive indices of glasses prepared at different pressures

Composition:	$LiAlSi_2O_6$			$Li_{1.5}AlSi_2O_{6.25}$
Pressure (kbar):	0.001	10	20	0.001
Density (g/cm^3):	2.340	2.435	2.485	2.375
Refractive index:	1.518	1.529	1.536	1.527
		Frequencies*		
	...	∿80 s	∿80 s	∿100 s
	∿380 (sh),p†	...	...	...
	476 s,p	480 s,p	476 s,p	490 s,p
	∿588 (sh),p	588 (sh),p	588 (sh),p	∿568 (sh),p
	∿760 w,bd	∿756 w,bd	∿764 w,bd	∿744 w,bd
	∿980 w,bd,wp	∿964 w,p	∿964 w,bd,p	∿1012 w,bd,p
	∿1052 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 $LiAlSi_2O_6$-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 Al^{3+} is present in four-fold coordination. In $LiAlSi_2O_6$-II the strong band due to the ν_s (T–O–T) mode appears at 492 cm^{-1}, and the ν_{as} (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 $LiAlSi_2O_6$-II and - III are responsible for the differences in the positions of the bands in these polymorphs.

$LiAlSi_2O_6$-I (α-spodumene). This phase has a monoclinic structure of pyroxene chains, and Al^{3+} is present in six-fold coordination. Change in the coordination of Al^{3+} from four- to six-fold has a drastic effect on the Raman spectrum of spodumene (Fig. 1). In the spectrum of $LiAlSi_2O_6$-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 *C*2/*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):

$$\Gamma = 14A_g(\mathrm{R}) + 16B_g(\mathrm{R}) + 13A_u(\mathrm{IR}) + 14B_u(\mathrm{IR})$$

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

Etchepare (1972) studied Raman spectra of an oriented single crystal of diopside ($CaMgSi_2O_6$) and detected 13 A_g and 15 B_g modes. In polycrystalline diopside samples, however, only 23 Raman modes were detected because some of the bands overlap. In $LiAlSi_2O_6$-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 *C*2 rather than to space group *C*2/*c* (Clark *et al.*, 1969). For space group *C*2 all the 57 optic modes should be both Raman- and infrared-active. If the deviation of the structure from the *C*2/*c* space group is small, the A_u and B_u 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 spondumene from the *C*2/*c* space group is small, if present. Graham (1975) has pointed out that spodumene belongs to the *C*2/*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 $LiAlSi_2O_6$-I are needed to resolve the question of the space group of spodumene.

The strong band at 707 cm^{-1} in the spectrum of $LiAlSi_2O_6$-I is a characteristic band of pyroxene chains and is due to symmetric stretch of the bridging oxygen ν_s (Si–O–Si) in the chain (White, 1975). In the Raman spectra of other pyroxene minerals, *e.g.*, diopside ($CaMgSi_2O_6$), clinoenstatite ($MgSiO_3$), and enstatite ($MgSiO_3$), one or two intense bands in the 650–680 cm^{-1} range were also observed and were assigned 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 [ν_s(Si–O$^-$)] in the chain. In diopside and other pyroxenes, which do not contain Al^{3+} ions, the ν_s (Si–O$^-$) mode appears near 1000 cm^{-1} and is very intense (White, 1975). In the $LiAlSi_2O_6$-I spectrum the medium intensity of this band compared with the ν_s (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 *et al.*, 1969) has indicated that in $LiAlSi_2O_6$-I the Al–O bond lengths in AlO_6 octahedra vary (two Al–O distances of 1.818, two of 1.943, and two of 1.997 ± 0.002Å).

Raman bands due to the AlO_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 AlO_6 group are 520, 474, and 438 cm^{-1} (Adams, 1975). In the spectra of $LiAlSi_2O_6$-I, the AlO_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 $LiAlSi_2O_6$ 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 AlO_4 and SiO_4 tetrahedra are coupled, and the vibrational modes due to AlO_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 AlO_4 and AlO_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 $LiAlSi_2O_6$ (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 ν_s (Si–O–Si) stretching mode in $LiAlSi_2O_6$-I appears at 707 cm^{-1}, whereas the ν_s (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 1000–12000 cm^{-1} region relative to the band associated with the motion of bridging oxygen. The band at 1066 cm^{-1} in the spectrum of $LiAlSi_2O_6$-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 $LiAlSi_2O_6$ and $Li_{1.5}AlSi_2O_{6.25}$ composition quenched at 1 atm. The prominent features in the Raman spectrum of glass of $LiAlSi_2O_6$ 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 $LiAlSi_2O_6$-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 $LiAlSi_2O_6$-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 $LiAlSi_2O_6$ composition to their counterparts in the spectra of $LiAlSi_2O_6$-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 $LiAlSi_2O_6$ 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 ν_s

[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_s [Si(Al)–O–Si(Al)] band in the spectrum of $LiAlSi_2O_6$-III. It seems, therefore, that the most probable T–O–T angle in the glass of $LiAlSi_2O_6$ composition is close to that of $LiAlSi_2O_6$-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 $LiAlSi_2O_6$ 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 $LiAlSi_2O_6$-II [4Si(Al) at the C_2 site and 8 at the C_1 site]. The glass may, therefore, have $LiAlSi_2O_6$-II-like and -III-like arrangements in which clusters having $LiAlSi_2O_6$-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 $LiAlSi_2O_6$-II crystals grow rapidly when the temperature of the melt is lowered 25°–50°C below the liquidus, 1429° ± 1°C (Munoz, 1967; Li and Peacor, 1968), whereas the crystallization of $LiAlSi_2O_6$-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_2O was added to the melt of $LiAlSi_2O_6$ 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_s [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 $Li_{1.5}AlSi_2O_{6.25}$ composition the ratio r_i 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 $LiAlSi_2O_6$ 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 $Li_{1.5}AlSi_2O_{6.25}$ composition the strong and broad band at 100 cm^{-1}, which is easily resolved from the descending Rayleigh tail (Fig. 2), is characteristic of the glassy state. Similar low-frequency bands have been observed in the spectra of pure B_2O_3, SiO_2, and GeO_2 glasses (Stolen, 1970) and also in spectra of glasses of diopside ($CaMgSi_2O_6$) (Etchepare, 1972), akermanite ($Ca_2MgSi_2O_7$), and sodium melilite (Sharma and Yoder, 1979) compositions. It has been shown that these low-frequency bands in the glasses and melts are due to disorder-induced phonon density of states arising from low-lying optic modes as well as the higher-lying acoustic modes (Shuker and Gammon, 1970, 1971; Winterling, 1975). A close examination of the spectrum of glass of spodumene composition (Fig. 1) shows that a very low-frequency band, which is not well resolved from the Rayleigh tail, is present. The shift in the band position to higher frequency in the spectrum of $Li_{1.5}AlSi_2O_{6.25}$ composition is partly due to the higher density of this glass (D = 2.375) compared with that of 1 atm glass of $LiAlSi_2O_6$ composition (D = 2.340). These very low-frequency bands in the spectra of glasses correspond to intramolecular motions. These motions are not well understood but are very important because they dominate the thermodynamical properties of melts (Shuker and Gammon, 1971; Angell *et al.*, 1969). It should be emphasized that these low-frequency bands do not influence the high-frequency intermolecular modes that provide information about the structural units in the glasses and melts.

Glasses of $LiAlSi_2O_6$ composition quenched at high pressures. Both the density and the refractive index of the glasses of spodumene composition formed by quenching the melt at high pressure increase with increasing pressure (Table 2). The spectra of these high-pressure glasses in the 300–1200 cm^{-1} region are, however, similar to that of the quenched 1 atm glass except that with increasing pressure the weak and broad T–O–T asymmetric stretch bands at ~980 and ~1052 cm^{-1} in the 1 atm glass shift to lower frequency and show strong polarization (Table 2).

In general, the change in the polarization character of the Raman band in the 900–1200 cm^{-1} region in the spectra of high-pressure glasses can be attributed to a further lowering of local symmetry of the tetrahedrally-coordinated units in the network with increasing pressure.

The ratios r_i, 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} in the spectra of glasses of $LiAlSi_2O_6$ composition 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_i is 34 percent less than the value of r_i (0.52) for the 1-atm glass and is in contrast to the observed 35 percent increase in the value of r_i in the spectrum of glass of $Li_{1.5}AlSi_2O_{6.25}$ 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_i 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 $LiAlSi_2O_6$ glasses.

In the spectra of high-pressure glasses of $LiAlSi_2O_6$ 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 $LiAlSi_2O_6$ 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 ν_{as} (T–O–T) in the spectra of high-pressure $LiAlSi_2O_6$ 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 $LiAlSi_2O_6$ glasses may also have, in part, a coesite-like arrangement. A coesite model of the structure of high-pressure $LiAlSi_2O_6$ glasses is consistent with the observed increase in density and refractive index of the $LiAlSi_2O_6$ glasses with increasing pressure.

It should be pointed out that within the accessible pressure range in the apparatus used for the present work α-spodumene ($LiAlSi_2O_6$-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 $LiAlSi_2O_6$-I melts congruently.

Conclusions

The spectra of $LiAlSi_2O_6$-II and -III polymorphs show a close resemblance but differ greatly from the spectrum of $LiAlSi_2O_6$-I (α-spodumene), owing to Al^{3+} coordination and Si–Al ordering. The positions and number of Raman bands in the spectrum of α-spodumene are compatible with the pyroxene structure having the *C*2/*c* space group.

This study of different polymorphs of $LiAlSi_2O_6$ 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 nonbridging 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 $LiAlSi_2O_6$ glasses, prepared by quenching up to 20 kbar pressure, and that of $LiAlSi_2O_6$-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 position of the ν_s (T–O–T) mode, we propose that the 1-atm glass has $LiAlSi_2O_6$-II-like and -III-like arrangements in which the clusters having $LiAlSi_2O_6$-II-like arrangements dominate. With increasing pressure the local symmetry of Si,Al in the network is lowered compared with that of $LiAlSi_2O_6$-III, and the glass structure at high pressures may in part resemble that of coesite.

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