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Raman study of anorthite, calcium Tschermak's pyroxene, and gehlenite in crystalline and glassy states

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Abstract

Raman spectra are reported for crystalline anorthite (An), calcium Tschermak's pyroxene (CaTs), gehlenite (Geh), and glasses of $CaAl_2Si_2O_8$ (An), $CaAlAlSiO_6$ (CaTs), and $Ca_2AlAlSiO_7$ (Geh) composition. A small degree of Si–Al disorder in anorthite is indicated by the presence of weak Si–O–Si antisymmetric stretching modes in its spectrum. The spectrum of the glass of An composition closely resembles that of crystalline An. This correspondence indicates that the predominant species in An glass is composed of a random network of four-membered rings of TO_4 tetrahedra (where T = Si or Al). The spectra of glasses of CaTs and Geh compositions do not resemble the spectra of their respective crystals.

In the spectrum of glass of CaTs composition the ν_s(T–O–T) band appears at lower frequency (~564 cm^{-1}) than the ν_s(T–O–T) band of crystalline CaTs (651 cm^{-1}). The ν_{as}(T–O–T) bands in the 900–1200 cm^{-1} region are also at lower frequencies and are relatively stronger than the ν_{as}(T–O–T) bands in the glass of An composition. The lower frequency of the ν_{as}(T–O–T) is due to an increase in Al/Si from 1 in An glass to 2 in CaTs glass. The increase in the relative intensity of the ν_{as}(T–O–T) bands is due to nonbridging oxygens. The presence of free Ca^{2+} ions, and possibly a small amount of Al^{3+} in six-fold coordination, is responsible for these nonbridging oxygens in the glass.

In the spectrum of glass of Geh composition the ν_s(T–O–T) band appears at lower frequency (552 cm^{-1}) than in the spectrum of crystalline Geh (626 cm^{-1}). The shift of the band toward lower frequencies in the spectrum of the glass of Geh composition indicates that most of the Al^{3+} ions are tetrahedrally coordinated and act as network formers. A strong band at ~896 cm^{-1} in the spectrum of Geh glass is attributed to the presence of an appreciable amount of SiO_4^{4-} groups in the glass network. The structure of glass of Geh composition is thus highly polymerized with $CaAl_2O_4$ present in the network. The 0.33 nonbridging oxygen per network-forming cation (Si–Al), as required by the stoichiometry of the glass to charge-balance the Ca^{2+} ion, exists in the form of SiO_4^{4-} groups in the glass network.

Introduction

On the basis of geometrical packing, aluminum has an ionic radius intermediate between the optimum radii for four-fold and six-fold coordination (Hess, 1980). In this sense and also due to the amphoteric nature of aluminum oxide, Al^{3+} can assume the role of either a network-forming or a network-modifying cation in aluminosilicate melts. As a tetrahedrally coordinated cation within a silicate network, Al^{3+} is typically associated with a charge balancing cation such as an alkali or alkaline-earth cation. It has been suggested that when pressure is

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applied to aluminosilicate melts some or all of the Al^{3+} may change to higher coordinations (Waff, 1975; Kushiro, 1976, 1978; Mysen, 1976; Mysen and Virgo, 1978; Boettcher, 1981). It has been further proposed that such changes in coordination of Al^{3+} would depolymerize the melt, thus lowering its viscosity and diminishing the stability of highly polymerized liquid melts (Waff, 1975; Kushiro, 1975). Structural investigations of melts of jadeite (Sharma *et al.*, 1979; Hochella and Brown, 1981), spodumene (Sharma and Simons, 1981), and albite (Hochella and Brown, 1981) compositions quenched from higher pressure ($P < 40$ kbar), however, indicate that Al^{3+} ions remain tetrahedrally coordinated in these quenched melts. These observations imply that mechanisms other than a change in the Al^{3+} coordination from four- to six-fold may be responsible for the observed decrease in viscosity and increase in density at high pressures (Sharma *et al.*, 1979; Sharma and Simons, 1981; Hochella and Brown, 1981).

To aid in understanding the role of Al^{3+} in aluminosilicate melts, Raman spectra of anorthite (An, $Ca^{IV}Al_2Si_2O_8$), calcium Tschermak's pyroxene (CaTs, $Ca^{VI}Al^{IV}AlSiO_6$), and gehlenite (Geh, $Ca_2^{IV}Al^{IV}AlSiO_7$), in both crystalline and glassy states, have been measured in the present work. These aluminum-rich compositions were selected because Al^{3+} ions have different structural roles in crystalline phases and because these compositions represent important rock-forming minerals. In anorthite crystals, Al^{3+} ions act as network formers, are charge-balanced by Ca^{2+}, and obey the aluminum-avoidance rule, *i.e.*, have a high degree of Al and Si ordering (Kempster *et al.*, 1962; Megaw *et al.*, 1962). In CaTs, half the Al^{3+} ions are six-fold coordinated, acting as network modifiers and providing charge-balance to the remaining half of the aluminum ions, which are four-fold coordinated (Okamura *et al.*, 1974; Grove and Burnham, 1974). In crystalline gehlenite, both types of Al^{3+} ions are four-fold coordinated, with Al^{3+} at the site of symmetry $\bar{4}$ acting as network modifiers and providing charge-balance to the other Al^{3+} ions that are part of the ($AlSiO_7$) dimers. By examining the Raman spectra of crystalline anorthite and CaTs, the effect of Al^{3+} in four-fold and six-fold coordination on the spectra of these aluminum-rich minerals can be evaluated. Study of the Raman spectrum of gehlenite, on the other hand, provides a unique opportunity to evaluate the effect of a four-fold coordinated Al^{3+} acting as a network modifier, *i.e.*, not charge-balanced by another cation. Furthermore, a direct comparison of the Raman spectra of glasses of An, CaTs, and Geh compositions with the spectra of isochemical crystals can provide a better understanding of their local structures.

The Raman spectrum of crystalline anorthite was studied by Fabel *et al.* (1972) and McMillan *et al.* (1982). Virgo *et al.* (1979a) reported unpolarized Raman spectra of glasses of An and CaTs compositions and proposed that Al^{3+} ions are present in fourfold coordination in both the glasses. On the basis of polarized Raman spectra of glasses of CaTs and Geh composition, Piriou and Alain (1979) suggested that these glass spectra are characteristic of disordered- and ordered-chain structures, respectively. Taylor and Brown (1979) studied the structure of An glass by X-ray radial distribution function (RDF) analysis and proposed that the glass is composed of four-membered rings of TO_4 tetrahedra (where T = Si or Al) similar to those existing in crystalline feldspars.

Measurements of Raman spectra of crystalline An, CaTs, and Geh as well as polarized spectra of glasses of An, CaTs, and Geh composition synthesized at 1 atm are reported here. The Raman spectrum of crystalline CaTs is measured for the first time. For crystalline An, the higher resolution and low background from the sample used in this study resulted in a record of the spectrum below 100 cm^{-1} as well as resolution of the band structure in the 1000–1200 cm^{-1} region.

Experimental methods

Glasses of the compositions $CaAl_2Si_2O_8$ (An), $CaAlAlSiO_6$ (CaTs), and $Ca_2AlAlSiO_7$ (Geh) were prepared with appropriate oxides and carbonates of high purity. After decarbonation, the mixtures of An, CaTs, and Geh compositions were kept at 1575°, 1575°, and 1640°C, respectively, for 1 hr and subsequently quenched in air. A sample of glass of CaTs composition quenched from 1600°C, obtained from Prof. James F. Hays of Harvard University, consists of glass, corundum, β-Al_2O_3, or all three phases (Hays, 1966). The glass fragment free from crystalline inclusions that was used for Raman measurements was analyzed with an electron microprobe and was found to have a cationic composition of $CaAl_{1.9}Si_{0.99}$. Because the composition of this glass is close to that of CaTs, the glass is referred to in the text as a glass of CaTs composition. It should, however, be noted that the glass is deficient in aluminum and consequently has free Ca^{2+} (0.05 M).

Anorthite and gehlenite were crystallized from their respective glasses at 1000°C at 1 atm over a period of 48 hr. These samples were kindly provided by Prof. E. F. Osborn of the Geophysical Laboratory. Crystalline $CaAlAlSiO_6$ was prepared by crystallizing glass of CaTs composition at 20 kbar and 1400°C (Hays, 1966) for 24 hr in a solid-media, high-pressure apparatus (Boyd and England, 1960). The identifications of the synthetic gehlenite, anorthite and CaTs were verified by powder X-ray diffraction.

Raman spectra were recorded at room temperature with a Jobin-Yvon Raman spectrometer (HG · 2S). Samples were excited with the 488.0-nm line of an Ar^+ laser with laser power of about 500 mW at the sample. Scattered radiation was collected at 90° to the exciting beam. The spectra of the crystalline materials were recorded from the powdered samples in glass capillary tubes. Polarized spectra of the quenched glass fragments mounted on metallic needles were obtained with the electric vector of the exciting radiation in vertical orientation. A polarizer sheet in front of an optical scrambler was used to analyze separately the parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) components of scattered radiation. (For a detailed description of the Raman apparatus, see Sharma, 1978). The quenched glass samples used in the present study were not annealed. Presence of thermal stresses in these samples, especially in the glasses of CaTs and Geh composition, tend to scramble somewhat the polarization of the scattered radiation. As a result, $I_\perp$ spectra may contain a small contribution from the $I_\parallel$ component. For this reason these spectra are not used for estimating quantitatively the values of depolarization ratios ($\rho = I_\perp/I_\parallel$) of various bands. The quality of these spectra is, however, good enough for differentiating between polarized ($0 \leq \rho < 3/4$) and depolarized ($\rho = 3/4$) bands.

Results and discussion

The Raman spectra of crystalline An and glass of An composition are shown in Figure 1. The spectra of crystalline CaTs and glass of CaTs composition are depicted in Figure 2. The Raman spectra of crystalline Geh and glass of Geh composition are shown in Figure 3. The frequencies of Raman bands and their observed spectral characteristics in the spectra of crystalline phases and glasses are summarized in Tables 1 and 2, respectively. The assignment of various modes into lattice-like modes and molecular-like modes in Table 1 is only an approximation, especially in the case of the An spectrum where most of the modes are strongly coupled.

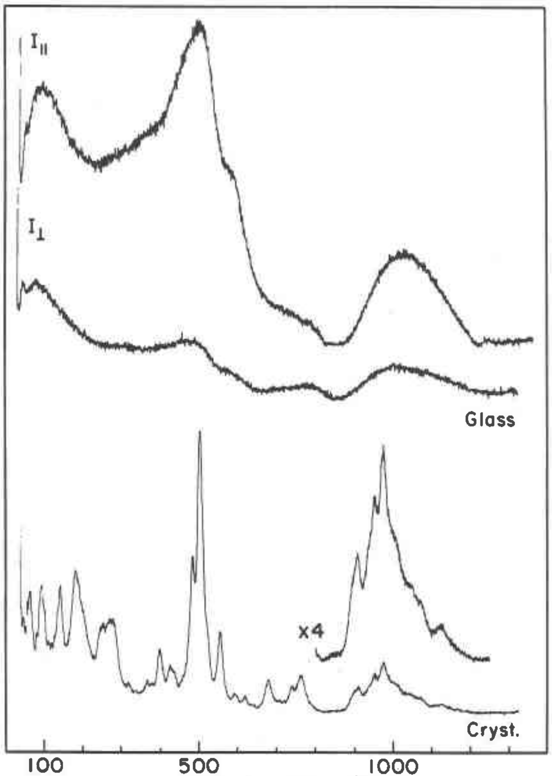

Fig. 1. Raman spectra of crystalline anorthite and of glass of the composition $CaAl_2Si_2O_8$. $I_\parallel$ and $I_\perp$ on the glass spectra, respectively, refer to the spectra recorded with the electric vector of the scattered light parallel to and perpendicular to the electric vector of the laser beam (laser 488.0 mm, Ar^+ ion, 500 mW, slit widths 3.5 cm^{-1} for the crystal spectrum and 8 cm^{-1} for the glass spectra).

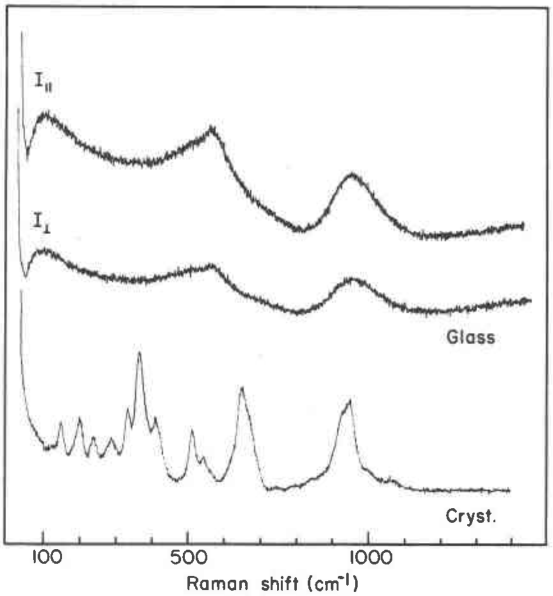

Fig. 2. Raman spectra of crystalline calcium Tschermak's pyroxene and of glass of approximately the CaTs composition. For symbols and experimental conditions refer to Fig. 1.

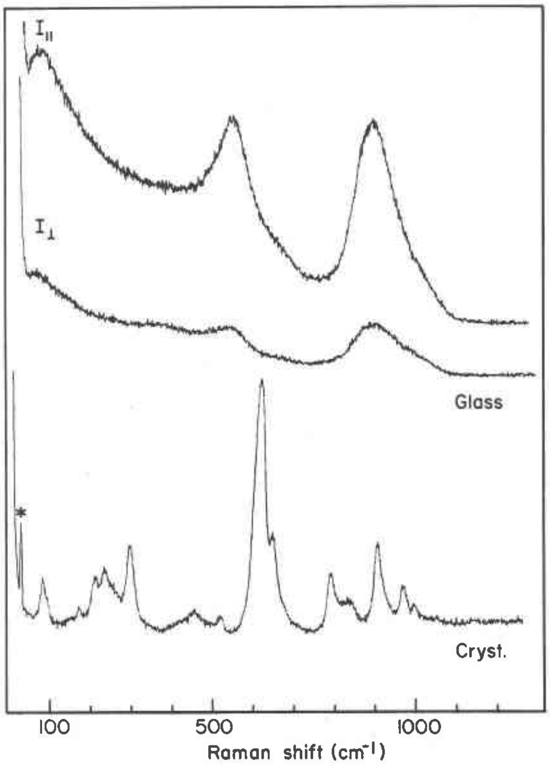

Fig. 3. Raman spectra of crystalline gehlenite and of glass of $CaAlAlSiO_7$ composition. For symbols and experimental conditions refer to Fig. 1. (Asterisk marks a plasma line from the laser.)

Table 1. Raman frequencies* (cm^{-1}) of crystals

Anorthite ($CaAl_2Si_2O_8$)		Calcium Tschermak's pyroxene ($CaAlAlSiO_6$)		Gehlenite ($Ca_2AlAlSiO_7$)	
Band positions	Tentative assignments	Band positions	Tentative assignments	Band positions	Tentative assignments
63 m†	lattice modes	...	lattice modes	...	lattice modes
88 m		...		89 m	
139 m		132 vw		...	
...		155 m		150 vw	
182 m		...		180 w	
200 (sh)		206 m		218 m	
...		244 w		240 m	
253 m		...		254 (sh)	
273 m		...		...	
281 m		296 w		...	
316 vw		...		303 m	
...		338 m (sh)		...	
369 vw		370 s		...	
400 w		414 m (sh)		425 vw (sh)	
427 w		...		...	
484 (sh)	$\nu_s(T\text{-O-}T)$	...		459 w, bd	
503 vs		...		...	
...		518 m		528 w	
553 m		549 w (sh)		...	
590 vw		...		...	
620 vw		...		626 vs	$\nu_s(T\text{-O-}T)$
...		651 s	$\nu_s(T\text{-O-}T)$	655 m (sh)	$\nu_s(AlO_4)$
681 m		676 (sh)		...	
741 (sh)		...		...	
756 w		...		...	
...		802 vw		796 m	$\nu(AlO_4)$
...		843 vw		841 w (sh)	
908 w (sh)	$\nu_{as}(\text{Si-O-Al})$	...		914 m	$\nu_s(T\text{-O}^-)$
...		922 s (sh)	$\nu_s(T\text{-O}^-)$	...	
949 w (sh)		953 s		...	
974 m		...		977 m	
998 (sh)		...		998 w	$\nu_{as}(\text{Si-O-Al})$
...		1004 vw	$\nu_{as}(\text{Si-O-Al})$	1005 vw	
1044 (sh)	$\nu_{as}(\text{Si-O-Si})$	...		...	
1072 (sh)		1071 vw	$\nu_{as}(\text{Si-O-Si})$	...	
1124 w		...		...	

*Measurement accuracy is ±2 cm^{-1} for strong and medium intensity bands and ±4 cm^{-1} for weak bands.
†Abbreviations: v, very; w, weak; m, medium; s, strong; sh, shoulder.

Raman spectrum of crystalline anorthite

Crystalline anorthite ($CaAl_2Si_2O_8$), a member of the feldspar family, belongs to the triclinic space group $P\bar{1}$ (C_i^1) with Z = 8, and is believed to transform on heating to a body-centered structure $C\bar{1}$ (C_i^1) with Z = 8 (Smith, 1974). Within the accuracy of X-ray crystal-structure determination, there is no Al–Si disorder because Al atoms alternate with Si atoms (Kempster *et al.*, 1962; Megaw *et al.*, 1962). From factor-group analysis, 156 A_g + 156 A_u optic modes are predicted for primitive anorthite, and 78 A_g + 78 A_u optic modes for body-centered anorthite (White, 1975), where all g modes are Raman active and u modes are infrared active.

Table 2. Raman frequencies* (cm^{-1}) of glasses

Anorthite, $CaAl_2Si_2O_8$	Calcium Tschermak's pyroxene, $CaAlAlSiO_6$	Gehlenite, $Ca_2AlAlSiO_7$
100 s, p†	96 s, p	84 s, p
300 w	...	371 w
508 vs, p	∿512 (sh), p	...
...	...	552 s, p
...	564 s, p	...
∿572 (sh)	...	...
...	...	662 (sh), p
∿770 w, bd, p/dp	...	...
...	...	896 s, p
974 m, p	948 m, p	∿1004 w (sh), p
∿1100 w (sh)	∿1048 w (sh)	...

*Measurement accuracy is ±4 cm^{-1} for strong bands and ±10 cm^{-1} for weak and broad bands.
†Abbreviations: w, weak; m, medium; s, strong; bd, broad; (sh), shoulder; p, polarized; dp, depolarized.

In the Raman spectrum of crystalline An, only 27 modes were observed (Table 1). In the infrared spectrum (60–1300 cm^{-1} range), only 35 bands were observed (Iishi *et al.*, 1971). The frequencies of the observed Raman bands do not coincide with the frequencies of infrared bands reported by Iishi *et al.* (1971), as is expected because of the centro-symmetric space group of this mineral. The observed number of Raman and infrared bands is, however, much smaller than the predicted number of modes. Accidental degeneracies and weak intensities may be responsible for the observation of fewer bands. It is also likely that the much smaller pseudo-cell in crystalline An determines the vibrational spectrum. White (1975) compared the Raman spectra of feldspars and pointed out that, although additional bands are required in the spectrum for a large unit cell in high-calcium plagioclase crystals, the frequencies of these bands fall into sets that nearly match the modes of a much smaller structural unit.

The strongest band at 503 cm^{-1} in the spectrum of crystalline An corresponds to motion of the oxygen atom along a line bisecting the T–O–T angle (where T = Si or Al) (see Galeener, 1979; Galeener and Mikkelsen, 1981) and is characteristic of the feldspar structure, which contains four-membered rings of tetrahedra. This symmetric stretch [ν_s(T–O–T)] mode appears as the strongest band at 506 cm^{-1} in low albite and at 513 cm^{-1} in orthoclase (White, 1975). These data imply that changes in cation and Si/Al in feldspar have little influence on the position of the ν_s(T–O–T) band. In the Raman spectra of coesite, a silica polymorph whose smallest ring contains four tetrahedra (Zoltai and Buerger, 1959), the ν_s(Si–O–Si) mode appears as the strongest band at 521 cm^{-1} (Sharma *et al.*, 1981). Table 3 summarizes the observed frequencies of the ν_s(T–O–T) bands for framework aluminosilicates with the smallest rings containing four, five, and six TO_4 tetrahedra. It is evident from Table 3 that, although there appears to be some fluctuation in the ν_s(T–O–T) band position for a given ring size, a trend emerges indicating an appreciable increase in the frequency of ν_s(T–O–T) with reduction in the ring size among crystals of isochemical compositions.

The highest frequency modes in the 900–1200 cm^{-1} region that give rise to relatively weak Raman bands but strong infrared bands are associated with the motion of the oxygen atom along the line parallel to T–T and are assigned to the antisymmetric stretch [ν_{as}(T–O–T)] mode. The ν_{as}(T–O–T) mode involves motion of both O and T atoms (for similar assignment in SiO_2 glass see Bell and Dean, 1970; Galeener, 1979). The seven well-defined Raman bands in the 900–1200 cm^{-1} region (Fig. 1, Table 1) of the spectrum of crystalline An reflect the high degree of Al–Si ordering in the anorthite crystal. By comparing the infrared spectra of natural feldspars and synthetic isomorphous materials in which Ga^{3+} was substituted for Al^{3+}, and Ge^{4+} for Si^{4+}, Iishi *et al.* (1971) found that the highest frequency bands can be attributed to nearly pure ν_{as}(Si–O–Si) (A_u) modes and the bands at relatively lower frequencies to ν_{as}(Si–O–Al) (A_u) modes. In the spectrum of crystalline An, these bands, $\nu_{as}(A_g)$, appear at 1124, 1072, 1044, 998, 974, 949, and 908 cm^{-1} (Table 1).

On the basis of theoretical model calculations of the frequency and normal modes of vibration for vitreous silica, Bell and Dean (1970, 1972a) concluded that the vibrational modes in the low-frequency region (200–600 cm^{-1}) of the glass spectrum are strongly coupled, whereas in the high-frequency region (900–1200 cm^{-1}) of the spectrum, the vibrational modes are much more localized. Substitution of Al^{3+} for Si^{4+} may further increase the localization of these modes. It is probably the localized nature of the ν_{as}(T–O–T) modes that causes the ν_{as}(Si–O–Al) and ν_{as}(Si–O–Si) modes to appear at different frequencies. In the Raman spectrum of low albite (White, 1975) the ν_{as}(T–O–T) bands were observed at 1099, 1031 and 977 cm^{-1}. The increase in the number of ν_{as}(T–O–T) Raman bands in the spectrum of An compared with that of albite is due to an increase in the population of the unit cell of An (Z = 8, for An, whereas Z = 4 for Ab). The shifts in the positions of the ν_{as}(Si–O–Al) bands of An toward lower frequencies relative to the positions of corresponding bands of albite are due to an increase in Al/Si. If there had been a perfect ordering of Al–Si in the synthetic anorthite used in the present study, all the ν_{as}(T–O–T) mode should have appeared at a lower frequency than that of the ν_{as} of albite. The presence of weak bands at 1124, 1072, and 1044 cm^{-1} possibly indicates that a small degree of Al–Si disorder exists in the synthetic anorthite sample. Robie *et al.* (1978) have also pointed out that in an anorthite crystal, crystallized from a glass at 1060°C and 10 kbar H_2O pressure for 2 hr, the Al–Si order was incomplete.

Table 3. Relationship between $\nu_s(T\text{-O-}T)$ frequency and the structural parameters in some tectosilicates

Minerals	$\nu_s(T\text{-O-}T)$ in crystalline phase[a]	Repeat units and shortest rings of tetrahedra[b]	$\nu_s(T\text{-O-}T)$ in glassy phase	Prominent ring structures in glassy phase
1. α-quartz	464 vs*	6	437 vs, bd	6[a]
2. β-quartz (700°C)	462 vs	6		
3. α-cristobalite	416 vs	6		
4. Coesite	521 vs	4		
5. $LiAlSi_2O_6$-III	480 vs	6	476 vs, bd	6[c]
6. $LiAlSi_2O_6$-II	492 vs	5		
7. Low albite, $NaAlSi_3O_8$	506 vs	4	472 vs, bd	6[d,e]
8. Orthoclase, $KAlSi_3O_8$	513 vs	4	...	6[f]
9. Anorthite	503 vs	4	508 vs, bd	4[e,f]

[a] Sharma *et al.* (1981); [b] Zoltai (1960); [c] Sharma and Simons (1981); [d] Sharma *et al.* (1978); [e] present work; [f] Taylor and Brown (1979).

*Abbreviations: vs, very strong; bd, broad.

Kempster *et al.* (1962) and Megaw *et al.* (1962) have examined the structure of An by single-crystal X-ray diffraction and have discussed the results in detail. These workers indicate that the ordering of Si and Al in An is perfect within the limits of experimental error; that is, the disorder is in any case less than 10% (see Megaw *et al.*, 1962, p. 1023). The weak intensities of the Raman bands at 1124, 1072, and 1044 cm^{-1} in the spectrum of crystalline An (Fig. 1) also imply that the degree of Al–Si disorder in the An crystal is small. Although it is not yet possible to provide a quantitative estimate of Al–Si disorder from the Raman spectra, the results of this study indicate that Raman spectroscopy could be useful in detecting relatively small degrees of Al–Si disorder in crystalline minerals.

Raman spectrum of the glass of An composition

The prominent features in the Raman spectrum of the glass of An composition are the strong band at 100 cm^{-1}, a very strong band at 508 cm^{-1}, and a doublet in the 900–1200 cm^{-1} region composed of a band of medium intensity at ~974 cm^{-1} and a weak shoulder at ~1100 cm^{-1} (Fig. 1, Table 2). The positions and intensities of the Raman bands in the glass of An composition are closely related to those of the most prominent bands observed in the spectrum of crystalline An (Fig. 1). The bands in the glass spectrum, however, are much broader than their counterparts in the spectrum of crystalline An. As explained below, the broadening of Raman bands in the spectrum of glass is presumably due to short-range variability and the absence of long-range order in the glass structure.

The close resemblance of the relative intensities and positions of the Raman bands in the spectrum of glass of $CaAl_2Si_2O_8$ composition to their counterparts in the spectrum of An indicates that Al^{3+} ions in the glass are present in four-fold coordination and act as network formers. The local structure in the three-dimensional network of $CaAl_2Si_2O_8$ glass can be qualitatively described by taking into account the positions and polarization of the Raman bands. It is known that the intertetrahedral T–O–T angle in glasses is not the same everywhere but ranges about some most likely value, estimated to be 144° in SiO_2, 133° in GeO_2, and 143° in An glass (Taylor and Brown, 1979). The glass probably has an ensemble of local environments with a statistical distribution of the intertetrahedral angles. The variation of the T–O–T angle is the basis of the short-range variability and long-range disorder as well as the broadening of the Raman bands. In this situation, the peak position of the ν_s(T–O–T) 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 of An composition is close to that of ν_s(T–O–T) in the spectrum of crystalline $CaAl_2Si_2O_8$ (Fig. 1). It is evident, therefore, that the most probable T–O–T angle in the glass of $CaAl_2Si_2O_8$ composition is close to that of crystalline anorthite.

In addition to the T–O–T bond angle, another important factor that can affect many physical and chemical properties of the melts and glasses is the network connectivity (Bell and Dean, 1972b; Sharma *et al.*, 1981). In the classification of the three-dimensional network of tetrahedra of minerals, the size of a tetrahedral ring is found to be related to the energies of the tetrahedral structure (Zoltai and Buerger, 1960; Zoltai, 1960). In minerals of isochemical composition, the frequency of ν_s(T–O–T) increases with decreasing ring size (Table 3). The positions of the ν_s(T–O–T) in the spectra of An in the crystalline and glassy phases are very close (Table 3). It can be concluded, therefore, that the glass of An composition consists predominantly of four-membered rings of SiO_4 and AlO_4 tetrahedra that are connected in a more or less random fashion. Close resemblance between the short-range structure in the glass and anorthite crystals is also consistent with the relatively small difference in the density and refractive index of An glass (D = 2.69 g/cm³; n = 1.574) relative to that of the anorthite crystal (D = 2.76 g/cm³; $n_\alpha = 1.577$, $n_\beta = 1.585$, $n_\gamma = 1.590$) (Smith, 1974; Deer *et al.*, 1977), and the observed rapid crystallization of anhydrous An glass above 845°C, the glass transition point (Kirkpatrick *et al.*, 1976, 1979).

The ν_s(T–O–T) appears at a lower frequency (472 cm^{-1}) in the spectrum of albite glass than the corresponding band (506 cm^{-1}) in the spectrum of crystalline albite (Sharma *et al.*, 1978). The frequency of ν_s(T–O–T) for the glass is close to that for crystalline $LiAlSi_2O_6$-III (Table 3), which is composed of six-membered rings of SiO_4 and AlO_4 tetrahedra. The correlation between ν_s(T–O–T) and ring size in three-dimensional network structures thus indicates that albite glass is composed predominantly of six-membered rings of SiO_4 and AlO_4 tetrahedra. Similar conclusions about the structure of albite glass were reached by Sharma *et al.* (1978) by comparing the Raman spectrum of albite with that of SiO_2 glass. On the basis of X-ray radial distribution function (RDF) analyses of feldspar glasses, Taylor and Brown (1979) also proposed that the structure of calcic feldspar (An) glass is consistent with a four-membered ring structure of the type found in crystalline anorthite, whereas that of the alkali feldspar glasses is consistent with the six-membered rings of the type found in tridymite, nepheline, and kalsilite. The results of the present investigation provide further support to the above structural models of glasses of An and Ab compositions.

Another aspect of An glass structure that requires further discussion is the degree of Si and Al disorder. The ν_{as}(T–O–T) modes in the spectrum of An appear as a strong band at ~974 cm^{-1} and a weak shoulder at ~1100 cm^{-1}. In the Raman spectrum of albite glass, these bands appear as a doublet composed of a weak band at ~1012 cm^{-1} and a medium-intensity band at ~1108 cm^{-1} (Sharma *et al.*, 1978). Theoretical calculations have shown that, even in the spectra of glasses, vibrational modes in the 900–1200 cm^{-1} region are localized (Bell and

Dean, 1970, 1972a). In analogy with the crystalline An bands in the 900–1200 cm^{-1} region, the strong band at ~974 cm^{-1} in the spectrum of An glass may be attributed to the antisymmetric Si–O–Al stretch mode. The ~974 band is at lower frequency than its counterpart in the spectrum of Ab glass (1012 cm^{-1}). The weak shoulder at ~1100 cm^{-1} in the spectrum of An glass is very close in position to the medium band at 1108 cm^{-1} in the spectrum of Ab glass; consequently, these bands may be assigned to nearly pure ν_{as}(Si–O–Si) stretch modes.

In the spectrum of glass of Ab composition (Si:Al = 3), the low-frequency band at 1012 cm^{-1} is less intense than the high-frequency band at ~1108 cm^{-1}. The observed reversal in the intensity of the high-frequency band at ~1100 cm^{-1} in the anorthite glass (Si:Al = 1) clearly shows that this band is the nearly pure ν_{as}(Si–O–Si) stretch and the low-frequency component belongs to the ν_{as}(Si–O–Al) stretch mode. A comparison of the Raman spectra of the glasses along the joins $NaAlSi_3O_8$–$Na_2Al_2Si_2O_8$ and $NaGaSi_3O_8$–$Na_2Ga_2Si_2O_8$ shows that, when Ga^{3+} is substituted for Al^{3+}, the low-frequency component of the ν_{as}(T–O–T) stretch mode shows a larger shift than the high-frequency ν_{as}(T–O–T) component (Virgo *et al.*, 1979b; Sharma, unpublished data), as is expected on the basis of the present assignment of these bands. The weak shoulder at ~1100 cm^{-1} in the spectrum of An glass indicates that, although a high degree of Si–Al order exists in the An glass, the Si–Al ordering is far from perfect.

Raman spectrum of crystalline calcium-Tschermak's pyroxene

CaTs has a monoclinic structure, space group C^6_{2h} (*C*2/*C*) with Z = 2, that is composed of pyroxene chains of SiO_4 and AlO_4 tetrahedra with Ca^{2+} and half the Al^{3+} in six-fold coordination acting as network modifiers (Grove and Burnham, 1974; Okamura *et al.*, 1974). The presence of half the Al^{3+} ions in six-fold coordination in CaTs gives rise to distinct spectral features in the Raman spectrum (Fig. 2). As a result, the spectrum of CaTs is easily distinguished from spectra of other crystalline aluminosilicates, *e.g.*, An (Fig. 1), which have all the Al^{3+} in four-fold coordination. In the spectrum of CaTs, the bands in the 900–1200 cm^{-1} region are much stronger because of nonbridging oxygens, and the symmetrical stretching mode of O(br), ν_s(T–O–T), appears as a strong band at higher frequency, 651 cm^{-1} (Table 1), as compared with the frequency of the ν_s(T–O–T) bands of aluminosilicate minerals in which Al^{3+} ions are present as network-forming cations (see below).

Factor-group analysis of CaTs indicates that 57 optic modes will be distributed among the following symmetry species (Rutstein and White, 1971; Adams and Hills, 1977): $\Gamma = 14A_g\ (R) + 16B_g\ (R) + 13A_u\ (IR) + 14B_u\ (IR)$, where R and IR refer to Raman and infrared active modes, respectively. Only 18 of the 30 bands were detected in the Raman spectrum of polycrystalline CaTs. The absences may be attributed to accidental degeneracies of modes, low intensities, or both. The strong band at 651 cm^{-1} is characteristic of pyroxene chains and corresponds to symmetric stretch of the bridging oxygen ν_s(T–O–T). Raman spectra of other pyroxene minerals—*e.g.*, diopside ($CaMgSi_2O_6$), clinoenstatite ($MgSiO_3$), and enstatite ($MgSiO_3$)—include one or two intense bands in the 650–680 cm^{-1} range that have been assigned to the motion of bridging oxygens in the chains (Fabel *et al.*, 1972; White, 1975). The strong band at 953 cm^{-1} is due to symmetrical stretching of the terminal nonbridging oxygens, ν_s(T–O^-), in the chains. In pure diopside and other alkaline-earth pyroxenes not containing Al^{3+} ions, ν_s(Si–O^-) appears near 1000 cm^{-1} and is very intense (White, 1975). The appearance of the ν_s(T–O^-) band at lower frequency in the CaTs spectrum than in spectra of nonaluminum-bearing pyroxenes can be attributed to isomorphous substitution of Al^{3+} for Si^{4+} in the chains that results in longer T–O bonds (1.686Å) in CaTs than the average Si–O bond length (1.634Å) in diopside. With the exception of the very weak band at 1071 cm^{-1}, all other bands between 900 and 1200 cm^{-1} appear at lower frequencies in the CaTs spectrum than the corresponding bands of the α-spodumene spectrum (Sharma and Simons, 1981). If the very weak band at 1071 cm^{-1} is a fundamental mode, it may be attributed to the ν_{as}(Si–O–Si) mode, indicating the presence of a small degree of Al–Si disorder in the chains.

The intensity of the 953 cm^{-1} band in the CaTs spectrum is 0.76 times the intensity of the 651 cm^{-1} ν_s(T–O–T) band. In the spectra of jadeite, α-spodumene ($LiAlSi_2O_6$-I) and diopside, the corresponding relative intensities, r_i (= $I[\nu_s(Si–O^-)]/I[\nu_s(Si–O–Si)]$), are 0.45, 0.51 and 1.67, respectively (Sharma and Simons, 1981; Sharma, 1981).

In order to understand the difference in the relative intensities of the $\nu_s(SiO^-)$ bands of $(T_2O_6)_\infty$ chains in the spectra of isostructural pyroxene crystals, the factors responsible for the intensity of Raman bands of interatomic vibrations of a complex ion or molecule must be considered. It is known that the intensity of a Raman band is proportional to $(\partial\alpha_{ij}/\partial Q_k)^2$, where $\partial\alpha_{ij}/\partial Q_k$ is the derivative of the *ij* component of the polarizability tensor with respect to the normal coordinate of vibration Q_k, taken at the equilibrium position (Long, 1977, p. 51–71), and the Raman intensities from vibrations of electrostatic linkages are probably 100 times less than the intensities from the vibrations of covalent bonds (George *et al.*, 1953; Hester, 1967). Because of these factors the intermolecular vibrational modes of silicate anions dominate the Raman spectra of silicate crystals and glasses. The intensities of the modes from the vibrations of largely ionic bonds, such as alkali and alkaline-earth metal ions and nonbridging oxygens, are so weak that they are not usually observed in the spectra. These cations, can, however, influence the intensity of the ν_s(Si–O^-) bands if the degree of electron sharing or covalent character between nonbridging oxygen and the metal ion increases because increase in the covalent character between nonbridging oxygen and the metal ion will tend to reduce the electron sharing in the Si–O$^-$ bonds. Sharma (1981) has shown that there is a correlation between the (M$_I$–O) bond distance (where M = Mg^{VI} or Al^{VI}) in pyroxenes and the intensity of the ν_s(T–O$^-$) bands of pyroxene chains. The average (M$_I$–O) bond lengths for α-spodumene (Sp), jadeite (Jd), CaTs and diopside (Di) are 1.919, 1.928, 1.947, 2.077Å, respectively (Clark *et al.*, 1969; Okamura *et al.*, 1974). Although the variation in the average bond length between nonbridging oxygen and M$_I$ cation in clinopyroxenes may be due to the compositional change or to other structural factors, this variation implies that the degree of covalent character in the M$_I$–O bonds of the cation in clinopyroxene increases in the order Di < CaTs < Jd < Sp. This effect will result in a decrease in electron sharing in the average T–O$^-$ bond of the $(T_2O_6)_\infty$ chains in the reverse order, *i.e.*, Di > CaTs > Jd > Sp, and therefore the $(\partial\alpha_{ij}/\partial Q_k)$ for the ν_s(T–O$^-$) mode of the chain is expected to decrease in the same order. This deduction is consistent with the observed decrease in the intensity ratio r_i in the order r_i (Di) > r_i (CaTs) > r_i (Jd) > r_i (Sp). The relative intensities of symmetrical stretch modes of nonbridging and bridging oxygen for pyroxene indicate that the relative intensities of the nonbridging oxygen bands in the Raman spectra of pyroxenes are affected by the degree of covalency of the Al–O bonds even when Al^{3+} is six-fold coordinated and acts as a network-modifying cation. This fact should be considered when the structure of aluminosilicate melts and glasses is inferred from the Raman spectra.

Raman spectra of a glass of CaTs composition

Polarized Raman spectra of CaTs glass, free from corundum inclusions and with a composition close to that of CaTs (Fig. 2), indicate that all bands are polarized, and bands in the 450–600 cm^{-1} region appear at lower frequencies (512 and 564 cm^{-1}) than the ν_s(T–O–T) band (651 cm^{-1}) in the spectrum of crystalline CaTs (see Tables 1 and 2). The $I_{\|}$ spectrum of CaTs glass closely resembles the VV spectrum of CaTs glass reported by Piriou and Alain (1979). The higher intensities of bands in the $I_\perp$ CaTs glass spectrum (Fig. 2) as compared with the intensities of corresponding bands in the VH CaTs glass spectrum of Piriou and Alain (1979) indicates some contribution of $I_{\|}$ components to the $I_\perp$ spectrum in Figure 2. In the 900–1100 cm^{-1} region of the CaTs glass spectrum, a band envelope that is composed of a broad band at ~948 cm^{-1} and a shoulder at ~1048 cm^{-1}, is observed. In the Raman spectra of crystalline aluminosilicates involving polymerized network structures, ν_s(T–O–T) bands appear at lower frequencies than the corresponding bands in the spectra of crystals having less polymerized structures, such as Si–Al sheets or chains. Furthermore, in the 1000–1200 cm^{-1} region of the spectra the antisymmetric stretching modes of bridging oxygens appear at higher frequencies than the ν_s(T–O$^-$) bands (White, 1975). For these reasons the CaTs glass has a more polymerized structure than that of crystalline CaTs. As discussed in the section on An glass, the weak polarized shoulder at ~1048 cm^{-1} in the spectrum of CaTs glass can be assigned to the ν_{as}(Si–O–Si) and indicates an increase in Al–Si disorder in the CaTs glass relative to crytalline CaTs. The band at ~948 cm^{-1} represents a coupled antisymmetric stretch mode of SiO$_4$ and AlO$_4$ tetrahedra.

In the CaTs glass spectrum ($I_{\|}$), the ratio r_i, corresponding to the ratio of the integrated intensity of the band contour from 800 to 1200 cm^{-1} to the integrated intensity of the band envelope from 200 to 700 cm^{-1}, is estimated to be 0.69. For the glass of anorthite composition, the r_i value is 0.43. This higher value of r_i for CaTs glass probably indicates the presence of a small number of nonbridging oxygens in the CaTs glass. As pointed out in the section on experimental methods, the exact cationic composition of the CaTs glass is estimated to be $CaAl_{1.9}Si_{0.99}$. If all the remaining Al^{3+} ions were in four-fold coordination and acting as network formers, the CaTs glass would have on the average 0.034 nonbridging oxygen per tetrahedron. The high ratio, r_i, for the CaTs glass, however, cannot be accounted for by only 0.034 nonbridging oxygen per tetrahedron. It seems, therefore, that a small fraction (≲1 mol%) of the Al^{3+} ions may still be present in five- or six-fold coordination in the glass, and these act as network modifiers. The formation of a small amount of crystalline Al$_2$O$_3$ in quenched melts of CaTs composition (Hays, 1966; Kirkpatrick and Steele, 1973) also indicates that at least some Al^{3+} ions in the melt must have had coordination numbers higher than four.

Raman spectrum of crystalline gehlenite

Crystalline gehlenite is a member of the melilite family and has a tetragonal cell, space group D^3_{2d} ($P\bar{4}2m$), Z = 2 (Louisnathan, 1969, 1970). Factor-group analysis shows that the symmetry species of the (3N-3) optic modes in the gehlenite crystal are distributed among the following symmetry species:

$$\Gamma = 10A_1\ (R) + 6A_2\ (i.a.) + 7B_1\ (R) + 10B_2\ (R, IR) + 18E\ (R, IR)$$

where R is Raman-active; IR, infrared-active; and i.a., inactive mode. Only 18 of the 45 expected Raman-active modes were detected in the Raman spectrum of Geh. Similarly, in the Raman spectra of akermanite (Ak) and sodium melilite (SM) only 12 and 17 bands, respectively, were observed (Sharma and Yoder, 1979). The absences may be due to accidental degeneracies of some modes, their weak intensities, or both.

In the spectrum of gehlenite the strongest band at 626 cm^{-1} is a symmetrical stretching, ν_s(T–O–T), mode of bridging oxygen of the pyrosilicate anions. In the spectra of akermanite and sodium melilite, the ν_s(Si–O–Si) bands of the $Si_2O_7^{6-}$ group appear at 661 and 648 cm^{-1}, respectively (Sharma and Yoder, 1979). In the Raman spectra of crystalline pyrosilicates of the type $A_2Pb_2Si_2O_7$ (where A = K, Rb, or Cs) the ν_s(Si–O–Si) stretch modes appear at 669, 668, and 666 cm^{-1}, respectively (Tarte *et al.*, 1973). The T–O–T bond angle in Geh is estimated to be 130.6° (Louisnathan, 1969) and is smaller as compared to T–O–T bond angle in akermanite (143°) and sodium melilite (136.2°) (Louisnathan, 1970). The decrease in the T–O–T bond angle is expected to decrease the frequency of the ν_s(T–O–T) mode of the T_2O_7 group (Lazarev, 1972). Substitution of Al for Si in the pyrosilicate unit may further lower the frequency of the ν_s(T–O–T) mode because this mode involves motion of both O and T atoms (Tarte *et al.*, 1973). Evidently, the decrease in the T–O–T bond angle and substitution of Al for Si ion in pyrosilicates shifts the ν_s(T–O–T) band toward lower frequencies. The shoulders at 655 and 841 cm^{-1} and the band at 796 cm^{-1} in the spectrum of Geh do not have counterparts in the spectrum of the Ak crystal, but shoulders at 665, 724, and 894 cm^{-1} were detected in the spectrum of SM (Sharma and Yoder, 1979). The shoulders at 655 and 841 cm^{-1} and the band at 796 cm^{-1} may therefore be assigned to vibrational modes involving AlO_4 tetrahedra that are present in both crytalline SM and Geh at a site having the point-group symmetry of $\bar{4}$ (Louisnathan, 1969, 1970).

In the 900–1200 cm^{-1} region of the Geh spectrum, bands of medium intensity appear at 914 and 977 cm^{-1}, and weak bands appear at 998 and 1005 cm^{-1} (Table 1, Fig. 3). In the spectrum of crystalline akermanite, corresponding bands appear at 904 (vs), 986 (w), 1023 (vw), and 1067 (w) cm^{-1} (where the letters in parentheses refer to band intensities, *i.e.*, v, very; w, weak; s, strong) (Sharma and Yoder, 1979). The bands at 904 and 986 cm^{-1} were assigned to symmetrical stretching modes of terminal oxygens, whereas the bands at 1023 and 1067 cm^{-1} were assigned to antisymmetric stretching of oxygens in akermanite. Accordingly, in the spectrum of Geh, the 914 and 977 cm^{-1} bands and the 998 and 1005 cm^{-1} bands are attributed to symmetric stretch of nonbridging oxygen and antisymmetric stretch of oxygen of the pyrosilicate group, respectively. The intensity ratio r_i, *i.e.*, the intensity at 914 cm^{-1} relative to that at 626 cm^{-1}, in the spectrum of Geh is estimated to be 0.35 (Fig. 3). In the spectrum of Ak and SM, r_i are 1.28 and 0.25, respectively. In the spectrum of SM the ν_s(Si–O$^-$) band at 930 cm^{-1} is also much weaker than the ν_s(Si–O$^-$) in the spectrum of Ak (Sharma and Yoder, 1979).

These differences in the relative intensities of the ν_s(Si–O$^-$) bands of T_2O_7 groups in the spectra of isostructural melilite crystals are similar to the differences observed in the relative intensities of the ν_s(Si–O$^-$) bands of $(T_2O_6)_\infty$ pyroxene chains, and are discussed in the section on the Raman spectrum of crystalline CaTs. Sharma (1981) has shown that there is a correlation between the (M–O) bond distances (where M = Mg or Al at the site of point-group symmetry $\bar{4}$) in melilites and the intensities of the ν_s(T–O$^-$) bands. The average (M–O) bond lengths in Geh (1.785Å) and SM (1.762Å) are smaller than the average (M–O) bond length in Ak (1.87Å) (Louisnathan, 1969, 1970). Although the variation in the average bond length between nonbridging oxygen and the M cation in melilite may be due to compositional change or to other structural factors, this variation implies that the degree of covalent character in the M–O bonds of the cation at the $\bar{4}$ site in melilite increases in the order Ak < Geh < SM. This effect will result in a decrease in electron sharing in the average T–O$^-$ bond of theT_2O_7 ion in the reverse order, *i.e.*, Ak > Geh > SM, and therefore the $(\partial\alpha_{ij}/\partial Q_k)$ for the ν_s(T–O$^-$) mode is expected to decrease in the same order. This deduction is consistent with the observed decrease in the intensity ratio r_i in the order r_i(Ak) > r_i(Geh) > r_i(SM). In the spectrum of crystalline Geh the bands at 998 and 1005 cm^{-1} assigned to ν_{as}(Si–O–Al) modes (Table 1) appear at lower frequencies than the corresponding ν_{as}(Si–O–Si) bands (1023 and 1067 cm^{-1}) in the spectrum of crystalline Ak. This shift is expected because one Si^{4+} in the pyrosilicate group of Geh is substituted for by a four-fold coordinated Al^{3+} ion, charge-balanced by a calcium ion (Sharma *et al.*, 1978).

The data outlined above clearly show that the degree of covalency between nonbridging oxygens of the T_2O_7 pyrosilicate anion and a four-fold coordinated network modifying Al^{3+} cation at the site of symmetry $\bar{4}$ decreases the intensity of the symmetric stretching mode of nonbridging oxygens in the spectra of melilite. The degree of covalency between the terminal oxygen of the pyroxene chain and the six-fold coordinated Al^{3+} cation also has a similar effect on the intensity of the ν_s(Si–O$^-$) band in the spectra of pyroxenes (Sharma, 1981). The effect of the degree of covalency of the Al–O bonds of the aluminum ion at the $\bar{4}$ site in melilites on the intensity and position of the symmetrical stretching mode of nonbridging oxygen, ν_s(T–O–T), is, however, small—the ν_s(T–O–T) mode gives rise to a strong band at 661 (Ak), 648 (SM), and 626 (Geh) cm^{-1}. For Al^{3+} ions, the concept of network-modifying and network-forming cations is only an approximation; both the coordination number and the degree of covalency in the Al–O bonds are important when the role of Al^{3+} is inferred from the Raman spectra.

Raman spectrum of glass of Geh composition

The prominent features in the spectrum of Geh composition are strong and polarized bands at 84 and 552 cm^{-1} and a very strong and polarized band at 896 cm^{-1} (Fig. 3, Table 2). In addition, weak bands appear at ~371 cm^{-1}, best seen in the $I_\perp$ spectrum (Fig. 3), and two weak and polarized shoulders, at ~662 and 1004 cm^{-1} (Fig. 3, Table 2).

A comparison of the spectrum of glass of Geh composition with that of crystalline Geh (Fig. 3) clearly shows that the ν_s(T–O–T) band appears at lower frequency (552 cm^{-1}) than that of crystalline Geh (626 cm^{-1}, Table 1) and that the intensity of the band in the 900–1200 cm^{-1} range in the glass spectrum is much stronger than the intensities of the corresponding bands in the spectrum of crystalline Geh. It is evident, therefore, that there is no correlation between the intensities and positions of the most prominent bands in the spectra of glass of Geh composition and crystalline Geh (Table 1, Fig. 3).

In the spectrum of Geh glass the appearance of the ν_s(T–O–T) band at lower frequency than in the spectrum of crystalline Geh indicates that the structure of Geh glass is more polymerized than that of crystalline Geh. The ratio r_i in the spectrum of Geh glass, corresponding to the ratio of the integrated intensity of the band contour from 800 to 1150 cm^{-1} to the integrated intensity of the band envelope from 354 to 730 cm^{-1}, is estimated to be 1.64. The value of r_i for Geh glass is much higher than for glasses of An (r_i = 0.43) and CaTs (r_i = 0.69) compositions.

Raman measurements on a number of silicate and aluminosilicate glasses have shown that the value of r_i in the glass spectrum increases with increase in the number of nonbridging oxygens in the glass (Brawer and White, 1975, 1977; Verweij and Konijnendijk, 1976; Sharma *et al.*, 1978; Mysen *et al.*, 1980; Sharma and Simons, 1981). Evidently, the Geh glass has a higher number of nonbridging oxygens than glasses of An and CaTs composition. In the spectrum of crystalline Geh (Fig. 3) the value of r_i, the intensity of 914 cm^{-1} relative to that of 626 cm^{-1}, is 0.35. The higher value of r_i for glass of Geh composition than for crystalline Geh indicates that the nonbridging oxygens of the Geh glass have a higher degree of covalent character in the nonbridging bonds to T (where T = Si, Al) than the corresponding bonds in crystalline Geh. It appears that to a large extent Al^{3+} ions in the Geh glass act as network formers and are charge-balanced by Ca^{2+} ions. In an aluminosilicate network structure such as the Geh glass, there is one Ca^{2+} ion per formula unit ($Ca_2AlAlSiO_7$) to be charge-balanced by nonbridging oxygens. One would expect from the stoichiometry of Geh glass, therefore, that there would be on the average 0.33 O$^-$ ion per TO$_4$ tetrahedron (where T = Si or Al). The position of the ν_s(T–O$^-$) band in the 900–1200 cm^{-1} region of the spectrum can provide information about the number of nonbridging oxygens attached to silicon atoms. In the spectrum of Geh glass the strong band appears at 896 cm^{-1} accompanied by a weak shoulder at 1004 cm^{-1}. In the spectrum of crystalline CaTs, the band appears at 953 cm^{-1} (Fig. 2, Table 1) and corresponds to two nonbridging oxygens per TO$_4$ tetrahedron. The strong ν_s(T–O$^-$) band in the spectrum of Geh glass and the appearance of the band at much lower frequency indicate that the species responsible has more than two nonbridging oxygens.

In the spectrum of glass of monticellite composition ($CaMgSiO_4$) the ν_s(Si–O$^-$) mode of SiO_4^{4-} was observed at 850 cm^{-1} (McMillan *et al.*, 1981). In the spectra of glasses of Ak and diopside compositions, polarized shoulders at ~858 and 885 cm^{-1}, respectively, have been attributed to the ν_s(Si–O$^-$) mode of the randomly oriented SiO_4^{4-} groups in the glass (Sharma and Yoder, 1979). It seems that the frequency of the ν_s(Si–O$^-$) mode of the SiO_4^{4-} group in the glass increases with increase in the degree of polymerization of the silicate network. In the spectra of glasses along the joins CaO–SiO$_2$ and MgO–CaO–SiO$_2$ the presence of a sharp band at 870 cm^{-1} has been attributed to the ν_s(Si–O$^-$) mode of SiO_4^{4-} groups (Mysen *et al.*, 1980). By analogy, the strong band at 896 cm^{-1} in the spectrum of Geh glass is assigned to the presence of SiO_4^{4-} groups in the aluminosilicate network structure of the glass. The weak shoulder at ~1004 cm^{-1} may be attributed to the antisymmetric stretch of bridging oxygen, ν_{as}(T–O–T). If there are a few tetrahedra having one nonbridging oxygen (T–O$^-$) in the network of Geh glass, the stretching of these nonbridging oxygens may also contribute to the shoulder at ~1004 cm^{-1}.

In summary, the Raman spectra of crystalline Geh and glass of Geh composition indicate that the structure of Geh glass is more polymerized than that of the crystalline Geh and contains an appreciable amount of the SiO_4^{4-} group randomly oriented in the glass network, charge-balanced by the Ca^{2+} ion. De Jong *et al.* (1981) have also pointed out that, although the number of bridging [O(br)] and nonbridging oxygens [O(nbr)] in the glass is fixed by the stoichiometry of the glass, the distribution of O(nbr) in the glass varies with the kind of alkali or alkaline-earth atom present. It appears from the present Raman data that in the Geh glass the Ca^{2+} ions prefer SiO_4^{4-} monomers (Q_0 species), and therefore the glass has a minimum dispersion of Ca^{2+} ions (Engelhardt *et al.*, 1975; de Jong *et al.*, 1981).

In the spectrum of Geh glass a strong and broad band at 85 cm^{-1}, which is easily resolved from the descending Rayleigh tail (Fig. 3), is characteristic of glass spectra and corresponds largely to the thermal population of disorder induced, density-of-states of the vibrational modes arising from low-lying optic modes as well as the higher-lying acoustic modes (Shuker and Gamon, 1970, 1971; Winterling, 1975). In the spectra of glasses of An and CaTs the low-frequency bands appear at 100 and 96 cm^{-1} respectively (Table 2, Figs. 1 and 2). These low-frequency bands correspond to intramolecular motions and are very important because they dominate the thermodynamic properties of melts (Angell *et al.*, 1969; Shuker and Gammon, 1971). 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.

In the spectra of the glasses of Ak and diopside composition, weak and broad bands at 358 and ~340 cm^{-1}, respectively, were observed and assigned to ν(Ca–O) modes. The weak band at ~371 cm^{-1} in the spectrum of Geh may be assigned to the ν(Ca–O) stretching mode. The presence of the ν(Ca–O) band of Geh glass at higher frequency than the corresponding band of the glasses of

Ak and Di composition may be attributed to the shorter Ca–O bond lengths in the Geh glass as compared with Ca–O bonds in the Ak and Di glasses.

Conclusions

The Raman spectra of crystalline $CaAl_2Si_2O_8$, $CaAlSiO_6$, and $Ca_2AlAlSiO_7$ show characteristic bands of feldspar, pyroxene, and melilite, respectively. Raman spectroscopy can be used, therefore, as one of the techniques to distinguish these minerals from each other and also to provide indirect information about the structural role of the Al^{3+} ions. The presence of weak bands corresponding to ν_{as}(Si–O–Si) modes, in addition to the sharp and well-defined ν_{as}(Si–O–Al) bands in the spectrum of crystalline anorthite, implies a small degree of Si–Al disorder in the sample used in the present study. In CaTs, the presence of half the Al^{3+} ion in six-fold coordination enhances the intensities of the bands resulting from the nonbridging oxygens in the 900–1200 cm^{-1} region of the spectrum. In Geh, however, the presence of half the Al^{3+} ions as tetrahedrally coordinated network modifiers at the $\bar{4}$ site in the structure decreases the intensities of the symmetrical stretching bands of nonbridging oxygens compared with those of the corresponding bands in the spectrum of non-Al-bearing melilite, *e.g.*, akermanite. Substitution of Al^{3+} ions for alkali and alkaline-earth network modifiers in pyroxenes and melilites affects the positions and intensities of the ν_s(T–O–T) Raman bands to a lesser extent. The intensities of the bands associated with the motion of nonbridging oxygens are, however, considerably decreased because of the more covalent character of Al–O(nbr) bonds. In the light of these observations, it is suggested that when inferences are made from the Raman spectra on the role of the Al^{3+} ion in aluminosilicate melts, both the positions and the relative intensities of the bands associated with the motion of bridging and nonbridging oxygens should be considered.

On the basis of similarity in the Raman spectra of crystalline An and glass of An composition, it has been confirmed that the random network of the glass contains predominantly four-membered rings of TO_4 tetrahedra similar to those present in crystalline An. A high degree of Si–Al order exists in the An glass; this order is, however, far from perfect.

There is no similarity between the Raman spectra of glasses and those of isochemical crystals of CaTs and Geh compositions. In the spectrum of glass of approximately CaTs composition the ν_s(T–O–T) bands appear at lower frequency than the corresponding bands in the spectrum of crystalline CaTs, indicating that the structure of the glass is more polymerized than that of the crystal. On the basis of the relative intensity of the Raman bands associated with the antisymmetric and symmetric stretching motion of bridging oxygen, it is proposed that in the CaTs glass Al^{3+} remains predominantly in tetrahedral coordination, and only a small fraction ($\lesssim$1 mol%) of the Al^{3+} ion has five- or six-fold coordination and acts as a network modifier. Similarly, the presence of the ν_s(T–O–T) band in the spectrum of Geh glass at much lower frequency than the corresponding band in the spectrum of crystalline gehlenite has been attributed to predominantly tetrahedrally coordinated Al^{3+} charge-balanced by Ca^{2+} in the aluminosilicate network of the glass. The 0.33 nonbridging oxygen per tetrahedron required by the stoichiometry of gehlenite glass exists largely in the form of SiO_4^{4-} monomers in the polymerized network, and because of these monomeric silicate species, Ca^{2+} has minimum dispersion in the glass.

In summary, the present study has shown that Raman spectroscopy not only is a sensitive tool for detecting the presence of nonbridging oxygen in the aluminosilicate network but also provides information about the distribution of the local Si environment and in favorable cases about the coordination of alkaline-earth cations.

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