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# Raman spectra of some tectosilicates and of glasses along the orthoclase-anorthite and nepheline-anorthite joins

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## ABSTRACT

Raman spectra are reported for powdered crystalline anorthite, sanidine, leucite, α-nepheline, and α-carnegieite and glasses of $CaAl_2Si_2O_8$ (An), $KAlSi_3O_8$ (Or), and $NaAlSiO_4$ (Ne) compositions. Qualitative comparisons between features in the spectra of the isochemical crystals and glasses indicate that the glasses maintain short-range (coordination) relationships similar to those of the crystalline polymorphs. Intermediate-range order ($TO_4$ ring structures; T = Si,Al) of the glasses is inferred from the frequency of the dominant symmetric stretch $\nu_s$(T-O-T) band in their Raman spectra. The ring structure of An glass is similar to that of the crystalline feldspars, consisting predominantly of four-membered $TO_4$ rings. Its Raman spectrum indicates that the melt-quenched glass of Or composition contains domains of leucite-like structure, consisting of alternating four- and six-membered $TO_4$ rings, and regions of predominantly six-membered ring structures. The ring structure of Ne glass consists of six-membered $TO_4$ rings, similar to its isochemical crystalline polymorphs, although the rings are highly puckered. High-frequency antisymmetric-stretching features in the spectra of the tectosilicate glasses are explained in terms of site symmetries of $TO_4$ tetrahedra due to the distribution of $SiO_4$ and $AlO_4$ units in the glass. Variations in the ring sizes in glasses along the Or-An and Ne-An joins are reflected by shifts of the $\nu_s$(T-O-T) bands in the glass spectra. Antisymmetric-stretching features in the spectra of glasses along the Or-An join vary systematically as Si:Al changes from 3:1 in Or to 1:1 in An but vary only slightly in the spectra of glasses along the Ne-An join because of the common Si:Al of all glasses along that join.

## INTRODUCTION

Crystalline tectosilicates consist of three-dimensional framework structures containing fully polymerized $TO_4$ tetrahedra (T = $Si^{4+}$,$Al^{3+}$). Such frameworks generally consist of rings of $TO_4$ tetrahedra enclosing void spaces in which nontetrahedrally coordinated cations may reside. The structures of glasses (quenched melts) having tectosilicate-forming compositions are of interest to petrologists and geochemists studying the physical and chemical properties of aluminosilicate melt structures because the majority of natural magmas are highly polymerized, containing less than one nonbridging oxygen per tetrahedral cation (Mysen et al., 1981). Although it is generally accepted that both Si and Al cations maintain fourfold coordination in glasses quenched at ambient and high pressures from melts having tectosilicate-forming compositions (Day and Rindone, 1962; Sharma et al., 1978b; Mysen et al., 1981; Seifert et al., 1982; Navrotsky et al., 1982; Fleet et al., 1984; Hochella and Brown, 1985), the intermediate-range order (ring structure) of these glasses has yet to be fully investigated.

Tetrahedrally coordinated cation populations vary widely among the various tectosilicates. Tetrahedral sites in the structures of the pure silica crystalline polymorphs are completely occupied by $Si^{4+}$ cations. Among the feldspars, $Si^{4+}:Al^{3+}$ ranges from 3:1 for albite (Ab; $NaAlSi_3O_8$) and orthoclase (Or; $KAlSi_3O_8$) to 1:1 for anorthite (An; $CaAl_2Si_2O_8$). Sodic nepheline (Ne; $Na_2Al_2Si_2O_8$) also contains a 1:1 Si:Al population, and other crystalline aluminosilicates such as leucite (Lc; $KAlSi_2O_6$; Si:Al = 2:1) have intermediate cation populations.

In this study we investigate the Raman spectra of glasses having Or, Ne, and An compositions and the spectra of crystalline phases having Or, Ne, An, and Lc compositions, which are characterized by variations in both $TO_4$ ring structures and Si:Al. A systematic investigation of the spectra of glasses having compositions along the Or-An and Ne-An joins has also been undertaken to elucidate structural variations resulting from the compositional changes in these glasses.

## EXPERIMENTAL METHOD

The compositions and preparation conditions of the glasses used in this investigation are presented in Table 1. Starting materials for the endmember-composition glasses were high purity (>99.9%) oxides and carbonates. Mixes of the appropriate compositions were ground under acetone in an agate mortar for not

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Table 1. Compositions and preparation conditions of aluminosilicate glasses used to obtain Raman spectra

| Composition | Starting components | Fusion temp. (°C) | Time at fusion temp. (hr.) |
|---|---|---|---|
| $NaAlSiO_4$ (Ne) | $Na_2CO_3+SiO_2+Al_2O_3$ | 1620 | 2 |
| $KAlSi_3O_8$ (Or) | $K_2CO_3+SiO_2+Al_2O_3$ | 1600<br>1625 | 1.0<br>2.0† |
| $CaAl_2Si_2O_8$ (An) | $CaCO_3+SiO_2+Al_2O_3$ | 1625 | 3.5 |
| $Ne_{20}An_{80}$ | endmember glasses | 1600 | 1.0 |
| $Ne_{40}An_{60}$ | endmember glasses | 1500 | 1.0 |
| $Ne_{60}An_{40}$ | endmember glasses | 1500 | 1.0 |
| $Ne_{80}An_{20}$ | endmember glasses | 1500 | 1.0 |
| $Or_{20}An_{80}$ | endmember glasses | 1600 | 1.0 |
| $Or_{40}An_{60}$ | endmember glasses | 1550 | 1.0 |
| $Or_{60}An_{40}$ | endmember glasses | 1500 | 1.0 |
| $Or_{80}An_{20}$ | endmember glasses | 1500 | 1.0 |

†Indicates multiple heatings with sample powdered between each.

less than 10 min, dried, and loaded into platinum crucibles. The mixtures were allowed to stand at 700–900°C for several hours to ensure complete removal of $CO_2$ from the carbonates prior to fusion at the conditions listed in Table 1. Glasses having compositions along the Or-An and Ne-An joins were prepared from the powdered endmember glasses under similar conditions, omitting the decarbonation step. The glasses were quenched either by removing the crucible and allowing it to cool in air or by immersing its base in water. All glasses appeared clear and optically homogeneous with the exception of the Or-composition glass which contained minute bubbles dispersed throughout, but which was otherwise clear.

Polycrystalline samples used to obtain Raman spectra were crystallized from their isochemical glasses or were naturally occurring minerals. Anorthite was crystallized from the glass at 1000°C and 1 atm over a 48-h period (Sharma et al., 1983). Nepheline and carnegieite were crystallized at 1 atm from Ne glass at 1100°C for 4 h and at 1400°C for 5 d, respectively. The sanidine and leucite used for this study were natural minerals from Civitacastellana, Italy, and from Swan City, Colorado, respectively.

Spectra of all samples were collected using a computer-controlled Spex 1403 Raman spectrometer. The 488.0-nm line of an $Ar^+$ laser having a source power of approximately 600 mW was used to excite the samples, and a 90° scattering geometry was employed. The unpolarized spectra of powdered crystalline samples (loaded in glass capillary tubes) were collected using 2 $cm^{-1}$ slits. Glass spectra were obtained, with 5 $cm^{-1}$ slits, from unannealed glass fragments mounted on metal needles. A polarizer sheet mounted in front of an optical scrambler was used to analyze the parallel ($I_\parallel$) and perpendicular ($I_\perp$) components of the radiation scattered from the glasses, although only the $I_\parallel$ data are reported here.

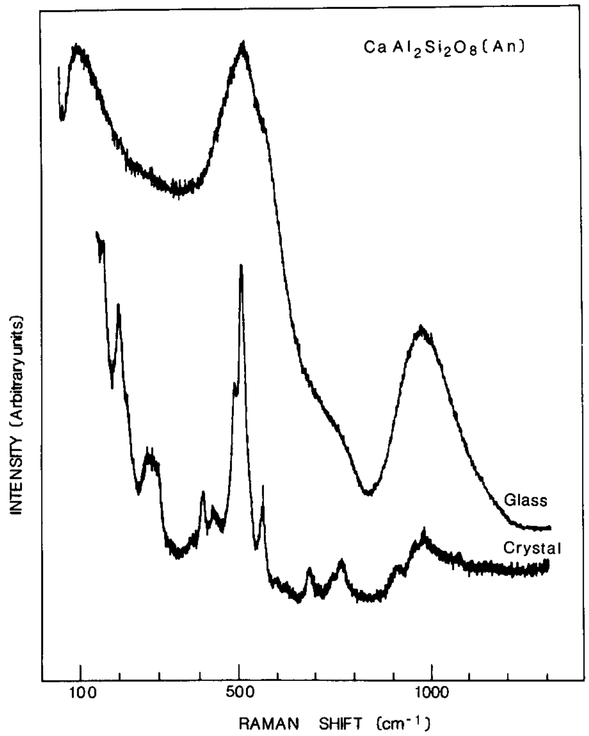

Fig. 1. The Raman spectra of crystalline anorthite and glass ($I_\parallel$) of An composition.

## RAMAN SPECTRA OF TECTOSILICATE CRYSTALS AND THEIR ISOCHEMICAL GLASSES

### Comparison of tectosilicate crystal and glass spectra

The polarized Raman spectra ($I_\parallel$) of glasses having An, Or, and Ne compositions are presented in Figures 1–3. Each glass spectrum is accompanied by the powder Raman spectrum of one or more related crystalline phases having fully polymerized tetrahedral framework structures.

The broadness of bands in the spectra of glasses compared to those in the spectra of their isochemical crystalline phases (Figs. 1–3) results from the inherent disorder of glass networks relative to the highly ordered structures of crystalline materials. Structural disorder contributes to the broadening of glass spectral bands because of the relatively wide range of structural parameters (T-O-T bond angles and T-O bond lengths) in the glass that determine its vibrational characteristics. The mean values of these structural parameters of the glass networks can be estimated using X-ray or neutron-diffraction techniques (Wright and Leadbetter, 1976; Taylor and Brown, 1979a, 1979b), but estimates of their distributions require statistical modeling (e.g., Soules, 1979).

An initial comparison reveals that the spectra of the crystalline tectosilicates and their isochemical glasses exhibit strong similarities in terms of the frequencies and relative intensities of major features. This indicates distinct structural similarities between the crystalline and glass phases in these systems, at least over the distances to which the Raman spectra are sensitive. Specifically, the next-nearest-neighbor (cation-oxygen coordination) relationships characteristic of the crystalline phases are likely retained, and these glasses consist of fully polymerized tetrahedral framework structures. Nonbridging oxygen (NBO) bonds, which would form if the tetrahedral frame-

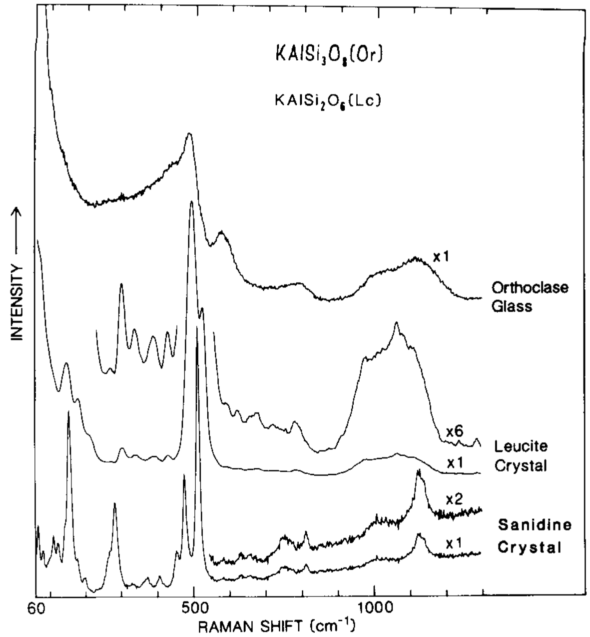

Fig. 2. The Raman spectra of crystalline sanidine and leucite, and glass ($I_\parallel$) of Or composition.

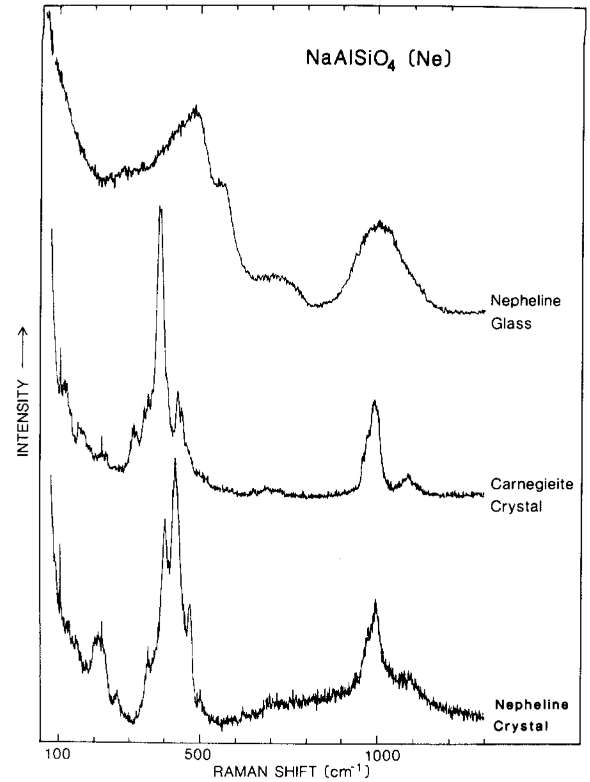

Fig. 3. The Raman spectra of crystalline $\alpha$-carnegieite and $\alpha$-nepheline, and glass ($I_\parallel$) of Ne composition.

work structures were not maintained by the glasses, have been shown to produce strong, polarized bands at characteristic frequencies (800–1200 cm$^{-1}$) in the Raman spectra of both silicate crystals and glasses (Brawer and White, 1975; Matson et al., 1983). The presence of either sixfold coordinated Al or fourfold coordinated Al acting as a network modifier is also known to have a dramatic effect on the Raman spectrum, particularly below 800 cm$^{-1}$ where these species cause the dominant low-frequency spectral band to shift strongly to higher frequency (Sharma et al., 1983). Although the general correspondence between features in the spectra of the crystalline tectosilicates and their isochemical glasses confirms the similar structural roles of cationic species in these phases, the spectra must be more carefully scrutinized to determine the effect of vitrification on intermediate-range order (i.e., ring structures).

Features in the spectra of all fully polymerized tetrahedral framework silicate and aluminosilicate glasses originate from similar vibrational modes but may vary somewhat in intensities or frequencies as a result of compositional differences (Sharma et al., 1985; Matson and Sharma, 1985). The dominant band in the spectra of all the tetrahedral framework glasses appears in the 450 to 520 cm$^{-1}$ range and is attributed to a delocalized vibrational mode involving the symmetric stretching of bridging oxygens in T-O-T linkages ($\nu_s$(T-O-T)) (Galeener, 1979; Sharma et al., 1983). Because of the similarity between features in the spectra of crystalline tectosilicates and their isochemical glasses, the corresponding dominant low-frequency bands in the crystalline tectosilicate spectra are also attributed to the $\nu_s$(T-O-T) vibrational mode (Sharma et al., 1981, 1983). Other features having similar relative intensities and frequencies in the Raman spectra of tectosilicate crystals and their glasses also likely originate from corresponding types of vibrational modes in their structures.

## Tectosilicate crystal spectra

Before beginning a detailed examination of the structural information encoded in the spectra of the tectosilicate glasses, we briefly discuss the spectra of the polycrystalline tectosilicates shown in Figures 1–3. The Raman spectra of some of these materials (anorthite and sanidine) have been presented and discussed elsewhere (e.g., Fabel et al., 1972; McMillan et al., 1982; Sharma et al., 1983; von Stengel, 1977) but are included here for the sake of completeness. To our knowledge the Raman spectra of leucite and the nepheline polymorphs have not been reported previously.

The vibrational spectrum of a crystalline material is determined by the characteristic vibrations of the crystal's unit cell and should therefore account for all degrees of freedom of the entire cell. The number of vibrational modes expected to be Raman and infrared active may be determined by factor group analysis if the unit-cell parameters are precisely known from X-ray crystallographic studies (White and DeAngelis, 1967; Adams, 1973). Careful examinations of the Raman spectra of single-crystal

Table 2. Factor group analysis of vibrational modes, and observed frequencies* and relative intensities** of bands in the Raman spectra of some powdered crystalline aluminosilicates

Anorthite ($P\bar{1}$, z = 8[a]; $\Gamma$[b] = 78 $A_g$ (R[†]) + 75 $A_u$ (i.r.)); 63 m, 88 m, 139 m, 182 m, 200 (sh), 253 m, 273 m, 281 m, 316 vw, 369 vw, 400 w, 427 w, 484 (sh), 503 vs, 553 m, 590 vw, 620 vw, 681 m, 741 (sh), 756 w, 908 w(sh), 949 w(sh), 974 m, 998 (sh), 1044 (sh), 1072 (sh), 1124 w.

Sanidine ($C2/m$, z = 4[c]; $\Gamma$[b] = 20 $A_g$ (R) + 19 $B_g$ (R) + 17 $A_u$ (i.r.) + 19 $B_u$ (i.r.)); 68 w, 80 vw, 110 w, 124 w, 142 w(sh), 156 m, 178 w(sh), 198 w(sh), 228 vw, 270 w(sh), 282 m, 330 vw, 336 vw, 372 vw, 406 vw, 454 w(sh), 476 m, 514 vs, 584 vw, 632 vw, 658 vw, 754 w, 812 w, 1008 w(sh), 1122 m.

Leucite ($I4_1/a$; z = 16[d]; $\Gamma$[e] = 30 $A_g$ (R) + 30 $B_g$ (R) + 30 $E_g$ (R) + 29 $A_u$ (i.r.) + 30 $A_u$ (i.a.) + 29 $E_u$ (i.r.)); 76 w, 112 w, 152 m, 180 w, 216 w, 266 vw, 272 vw, 304 w, 338 w, 394 vw, 432 vw, 498 vs, 528 m(sh), 618 vw, 678 vw, 786 vw, 984 w(bd)(sh), 1066 w(bd).

$\alpha$-Nepheline ($P6_3/m$, z = 2[f]; $\Gamma$[e] = 14 $A_g$ (R) + 14 $B_g$ (i.a.) + 13 $E_{1g}$ (R) + 15 $E_{2g}$ (R) + 13 $A_u$ (i.r.) + 14 $B_u$ (i.a.) + 13 $E_{1u}$ (i.r.) + 13 $E_{2u}$ (i.a.)); 123 w, 138 vw, 151 w, 214 m(bd), 264 w, 331 w(sh), 399 w, 427 vs, 469 m, 497 w, 616 vw, 690 vw(bd), 973 w(sh), 984 m(bd), 1081 w(bd).

$\alpha$-Carnegieite (low symmetry); 114 w, 154 w(bd), 217 w(bd), 262 vw, 313 w(sh), 340 w(sh), 347 vw(sh), 379 vs, 404 w(sh), 433 w, 444 w(sh), 487 w(sh), 637 vw, 685 w(bd), 721 vw, 803 vw(bd), 949 w(sh), 964 w(sh), 982 m(bd), 1072 w(bd).

[a] Smith (1974); [b] White (1974); [c] Deer et al. (1966); [d] Wyart (1940, 1941); [e] this study; [f] Dollase (1970), Foreman and Peacor (1970).

*Measurement accuracy is ±2 $cm^{-1}$ for strong bands and ±4 $cm^{-1}$ for very weak or broad bands.

**Abbreviations: s, strong; m, moderate; w, weak; v, very; (sh), shoulder; (bd), broad.

†R, Raman active; i.r., infrared active; i.a., inactive mode.

olivines and pyroxenes have shown, however, that accidental degeneracies may account for the appearance of fewer bands then expected on the basis of factor group analysis (White, 1975). A summary of the vibrational modes calculated on the basis of factor group analysis and of the experimentally observed frequencies and intensities of bands in the Raman spectra of the crystalline samples investigated here is presented in Table 2.

Crystalline An and Or are feldspars whose structures consist of four-membered rings of $TO_4$ tetrahedra interconnected to form characteristic crankshaft-like arrangements (Deer et al., 1966; Smith, 1974). The Ca and K cations occupy cavities in the framework and balance the charges of $Al^{3+}$ in tetrahedral coordination. Crystalline anorthite, containing half $Al^{3+}$ and half $Si^{4+}$ in its tetrahedral sites, exhibits a high degree of Si-Al order, largely obeying the aluminum avoidance rule proposed by Lowenstein (1954) (Kempster et al., 1962; Megaw et al., 1962; Smith, 1974). Orthoclase contains Si and Al in a 3:1 ratio, and its tetrahedral cation distribution is not so constrained. The orthoclase structure may, however, exhibit cation bias because of crystallographic site preferences and bonding-energy considerations. Consequently, the cation distribution in the high-temperature (sanidine) form of this composition is relatively random, although the low-temperature form (microcline) exhibits a high degree of tetrahedral cation order (Stewart and Ribbe, 1969).

Crystalline leucite (which the orthoclase composition melts incongruently to form; Schairer and Bowen, 1947) contains alternating four- and six-membered rings of $TO_4$ tetrahedra, with K ions occupying cavities along the lines joining the centers of the six-membered rings (Zoltai, 1960; Papike and Cameron, 1976). The broadness of the bands in the spectrum of crystalline leucite (Fig. 2) indicates that the natural sample used in the present study likely has significant Si-Al cation disorder, causing some loss of spectral resolution.

Four polymorphs of the nepheline composition are known (Smith and Tuttle, 1957). $\beta$-carnegieite is stable from the liquidus to ~1250°C where it transforms to $\beta$-nepheline. At ~900°C $\beta$-nepheline inverts to $\alpha$-nepheline which is hexagonal and stable to room temperature. The transformation from $\beta$-carnegieite is sluggish, and by rapid cooling it may be obtained in the stability field of nepheline. At ~690°C $\beta$-carnegieite undergoes a displacive inversion to $\alpha$-carnegieite which has low symmetry. The structures of nepheline and carnegieite may be described in terms of stuffed derivatives of the high-temperature silica polymorphs tridymite and cristobalite, respectively. These, unlike the $\alpha$- and $\beta$-quartz structures, are sufficiently open to accommodate interstitial Na ions (Buerger, 1954). Both structures are dominated by six-membered rings of $TO_4$ tetrahedra (Papike and Cameron, 1976). The alternation of Si and Al cations in the crystalline nepheline structure is mandated by the aluminum avoidance rule, and high degrees of Si-Al ordering have been observed in natural nephelines to temperatures in excess of 900°C (Foreman and Peacor, 1970).

The structure of pure synthetic sodic nepheline has not been thoroughly investigated. Naturally occurring nepheline ($Na_3(Na,K)Al_4Si_4O_{16}$) is hexagonal and belongs to the $P6_3$ space group, although some specimens may possess higher pseudosymmetry close to $P6_3/m$ (Dollase, 1970; Foreman and Peacor, 1970). The structure of the Na end-member is closely related to that of the natural mineral (Smith and Tuttle, 1957). A general lack of coincidence between the positions of bands in the Raman spectrum of nepheline presented here (Table 2) and the bands observed in the infrared spectrum of a naturally occurring nepheline (Moenke, 1974) indicates that the synthetic sample likely belongs to the $P6_3/m$ space group in which the Raman and infrared active modes are mutually excluded (Table 2).

In nearly all cases presented here, the number of detected Raman bands is less than predicted on the basis of group theoretical considerations (Table 2). This may result, in part, from accidental degeneracies between bands in the spectra or from the inability to distinguish weak bands from background noise (Sharma et al., 1983). Alternatively, the spectra of some of the crystalline materials, particularly those having larger unit cells, may be determined by smaller (pseudo) unit cells (White, 1974).

Table 3. Relationship between $\nu_s$(T-O-T) and ring structures in some tectosilicates and their isochemical glasses

| | Crystal | | | Glass | | |
|---|---|---|---|---|---|---|
| Mineral | $\nu_s$(T-O-T) (cm$^{-1}$) | Smallest TO$_4$ ring size$^{(k)}$ | Density (g/cm$^3$) | $\nu_s$(T-O-T) (cm$^{-1}$) | Density (g/cm$^3$) | Prominent ring structure |
| α-Quartz | 464 | 6 | 2.65 (m) | | | |
| β-Quartz (700°C) | 464 (a) | 6 | -- | | | |
| α-Cristobalite | 416 | 6 | 2.33 (m) | 437 (c) | 2.21 (v) | 6 (c) |
| α-Tridymite | 407 (b) | 6 | 2.26 (m) | | | |
| Coesite | 521 (c) | 4 | 3.01 (n) | | | |
| γ-Spodumene<br>(LiAlSi$_2$O$_6$-III) | 480 | 6 | 2.399 (p) | | | |
| β-Spodumene<br>(LiAlSi$_2$O$_6$-II) | 492 (d) | 5 | 2.374 (r) | 476 (d) | 2.34 (d) | 6 (d) |
| Low albite<br>(NaAlSi$_3$O$_8$) | 506 (e,f) | 4 | 2.63 (m) | 480 (u) | 2.38 (w) | 6 (w) |
| Sanidine<br>(KAlSi$_3$O$_8$) | 513 (e,f,g) | 4 | 2.563 (m) | 491 (g) | 2.37 (w) | 6 (g,w) |
| Anorthite<br>(CaAl$_2$Si$_2$O$_8$) | 503 (e,g,h) | 4 | 2.76 (m) | 508 (g,h) | 2.69 (w) | 4 (g,h,w) |
| Leucite<br>(KAlSi$_2$O$_6$) | 498 (g) | 4 + 6 | 2.47-2.50 (m) | -- | -- | -- |
| α-Carnegieite<br>(NaAlSiO$_4$) | 381 (g) | 6 | 2.513 (s) | | | |
| α-Nepheline<br>(NaAlSiO$_4$) | 427 (g) | 6 | 2.598 (t) | 485 (g) | 2.50 (t) | 6 (g,t) |

(a) Bates and Quist (1972)
(b) Etchepare et al. (1978)
(c) Sharma et al. (1981)
(d) Sharma and Simons (1981)
(e) White (1975)
(f) von Stengel (1977)
(g) This study
(h) Sharma et al. (1983)
(k) Zoltai (1960)
(m) Deer et al. (1966)
(n) Zoltai and Buerger (1959)
(p) Li and Peacor (1968)
(r) Li (1968)
(s) Bowen (1912)
(t) Taylor and Brown (1979b)
(u) Sharma et al. (1985)
(v) Seifert et al. (1983)
(w) Taylor and Brown (1979a)

## Interpretation of ring structures in tetrahedral framework crystals and glasses

It has been demonstrated (Sharma et al., 1981, 1983, 1985) that a relationship exists between the intermediate-range TO$_4$ ring structures of crystalline tectosilicates and the frequencies of $\nu_s$(T-O-T) bands in their Raman spectra. Those tectosilicates consisting of structures containing four-membered rings (e.g., coesite and the feldspars) have $\nu_s$(T-O-T) modes appearing above 500 cm$^{-1}$ whereas those containing six-membered ring structures (e.g., α- and β-quartz, cristobalite, tridymite, γ-spodumene, α-carnegieite, and β-nepheline) have $\nu_s$(T-O-T) modes ranging from 381 to 480 cm$^{-1}$. $\nu_s$(T-O-T) bands in the spectra of other crystalline tectosilicate phases whose structures consist of five-membered rings (e.g., β-spodumene) or alternating four- and six-membered rings (e.g., leucite) appear at intermediate frequencies (Table 3). Comparisons between the spectra of crystalline tectosilicates and their isochemical glasses have led to the conclusion that the frequencies of $\nu_s$(T-O-T) bands in the spectra of tetrahedral framework glasses are also indicators of ring structures in the glass networks (Sharma et al., 1981, 1983, 1985).

Frequencies of the $\nu_s$(T-O-T) bands in the spectra of anorthite crystal and glass agree closely (503 vs. 508 cm$^{-1}$, respectively; Table 3), indicating a close correspondence between the ring structures in the two phases of this material. On the basis of $\nu_s$(T-O-T) band positions alone, it is inferred that four-membered rings of TO$_4$ tetrahedra characteristic of the crystalline feldspar structure likely predominate in the isochemical An glass. This interpretation is supported by X-ray RDF (Taylor and Brown, 1979a) and thermochemical studies (Navrotsky et al., 1980) of anorthite glass and is also consistent with a number of physical, chemical, and optical properties of An glass summarized by Sharma et al. (1983).

The $\nu_s$(T-O-T) band frequency of Or glass (491 cm$^{-1}$) is significantly lower than that of its crystalline feldspar analogue, sanidine (513 cm$^{-1}$; Table 3). The frequency of the Or glass band is, however, considerably closer to that observed in the spectrum of its liquidus phase, leucite (498 cm$^{-1}$). Careful inspection of the low-frequency features in the spectrum of Or glass (Fig. 2) indicates that the relatively sharp $\nu_s$(T-O-T) band appearing at 491 cm$^{-1}$ is probably superimposed over a much broader feature centered at approximately 15 to 20 cm$^{-1}$ lower frequency.

Because the $\nu_s$(T-O-T) band is believed to result from a delocalized vibrational mode occurring over a large number of tetrahedral linkages (Bell et al., 1970), the appearance of vibrationally distinct $\nu_s$(T-O-T) bands indicates that relatively large domains of more or less homogeneous ring structure must exist in the Or glass. The close correspondence in frequency between the $\nu_s$(T-O-T) band in the spectrum of leucite and the sharp $\nu_s$(T-O-T) feature in the Or glass spectrum suggests that domains of leucite-like structures consisting of alternating four- and six-membered rings may persist in the glass framework. The underlying broader feature indicates the presence of a vibrationally distinct structure containing a higher proportion of six-membered rings. The Raman spectrum of a glass prepared from a gel of Or composition (McMillan et al., 1982) exhibits only a single asymmetric $\nu_s$(T-O-T) feature, perhaps attesting to a greater structural homogeneity of gel-derived glasses as opposed to those quenched from melts (Mackenzie, 1982).

The presence of leucite-like structures in Or-rich melts having compositions along the Ab-Or join has also been proposed by Rammensee and Fraser (1982) to account for positive deviations in $\Delta H_{\mathrm{mix}}$ of the endmembers on the basis of high-temperature Knudsen cell mass-spectrometric measurements. The glasses of Rammensee and Fraser (1982) were carefully examined in transmitted light but reportedly showed no signs of leucite crystallization products and are considered to represent supercooled liquids above $T_g$, the glass transition temperature. Taylor and Brown (1979a) noted that the X-ray RDF of Or glass compared well with that of leucite to >4.5 Å, although beyond 5 Å the RDFs of the leucite structure and Or glass appear uncorrelated. These observations appear to support the proposal of Kushiro (1975) that in some cases the highest-temperature crystalline phase of a particular composition influences the melt structure.

The $\nu_s$(T-O-T) bands at 427 and 381 cm$^{-1}$ in the spectra of $\alpha$-nepheline and $\alpha$-carnegieite crystals, respectively, occur at low frequencies compared with the frequencies of corresponding bands in the spectra of $\alpha$- and $\beta$-quartz (464 cm$^{-1}$; Bates and Quist, 1972). The nepheline and carnegieite bands do correspond more closely with the frequencies of $\nu_s$(T-O-T) bands in the spectra of $\alpha$-tridymite (407 cm$^{-1}$; Etchepare et al., 1978) and $\alpha$-cristobalite (416 cm$^{-1}$; Bates and Quist, 1972), of which nepheline and carnegieite are stuffed derivatives (Buerger, 1954).

The $\nu_s$(T-O-T) band in the spectrum of Ne glass appears at considerably higher frequency (485 cm$^{-1}$; Table 3) than the corresponding band in the spectra of either of the crystalline polymorphs. This may result, in part, from a distribution of $TO_4$ ring sizes (including three-, five-, seven-, and larger-membered rings) in the disordered structure of Ne glass. Such a distribution could contribute to the relatively high frequency of the $\nu_s$(T-O-T) band in the spectrum of Ne glass because of the highly delocalized nature of this mode. However, the rapid crystallization behavior of the Ne glass to its isochemical crystalline phases containing six-membered rings (Bowen, 1912) suggests a predominance of six-membered rings in the glass structure because a redistribution of ring structures on crystallization would require the breaking of strong T-O bonds. Further support for the assignment of six-membered rings to the structure of Ne glass may be found in the Taylor and Brown (1979b) interpretation of the X-ray RDF data of this material.

The tendency of An glass (and melt) to retain the four-membered $TO_4$ ring configurations characteristic of its crystalline feldspar phase is probably related to the nature of its charge-balancing cation ($Ca^{2+}$). The divalent character of the Ca cations requires that two $AlO_4^-$ units be present in close proximity to satisfy charge-balance conditions. This—in addition to the small size of the $Ca^{2+}$ relative to the alkali cations and the tendency of the $SiO_4$ and $AlO_4$ tetrahedra to alternate in the structure owing to the Al avoidance principle—can account for the stability of four-membered rings in An glass. The larger size of $Na^+$ and $K^+$, the single charge on these cations, and/or the lower Si:Al ratio in Or and Ne glasses undoubtedly contribute to the greater stability of six-membered $TO_4$ rings in these materials.

With the exception of the $\nu_s$(T-O-T) band and the high-frequency antisymmetric-stretching bands discussed below, other features in the Raman spectra of the framework aluminosilicate glasses are not well understood. Shoulders appear on either side of the $\nu_s$(T-O-T) band in the spectra of each of the tectosilicate composition glasses studied (Figs. 1–3). If the $\nu_s$(T-O-T) vibrational modes of the ring structures in glasses were not strongly delocalized, it would be tempting to assign these features to contributions from larger (>6-membered) and smaller (3-membered) ring structures. We have previously shown, however, that the low-frequency features in the spectra of Ge-substituted-for-Si framework aluminosilicate glasses can be attributed to distinctive vibrational modes to which cation motion makes a significant contribution (Sharma and Matson, 1984; Matson and Sharma, 1985). Unresolved low-frequency shoulders in the spectra of the framework aluminosilicate glasses discussed here are considered to arise from corresponding modes. Similarly, we have argued (Matson and Sharma, 1985) that the shoulder appearing between 550 and 580 cm$^{-1}$ in the spectra of the aluminosilicate glasses corresponds to the 606 cm$^{-1}$ $SiO_2$ glass "defect" band, although its relative intensity appears to be related to the $Al^{3+}$ content of the glass. The specific nature of the "defect" responsible for this feature is not currently understood. We do not, however, consider it likely that this band can be accounted for by Al-O-Al linkages as proposed by McMillan et al. (1982) as this would require a highly localized $\nu_s$(T-O-T) vibrational mode. Intermediate-frequency features appearing between 700 and 800 cm$^{-1}$ (Figs. 1–3) are common to the spectra of tetrahedral network glasses and are attributed to an intertetrahedral deformation mode involving significant cation motion (Sharma et al., 1984; Sharma and Matson, 1984).

### High-frequency features

Systematic Raman spectral investigations of glasses having compositions along the $SiO_2$-$MAlO_2$ and $SiO_2$-$MAl_2O_4$ joins (Seifert et al., 1982; McMillan et al., 1982) have shown that both intensities and band contours of high-frequency features (850–1200 $cm^{-1}$) in the spectra of the framework aluminosilicate glasses are highly sensitive to the glass composition. Although strong bands attributed to the stretching modes of nonbridging oxygens (NBOs) appear in this spectral region (Brawer and White, 1975; Sharma et al., 1978a; Matson et al., 1983), it is unlikely that glasses having alkali or alkaline-earth cations present in just sufficient quantities to charge balance $Al^{3+}$ in fourfold coordination contain significant numbers of NBOs. Difference spectra between pure Ab glass and Ab glass containing excess $Na_2O$ or $Al_2O_3$ (Matson, 1984) clearly show that high-frequency features in the spectrum of pure Ab glass do not result from NBO stretching modes. On this basis it is inferred that high-frequency features in the spectra of other tectosilicate-composition glasses result primarily from the antisymmetric-stretching modes of O atoms and network-forming cations in the three-dimensional aluminosilicate framework. These high-frequency glass modes correspond to similar vibrational modes of crystalline tectosilicates (White, 1975; Sharma et al., 1983).

The shape of the high-frequency envelope in the spectrum of Ab glass (McMillan et al., 1982) is similar to that in the spectrum of Or glass (Fig. 2). Both compositions contain Si:Al of 3:1. The high-frequency antisymmetric-stretching features in the spectra of both Ab and Or glasses consist of two dominant bands, the higher-frequency band having higher intensity and being more strongly polarized. Similarly, the high-frequency features in the spectra of An and Ne glasses (Si:Al = 1:1; Figs. 1 and 3) are comparable, consisting of a single predominant band with some small residual intensity on the high-frequency side. These observations suggest that the general shape of the antisymmetric-stretching features in the spectra of the framework aluminosilicate glasses can be directly related to the Si:Al of the glass.

High-frequency features in the Raman spectra of glasses along the $SiO_2$-$NaAlSiO_4$ join have been interpreted in terms of two variable-frequency bands (Virgo et al., 1979; Mysen et al., 1980), although that interpretation was subsequently abandoned in favor of a more complex model based on residual-minimized Gaussian curve fitting of the experimental data (Seifert et al., 1982; Mysen et al., 1982). More recently it has been shown that the high-frequency features in the Raman spectra of Ga- and/or Ge-substituted glasses are analogous to those in the spectra of the corresponding sodium aluminosilicate glasses and can also be interpreted in terms of two variable-frequency (and non-Gaussian) bands (Sharma and Matson, 1984; Matson and Sharma, 1985). This brings to question the validity of using residual-minimized fits of Gaussian-shaped bands to interpret features in the spectra of framework aluminosilicate glasses, or of glasses in general.

The predominance of two bands in the high-frequency region in the spectra of aluminosilicate glasses having Si:Al greater than 1:1 (e.g., Or; Fig. 2) can be accounted for, at least as a first approximation, by the lowering of the $SiO_4$ tetrahedra site symmetries resulting from the presence of adjacent $AlO_4$ tetrahedra (Sharma and Matson, 1984; Matson and Sharma, 1985). The presence of adjacent tetrahedra having distinct T-O bonding character produces a splitting of the high-frequency antisymmetric-stretching ($F$) mode of the tetrahedral species into modes of $A_1$ and $E$ character. The higher-frequency component of the aluminosilicate-glass antisymmetric-stretching envelope in the spectra of glasses having Si:Al > 1:1 is more strongly polarized than the lower-frequency component and has therefore been assigned to the mode having $A_1$ character. Glasses having Si:Al of 1:1 (An and Ne) are expected to have a relatively high degree of Si-Al ordering if the aluminum avoidance rule is invoked, and individual $TO_4$ units should therefore experience similar environments (e.g., $Si(OAl)_4$ units). This results in the appearance of a single antisymmetric-stretching feature in the spectra of An and Ne glasses (Figs. 1 and 3) although the polarized nature of this feature indicates that the symmetry of the $TO_4$ units is lower than $T_d$. A slight asymmetry of the high-frequency feature in the spectra of An and Ne glasses suggests some deviation from strict adherence to the aluminum avoidance rule. The spectra of glasses having compositions along the $GeO_2$-$NaAlGeO_4$ and $GeO_2$-$NaGaGeO_4$ joins (Sharma and Matson, 1984) clearly indicate that the frequencies of both bands in the doublet are affected by the aluminate content in the glasses, as had been originally proposed to account for features in the spectra of glasses along the $SiO_2$-$NaAlSiO_4$ join (Virgo et al., 1979; Mysen et al., 1980). This would strongly suggest that some degree of coupling exists between the high-frequency antisymmetric-stretching vibrational modes of the $AlO_4$ and $SiO_4$ tetrahedra. Coupling between the antisymmetric-stretching modes of $SiO_4$ and $AlO_4$ tetrahedra is also indicated by the lack of features between 800 and 900 $cm^{-1}$ in the spectra of the aluminosilicate glasses, which would correspond to the stretching of $AlO_4$ units, as observed in the spectrum of $CaAl_2O_4$ glass (McMillan et al., 1982).

## RAMAN SPECTRA OF GLASSES ALONG Or-An AND Ne-An JOINS

Systematic investigations of Raman spectra of glasses having compositions along the Or-An and Ne-An joins are of interest in light of the above interpretation of features in the endmember glass spectra. Intermediate-range ring species in the endmember glasses of both joins are distinct. The relative stabilities of those species in the structures of the glasses having compositions along the joins may be probed using the frequency of $\nu_s$(T-O-T) as an indicator of the $TO_4$ ring distributions in the glass structures. The Or-An join is also characterized by a change in Si:Al from 3:1 to 1:1 along the join, which should be reflected in the high-frequency features of the intermediate-composition glass spectra because of the contribu-

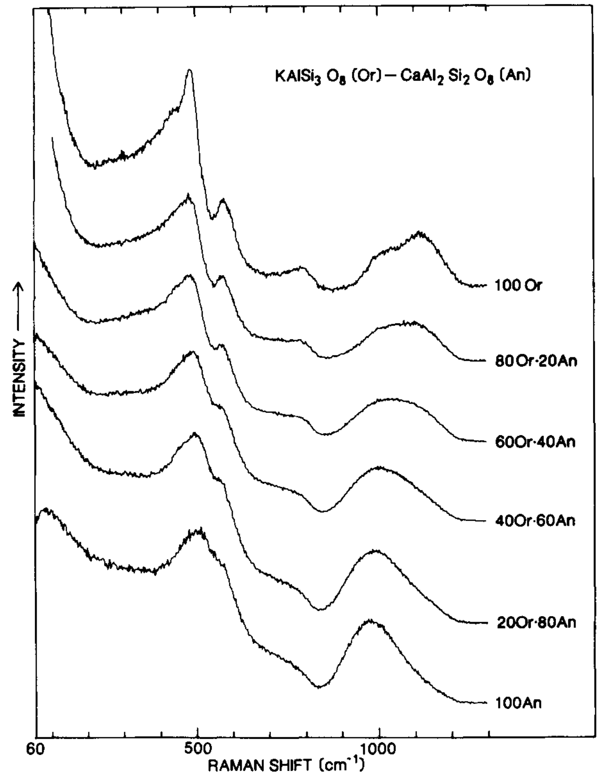

Fig. 4. Raman spectra ($I_{\|}$) of glasses having compositions along the Or-An join.

tion of both O and T cation motion to these modes. Changes in the spectra of glasses having compositions along the Ne-An join must be accounted for by factors other than changes in Si:Al because this parameter remains constant at 1:1 for all compositions along this join.

## Or-An system

The $I_{\|}$ Raman spectra of glasses along the Or-An join are presented in Figure 4. Refractive indices and spectral band positions of the glasses along the join are listed in Table 4. The refractive indices vary smoothly with nominal composition along the join and are consistent with those of both the endmember- and intermediate-composition glasses as reported by other workers (Schairer and Bowen, 1947; Taylor and Brown, 1979a).

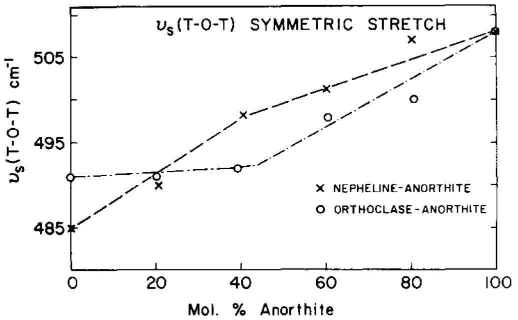

Fig. 5. $\nu_s$(T-O-T) as a function of composition in the spectra of glasses along the Or-An and Ne-An joins.

It is important to note that only a single broad $\nu_s$(T-O-T) band exists in the spectra of all of the intermediate-composition glasses (Fig. 4) despite the fact that the endmember glasses are interpreted as consisting of distinct ring structures. This indicates (1) that the intermediate-composition glasses must consist of mixtures of ring structures and (2) that the $\nu_s$(T-O-T) vibrational mode is sufficiently delocalized that individual rings cannot be distinguished. The nearly constant frequency of the $\nu_s$(T-O-T) band between the spectra of pure Or and $Or_{60}An_{40}$ glasses (Fig. 5) could be taken to indicate the retention of the leucite-like domains in these glasses without the incorporation of larger numbers of four-membered ring structures. This is unlikely since leucite does not appear as the liquidus phase beyond about 20% An content (Schairer and Bowen, 1947) and because the $\nu_s$(T-O-T) shoulder characteristic of the leucite structure does not appear in the spectra of either the $Or_{80}An_{20}$ or the $Or_{60}An_{40}$ glasses. The very small shift in frequency of the $\nu_s$(T-O-T) band in the spectra of glasses containing less than 60% An (Fig. 5) may result from a more random incorporation of the four-membered rings throughout the glass upon the loss of distinct structural domains of the $Or_{100}$ glass. Glasses having compositions beyond 40% An almost certainly revert back to random ring structures in which the concentration of four-membered rings increases as the pure An composition is approached. This is reflected by the

Table 4. Raman frequencies (cm$^{-1}$) and refractive indices of glasses along the Or-An join

| Composition: | $Or_{100}$ | $Or_{80}An_{20}$ | $Or_{60}An_{40}$ | $Or_{40}An_{60}$ | $Or_{20}An_{80}$ | $An_{100}$ |
|---|---|---|---|---|---|---|
| Refractive index: | 1.485 | 1.499 | 1.515 | 1.535 | 1.555 | 1.573 |
| | -- | -- | -- | 72 s,p | 68 s,p | 90 s,p |
| | ∿310 vw,bd† | ∿320 vw,bd | ∿324 vw,bd | ∿326 vw,bd | ∿320 vw,bd | ∿320 vw,bd |
| | 452 (sh),p | | | | | |
| | 491 vs,p | 491 vs,p | 492 vs,p | 498 vs,p | 500 vs,p | 508 vs,p |
| | 578 (sh),p | ∿576 (sh),p | ∿576 (sh),p | ∿568 (sh),p | ∿568 (sh),p | ∿572 (sh),p |
| | ∿802 w,bd | ∿790 vw,bd | ∿772 vw,bd | ∿768 vw, bd | ∿764 w,bd | ∿770 w,bd |
| | 1015 w,(sh),bd | 1012 w,(sh),bd | 1033 w,bd | | | |
| | | | | ∿1014 m,bd | ∿993 m,bd | ∿984 m,bd |
| | 1118 m,bd | 1104 w,bd | 1079 w,(sh) | | | |

*Accuracy: ±5 cm$^{-1}$ for strong and medium intensity bands and ±10 cm$^{-1}$ for weak bands and shoulders.
†Abbreviations: w, weak; m, medium; s, strong; v, very; bd, broad; (sh), shoulder; p, polarized.

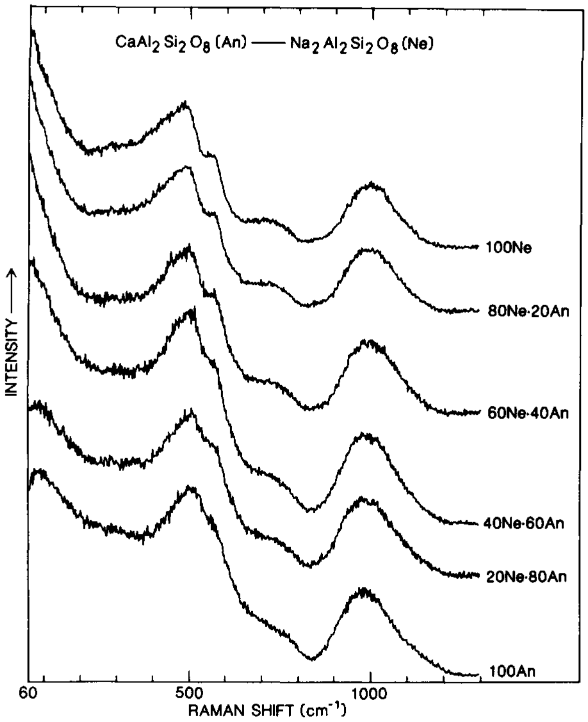

Fig. 6. Raman spectra ($I_\parallel$) of glasses having compositions along the Ne-An join.

sharp increase in frequency of the $\nu_s$(T-O-T) band in the spectra of glasses containing greater than 40% An (Fig. 5).

The spectrum in the high-frequency region (850–1250 cm$^{-1}$) is altered dramatically as the glass composition changes from pure Or to pure An (Fig. 4). The Or-glass spectrum contains a pair of unresolved high-frequency features that shift continuously in the spectra of glasses along the Or-An join to become a single asymmetric feature in the spectrum of An glass. Changes appearing in the high-frequency spectra of the glasses along the Or-An join reflect the changing concentration and distribution of $SiO_4$ and $AlO_4$ units in these glasses as Si:Al changes from 3:1 in Or to 1:1 in the An composition.

### Ne-An system

The polarized ($I_\parallel$) spectra of all the glasses along the Ne-An join are presented in Figure 6, and glass refractive indices and spectral band positions are recorded in Table 5. Refractive indices of the glasses along the join vary smoothly with composition and are in close agreement with those reported for glasses of these compositions by Gummer (1943) and Goldsmith (1947).

A shift in the frequency of the $\nu_s$(T-O-T) band from 485 cm$^{-1}$ at the pure Ne composition to 508 cm$^{-1}$ at the An composition (Table 5, Fig. 5) suggests a general increase in four-membered ring concentration in the glasses with increasing An content. An apparent break in the $\nu_s$(T-O-T) vs. An content observed near the $Ne_{60}An_{40}$ composition (Fig. 5) may reflect subtle changes in intermediate-range order near this composition. Clearly, differences in Si:Al cannot be invoked to account for these changes as all glasses along the join have the same Si:Al.

Other than a slight shift of the envelope toward lower frequency (Fig. 6, Table 5), there is little change in the high-frequency antisymmetric-stretching region of the spectra of the glasses along the Ne-An join. This is expected because the constant Si:Al (= 1:1) of all the glasses produces a single antisymmetric-stretching mode from $TO_4$ tetrahedra surrounded by four other similar tetrahedra as mandated by the aluminum avoidance rule.

## CONCLUSIONS

Similarities between the spectra of the crystalline tectosilicates and those of their isochemical glasses are taken to indicate that structural similarities exist between the two phases, at least in terms of the maintenance of $SiO_4$ and $AlO_4$ units that are interconnected to form continuous three-dimensional framework structures. The broadness of the bands and the lack of fine structure in the spectra of glasses relative to the isochemical crystal spectra result directly from the disordered state of the glassy material.

The frequencies of the $\nu_s$(T-O-T) bands in the spectra of the crystalline tectosilicates are sensitive to the size of the $TO_4$ rings present in their structures. Crystalline tectosilicates whose structures are dominated by four-membered rings of $TO_4$ tetrahedra have $\nu_s$(T-O-T) frequencies above 500 cm$^{-1}$ whereas those containing six-membered and larger rings have $\nu_s$(T-O-T) bands which appear below 480 cm$^{-1}$. Using a similar criterion to determine the $TO_4$ ring distribution in the structures of aluminosilicate glasses, it is clear that An glass contains four-membered $TO_4$ rings similar to those in the crystalline feldspar phase, whereas Ne glass probably consists predominantly of six-

Table 5. Raman frequencies (cm$^{-1}$) and refractive indices of glasses along the Ne-An join

| Composition: | $Ne_{100}$ | $Ne_{80}An_{20}$ | $Ne_{60}An_{40}$ | $Ne_{40}An_{60}$ | $Ne_{20}An_{80}$ | $An_{100}$ |
|---|---|---|---|---|---|---|
| Refractive index: | 1.513 | 1.523 | 1.533 | 1.546 | 1.559 | 1.573 |
| | -- | -- | -- | -- | 74 s,p | 90 s,p |
| | ∿285 vw,bd† | ∿283 vw, bd | ∿304 vw,bd | ∿300, vw,bd | ∿313 vw,bd | ∿320 vw,bd |
| | 485 vs,p | 490 vs,p | 498 vs,p | 502 vs,p | 508 vs,p | 508 vs,p |
| | 558 (sh),p | 565(sh),p | 560 (sh),p | 564 (sh),p | 570 (sh),p | ∿572 (sh),p |
| | ∿735 w,bd | ∿741 w,bd | ∿745 w,bd | ∿760 w,bd | ∿759 w,bd | ∿770 w,bd |
| | 1005 m,bd | 990 m,bd | 994 m,bd | 988 m,bd | 980 m,bd | 985 m,bd |

*Accuracy: ±5 cm$^{-1}$ for strong and medium intensity bands and ±10 cm$^{-1}$ for weak bands and shoulders.
Abbreviations: w, weak;, m, medium; s, strong; v, very; bd, broad; (sh), shoulder; p, polarized.

membered rings. Or glass quenched from melt of Or composition may contain domains of leucite-like structure as well as domains consisting largely of six-membered rings.

High-frequency features in the spectra of the tetrahedral framework aluminosilicate glasses result from the antisymmetric-stretching modes of the bridging oxygens and network-forming cations. Variations in frequencies and intensities of high-frequency antisymmetric-stretching bands with changes in Si:Al in these glasses indicate that the higher-frequency feature of the antisymmetric-stretching envelope corresponds to the $A_1$ component, whereas the lower-frequency feature can be attributed to the $E$ mode component of this mode which is split by a lowered symmetry of $TO_4$ species in aluminosilicate glass networks. Shifts of these bands to lower frequency with increasing Al content of the glasses indicate that both components of the antisymmetric-stretching mode are sensitive to the overall T-O bond strength of the glass and therefore must be at least partially delocalized.

The above interpretations are consistent with observed changes in the spectra of glasses having compositions along the Or-An and Ne-An joins. Variations in $\nu_s$(T-O-T) band frequencies with compositional changes in the spectra of glasses along these joins reflect changes in the $TO_4$ ring distributions in these materials and indicate the delocalized nature of the $\nu_s$(T-O-T) mode. Variations in the shape of the high-frequency antisymmetric-stretching envelope with changes in composition in the spectra of glasses along the Or-An join are most likely related to the changes in Si:Al of these glasses.

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