

Structure of Na in aluminosilicate glasses: A far-infrared reflectance spectroscopic study

CELIA I. MERZBACHER,* WILLIAM B. WHITE**

Department of Geosciences, The Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

ABSTRACT

Infrared reflectance spectra of two strategically selected series of glasses in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system have been measured. One series is along the $\text{SiO}_2-\text{NaAlO}_2$ join with $\text{NBO/T} = 0$. The other series is on the $\text{Na}_2\text{O}-\text{SiO}_2$ binary with NBO/T from 0.67 to 1.33. Kramers-Kronig analysis was performed, and the far-infrared region of the computed dielectric loss function is interpreted in terms of changes in the Na structural environment. On the basis of the strong, positive, linear correlation between peak height and Na content, the observed far-infrared peak is assigned to vibration of the Na ions. The Na mode occurs at 85 cm^{-1} in the spectra of all the fully polymerized glasses. The vibrational energy increases with depolymerization, to 150 cm^{-1} for the most depolymerized glass, owing to the gradual collapse of the tetrahedral framework structure. Calculated Na-O force constants range from 10 N/m for the fully polymerized glasses to 30 N/m for the most depolymerized composition. The results of this study agree with a structural model, for glasses with $\text{Na/Al} \geq 1.0$, in which Na charge-balances tetrahedral Al, with excess Na acting as network modifiers and depolymerizing the structure.

INTRODUCTION

The interest in understanding properties of various materials, including silicate glasses and melts, in terms of their structures has spawned numerous spectroscopic investigations. In addition, recent calculations of thermodynamic functions emphasize the need for complete vibrational spectra in the far- and mid-infrared regions (Hofmeister et al., 1987).

In general, the structure of alkali aluminosilicate melts and glasses is believed to consist of a framework of AlO_4 and SiO_4 tetrahedra, with alkali ions residing in the interstices, acting either as network-modifying or charge-balancing cations. Structural details of the alkali site have proven to be elusive. In the radial distribution functions of alkali glasses, the contribution by the alkali ions is buried beneath the stronger peaks owing to the tetrahedral network (Taylor and Brown, 1979; Hochella and Brown, 1984). Similarly, in the numerous Raman spectra of alkali aluminosilicate glasses that have been published (e.g., Brawer and White, 1977; Mysen et al., 1980, 1983, 1985; McMillan et al., 1982; Seifert et al., 1982; DiSalvo et al., 1982; McKeown et al., 1984), all bands were assigned to vibrations of the tetrahedral framework. This interference problem is surmounted by element-specific techniques such as EXAFS and magic-angle spinning nuclear magnetic resonance (MAS NMR). Theoretically, the X-ray absorption techniques, EXAFS and XANES, can be

used to determine Na coordination and Na-O bond lengths in silicate glasses (e.g., Greaves et al., 1981; McKeown et al., 1985). The wide range and unknown distribution of Na-O bond lengths, however, adds uncertainty to the interpretation of the absorption data (Calas and Petiau, 1983). MAS NMR is a relatively new technique for studying glass structure. Unfortunately, because of quadrupolar effects, the ^{23}Na NMR peak is very broad, thereby reducing the sensitivity to small variations in chemical shift (Dupree et al., 1984; Kirkpatrick et al., 1985).

Far-infrared spectroscopy has been used, with success, to study the modifier motion in some alkali silicate glasses (Exarhos and Risen, 1972; Kamitsos and Risen, 1984; Gervais et al., 1987) and alkali-phosphate and borate glasses (Exarhos et al., 1974; Rouse et al., 1978; Nelson and Exarhos, 1979; Rao and Elliott, 1981; Kamitsos et al., 1987). By and large, these previous studies have been based on transmission measurements. The line shapes of transmission spectra are a combination of reflectance and absorption that cannot be separated. Furthermore, peak intensities are not easily reproduced owing to sample-preparation techniques.

Reflectance infrared spectroscopy yields very reproducible spectra, and with additional transformation, the true line shapes of the infrared active modes may be extracted. In this study, reflectance infrared spectroscopy has been used to examine the structural environment of Na in several glasses from the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. The observed vibrational energy is a function of chemistry—that is, ionic charge and mass—and structural parameters such as bond length, bond angle, and coordi-

* Present address: Lawrence Livermore National Laboratory, Livermore, California 94550, U.S.A.

** Also affiliated with the Materials Research Laboratory, The Pennsylvania State University.

TABLE 1. Glass compositions and calculated Na-O force constants

Sample	Mole fraction			NBO/T	$\bar{\nu}$ (cm ⁻¹)	k* (N/m)	k** (N/m)
	Na ₂ O	Al ₂ O ₃	SiO ₂				
Albite glass	0.125	0.125	0.75	0.0	83	9	2.8
Jadeite glass	0.167	0.167	0.67				
Nepheline glass	0.25	0.25	0.50				
Na ₂ O·3SiO ₂	0.25	0.0	0.75	0.67	125	21	6.2
Na ₂ O·2SiO ₂	0.33	0.0	0.67	1.0	136	25	7.3
Na ₂ O·1.5SiO ₂	0.40	0.0	0.60	1.33	197	53	15.3

* Assuming oxygens are immobile.

** Assuming oxygens are vibrating.

nation number. By considering glasses in which Na is the only nonframework cation, the chemical effects are held constant, and information about the Na site structure is obtained.

COMPOSITIONS

Two compositional series were selected in the Na₂O-Al₂O₃-SiO₂ ternary system such that the role of Na as network modifier and charge balancer would be discriminated (see Table 1). In the first series, along the Na₂O-SiO₂ join, Na enters the melt as a modifying cation, causing formation of nonbridging oxygens and progressively depolymerizing the structure. The second series lies on the SiO₂-NaAlO₂ join with compositions corresponding to the mineral phases albite (NaAlSi₃O₈), jadeite (NaAlSi₂O₆), and nepheline (NaAlSiO₄). All of these mineral glasses are fully polymerized, with Al³⁺ + Na⁺ increasingly substituting for Si⁴⁺. In these aluminous melts, Na acts only as a charge-compensating cation and resides in the interstices of the tetrahedral framework, near Al in fourfold coordination (Onorato et al., 1985, and references therein).

EXPERIMENTAL PROCEDURES

Jadeite and nepheline glasses were prepared from SiO₂ floated-powder and reagent-grade Na₂CO₃ and Al₂O₃. Both samples were melted at approximately 100 °C above the liquidus (1350–1625 °C) in a Pt crucible, ground, and remelted several times. The intermediate grinding was begun in a steel mortar and completed in an agate mortar, after passing over a magnet to remove any steel filings. The melts were too viscous to pour from the crucible; therefore, the final melting was in a Pt-foil mold. Several glasses, made according to this procedure and having similar melt viscosities, were shown to be homogeneous by microprobe analysis and refractive-index measurements (Merzbacher, 1987). This process yielded a 2.5-cm disk-shaped sample with 1–2-mm bubbles at the glass-foil interface, leaving the remainder of the sample glassy, bubble-free, and suitable for reflectance measurement. Samples were prepared for infrared analysis by grinding a flat face (~2 cm in diameter) on the top surface of the disks, and polishing to 1 μm with diamond paste.

The albite glass sample was the same material used by Zellmer (1986). The glass was prepared by grinding a specimen of Amelia albite and melting at 1300 °C, grinding and remelting several times. In order to eliminate microscopic bubbles in the glass, which caused cloudiness and degraded the quality of the reflectance spectra, the sample was treated in a hot isostatic press at 1300 °C and 2500 psi (172 bars). This technique produced a

bubble-free sample that was polished in the same manner as the jadeite and nepheline glasses.

Infrared spectra in the region from 25 to 4000 cm⁻¹ were collected on an IBM IR98 Fourier transform infrared spectrometer. The reflectance spectrum for each sample represents 256 coadded scans that were then normalized to the reflectance spectrum of a front-surface Al mirror. The spectral resolution is 1–2 cm⁻¹, with highest resolution in the far-infrared. Because of the broad line shapes, however, peak positions are only accurate to within ±5 cm⁻¹.

The Kramers-Kronig transformation was performed on the observed reflectance spectra using the correction scheme of Andermann et al. (1965). The transformation yields the phase-angle shift upon reflection as a function of energy. A more detailed description of the transformation and the calculation of various optical parameters is given elsewhere (cf. Merzbacher, 1987; Gervais et al., 1987). The entire reflectance spectrum was used in the Kramers-Kronig transformation in order to minimize the necessary corrections and to obtain the most accurate results in the region of interest, i.e., the far-infrared at 300 cm⁻¹ or less. For crystalline solids, the vibrational frequency of the transverse optic (TO) modes correspond to the maxima in the imaginary part of the dielectric function (ϵ'') vs. wavenumber. The vibrational mode does not correspond to the wavenumber of maximum reflectance. Although the relationships between the TO modes and ϵ'' cannot be derived rigorously for noncrystalline solids, the dielectric loss function may nevertheless be analyzed to elucidate the vibrational characteristics of the glasses studied.

RESULTS AND DISCUSSION

The reflectance spectra for albite (Ab), jadeite (Jd), and nepheline (Ne) glasses (Fig. 1) are dominated by two peaks near 1000 and 450 cm⁻¹. Spectral variation of these modes is due primarily to the change in Si:Al. A weak mode is observed near 650 cm⁻¹, but there are no well-defined reflectance maxima below 300 cm⁻¹.

Kramers-Kronig transformation of the reflectance spectra, however, reveals a moderately strong low-frequency mode at 83 cm⁻¹, visible in all three spectra of ϵ'' (Fig. 2). The strong linear correlation between the intensity of this peak and the Na content, shown in Figure 3, confirms the relationship between this band and the Na vibration.

The observed maximum at 83 cm⁻¹ in the albite glass spectrum agrees very well with the low-frequency Raman line, also at 83 cm⁻¹, reported by Kieffer (1982) for crystalline albite. Low-frequency modes contribute significantly to the total heat capacity. In fact, Kieffer (1982)

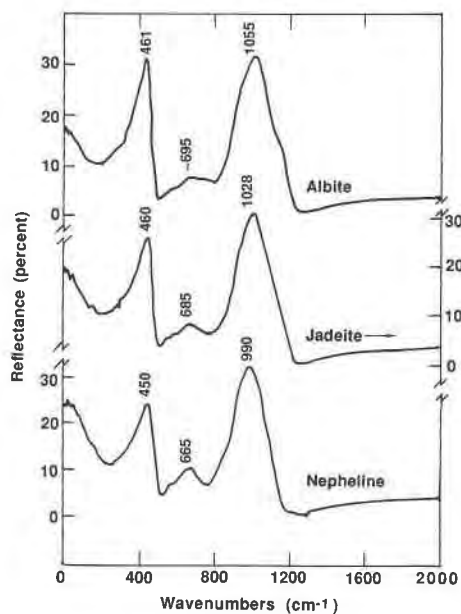


Fig. 1. Infrared reflectance spectra of albite, jadeite, and nepheline glass. The abscissa is scaled on the left for albite and nepheline and on the right for jadeite.

successfully predicted the experimental heat-capacity values only after the low-frequency mode was included in the calculation.

The identical vibrational frequency of the far-infrared mode indicates that the Na ions are in similar local environments in all three mineral glasses. The nature of the

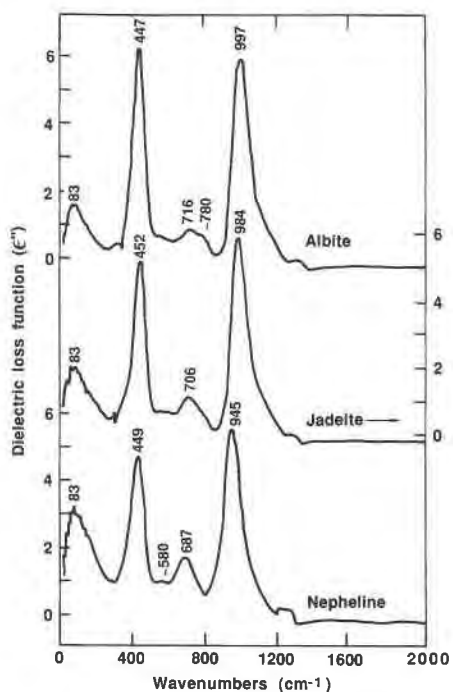


Fig. 2. Dielectric loss functions (ϵ'') of albite, jadeite, and nepheline glass. The abscissa is scaled as for Fig. 1.

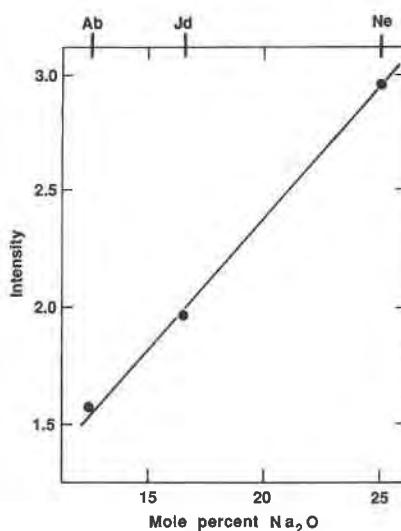


Fig. 3. Peak height of the low-frequency mode in ϵ'' as a function of Na content.

Na ion environment is constrained in part by the composition. Ideally, these glasses have no (negatively charged) nonbridging oxygens, and all of the Na ions are situated interstitially, near tetrahedral Al. The maximum observed for albite, jadeite, and nepheline, therefore, represents the vibrational energy of charge-compensating Na cations in fully polymerized aluminosilicate glasses.

The ϵ'' functions for glasses along the $\text{Na}_2\text{O}-\text{SiO}_2$ binary, drawn from the data of Minser and White (1984), are shown in Figure 4. The low-frequency bands in these spectra are considerably broader than the corresponding mode in the fully polymerized glasses and are at higher frequency (125–200 cm^{-1}). There is some evidence, particularly in lithium silicate as well as sodium silicate glasses, that these bands result from two overlapping

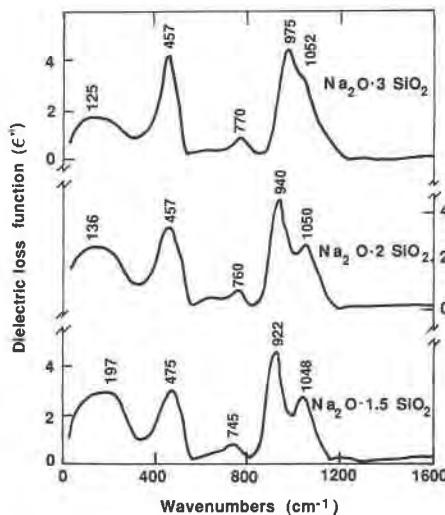


Fig. 4. Dielectric loss functions (ϵ'') of glasses along the $\text{Na}_2\text{O}-\text{SiO}_2$ join. The values of ϵ'' for $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ and $\text{Na}_2\text{O}\cdot 1.5\text{SiO}_2$ are shown on the left, and those for $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ are on the right.

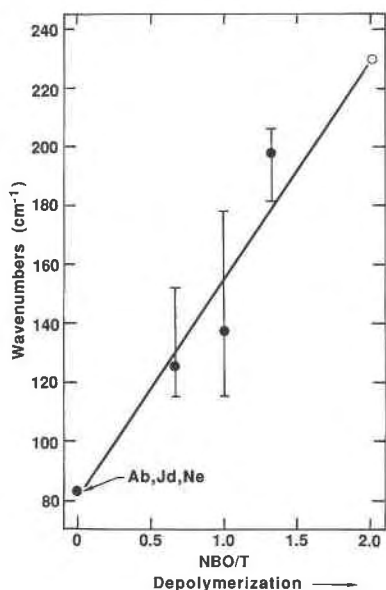


Fig. 5. Position of the low-frequency mode as a function of depolymerization. Open circle is a value from Exarhos and Risen (1972). Error bars indicate uncertainty in the position of the broader peaks in the sodium silicate glass spectra. Error in the peak positions in the mineral-glass spectra is approximately the size of the closed circle.

modes (Minser, in prep.; Exarhos and Risen, 1972). Because of poor constraints on the background in the far-infrared, and in order to be consistent with the procedure used in evaluation of the mineral-glass spectra, the position of the broad peak in the sodium silicate spectra corresponds to the frequency of maximum intensity in ϵ'' .

The frequency of the Na vibration is plotted against polymerization in Figure 5, including a value for sodium metasilicate (NBO/T = 2.0) from Exarhos and Risen (1972). With increasing depolymerization there is a continuous increase in the energy of the modifying cation vibration. This rise is attributed to the collapse of the tetrahedral network and the corresponding increase in the anionic charge density surrounding the Na ions.

The gradual change in the structure indicated by the far-infrared data is consistent with the MAS NMR results of Dupree et al. (1984). Those authors measured the ^{23}Na NMR spectra of several sodium silicate glasses with the results plotted in Figure 6. With the exception of the sample at 28.6 mol% Na_2O , the chemical shift increases linearly with depolymerization. This trend is in the same sense, although smaller in magnitude, as that reported for the ^{29}Si chemical shift as a function of polymerization (Lippmaa et al., 1980, 1981; Grimmer et al., 1984; Engelhardt et al., 1985).

Whereas the far-infrared data show a definite change in the Na environment with polymerization, McKeown et al. (1985) were unable to detect any significant change in the EXAFS and XANES spectra of several sodium aluminosilicate glasses with varying polymerization. Con-

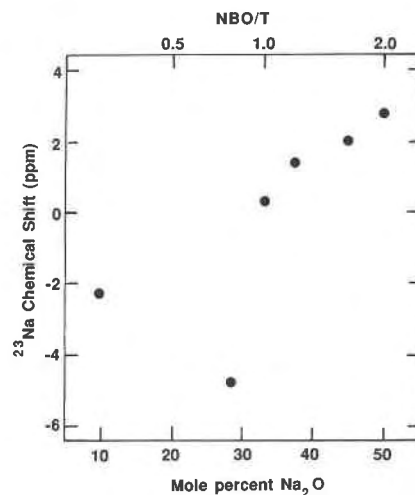


Fig. 6. ^{23}Na chemical shift for $\text{Na}_2\text{O}-\text{SiO}_2$ glasses as a function of Na content. Data from Dupree et al. (1984).

versely, Greaves et al. (1981) determined significant differences in the short-range order around Na as a function of composition on the basis of EXAFS analysis of $\text{Na}_2\text{CaSi}_2\text{O}_{12}$ (NBO/T = 0.8) and $\text{Na}_2\text{Si}_2\text{O}_5$ (NBO/T = 1.0) glasses. The discrepancy in these studies indicates the uncertainty that is inherent in EXAFS and XANES results at this time.

Na-O force constants

The far-infrared peak may be treated as the motion of a single forced, damped harmonic oscillator (Exarhos et al., 1974). The energy of the oscillatory motion between a Na ion and surrounding oxygens depends on several factors including mass, ionic charge, bond length, and bond strength. All of these influences, except mass, are incorporated in the force constant, k , which is defined by the relationship

$$\omega^2 = k/\mu, \quad (1)$$

where ω is the angular frequency of vibration. If the cage of oxygens surrounding the Na ion are assumed to be immobile, owing to their relatively large mass, then μ is simply the mass of the Na cation. If the Na site is approximated by an octahedron, with the oxygens free to vibrate, then $\mu = (m_{\text{Na}}m_{\text{O}})/(m_{\text{Na}} + 2m_{\text{O}})$ (Exarhos et al., 1974). Force constants calculated with both stationary and vibrating oxygens are presented in Table 1. These values are relatively low, confirming the large loosely bound nature of the Na site. Furthermore, the force constants are similar in magnitude to values derived for Na-O bonds in phosphate glasses (Exarhos et al., 1974; Rao and Elliott, 1981).

The empirical relationship between interatomic distances and bond force constants known as "Badger's rule" (Badger, 1934) states that

$$k = 186/(r_0 - d_0)^3, \quad (2)$$

where the force constant, k , is in N/m, r_0 is the interionic distance in Å, and d_{ij} is a constant for ions i and j equal to 0.90 for Na and O (Berry et al., 1980, p. 268). Some assumptions were made in extending the relationship from ion pairs to polyatomic systems (Badger, 1935). The mean Na–O bond length (r_0) in high albite is 2.8–2.9 Å (Prewitt et al., 1976), which corresponds to a force constant of 27–23 N/m. The Na–O distance in several sodium aluminosilicate glasses is 2.56 to 2.62 Å as determined by EXAFS (McKeown et al., 1985), which is equivalent to a force constant of nearly 38 N/m. These force constants, predicted using Badger's rule, are closer to the values for the glasses in this study that were calculated by assuming that the oxygens are immobile, rather than free to vibrate (Table 1), suggesting that the rigid model is more accurate.

The direct relationship between the cation-anion force constant and ionic charge (Exarhos et al., 1974) suggests that singly charged Na⁺ should vibrate at roughly half the frequency of Ca²⁺ if the structures are otherwise similar. A far-infrared mode is in fact observed at 175–250 cm⁻¹, depending on polymerization, in the spectra of some calcium aluminosilicate glasses (Merzbacher and White, in prep.) A weak Raman band at 350–400 cm⁻¹ in the spectra of some calcium silicate glasses has been assigned to motion of Ca ions (Mysen et al., 1981; Sharma et al., 1983). There is no evidence in the Raman spectra, however, of Na modes in the region of 150–200 cm⁻¹, even in simple Na₂O–SiO₂ glasses with up to nearly 50 mol% Na₂O (Furukawa et al., 1981).

CONCLUSIONS

A vibrational mode in the far-infrared spectra of some sodium aluminosilicate glasses has been assigned to the motion of network-modifying Na ions in large, interstitial sites. This assignment is confirmed by the direct relationship between Na content and peak intensity. In fully polymerized glasses along the SiO₂–NaAlO₄ join, the number of network modifiers changes, but the environment surrounding each Na ion is the same. In simple Na₂O–SiO₂ glasses, depolymerization increases with added Na₂O, leading to a gradual collapse of the tetrahedral structure around the Na ions and a rise in the vibrational energy.

Assuming that the oxygens form a rigid cage around the Na ions, the average force constant for the Na–O bonds ranges from 10 N/m in the fully polymerized glasses to 30 N/m in the most depolymerized sodium silicate glass.

The results of this study by far-infrared reflectance spectroscopy are in general agreement with conclusions based on MAS NMR and EXAFS analysis. These results are also consistent with the basic structural model in which Na acts as charge-compensating and/or network-modifying cation in glasses with Na/Al ≥ 1. At present, interpretation is often constrained by the limited range of minerals and glass compositions analyzed.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy (contract DE/FG02/84ER45077). We would like to acknowledge D. G. Minser for

preparation and spectroscopic analysis of the sodium silicate glasses, and L. Zellmer for supplying the albite glass sample. We also thank B. L. Walden for improving the software used to perform the Kramers-Kronig analysis. Review of an early version by A. M. Nitkiewicz greatly improved the manuscript, and critical reviews by J. A. Peck and F. Gervais are appreciated.

REFERENCES CITED

- Andermann, G., Caron, A., and Dows, D.A. (1965) Kramers-Kronig dispersion analysis of infrared reflectance bands. *Journal of the Optical Society of America*, 55, 1210–1216.
- Badger, R.M. (1934) A relation between internuclear distance and bond force constants. *Journal of Chemical Physics*, 2, 128–131.
- (1935) The relation between the internuclear distances and force constant of molecules and its application to polyatomic molecules. *Journal of Chemical Physics*, 3, 710–714.
- Berry, R.S., Rice, S.A., and Ross, J. (1980) *Physical chemistry*. Wiley, New York.
- Brawer, S.A., and White, W.B. (1977) Raman spectroscopic investigation of silicate glasses. (II) Soda-alkaline earth-alumina ternary and quaternary glasses. *Journal of Non-Crystalline Solids*, 23, 261–278.
- Calas, G., and Petiau, J. (1983) Coordination of iron in oxide glasses through high-resolution K-edge spectra: Information from the pre-edge. *Solid State Communications*, 48, 625–629.
- DiSalvo, R., Furukawa, T., Nelson, C., and White, W.B. (1982) Raman spectra and structure of aluminosilicate glasses. In *Structure of glasses containing transition metal ions*. U.S. Department of Energy Annual Report No. COO-2754-7.
- Dupree, R., Holland, D., McMillan, P.W., and Pettifer, R.F. (1984) The structure of soda-silica glasses: A MAS NMR study. *Journal of Non-Crystalline Solids*, 68, 399–410.
- Engelhardt, G., Nofz, M., Forkel, K., Wihsman, F.G., Magi, M., Samoson, A., and Lippmaa, E. (1985) Structural studies of calcium aluminosilicate glasses by high-resolution solid-state ²⁹Si and ²⁷Al magic angle spinning nuclear magnetic resonance. *Physics and Chemistry of Glasses*, 26, 157–165.
- Exarhos, G.J., and Risen, W.M., Jr. (1972) Cation vibrations in inorganic oxide glasses. *Solid State Communications*, 11, 755–758.
- Exarhos, G.J., Miller, P.J., and Risen, W.M., Jr. (1974) Interionic vibrations and glass transitions in ionic oxide metaphosphate glasses. *Journal of Chemical Physics*, 60, 4145–4155.
- Furukawa, T., Fox, K.E., and White, W.B. (1981) Raman spectroscopic investigation of the structure of silicate glasses. III. Raman intensities and structural units in sodium silicate glasses. *Journal of Chemical Physics*, 75, 3226–3237.
- Gervais, F., Blin, A., Massiot, D., Coutures, J.P., Chopinet, M.H., and Naudin, F. (1987) Infrared reflectivity spectroscopy of silicate glasses. *Journal of Non-Crystalline Solids*, 89, 384–401.
- Greaves, G.N., Fontaine, A., Lagarde, P., Raoux, D., and Gurman, S.J. (1981) Local structure of silicate glasses. *Nature*, 293, 611–616.
- Grimmer, A.-R., Magi, M., Hahnert, M., Stade, H., Samoson, A., Wieker, W., and Lippmaa, E. (1984) High-resolution solid-state ²⁹Si nuclear magnetic resonance spectroscopic studies of binary alkali silicate glasses. *Physics and Chemistry of Glasses*, 25, 105–109.
- Hochella, M.F., Jr., and Brown, G.E., Jr. (1984) Structure and viscosity of rhyolitic composition melts. *Geochimica et Cosmochimica Acta*, 48, 2631–2640.
- Hofmeister, A.M., Hoering, T.C., and Virgo, D. (1987) Vibrational spectroscopy of beryllium aluminosilicates: Heat-capacity calculations from band assignments. *Physics and Chemistry of Minerals*, 14, 205–224.
- Kamitsos, E.I., and Risen, W.M., Jr. (1984) Vibrational spectra of single and mixed alkali pentasilicate glasses. *Journal of Non-Crystalline Solids*, 65, 333–354.
- Kamitsos, R.I., Chryssikos, G.D., and Karakassides, M.A. (1987) Vibrational spectra of magnesium-sodium-borate glasses. I. Far-infrared investigation of the cation-site interactions. *Journal of Physical Chemistry*, 91, 1067–1073.
- Kieffer, S.W. (1982) Thermodynamics and lattice vibrations of minerals: 5. Applications to phase equilibria, isotopic fractionation, and high-

- pressure thermodynamic properties. *Reviews of Geophysics and Space Physics*, 20, 827–849.
- Kirkpatrick, R.J., Kinsey, R.A., Smith, K.A., Henderson, D.M., and Oldfield, E. (1985) High resolution solid-state sodium-23, aluminum-27, and silicon-29 nuclear magnetic resonance spectroscopic reconnaissance of alkali and plagioclase feldspars. *American Mineralogist*, 70, 106–123.
- Lippmaa, E., Magi, M., Samoson, A., Engelhardt, G., and Grimmer, A.-R. (1980) Structural studies of silicates by solid-state high-resolution ^{29}Si NMR. *Journal of the American Chemical Society*, 102, 4889–4893.
- Lippmaa, E., Magi, M., Samoson, A., Tarmak, M., and Engelhardt, G. (1981) Investigation of the structure of zeolites by solid-state high-resolution ^{29}Si NMR spectroscopy. *Journal of the American Chemical Society*, 103, 4992–4996.
- McKeown, D.A., Galeener, F.L., and Brown, G.E., Jr. (1984) Raman studies of Al coordination in silica-rich sodium aluminosilicate glasses and some related minerals. *Journal of Non-Crystalline Solids*, 68, 361–378.
- McKeown, D.A., Waychunas, G.A., and Brown, G.E., Jr. (1985) EXAFS and XANES study of the local coordination environment of sodium in a series of silica-rich glasses and selected minerals within the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. *Journal of Non-Crystalline Solids*, 74, 325–348.
- McMillan, P., Piriou, B., and Navrotsky, A. (1982) A Raman spectroscopic study of glasses along the joins silica–calcium aluminate, silica–sodium aluminate, and silica–potassium aluminate. *Geochimica et Cosmochimica Acta*, 46, 2021–2037.
- Merzbacher, C.I. (1987) The structure of alkaline earth aluminosilicate glasses and melts: A spectroscopic study. Ph.D. thesis, The Pennsylvania State University, University Park, Pennsylvania.
- Minser, D.G., and White, W.B. (1984) Alkali ion environments in alkali silicate glasses: Far-infrared spectra. In *Spectroscopic Investigations of Glass Structure*, U.S. Department of Energy Annual Report no. DOE/ER/45077-1.
- Mysen, B.O., Virgo, D., and Scarfe, C.M. (1980) Relations between the anionic structure and viscosity of silicate melts—A Raman spectroscopic study. *American Mineralogist*, 65, 690–710.
- Mysen, B.O., Virgo, D., and Kushiro, I. (1981) The structural role of aluminum in silicate melts—A Raman spectroscopic study at 1 atmosphere. *American Mineralogist*, 66, 678–701.
- Mysen, B.O., Virgo, D., Danckwerth, P., Seifert, F.A., and Kushiro, I. (1983) Influence of pressure on the structure of melts on the joins $\text{NaAlO}_2-\text{SiO}_2$, $\text{CaAl}_2\text{O}_4-\text{SiO}_2$, and $\text{MgAl}_2\text{O}_4-\text{SiO}_2$. *Neues Jahrbuch für Mineralogie Abhandlung*, 147, 281–303.
- Mysen, B.O., Virgo, D., and Seifert, F.A. (1985) Relationships between properties and structure of aluminosilicate melts. *American Mineralogist*, 70, 88–105.
- Nelson, B.N., and Exarhos, G.J. (1979) Vibrational spectroscopy of cation-site interactions in phosphate glasses. *Journal of Chemical Physics*, 71, 2739–2747.
- Onorato, P.I.K., Alexander, M.N., Struck, C.W., Tasker, G.W., and Uhlmann, D.R. (1985) Bridging and nonbridging oxygen atoms in alkali aluminosilicate glasses. *Journal of the American Ceramic Society*, 68, C-148–C-150.
- Prewitt, C.T., Sueno, S., and Papike, J.J. (1976) The crystal structure of high albite and monalbite at high temperatures. *American Mineralogist*, 61, 1213–1225.
- Rao, K.J., and Elliott, S.R. (1981) Characteristic vibrations of cations in glasses. *Journal of Non-Crystalline Solids*, 46, 371–378.
- Rouse, G.B., Jr., Miller, P.J., and Risen, W.M., Jr. (1978) Mixed alkali glass spectra and structure. *Journal of Non-Crystalline Solids*, 28, 193–207.
- Seifert, F.A., Mysen, B.O., and Virgo, D. (1982) Three-dimensional network structure of quenched melts (glass) in the systems $\text{SiO}_2-\text{NaAlO}_2$, $\text{SiO}_2-\text{CaAl}_2\text{O}_4$, and $\text{SiO}_2-\text{MgAl}_2\text{O}_4$. *American Mineralogist*, 67, 696–717.
- Sharma, S.K., Simons, B., and Yoder, H.S., Jr. (1983) Raman study of anorthite, calcium Tschermak's pyroxene, and gehlenite in crystalline and glassy states. *American Mineralogist*, 68, 1113–1125.
- Taylor, M., and Brown, G.E., Jr. (1979) Structure of mineral glasses—II. The $\text{SiO}_2-\text{NaAlSiO}_4$ join. *Geochimica et Cosmochimica Acta*, 43, 1467–1473.
- Zellmer, L. (1986) Dissolution kinetics of crystalline and amorphous albite. M.S. thesis, The Pennsylvania State University, University Park, Pennsylvania.

MANUSCRIPT RECEIVED DECEMBER 18, 1987

MANUSCRIPT ACCEPTED MAY 13, 1988