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Raman study of the coordination of aluminum in jadeite melts as a function of pressure

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Abstract

The coordination of Al^{3+} in glasses of jadeite composition, synthesized at 1450° and 1550°C and over the pressure range 0.001–40 kbar, has been determined using laser Raman spectroscopy. The Raman spectrum of glass of jadeite composition at 1 atm resembles that of SiO_2 glass, except that the Si–O stretching bands occur at lower frequencies than in SiO_2 glass and are weakly polarized in contrast to the depolarized bands in SiO_2 glass. The shift of the Si–O bands in the jadeite glass to lower frequencies is due to Si(Al)–O coupled modes. The weakly polarized stretching bands indicate that the local ordering in jadeite glass may resemble that of α-cristobalite.

The spectra of jadeite glasses formed from liquids quenched at high pressure are similar to that of glass formed from liquid quenched at 1 atm, except that the Si(Al)–O stretching bands become strongly polarized with increasing pressure and are shifted to lower frequencies. There is also a decrease in the intensity of the Rayleigh tail. The major spectral differences between the 1-atm and high-pressure glasses are explained in terms of differences in the symmetry of the local ordering of the network structure and a systematic decrease in the bond angle at the oxygen atom shared by two adjacent silicon atoms. Overall, the effect of pressure on the structure of $NaAlSi_2O_6$ melts is to increase the degree of local ordering and to change the local network structure to a coesite-type structure.

Al^{3+} remains tetrahedrally coordinated over the pressure range investigated; there is no support for the hypothesis that a pressure-induced coordination change of Al^{3+} from fourfold to sixfold is responsible for the observed decrease in viscosity of melts of jadeite composition at elevated pressures.

Introduction

It is important to know the structure of chemically simple silicate melts in order to form a basis for interpreting the physical and chemical properties of melts as a function of pressure, temperature, and bulk composition. Recently it has been suggested that the anomalous behavior of certain physical and chemical properties of silicate melts as a function of pressure is due to a change in the aluminum coordination in the melt from fourfold to sixfold, with an accompanying decrease in the degree of polymerization of the melt. The suggested pressure-induced cationic coordination changes in the melt are based on analogous changes that occur in solid-state reactions (Waff, 1975). Specific melt properties that have been related to changes in cation coordination polyhedra with increasing pressure include (1) decreases in the viscosity of aluminosilicate melts (Kushiro, 1976, 1978; Kushiro *et al.*, 1976), (2) changes in CO_2 solubility in albite melt (Mysen, 1976), (3) decreases in $Fe^{3+}/\Sigma Fe$ in melts for iron-rich compositions along the $NaAlSi_2O_6$–$NaFeSi_2O_6$ join (Mysen and Virgo, 1978), and (4) significant decreases in Ni partitioning between crystals and melts along the $NaAlSi_2O_6$–$MgSi_2O_4$ join (Mysen and Kushiro, 1978).

Structural data are generally not available for evaluating proposed mechanisms associated with many of the above-mentioned physical and chemical melt properties. In this connection, Velde and Kushiro (1978) have attempted to show, on the basis of measurements of the wavelength shift of Al*K*α and Al*K*β radiation and changes in the intensity of bands in the infrared spectra of glasses of jadeite composition formed by quenching at high pressure, that there

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is a continuous shift in the coordination of Al from 4 to 6 with pressure in melts of jadeite composition ($NaAlSi_2O_6$).

In this study, Raman spectroscopy is used as a tool for determining the network structure of supercooled melts. This technique has already proved to be highly successful as a structural probe of the amorphous state (*cf.* review by Wong and Angell, 1976) and has distinct advantages over the X-ray diffraction method that traditionally includes the analysis of average radial distribution functions (RDF's). A radial distribution function refers to the average glass structure and does not provide a unique description of the structure. For example, on the basis of similar experimental RDF's, a variety of structural models have been proposed for SiO_2 glass (*e.g.*, Konnert and Karle, 1973; Konnert *et al.*, 1973; Narten, 1972; Nukui *et al.*, 1978; Mozzi and Warren, 1969; Bell and Dean, 1972). On the other hand, Narten (1972) has proposed the β-quartz model of SiO_2 glass to calculate the RDF by taking into account the infrared and Raman spectra of SiO_2 glass and the depolarization ratio of the Raman bands (*e.g.*, Bates, 1972; Wong and Angell, 1976).

Raman spectra of melts of $NaAlSi_2O_6$ composition quenched at high pressure were measured with the objective of determining the structural changes in these melts, including the coordination of aluminum. These results were expected to have direct bearing on changes in the viscosity of aluminosilicate melts with increasing pressure (*e.g.*, Kushiro, 1976).

Experimental techniques

Sample preparation

Starting material for the high-pressure runs was a glass of $NaAlSi_2O_6$ composition prepared from an oxide mix of Johnson-Matthey high-purity SiO_2, Al_2O_3, and reagent-grade Na_2CO_3. The starting material for the high-pressure experiments was prepared by melting the oxide mixture in sealed $Pt_{95}Au_5$ capsules at 1 atm and 1450°C for 1 hr followed by rapid quenching. A sealed capsule was used to eliminate alkali loss during melting. The high-pressure experiments were made on aliquots ($\sim$10 mg) in solid-media, high-pressure apparatus (Boyd and England, 1960) at 10, 15, 20, and 30 kbar at 1450° and 40 kbar at 1550°C. Glass of diopside composition was obtained by melting an oxide mix prepared from Johnson-Matthey high-purity SiO_2, $CaCO_3$, and MgO at 1 atm and 1450°C followed by rapid quenching.

Raman spectroscopy

The Raman spectra were measured on a Jobin-Yvon double-grating spectrometer. The source was an Ar^+ ion laser operating at 300–400 MW and 488 nm. The measurements were made by collecting the scattered radiation at 90° to the exciting beam. The scattered radiation was detected with a photon-counting detection system. The polarization spectra were obtained with the focused exciting beam parallel to the horizontal spectrometer slit and with the electric vector of the exciting radiation in a vertical orientation. A polarized disk in front of an optical scrambler was used to record separately the parallel and perpendicular components of the scattered radiation. The spectra were recorded with the sample at room temperature.

Results

Raman spectra of the jadeite melts quenched to glass from 1450°C and under various pressures are given in Figure 1. The spectra of the glasses prepared at 10 and 20 kbar but with the electric vector of the scattered light both parallel and perpendicular to the electric vector of the laser beam are shown in Figure 2. The band positions and their polarization characteristics are listed in Table 1.

Figure 1 and Table 1 show that the unpolarized Raman spectra of the jadeite melts quenched over the pressure range 1 atm to 40 kbar have similar characteristics, except that the components of the weak, broad band in the 900–1200 cm^{-1} region are shifted toward lower frequencies with increasing pressure and the strong band at 472 cm^{-1} (1 atm) is shifted toward higher frequencies (496 cm^{-1} at 40 kbar). All bands in the spectra of the melts quenched at pressures above ambient are strongly polarized. Polarization data for glasses prepared at 10 and 20 kbar are shown in Figure 2. The glass of jadeite composition quenched at 1 atm shows only weak polarization of the 900–1200 cm^{-1} band (Sharma *et al.*, 1978b). This difference between the low- and high-pressure glasses was found to be reproducible from replicate analyses of both low- and high-pressure glasses prepared under specific pressure–temperature conditions but for different run durations.

In all glasses of jadeite composition, the broad polarized band in the 900–1200 cm^{-1} region (half-width at half-peak height is 212 cm^{-1} in the 10-kbar sample) seems to be composed of at least two overlapping peaks. Because of this strong overlap, it is not possible to measure accurately the position of the component peaks of the doublet. Nevertheless, the positions of component peaks progressively shift to lower frequencies in samples quenched at progressively higher pressures (Table 1). No band in the Raman spectra of the jadeite melts quenched at high pressure can be attributed to AlO_6 groups.

Discussion

Interpretation of Raman spectra of $NaAlSi_2O_6$ glasses

The prominent features in the Raman spectra of the jadeite melt quenched at 1 atm are the strong band at 475 cm^{-1} and the broad, weakly polarized bands in the 900–1200 cm^{-1} region. It is known, for example, in SiO_2 glass that the presence of SiO_4 units in a three-dimensional network is characterized by the presence of weak bands in the Si–O stretching region compared with the low-frequency bands at ~500 cm^{-1}. Furthermore, the creation of nonbridging oxygens in the network (*e.g.*, sodium silicate glasses) results in a marked increase in the relative intensity of Si–O stretching modes and the appearance of a new band at ~950 cm^{-1} due to $Si–O^-$ (nonbridging) stretch (Simon, 1960). We suggest, therefore, that the spectral features evident in the jadeite melt quenched at 1 atm are indicative of a three-dimensional network structure. In this interpretation, the weak shoulder at 575 cm^{-1} in the spectra of jadeite glass results from a defect structure involving a nonbridging oxygen (Bates *et al.*, 1974). In this respect the spectra of the jadeite glass are similar to those of SiO_2 glass (*e.g.*, Bates, 1972). In SiO_2 glass, however, the bands in the 900–1200 cm^{-1} region are shifted to higher frequencies and are depolarized compared with the jadeite glass at 1 atm (Bates, 1972; Wong and Angell, 1976).

The lowering of the Si–O stretch frequency in aluminosilicate glasses can be attributed to the isomorphous substitution of Al for Si in the glass network. In this connection, Milkey (1960) has investigated the infrared spectra of 57 tectosilicate crystals and has found that the Si–O absorption peaks show an irregular but systematic shift to lower frequencies as Al/Si increases. It has also been established from infrared studies of aluminosilicates that the modes of vibration of SiO_4 and AlO_4 tetrahedra interact strongly and produce coupled modes (Moenke, 1974; Iishi *et al.*, 1971). A similar effect can also be expected to occur in glasses. In fact, the above interpretation (Sharma and Virgo, unpublished data) has been confirmed in Raman studies of glasses analogous to jadeite composition, but in which Ge^{4+} is substituted for Si^{4+} and Ga^{3+} for Al^{3+}. The systematic differences in the polarization data for $NaAlSi_2O_6$ and SiO_2 glasses, noted above, can be explained in terms of differences in the symmetry of the local ordering of the network structures in the two glasses. The presence of only polarized bands in the Raman spectra of $NaAlSi_2O_6$ glass indicates a lower site symmetry of silicon than that in the β-quartz model of SiO_2 glass (Narten, 1972; Bates, 1972). In general, however, it appears that $NaAlSi_2O_6$ glass quenched at 1 atm has a three-dimensional network structure composed of AlO_4 and SiO_4 tetrahedra with sodium ions present in cavities.

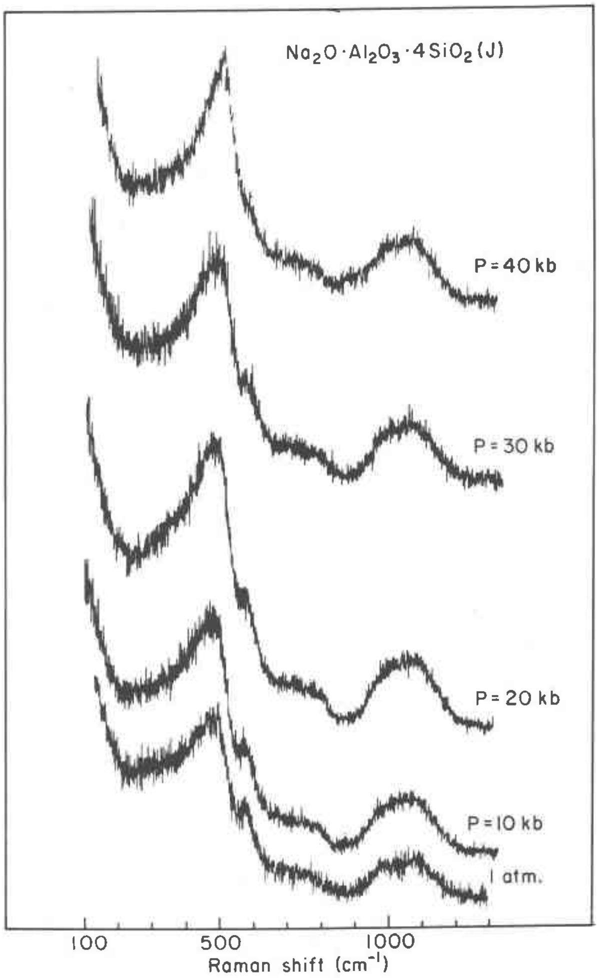

Fig. 1. Raman spectra of $NaAlSi_2O_6$ glasses formed from liquids quenched at 1 bar and 10, 15, 20, 30, and 40 kbar (laser 488.0 nm Ar ion, 200 MW, slit 6 cm^{-1}).

As stated above, the spectra of the jadeite melts quenched at high pressure are similar to that of the

Table 1. Raman frequencies* of $Na_2O \cdot Al_2O_3 \cdot 4SiO_2$ glasses prepared at different pressures

0.001 kbar	10 kbar	20 kbar	30 kbar	40 kbar
∿300, w,bd†	340, w,bd	320, w,bd	...	...
472, s,p	475, s,p	478, s,p	480, s,p	496, s,p
572, (Sh),p	572, (Sh),p	568, (Sh),p	564, (Sh)	...
750, w,bd,dp	750, w,bd	760, w,bd	740, w,bd	748, w,bd
1010, w,bd,wp	992, w,bd,p	1008, w,bd,p	996, w,bd,p	984, w,bd,p
1084, w,bd,wp	1050, w,bd,p	1080, w,bd,p	1054, w,bd,p	1056, w,bd,p

*Measurement accuracy is ±10 cm^{-1} for weak and broad bands and ±4 cm^{-1} for sharp and strong bands.

†Abbreviations: w, weak; s, strong; bd, broad; p, polarized; dp, depolarized; wp, weakly polarized; Sh, shoulder.

quenched 1-atm melt, except that with increasing pressure the weak and broad Si–O and Si(Al)–O stretching modes at 1084 and 1010 cm^{-1}, respectively, in the 1-atm glass shift to lower frequencies and show strong polarization, and the strongly polarized band at 472 cm^{-1} in the 1-atm glass shifts to higher frequencies at higher pressures (Table 1). There is no appreciable increase in the intensity of the 572 cm^{-1} band attributed to a defect structure in the network. In general, the change in the polarization character of the Raman bands in the 1000–1100 cm^{-1} region in the high-pressure glasses can be attributed to a further lowering of local symmetry of the tetrahedrally-coordinated units in the network with increasing pressure.

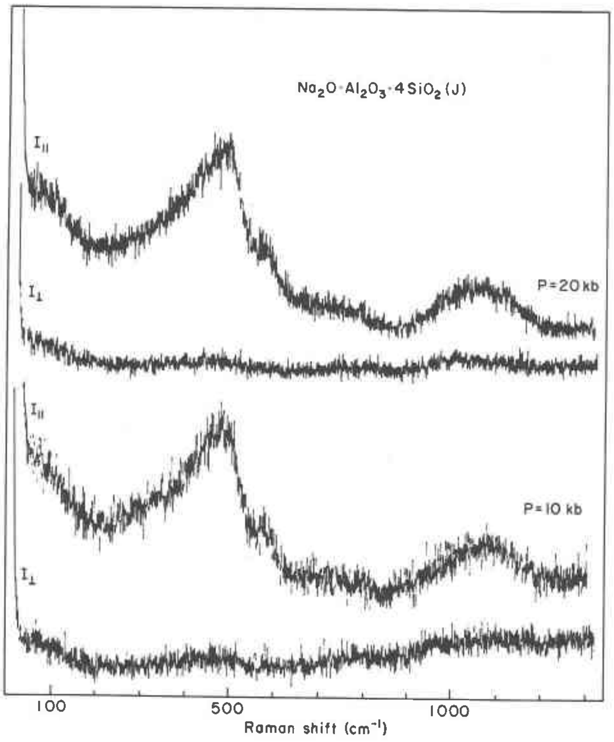

Fig. 2. Polarized Raman spectra of $NaAlSi_2O_6$ glasses formed from liquids quenched at 10 and 20 kbar (laser 488.0 mn Ar ion, 150 MW, slit 6 cm^{-1}).

Relationship between the shift of Raman bands as a function of pressure and the network structure

The observed shift in the position of the bands in the 1000–1100 cm^{-1} region and of the strong band at 472 cm^{-1} in the 1-atm glasses with increasing pressure can be compared with similar changes observed in the Raman spectra of neutron-compacted SiO_2 glasses (Stolen *et al.*, 1970; Bates *et al.*, 1974). For example, Bates *et al.* found that for SiO_2 glass that undergoes a density increase of ~2 percent upon neutron irradiation, the Raman bands in the Si–O stretching region of unirradiated SiO_2 glass (at ~1060 and 1200 cm^{-1}) shift significantly to lower frequencies (1038 and 1175 cm^{-1}, respectively) in densified SiO_2 glass. Also, the strongly polarized band at 435 cm^{-1} shifts to higher frequency and occurs at 460 cm^{-1} in the neutron-compacted glass. Similar shifts in the Si–O stretching modes are also observed in the infrared spectra of neutron-compacted SiO_2 (Simon, 1957) and in SiO_2 glass densified by the application of high pressure and moderate temperature (*e.g.*, Cohen and Roy, 1965; Arndt *et al.*, 1971).

The behavior of the Si–O stretching modes in densified SiO_2 and $NaAlSi_2O_6$ glasses appears to be systematic (this paper; Cohen and Roy, 1965; Velde and Kushiro, 1978). This similarity in behavior should not be surprising, because all these glasses have a three-dimensional network structure. We suggest, therefore, that the observed decreases in the frequencies of the Si–O mode in high-density SiO_2 glass and the Si(Al)–O modes in the high-pressure $NaAlSi_2O_6$

glasses are in response to similar structural modifications that accompany the increase in density.

Two distinct structural models have been proposed to explain the observed changes in the infrared and Raman spectra of compacted SiO_2 glass. Our preferred interpretation is based on X-ray radial distribution studies of unirradiated and neutron-irradiated SiO_2 glass (Stolen *et al.*, 1970; Simon, 1957), in which the primary structural change in SiO_2 glass after neutron irradiation, as reflected in the increase in density of the glass, is a decrease in the average Si–O–Si bond angle from 142° to 138°. In those studies, however, there appeared to be no evidence for a change in the Si–O bond length. An alternative interpretation of the structural changes in SiO_2 glass densified by neutron bombardment is offered by Leadbetter and Wright (1977), in terms of the presence of interstitially located SiO_2 molecules. This interpretation can be ruled out, because the presence of interstitial SiO_2 requires the creation of nonbridging oxygens in the network structure, an effect that is not observed in the Raman spectra of neutron-irradiated SiO_2 glasses (Bates *et al.*, 1974). The speculation that the major structural change in both SiO_2 and $NaAlSi_2O_6$ glasses, in which the density has been increased, is a change in the bond angle between the tetrahedra can be further substantiated. It can be unequivocally shown that the specific bands in the infrared and Raman spectra are indeed especially sensitive to variation of the Si–O–Si bond angle.

For example, it is known from X-ray diffraction studies that the Si–O–Si bond angle increases across the $\alpha \rightarrow \beta$ phase transition in quartz (Yong, 1962; Taylor, 1972). In this connection, in an infrared study of the SiO_2 system, Gaskell (1966) found that the frequency of the Si–O stretching mode in α-quartz first decreases with increasing temperature, consistent with the increase in Si–O bond length with temperature. At the temperature of the $\alpha \rightarrow \beta$ transition, the Si–O stretching band shows a sharp increase in the frequency of this mode, whereas under the same conditions the band at 450 cm^{-1} actually appears at a lower frequency. Note that the application of pressure or neutron irradiation of SiO_2 produces changes in the infrared spectra that are exactly opposite to those observed in the infrared spectra after the α- to β-quartz transition. Similarly, Bates (1972) has compared the observed Raman spectra of α- and β-quartz. In going from α- to β-quartz, the 1162 cm^{-1} (e) mode of α-quartz appears at 1067 cm^{-1} (e_1) in β-quartz, and the 1072 cm^{-1} (e) band in α-quartz appears at the higher frequency, 1173 cm^{-1} (e_2), in the β-quartz spectrum. In addition, the 464 cm^{-1} (a_1) mode of α-quartz appears at 462 cm^{-1} (a_1) in the β-quartz spectrum. Evidently the increase in the Si–O–Si angle in β-quartz causes the e_2 mode to increase in frequency, but the e_1 mode in β-quartz appears at considerably lower frequency than observed in the Raman spectra of α-quartz. In the use of this example, however, we point out that in the Raman spectra of neutron-irradiated SiO_2 glass both of the bands in the Si–O stretching region show a decrease in their respective frequencies (Bates *et al.*, 1974). Thus we conclude that although the decrease in the frequency of the Si–O modes in compacted SiO_2 can be attributed to a decrease in the average Si–O–Si bond angle, the local ordering produced in the neutron-irradiated glasses must be different than in α-quartz and may resemble the structure of some high-pressure polymorph of SiO_2 in which Si is tetrahedrally coordinated.

From the above discussion, the spectral changes observed in the infrared and Raman spectra of SiO_2 and $NaAlSi_2O_6$ glasses, both having higher densities than their 1-atm analogues, can in general be attributed to a decrease in the average Si–O–Si angle. This effect will lead to closer packing and, therefore, to higher densities compared with those of the 1-atm glasses. Note that an increase in the degree of local ordering in the high-pressure $NaAlSi_2O_6$ glasses is indicated from the Raman spectra because of the sharpness of the band at 496 cm^{-1} in the glass quenched at 40 kbar (Fig. 1) compared with the same band in the 1-atm $NaAlSi_2O_6$ glasses.

Finally, we suggest, on the basis of the inverse relationship between the change of bond angle at the oxygen atom shared by the two adjacent silicon atoms and the Si(Al)–O bond length (*e.g.*, Taylor, 1972; Gibbs *et al.*, 1977) as established in crystals, that the decrease in the Si–O–Si angle in jadeite glasses noted above may in fact be associated with a slight increase in Si(Al)–O bond length.

Coordination of Al^{3+} in jadeite glasses

The above discussion of local ordering of the network structure of the high-pressure $NaAlSi_2O_6$ glasses implicitly assumes that Al^{3+} is predominantly tetrahedrally coordinated. A distinct peak that may be attributed to AlO_6 is not observed in the Raman spectra of the high-pressure $NaAlSi_2O_6$ glasses. Furthermore, the presence of Al in sixfold coordination must be accompanied by an increase in the number of nonbridging oxygen atoms. The Na^+ ions that are present in cavities when Al^{3+} is in fourfold coordination are also free to create nonbridging oxygen as soon as Al^{3+} shifts to sixfold coordination. If this were the case, the spectra of the high-pressure $NaAlSi_2O_6$ glasses should show an increase in the intensity of the bands in the 1100 cm^{-1} region, and the spectra could be expected to resemble that of diopside glass (Fig. 3), because both diopside and jadeite crystals consist in part of pyroxene chains. In brief, the spectrum of the diopside glass made at 1450°C, 1 atm, is similar to that reported by Etchepare (1972), but the spectral resolution in the region 800–1200 cm^{-1} is more distinct. In general, the glass spectrum of $CaMgSi_2O_6$ closely resembles that of crystalline diopside, and the broad peak in the 850–1100 cm^{-1} region is due to Si–O stretching modes at 890, 980, and 1008 cm^{-1} in the silicate chains that consist of two nonbridging and two bridging oxygen atoms. Furthermore, the Si–O stretching modes (1000–1200 cm^{-1}) in diopside glass are considerably more intense than in jadeite glasses because of the absence of a three-dimensional network (Etchepare, 1972). It is therefore evident that the spectra of diopside and jadeite glasses at high pressure are distinctly different. Also, we point out that the Si–O stretching modes in glasses of $Na_2O \cdot 2SiO_2$ and $Na_2O \cdot 3SiO_2$ composition are represented by peaks at ~950 and ~1100 cm^{-1}, corresponding to Si-nonbridging oxygen stretches (Brawer and White, 1977). From the latter studies, the intensity of the 950 cm^{-1} band relative to that of the 1100 cm^{-1} band increases with small additions of Al_2O_3 to these sodium silicate glasses with fixed Na_2O content, and this result implies the presence of octahedrally coordinated Al^{3+}. Increases in the intensity of the $Si–O^-$ stretch band were also observed with the addition of TiO_2 and B_2O_3 to SiO_2 glass (Kato, 1976). The presence of the analogous band due to nonbridging oxygen is not observed in jadeite spectra at any pressure, and these data reinforce the previous inference that Al^{3+} is predominantly in tetrahedral coordination. It should be mentioned, however, that the maximum amount of Al^{3+} in octahedral coordination in the jadeite glasses prepared at pressures up to 40 kbar must be less than 1 mole percent. This latter estimate is determined from the increase in the intensity of the high-frequency Si–O stretch band resulting from the presence of nonbridging oxygens in aluminosilicate glasses with Al/Na less than unity. The estimate of 1 mole percent $(AlO_6)^{3-}$ units in the high-pressure $NaAlSi_2O_6$ glasses excludes the possibility that the increase in the intensity of the Si–O stretch bands results from structural changes in the network as a function of pressure.

Our results are in direct contrast to the suggested role of Al^{3+} as a network modifier in jadeite melts at high pressure (Velde and Kushiro, 1978) as determined on the basis of the infrared spectra, in which it is observed that the intensity of the vibration involving a bridging oxygen of the tetrahedrally coordinated polyhedra decreases with increasing pressure. In addition, Velde and Kushiro found a continuous shift in the Al*Kα* and Al*Kβ* wavelengths in the high-pressure $NaAlSi_2O_6$ glasses, which they interpreted in terms of the Al(IV) to Al(VI) transition. Some comments can be made on these two lines of evidence that purportedly support the change of Al^{3+} coordination in jadeite melts with increasing pressure. In the first instance, the interpretation of the infrared spectra of high-pressure $NaAlSi_2O_6$ glasses by Velde and Kushiro is based on the fact that the addition of Na_2O to SiO_2 glass causes the band at ~800 cm^{-1}, attributed to the Si–O–Si stretch mode, to shift toward lower frequency and its intensity to decrease (Simon, 1960; Hanna and Su, 1964; Ferraro and Manghnani, 1972). Velde and Kushiro ignored the fact that the above-cited change in the infrared spectra of SiO_2 glasses with the addition of Na_2O is accompanied both by line broadening and a decrease in the intensity of the Si–O stretching mode at ~1100 cm^{-1} and by the appearance of a new band at ~950 cm^{-1} due to the $Si–O^-$ (nonbridging) stretch mode. The Raman spectra of the high-pressure $NaAlSi_2O_6$ glasses (Fig. 1) show neither an appreciable decrease in the intensity of the Si–O stretching mode nor any evidence for the presence of a band at ~950 cm^{-1} due to the $Si–O^-$ stretch mode. We therefore suggest that the decrease in the intensity of the band attributed to the Si–O–Si stretch mode observed by Velde and Kushiro in the spectra of high-pressure jadeite glasses is probably due to a change in the selection rules in response to subtle changes in the local ordering of the glass structure with increasing pressure.

In the second instance, Velde and Kushiro chose to interpret Al*Kα* and Al*Kβ* wavelength shifts of high-pressure $NaAlSi_2O_6$ glasses in terms of a systematic change from fourfold to sixfold coordination of Al^{3+}. The original data of Day and Rindone (1962) that purport to show shifts of Al*Kα* radiation in Na_2O–Al_2O_3–SiO_2 glasses as a function of Al/Na, however,

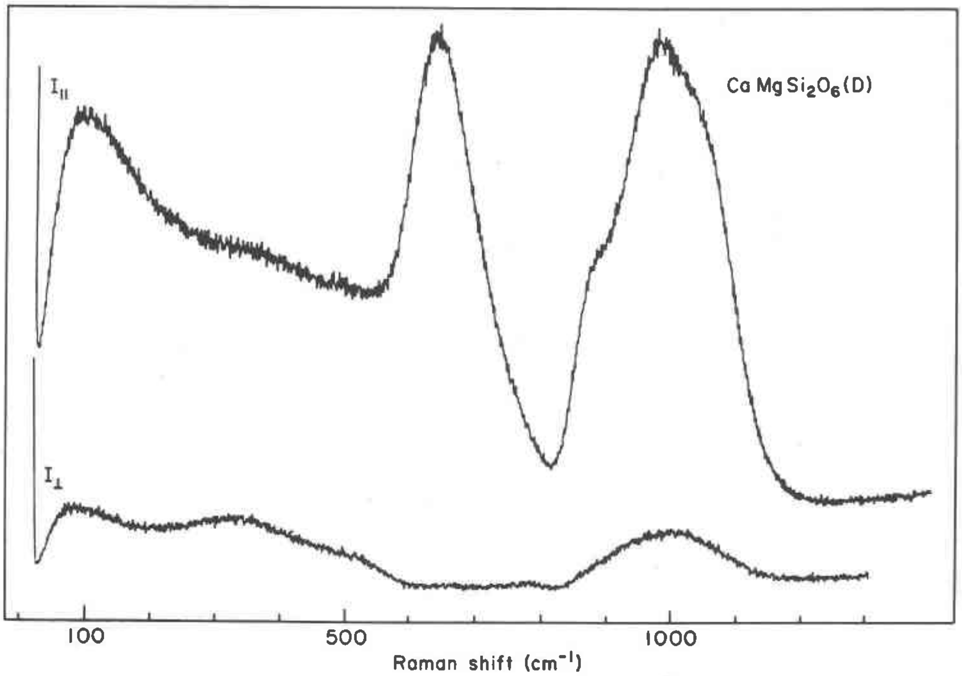

Fig. 3. Polarized Raman spectra of $CaMgSi_2O_6$ glass (laser 488.0 nm Ar ion, 350 MW, slit 8 cm^{-1}).

were not substantiated in later studies (Terai *et al.*, 1969). In addition, the data of White and Gibbs (1969) on the Al$K\beta$ X-ray emission band in aluminum-containing silicate crystals show that in the plot of Al$K\beta$ shifts *vs.* Al coordination there is some overlap of Al$K\beta$ shifts for compounds with Al^{3+} in both four- and sixfold coordination (*e.g.*, $Mg_3Al_2Si_3O_{12}$, $CaAl_2Si_2O_8$). The implication is that Al$K\alpha$ or Al$K\beta$ shifts require careful measurement and that the actual shifts may be dependent on other unknown factors (*e.g.*, bond character) in addition to bond length.

Proposed structural models of low- and high-pressure $NaAlSi_2O_6$ glasses

A quantitative explanation of the lower local symmetry of the network structure in both the low- and high-pressure $NaAlSi_2O_6$ glasses compared with the β-quartz model of SiO_2 glass is not possible at this time, but some constraints on the actual structures can be suggested.

The short-range ordering in the random network of SiO_2 glass closely resembles that of β-quartz (Wong and Angell, 1976). The SiO_2 polymorphs in which Si has a lower site symmetry than β-quartz are α-quartz, α-cristobalite, tridymite, coesite and keatite. Of these polymorphs, coesite has a center of inversion that implies the mutual exclusion of Raman and infrared activity of the vibration modes. A comparison of Raman frequencies with those observed in the infrared absorption spectra (Velde and Kushiro, 1978) of quenched high-pressure glasses of $NaAlSi_2O_6$ composition shows that the positions of the Raman and infrared bands are noncoincidental. This result implies that the short-range ordering in the network of the high-pressure $NaAlSi_2O_6$ glasses may resemble that of coesite. A coesite model of the structure of the high-pressure $NaAlSi_2O_6$ glasses is consistent with the increase in density of $NaAlSi_2O_6$ glasses with increasing pressure (Kushiro, 1976).

We further suggest that the structure of the 1-atm $NaAlSi_2O_6$ glass may in part resemble that of α-cristobalite. This latter suggestion is based on a Raman spectroscopic study of the structure of glasses along the join SiO_2–$NaAlSiO_4$ (Sharma *et al.*, 1978b). This study showed that the network structure becomes more open with the replacement of SiO_2 by $NaAlO_2$ and that the local ordering of the network in $NaAlSiO_4$ glass at 1 atm resembles that of the high-temperature polymorph, carnegieite, which has a stuffed cristobalite structure. Taylor and Brown (in preparation) have shown that the RDF of $NaAlSi_2O_6$ glass synthesized at 1 atm is considerably different from that calculated for the jadeite structure, and they conclude that $NaAlSi_2O_6$ melt at 1 atm has a stuffed tridymite-like structure with a more disordered and open network than that of SiO_2 glass. In general, the results of Taylor and Brown are in agreement with our results, but it should be noted that the conclusions drawn by Taylor and Brown are derived from a comparison of the RDF's of $NaAlSi_2O_6$ and SiO_2 glasses, in which it is implicitly assumed that SiO_2 glass has a tridymite-like structure (Konnert *et al.,* 1973). We contend, however, that the β-quartz model of SiO_2 glass is consistent not only with the Raman and infrared spectroscopic data but also with the X-ray radial distribution studies.

Summary and conclusions

The Raman spectra of jadeite glasses at pressures between 0.001 and 40 kbar are consistent with a three-dimensional network structure where Al^{3+} occurs predominantly in fourfold coordination. With increasing pressure, the local symmetry of Si,Al in the network is lowered compared with that in SiO_2 glass, and the glass structure at high pressure may in part resemble that of coesite. In addition, we show that the observed shift in the Si(Al)–O stretching frequencies with pressure is most likely due to a reduction in the Si–O–Si bond angle.

In general, on the basis of our structural results on $NaAlSi_2O_6$ melts and other structural data for high-pressure GeO_2 glass (Sharma *et al.,* 1978a), there is no direct support for the hypothesis proposed by Waff (1975) concerning the possibility of pressure-induced cationic coordination changes in melts and the effect of such changes on important melt properties. Some implications of the present results and the observed decreases in the viscosity of aluminosilicate melts can be made.

In view of the presence of tetrahedrally coordinated Al^{3+} in high-pressure $NaAlSi_2O_6$ glasses, the previously-observed decreases in the viscosity of silicate melts with pressure must be considered anomalous and in contradiction to the free-volume theory applied to the pressure-dependence of liquid viscosities (*e.g.,* Matheson, 1966). Most experimental viscosity measurements show that the viscosity of liquids increases with increasing pressure, H_2O being the only known exception. A possibly important point that may have been overlooked is that the pressure-dependence of viscosity reported to date has been observed for melts that have a three-dimensional network structure. It seems probable, therefore, that the viscosity changes with pressure in GeO_2 and silicate systems may in fact be related to the distinct three-dimensional network structure of these melts. In view of our results, a progressive collapse of the open network structure over a restricted pressure range, as suggested by a decrease in the Si(Al)–O–Si(Al) bond angle with a concomitant increase in melt density, is possibly the only major structural reorganization of the melt with pressure. If the progressive decrease in the Si(Al)–O–Si(Al) bond angle is accompanied by an increase in the Si(Al)–O bond length, then the systematic decreases in the melt viscosity could be explained in terms of the progressively weaker network structure. Finally, the above inferred relationship between the effect of pressure on viscosity and melt structure is possibly substantiated from the observed increases in viscosity with pressure in depolymerized melts of diopside and sodium metasilicate compositions (authors' unpublished data).

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References

Arndt, J., V. Hornemann and W. F. Muller (1971) Shock wave densification of silica glass. *Phys. Chem. Glasses, 12,* 1–7.

Bates, J. B. (1972) Dynamics of β-quartz structures of SiO_2 and BeF_2. *J. Chem. Phys., 56,* 1910–1917.

———, R. W. Hendricks and L. B. Shaffer (1974) Neutron irradiation effects and structure of noncrystalline SiO_2. *J. Chem. Phys., 61,* 4163–4176.

Bell, R. J. and P. Dean (1972) The structure of vitreous silica: validity of random network theory. *Phil. Mag., 25,* 1381–1398.

Boyd, F. R. and J. L. England (1960) Apparatus for phase-equilibrium measurements at pressures up to 50 kb and temperatures up to 1750°C. *J. Geophys. Res., 65,* 741–748.

Brawer, S. A. and W. B. White (1977) Raman spectroscopic investigation of the structure of silicate glasses. II. Soda–alkaline earth–alumina ternary and quaternary glasses. *J. Non-Crystalline Solids, 23,* 261–278.

Cohen, H. M. and R. Roy (1965) Densification of glass at very high pressure. *Phy. Chem. Glasses, 6,* 149–161.

Day, D. E. and G. E. Rindone (1962) Properties of soda aluminosilicate glasses: III. Coordination of aluminum ions. *J. Am. Ceram. Soc., 45,* 579–587.

Etchepare, J. (1972) Study by Raman spectroscopy of crystalline and glassy diopside. In R. W. Douglas and B. Ellis, Eds., *Amorphous Materials,* p. 337–346. Wiley, New York.

Ferraro, J. and M. Manghnani (1972) Infrared absorption spectra of sodium silicate glasses at high pressure. *J. Appl. Phys., 43,* 4595–4599.

Gaskell, P. H. (1966) Thermal properties of silica. Part 1. Effect of temperature on infrared reflection spectra of quartz, cristobalite and vitreous silica. *Trans. Faraday Soc., 62,* 1493–1504.

Gibbs, G. V., C. T. Prewitt and K. J. Baldwin (1977) A study of the structural chemistry of coesite. *Z. Kristallogr., 145,* 108–123.

Hanna, R. and G. J. Su (1964) Infrared absorption spectra of sodium silicate glasses from 4 to 30 μ. *J. Am. Ceram. Soc., 47,* 597–601.

Iishi, K., T. Tomisaka, T. Kato and Y. Unegaki (1971) Isomorphous substitution, and infrared and far infrared spectra of the feldspar group. *Neues Jahrb. Mineral. Abh., 115,* 98–119.

Kato, D. (1976) Raman spectrometric determination of additive concentration in high-silica-content glasses. *J. Appl. Phys., 47,* 2050–2055.

Konnert, J. H. and L. Karle (1973) The computation of radial distribution fractions for glassy materials. *Acta Crystallogr., A29,* 702–710.

———, ——— and G. A. Ferguson (1973) Crystalline ordering in silica and germania. *Science, 179,* 177–178.

Kushiro, I. (1976) Changes in viscosity and structure of melt of $NaAlSi_2O_6$ composition at high pressure. *J. Geophys. Res., 81,* 6347–6450.

——— (1978) Viscosity and structural changes of albite ($NaAlSi_3O_8$) melt at high pressures. *Earth Planet. Sci. Lett., 41,* 87–90.

———, H. S. Yoder, Jr. and B. O. Mysen (1976) Viscosities of basalt and andesite melts at high pressure. *J. Geophys. Res., 81,* 6351–6356.

Leadbetter, A. J. and A. C. Wright (1977) The structure of neutron irradiated silica. *Phys. Chem. Glasses, 18,* 79–80.

Matheson, A. J. (1966) Role of free volume in the pressure dependence of the viscosity of liquids. *J. Chem. Phys., 44,* 695–699.

Milkey, R. G. (1960) Infrared spectra of some tectosilicates. *Am. Mineral., 45,* 990–1007.

Moenke, H. W. (1974) Silica, the three-dimensional silicates, borosilicates and beryllium silicates. In V. C. Farmer, Ed., *Infrared Spectra of Minerals,* p. 365–382. Mineralogical Society, London.

Mozzi, R. L. and B. E. Warren (1969) Structure of vitreous silica. *J. Appl. Crystallogr., 2,* 165–172.

Mysen, B. O. (1976) The role of volatiles in silicate melts: solubility of carbon dioxide and water in feldspar, pyroxene, and feldspathoid melts to 30 kb and 1625°C. *Am. J. Sci., 276,* 969–996.

——— and I. Kushiro (1978) The effect of pressure on the partitioning of nickel between olivine and aluminous silicate melt. *Carnegie Inst. Wash. Year Book, 77,* 706–709.

——— and D. Virgo (1978) Influence of pressure, temperature and bulk composition on melt structures in the system $NaAlSi_2O_6$–$NaFe^{3+}Si_2O_6$. *Am. J. Sci., 278,* 1307–1322.

Narten, A. H. (1972) Diffraction pattern and structure of noncrystalline BeF_2 and SiO_2 at 25°C. *J. Chem. Phys., 56,* 1950–1909.

Nukui, A., H. Tagai, H. Morikawa and S. Iwai (1978) Structural study of molten silica by an X-ray radial distribution analysis. *J. Am. Ceram. Soc., 61,* 174–176.

Sharma, S. K., D. Virgo and I. Kushiro (1978a) The coordination of Ge in crystals and melts of GeO_2 composition at low and high pressures by Raman spectroscopy. *Carnegie Inst. Wash. Year Book, 77,* 665–672.

———, ——— and B. Mysen (1978b) Structure of melts along the join SiO_2–$NaAlSiO_4$ by Raman spectroscopy. *Carnegie Inst. Wash. Year Book, 77,* 652–658.

Simon, I. (1957) Structure of neutron-irradiated quartz and vitreous silica. *J. Am. Ceram. Soc., 40,* 150–153.

——— (1960) Infrared studies of glass. In J. D. Mackenzie, Ed., *Modern Aspects of the Vitreous State,* p. 120–151. Butterworth, Washington, D. C.

Stolen, R. H., J. T. Krause and C. R. Kurkjian (1970) Raman scattering and far infrared absorption in neutron compacted silica. *Disc. Faraday Soc., 50,* 103–107.

Taylor, D. (1972) The relationship between Si–O distances and Si–O–Si bond angles in the silica polymorphs. *Mineral. Mag., 38,* 629–631.

Terai, R., S. Kuroda and T. Ueno (1969) Coordination of aluminum ions in sodium–aluminosilicate glasses. *Bull. Gov. Ind. Res. Inst. Osaka, 20,* 172–176.

Velde, B. and I. Kushiro (1978) Structure of sodium alumino-silicate melts quenched at high pressure; infrared and aluminum *K*-radiation data. *Earth Planet. Sci. Lett., 40,* 137–140.

Waff, H. S. (1975) Pressure-induced coordination changes in magmatic liquids. *Geophys. Res. Lett., 2,* 193–196.

White, E. W. and G. V. Gibbs (1969) Structural and chemical effects on the Al$K\beta$ X-ray emission band among aluminum containing silicates and aluminum oxides. *Am. Mineral., 54,* 931–936.

Wong, J. and C. A. Angell (1976) *Glass Structure by Spectroscopy.* Marcel Dekker Inc., New York.

Yong, R. A. (1962) Mechanism of phase transition in quartz. *Defence Doc. Center Wash. Rep. No. AD276235.*

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