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

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Abstract

The coordination of Al³⁺ 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 SiO₂ glass, except that the Si–O stretching bands occur at lower frequencies than in SiO₂ glass and are weakly polarized in contrast to the depolarized bands in SiO₂ 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 NaAlSi₄O₈ melts is to increase the degree of local ordering and to change the local network structure to a coesite-type structure.

Al³⁺ remains tetrahedrally coordinated over the pressure range investigated; there is no support for the hypothesis that a pressure-induced coordination change of Al³⁺ 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 CO₂ solubility in albite melt (Mysen, 1976), (3) decreases in Fe³⁺/ΣFe in melts for iron-rich compositions along the NaAlSi₄O₈–NaFeSi₂O₆ join (Mysen and Virgo, 1978), and (4) significant decreases in Ni partitioning between crystals and melts along the NaAlSi₄O₈–MgSi₂O₆ 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 AlKα and AlKβ 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
is a continuous shift in the coordination of Al from 4 to 6 with pressure in melts of jadeite composition (NaAlSi$_2$O$_6$).

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$_2$O$_6$ 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$_2$O$_6$ composition prepared from an oxide mix of Johnson-Matthey high-purity SiO$_2$, Al$_2$O$_3$, and reagent-grade Na$_2$CO$_3$. The starting material for the high-pressure experiments was prepared by melting the oxide mixture in sealed Pt$_{10}$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 (~10 mg) in solid-media, high-pressure apparatus (Boyd and England, 1960) at 10, 15, 20, and 30 kbar at 1450°C 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 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$_2$O$_6$ 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 87 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$_2$O$_6$ 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$_2$O$_6$ glass indicates a lower site symmetry of silicon than that in the $\beta$-quartz model of SiO$_2$ glass (Narten, 1972; Bates, 1972). In general, however, it appears that NaAlSi$_2$O$_6$ 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.

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$_2$O·Al$_2$O$_3$·4SiO$_2$ glasses prepared at different pressures

<table>
<thead>
<tr>
<th>Pressure (kbar)</th>
<th>0.001</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman frequency (cm$^{-1}$)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>782, sh</td>
<td></td>
<td>340, w,bd</td>
<td>320, w,bd</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>472, s,p</td>
<td>475, s,p</td>
<td>478, s,p</td>
<td>480, s,p</td>
<td>496, s,p</td>
<td></td>
</tr>
<tr>
<td>572, (Sh), p</td>
<td>572, (Sh), p</td>
<td>568, (Sh), p</td>
<td>564, (Sh)</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>750, w,bd,p</td>
<td>750, w,bd,p</td>
<td>760, w,bd,p</td>
<td>740, w,bd,p</td>
<td>748, w,bd,p</td>
<td></td>
</tr>
<tr>
<td>1010, w,bd,p</td>
<td>992, w,bd,p</td>
<td>1008, w,bd,p</td>
<td>996, w,bd,p</td>
<td>984, w,bd,p</td>
<td></td>
</tr>
<tr>
<td>1084, w,bd,p</td>
<td>1050, w,bd,p</td>
<td>1080, w,bd,p</td>
<td>1054, w,bd,p</td>
<td>1056, w,bd,p</td>
<td></td>
</tr>
</tbody>
</table>

*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.

**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 $\sim$2 percent upon neutron irradiation, the Raman bands in the Si–O stretching region of unirradiated SiO$_2$ glass (at $\sim$1060 and 1200 cm$^{-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$_2$O$_6$ 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$_2$O$_6$
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 SiO₂ glass. Our preferred interpretation is based on X-ray radial distribution studies of unirradiated and neutron-irradiated SiO₂ glass (Stolen et al., 1970; Simon, 1957), in which the primary structural change in SiO₂ 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 SiO₂ glass densified by neutron bombardment is offered by Leadbetter and Wright (1977), in terms of the presence of interstitially located SiO₂ molecules. This interpretation can be ruled out, because the presence of interstitial SiO₂ requires the creation of nonbridging oxygens in the network structure, an effect that is not observed in the Raman spectra of neutron-irradiated SiO₂ glasses (Bates et al., 1974). The speculation that the major structural change in both SiO₂ and NaAlSi₃O₈ 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 α → β phase transition in quartz (Yong, 1962; Taylor, 1972). In this connection, in an infrared study of the SiO₂ 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 α → β 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 SiO₂ produces changes in the infrared spectra that are exactly opposite to those observed in the infrared spectra after the α → 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) in β-quartz, and the 1072 cm⁻¹ (e) band in α-quartz appears at the higher frequency, 1173 cm⁻¹ (e), in the β-quartz spectrum. In addition, the 464 cm⁻¹ (a₁) mode of α-quartz appears at 462 cm⁻¹ (a₁) in the β-quartz spectrum. Evidently the increase in the Si–O–Si angle in β-quartz causes the e₁ mode to increase in frequency, but the e₁ 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 SiO₂ 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 SiO₂ 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 SiO₂ in which Si is tetrahedrally coordinated.

From the above discussion, the spectral changes observed in the infrared and Raman spectra of SiO₂ and NaAlSi₃O₈ 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 NaAlSi₃O₈ 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 NaAlSi₃O₈ 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⁺⁺ in jadeite glasses

The above discussion of local ordering of the network structure of the high-pressure NaAlSi₃O₈ glasses implicitly assumes that Al⁺⁺ is predominantly tetrahedrally coordinated. A distinct peak that may be attributed to AlO₄ is not observed in the Raman spectra of the high-pressure NaAlSi₃O₈ 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 $Al^{1+}$ is in fourfold coordination are also free to create nonbridging oxygen as soon as $Al^{1+}$ shifts to sixfold coordination. If this were the case, the spectra of the high-pressure NaAlSi$_2$O$_6$ 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$_2$O$_6$ 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$_2$O · 2SiO$_2$ and Na$_2$O · 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$_2$O$_3$ to these sodium silicate glasses with fixed Na$_2$O content, and this result implies the presence of octahedrally coordinated $Al^{1+}$. Increases in the intensity of the Si–O$^-$ stretch band were also observed with the addition of TiO$_2$ and B$_2$O$_3$ 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 $Al^{1+}$ is predominantly in tetrahedral coordination. It should be mentioned, however, that the maximum amount of $Al^{1+}$ 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$_6$)$^{2-}$ units in the high-pressure NaAlSi$_2$O$_6$ 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 $Al^{1+}$ 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 AlK$\alpha$ and AlK$\beta$ wavelengths in the high-pressure NaAlSi$_2$O$_6$ 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 $Al^{1+}$ coordination in jadeite melts with increasing pressure. In the first instance, the interpretation of the infrared spectra of high-pressure NaAlSi$_2$O$_6$ glasses by Velde and Kushiro is based on the fact that the addition of Na$_2$O 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$_2$O 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$_2$O$_6$ 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 AlK$\alpha$ and AlK$\beta$ wavelength shifts of high-pressure NaAlSi$_2$O$_6$ glasses in terms of a systematic change from fourfold to sixfold coordination of $Al^{1+}$. The original data of Day and Rindone (1962) that purported to show shifts of AlK$\alpha$ radiation in Na$_2$O–Al$_2$O$_3$–SiO$_2$ glasses as a function of Al/Na, however,
were not substantiated in later studies (Terai et al., 1969). In addition, the data of White and Gibbs (1969) on the AlKβ X-ray emission band in aluminum-containing silicate crystals show that in the plot of AlKβ shifts vs. Al coordination there is some overlap of AlKβ shifts for compounds with Al³⁺ in both four-and sixfold coordination (e.g., Mg₂Al₂Si₃O₁₀, CaAl₂Si₂O₆). The implication is that AlKa or AlKB 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 NaAlSi₂O₆ glasses

A quantitative explanation of the lower local symmetry of the network structure in both the low- and high-pressure NaAlSi₂O₆ glasses compared with the β-quartz model of SiO₂ 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 SiO₂ glass closely resembles that of β-quartz (Wong and Angell, 1976). The SiO₂ 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 NaAlSi₂O₆ composition shows that the positions of the Raman and infrared bands are noncoincident. This result implies that the short-range ordering in the network of the high-pressure NaAlSi₂O₆ glasses may resemble that of coesite. A coesite model of the structure of the high-pressure NaAlSi₂O₆ glasses is consistent with the increase in density of NaAlSi₂O₆ glasses with increasing pressure (Kushiro, 1976).

We further suggest that the structure of the 1-atm NaAlSi₂O₆ 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 SiO₂–NaAlSiO₄ (Sharma et al., 1978b). This study showed that the network structure becomes more open with the replacement of SiO₂ by NaAlO₂ and that the local ordering of the network in NaAlSiO₄ 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 NaAlSi₂O₆ glass synthesized at 1 atm is considerably different from that calculated for the jadeite structure, and they conclude that NaAlSi₂O₆ melt at 1 atm has a
stuffed tridymite-like structure with a more disordered and open network than that of SiO₂ 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 NaAlSi₃O₈ and SiO₂ glasses, in which it is implicitly assumed that SiO₂ glass has a tridymite-like structure (Konnert et al., 1973). We contend, however, that the β-quartz model of SiO₂ 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 Al³⁺ occurs predominantly in fourfold coordination. With increasing pressure, the local symmetry of Si,Al in the network is lowered compared with that in SiO₂ 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 NaAlSi₃O₈ melts and other structural data for high-pressure GeO₂ 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 Al³⁺ in high-pressure NaAlSi₃O₈ 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, H₂O 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 GeO₂ 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 only the 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


