Application of infrared spectroscopy to studies of silicate glass structure: Examples from the melilite glasses and the systems $\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$

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Abstract. Infrared (IR) and Raman spectroscopic methods are important complementary techniques in structural studies of aluminosilicate glasses. Both techniques are sensitive to small-scale ($<15 \text{ \AA}$) structural features that amount to units of several SiO_4 tetrahedra. Application of IR spectroscopy has, however, been limited by the more complex nature of the IR spectrum compared with the Raman spectrum, particularly at higher frequencies ($1200\text{--}800 \text{ cm}^{-1}$) where strong antisymmetric Si–O and Si–O–Si absorptions predominate in the former. At lower frequencies, IR spectra contain bands that have substantial contributions from ‘cage-like’ motions of cations in their oxygen co-ordination polyhedra. In aluminosilicates these bands can provide information on the structural environment of Al that is not obtainable directly from Raman studies. A middle frequency envelope centred near 700 cm^{-1} is indicative of network-substituted AlO_4 polyhedra in glasses with $\text{Al}/(\text{Al} + \text{Si}) > 0.25$ and a band at $520\text{--}620 \text{ cm}^{-1}$ is shown to be associated with AlO_6 polyhedra in both crystals and glasses. The IR spectra of melilite and melilite-analogue glasses and crystals show various degrees of band localization that correlate with the extent of Al, Si tetrahedral site ordering. An important conclusion is that differences in Al, Si ordering may lead to very different vibrational spectra in crystals and glasses of otherwise gross chemical similarity.

Keywords. Infrared spectroscopy; silicate; aluminium co-ordination; aluminosilicate glasses; melilite; melilite-analogue glasses; akermanite; gehlenite; sodamelilite.

1. Introduction

In disordered silicate glasses there is no long-range structural periodicity. Methods of structural analysis that are applicable to crystalline solids e.g. conventional X-ray diffraction techniques, require the existence of order on a scale of hundreds of atomic spacings but in glasses no such order exists, and other techniques must be used as structural probes.

Models for the structure of silica and silica-metal oxide glasses range over two extremes. The random network hypothesis, originally proposed by Zachariasen (1932), has no provision for the presence of short range order or crystal-like features. In silica glass, the model assumes an arrangement of inter-connected $[\text{SiO}_4]$ tetrahedra completely lacking periodicity due to a random distribution of Si–O–Si bond angles. At the other extreme lies the crystallite theory (Randall *et al* 1930; illustrated by Wright and Leadbetter 1976) that proposes a glass structure based on highly ordered microcrystalline regions with dimensions of several tens of angstroms that strongly resemble the structure of the corresponding equilibrium solid. Much evidence exists to suggest that the real structure of silicate glasses lies between these two models, which really only represent extremes in the degree of the short range order present.

Bottinga *et al* (1981) have shown that the dimensions of short range structures are probably quite small and amount to several $[\text{SiO}_4]$ tetrahedra only ($\sim 5\text{--}15 \text{ \AA}$). The theory of vibrational spectroscopy as applied to silicate glasses (Brawer 1975; Brawer and White 1974) shows that infrared (IR) and Raman spectroscopy are sensitive to such small-scale structural features. For this reason, vibrational spectroscopic techniques have become very popular tools in experimental geochemistry over the last ten years (see review by McMillan and Piriou 1983) although they have their limitations. In this respect the extent to which vibrational spectroscopy can provide insights into the full bonding topology of silicate glasses has not yet been fully assessed.

The small-scale sensitivity, particularly at higher frequencies, of IR and Raman spectra, implies that information on the overall structure i.e. the interconnection between smaller structural units may not be readily obtainable (McMillan 1984a). However, this small-scale sensitivity can be used to advantage in studies on the solubility mechanisms of small molecules such as H_2O and CO_2 in silicate glasses. Molecular dynamic and Monte Carlo simulations (Woodcock *et al* 1976; Borgianni and Granati 1979; Matsui and Kawamura 1984) have shown some promise in providing an overall picture of silicate melts and glasses, emphasizing the need to employ a wide range of techniques in any structural study.

In the geological literature much effort has been placed on correlating structural information on silicate melts and glasses with observed physical properties such as viscosity-pressure relationships and diffusion coefficients (e.g. Mysen *et al* 1980, 1982). Considerable attention has also been devoted to understanding the effects of minor and volatile component additions to silicate liquids. It is well known that such components have an effect on natural and synthetic systems that is large in relation to their level of abundance (e.g. Kushiro 1975). The mechanisms of TiO_2 , P_2O_5 and oxidized volatile (H_2O , CO_2) dissolution have been investigated by Raman spectroscopy and the results have been summarized by Mysen *et al* (1982). More recent work on the H_2O solubility mechanism by Stolper (1982a, 1982b) and McMillan *et al* (1983) using IR spectroscopic techniques have found, contrary to the Raman investigations, that a substantial fraction of the dissolved water is present in molecular form. This highlights the importance of the complementary nature of Raman and IR techniques since use of one technique by itself may provide only part of the answer sought. The differing activity of Raman and IR vibrational modes makes the former technique more powerful in investigations of the silicate glass network structure but indirect and often ambiguous in studies of volatile solubility (e.g. Mysen *et al* 1980) and cation co-ordination environments (e.g. Sharma and Simons 1981; McMillan *et al* 1982).

In this paper the aim is to emphasize the range of structural information obtainable by IR spectroscopy mindful of the much larger data-base provided by Raman spectroscopic studies of silicate glasses. A comparison of the major IR and Raman absorption bands and their inferred structural assignment is presented in the next section, and examples of IR applications from the systems $\text{Na}_2\text{O}\text{--}\text{SiO}_2$, $\text{Na}_2\text{O}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2$ and from melilite glasses (akermanite, gehlenite, sodamelilite) are presented in following sections.

2. Background

The structure of disordered solids cannot be expressed explicitly in terms of nearest neighbour co-ordination numbers, bond lengths and bond angles as is the case with crystalline solids. Instead, one is faced with a statistical distribution about some mean structure pointing to the existence in melts and glasses of a range of easily accessible configurations separated by only small energy barriers. For example in vitreous silica a variety of techniques have shown that there is a broad distribution of Si–O–Si bond angles from 170 – 130° with the most probable angles in the range 155 – 140° (Greaves *et al* 1981; Dupree and Pettifer 1984). This variability leads to vibrational spectra that have broad, often poorly resolved, band envelopes with bandwidths of a half-height as much as 50 – 300 cm^{-1} , ten times more than the width of comparable crystalline compounds. The elucidation of structural information, therefore, frequently requires the use of special procedures such as spectral deconvolution and spectral subtraction. The question of whether these techniques can provide unique structural solutions is the subject of debate in the literature (McMillan *et al* 1982; McMillan and Piriou 1983). However it is clear that absorption bands must be assigned with reference to all available experimental and theoretical information. For Raman spectra, the arguments leading to band assignments have been discussed by McMillan (1984a). No detailed summary is as yet available for IR spectra although many bands are both IR- and Raman-active (though with differing intensities) and assignments will in many cases be applicable to both spectra.

In simple system silicate and aluminosilicate glasses, both IR and Raman spectra have prominent band envelopes (variably resolved into separate bands) in the high-frequency (1200 – 800 cm^{-1}), middle-frequency (800 – 650 cm^{-1}) and low frequency (650 – 400 cm^{-1}) regions. A brief description of their structural assignment is given below:

2.1 High-frequency band envelope

In the Raman spectra of silicate glasses the high frequency envelope is composed of polarized bands due to symmetric Si–O stretching motions of silicate units containing $[\text{SiO}_4]$ tetrahedra with: one (~ 1100 – 1050 cm^{-1}), two (~ 1000 – 950 cm^{-1}), three ($\sim 900\text{ cm}^{-1}$) and four ($\sim 850\text{ cm}^{-1}$) non-bridging oxygens (NBO). In the notation of Engelhardt *et al* (1975) these are designated Q_3 , Q_2 , Q_1 and Q_0 respectively. Mysen *et al* (1980) and Virgo *et al* (1980) ascribe these bands to the presence of a number of discrete anionic structural units i.e. 3-d networks, sheets, infinite chains, dimers and monomers with NBO/Si ratios of 0, 1, 2, 3 and 4 respectively. This interpretation has been questioned by McMillan (1984a, b) who presents strong evidence for the major high frequency bands being highly localized in character and as such, unable to provide any information on the linkage of adjacent tetrahedral groups. For example, McMillan (1984a) and McMillan and Piriou (1983) find that discrimination between infinite chains, $[\text{Si}_2\text{O}_6]_\infty$, and ring structures of equivalent NBO/Si ratio is not possible based solely on high frequency Raman bands. Thus an interpretation of the Raman bands in terms of Engelhardt *et al*'s Q-species, where there is no inherent assumption about the presence or absence of longer-range ($> 10\text{\AA}$) structures, may be most appropriate.

Unlike the relatively simple Raman high frequency envelope, the infrared spectrum in this region includes, in addition to symmetric Si–O stretching bands, a series of bands arising from antisymmetric stretches of non-bridging and bridging Si–O bonds; designated $\nu_{\text{as}}[\text{Si–O}^-]$ and $\nu_{\text{as}}[\text{Si–O–Si}]$ respectively.

In heteropolar solids, an absorption will be infrared-active when dissimilar atoms vibrate out-of-phase and Raman-active when they vibrate in-phase (Laughlin and Joannopoulos 1977). For example, strong negative correlations between silicon and oxygen displacements at 1080 cm^{-1} , 800 cm^{-1} and 450 cm^{-1} were found in the model of Laughlin and Joannopoulos (1977) for vitreous silica; all three values agree well with the observed IR activity.

Infrared spectra of silicate glasses in the high-frequency region tend to be much more complex than their Raman counterparts. In simple binary metal oxide-silica systems of high NBO/Si two distinct envelopes, corresponding to bridging and non-bridging Si–O vibrations, may be resolved in this region (e.g. Ferraro and Manghnani 1972; see later). For the same silica content, band shape is strongly influenced by the nature of the metal oxide present (Sanders *et al* 1974) with ions of largest z/r (e.g. Mg^{2+}) least disrupting the structural units present in vitreous silica (de Jong *et al* 1981).

2.2 Middle frequency envelope

The mid-range envelope ($800\text{--}650\text{ cm}^{-1}$) is of moderate strength in both temperature-corrected Raman (Seifert *et al* 1982) and infrared spectra. It is composed of at least two and probably more band components (Seifert *et al* 1982). McMillan *et al* (1982) have suggested that the band near 800 cm^{-1} in silica glass is mainly associated with motions of Si atoms against their tetrahedral oxygen cage, with little displacement of associated oxygen. This is consistent with observed isotope shifts (Galeener and Mikkelsen 1981; Galeener and Geissberger 1983) and with molecular dynamics calculations (Angell *et al* 1982; Giarofalini 1982).

In the case of melts lacking a semi-rigid polymerized network (i.e. those with $\text{NBO/Si} > 1$) McMillan (1984a) suggests that the mid-range vibrations might transform or couple to other modes having a greater degree of oxygen motion. This is evident in melts of NBO/Si approaching 4 where the mid-range band becomes progressively weaker with decreasing SiO_2 content; in vitreous fayalite, for example, the mid-range band is only present as a very weak shoulder (Kusabiraki and Shiraishi 1981).

Bell and Dean (1972) and Laughlin and Joannopoulos (1977) also describe the mid-range band as a vibration involving substantial Si motion but include an additional contribution from Si–O–Si “bridge bending” (i.e. in-plane oxygen motion bisecting the Si–O–Si bond angle). Ferraro and Manghnani (1972) found both strong pressure and compositional dependencies for the $800\text{--}700\text{ cm}^{-1}$ envelope in the system $\text{Na}_2\text{O–SiO}_2$. The effect of pressure is to compress the inter-tetrahedral linkages effectively decreasing the volume of the $[\text{SiO}_4]$ co-ordination polyhedra and thus raising the vibrational frequency. This behaviour together with the pronounced dependence of band position on NBO/Si led Ferraro and Manghnani (1977) to infer a strong degree of delocalization and hence a “pseudo-lattice-like” character for this band.

2.3 Low frequency envelope

The low frequency region ($650\text{--}400\text{ cm}^{-1}$) in Al-free silicate glasses includes a series of strong to moderate intensity unresolved bands that in the IR appear mostly below 550 cm^{-1} and in the Raman spectrum generally in the range $650\text{--}450\text{ cm}^{-1}$. In vitreous silica, the strong IR band near 470 cm^{-1} has been assigned largely to “rocking” motions of bridging oxygen where O vibrates in a direction perpendicular to the Si–O–Si plane (Laughlin and Joannopoulos 1977). A weak shoulder near 550 cm^{-1} in the IR is probably associated with vibrations of a predominantly “bending” character in which oxygen motion bisects the Si–O–Si bond angle. Two sharp bands at 604 cm^{-1} and 490 cm^{-1} in the Raman spectrum of vitreous silica have been attributed to localized modes associated with “broken bond” defects (Bates *et al* 1974). This assignment is, however, by no means certain and both absorption bands have been ascribed, on isotopic evidence, to the presence of 3- and 4-membered ring structures (Galeener and Geissberger 1983).

In the systems $\text{M}_2\text{O}\text{--}\text{SiO}_2$, $\text{MO}\text{--}\text{SiO}_2$ and in the fully polymerized $\text{MAIO}_2\text{--}\text{SiO}_2$, $\text{M}_{0.5}\text{AlO}_2\text{--}\text{SiO}_2$ aluminous systems, where M = monovalent or divalent alkali or alkaline earth cation, polarized bands of moderate to strong intensity appear in the Raman spectrum over the range $500\text{--}650\text{ cm}^{-1}$ (Seifert *et al* 1982; McMillan 1984a). These bands usually occur as an unresolved band envelope but in systems containing cations of low z/r , such as the $\text{K}_2\text{O}\text{--}\text{SiO}_2$ series glasses investigated by Verweij and Konijendijk (1976), they may be partly resolved. These absorptions are weakly active or inactive in the IR. Hass (1970); Mysen *et al* (1980) and Seifert *et al* (1982) have suggested a correlation with the “defect” bands of silica glass, however, McMillan (1984a) ascribes the observed absorptions to new bands unable to be simply derived from those of vitreous silica. McMillan (1984a) infers a high degree of vibrational localization for the $500\text{--}600\text{ cm}^{-1}$ bands and correlates absorption frequency with the presence of units of differing NBO/Si.

The most useful description of bands in the low frequency region, judging by the analysis of Furukawa *et al* (1981), is as bending plus stretching (deformation) modes involving a high degree of oxygen displacement at Si–O–Si bridges. “Rocking” describes predominantly out-of-plane motions of oxygen and “bending” *sensu stricto* describes in-plane motions.

2.4 Role of aluminium in aluminosilicate glasses

Many recent publications in the geological literature have been devoted to the understanding of the structural role of aluminium in aluminosilicate melts and glasses. The ionic radius of aluminium is such that it is found in four-, five- and six-fold co-ordination to oxygen in aluminate and aluminosilicate minerals. This variability coupled with aluminium’s known amphoteric behaviour, is good reason for presuming that Al^{3+} may adopt dual network-modifying and network-forming roles in the liquid or vitreous state. The usual interpretation (e.g. Mysen *et al*, 1982) is that when sufficient alkali or alkaline earth cations are present to charge compensate Al^{3+} , as NaAlO_2 or $\text{Ca}_{0.5}\text{AlO}_2$ complexes for example, then Al will be present in tetrahedral co-ordination. This idea is borne out by X-ray, thermochemical and Raman

spectroscopic studies of glasses in the system $\text{NaAlSiO}_4\text{--SiO}_2$ (Taylor and Brown 1979; Mysen *et al* 1980; Seifert *et al* 1982; Navrotsky *et al* 1982).

Interpretation of high frequency Raman spectrum of aluminosilicates is controversial. Mysen *et al* (1981) believe that the bands are a result of coupled (Si, Al)–O vibrations, but McMillan *et al* (1982) infer a dominant Si–O character modified only slightly by the Al^{3+} cation. McMillan *et al* (1982) believe Al–O stretching vibrations will occur at frequencies 20–30% less than Si–O vibrations; the authors expect components of Al–O stretching and Al “cage” motions to appear in the 700–900 cm^{-1} region with a weak Raman intensity but a strong to moderate IR activity. In the low frequency region associated dominantly with bridging oxygen motions, McMillan *et al* (1982) ascribe new bands at $\sim 590\text{ cm}^{-1}$ and $\sim 490\text{ cm}^{-1}$, occurring over a wide compositional range in system $\text{Ca}_{0.5}\text{AlO}_2\text{--SiO}_2$ and $\text{NaAlO}_2\text{--SiO}_2$ glasses, to the presence of Al–O–Al and Al–O–Si linkages respectively. These results together with ^{27}Al solid state NMR work (de Jong *et al* 1983) suggest that the “aluminium avoidance principle”, i.e. instability of aluminate condensates or clusters, is not a strict rule in aluminosilicate glasses (cf. Matsui and Kawamura 1984).

There has been considerable controversy in geological literature concerning pressure-induced Al co-ordination changes in silicate liquids (see Kushiro 1978, 1980, 1984; Velde and Kushiro 1978; Mysen *et al* 1982; Ohtani *et al* 1985). Part of this controversy concerns the suitability of Raman spectroscopy in detecting $\text{AlO}_4 \rightarrow \text{AlO}_6$ co-ordination changes. Due to weak band intensities and possible coupling effects in the Al–O region of the Raman spectrum (Sharma and Simons 1981; Sharma *et al* 1983), Al co-ordination changes can only be inferred indirectly by detecting changes in NBO content.

Infrared spectroscopy has been suggested by Tarte (1965, 1967) as useful for directly characterizing Al–O co-ordination polyhedra, provided the vibrating unit remains largely independent of other groups. This appears valid in the crystalline aluminosilicates and the few glasses investigated by Tarte (1967). Many cations in the glass phase, including Al, can be identified from their characteristic MO_n (M = metal cation, n = co-ordination number) “cage” vibrations which appear to be quite localized in character (Rao and Elliott 1981). The vibration frequency depends on the mass of the cation, the size of the oxygen polyhedron (both bond length and co-ordination number) and the nature of the co-ordinating oxygen ions (effective charge and type of network attachment). For Al, the approximation that these vibrations remain independent or localized breaks down for spinel minerals and other aluminate structures where substantial coupling with lattice modes is observed (cf. Jeanloz 1980).

IR techniques have been successfully employed in distinguishing six-fold from four-fold co-ordinated Al in synthetic aluminosilicate gels (Farmer *et al* 1979) and in aluminous serpentines (Serna *et al* 1977, 1979). But the technique has had only limited application to aluminosilicate glasses (Taylor and Green 1987). The suitability of IR spectroscopy in distinguishing Al co-ordination environments is discussed in §4 with reference to the systems $\text{Na}_2\text{O--SiO}_2$, $\text{Na}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2$ and data on the IR spectra of aluminosilicate minerals.

3. Experimental

To illustrate the usefulness of IR spectroscopy in aluminosilicate glass structural studies, a series of glasses in the systems $\text{Na}_2\text{O--SiO}_2$ (NS) and $\text{Na}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2$

(NAS) were synthesized at 1 atm. The glasses were prepared from analytical grade Na_2CO_3 , SiO_2 and Al_2O_3 . Appropriate proportions were ground in an agate mortar until sufficiently homogenized, they were then sintered at 800°C to drive off CO_2 , reground, then melted in a Pt crucible at 1100 – 1200°C and quenched in air. Glasses of $\text{NaCaAlSi}_2\text{O}_7$ (sodamelilite or Sm), $\text{NaAlSi}_2\text{O}_6$ (jadeite or Jd), $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (akermanite or Ak) and $\text{CaAl}_2\text{Si}_2\text{O}_7$ (gehlenite or Geh) composition were similarly prepared except that Ak and Geh were quenched from $\sim 1600^\circ\text{C}$. Crystalline jadeite and sodamelilite were prepared in piston cylinder apparatus at 25 kb and 30 kb respectively from the sintered oxides.

IR spectra were recorded over the range 4000 – 400 cm^{-1} , using a Digilab FTS-20E Fourier Transform IR spectrometer and employing the conventional KBr disc method. Approximately 2 mg (1 mg for crystalline compounds) of sample was ground together with 200 mg of IR-grade KBr in an agate mortar for 10 minutes. After drying the powder at 110°C , pellets were pressed between 1 cm diameter polished stainless steel dies; any cloudy discs were remade. Discs were then dried under P_2O_5 desiccant overnight to remove traces of absorbed water.

For the Na_2O – SiO_2 glasses, the KBr discs were prepared under a N_2 atmosphere with storage under NaOH desiccant to minimize the effects of atmospheric H_2O and CO_2 absorption to which these glasses are particularly susceptible. Spectrum acquisition was performed by signal-averaging 200 scans referenced against a blank KBr disc. A resolution of 4 cm^{-1} was employed.

4. Results and discussion

4.1 System Na_2O – SiO_2 (NS)

FTIR spectra of the compositions NS_5 (pentasilicate, $\text{Na}_2\text{Si}_5\text{O}_{11}$), NS_3 (trisilicate, $\text{Na}_2\text{Si}_3\text{O}_7$) and NS_2 (disilicate, $\text{Na}_2\text{Si}_2\text{O}_5$) having NBO/Si ratios of 0.4, 0.667 and 1.0 respectively are shown in figure 1. The effects of network depolymerization as $\text{Na}_2\text{O}/\text{SiO}_2$ increases are clearly illustrated in the high frequency (1200 – 800 cm^{-1}) region. In NS_5 only one band envelope, centred at 1046 cm^{-1} , is resolved in this region. It arises largely from antisymmetric stretching of Si–O–Si bridging groups and may be designated $\nu_{\text{as}}[\text{Si–O–Si}]$. With increasing amounts of NBO the shoulder seen near 1000 cm^{-1} grows into a visually resolvable band envelope centred at 982 cm^{-1} in NS_3 and 941 cm^{-1} in NS_2 . This causes the width of the high frequency envelopes to increase and extend below 800 cm^{-1} . The lower frequency band of the high frequency doublet may be assigned largely to antisymmetric stretching of Si–O[–] non-bridging bonds ($\nu_{\text{as}}[\text{Si–O}^-]$) with some contribution arising from symmetric Si–O[–] stretching (the strongly Raman active $\nu_{\text{s}}[\text{Si–O}^-]$ bands) in the unresolved lowest frequency portion of the envelope. In the intermediate frequency range, 800 – 650 cm^{-1} , a medium strength envelope appears at 781 , 768 and 760 cm^{-1} in the compositions NS_5 , NS_3 and NS_2 respectively. Vibrations contributing to this band are thought to be quite delocalized and involve substantial motion of Si atoms situated in their oxygen co-ordination cage (§2.2); additional contributions come from Si–O–Si in-plane bridge bending motions. Shoulders appearing near 660 cm^{-1} in NS_2 and other more depolymerized compositions accompany a decrease in intensity of the $\sim 750\text{ cm}^{-1}$ band. These probably arise from symmetric stretching of the Si–O–Si bridge bond in pyrosilicate (Si_2O_7) and other Q_1 -species that are likely

Figure 1. Fourier transform IR spectra ($1600\text{--}400\text{ cm}^{-1}$) of the sodium silicate glasses NS_2 , NS_3 , NS_5 , and the sodium aluminosilicate glasses N_3AS_{10} and N_3AS_4 ($\text{N}=\text{Na}_2\text{O}$, $\text{A}=\text{Al}_2\text{O}_3$, $\text{S}=\text{SiO}_2$). Prominent high frequency bands in N_3AS_4 occur at 1072 , 1034 , 937 , 870 (shoulder) and 698 cm^{-1} .

to be present in these depolymerized glasses. A weak shoulder at $\sim 550\text{ cm}^{-1}$ in NS_5 also occurs in pure silica glass and is assignable to in-plane Si–O–Si bridge bending vibrations. The low-frequency band envelope, $530\text{--}400\text{ cm}^{-1}$, is due to stretching plus bending-motions involving dominantly oxygen atom displacements. As predicted by Furukawa *et al* (1980), the low frequency bandwidth increases with increasing degree of depolymerization.

Bands present at $\sim 1430\text{ cm}^{-1}$ are due to small amounts of dissolved carbonate derived from absorbed atmospheric CO_2 . The amount present is not significant ($<1\text{ wt}\%$ carbonate) in terms of its effect on the volatile-free glass structure.

4.2 System $\text{Na}_2\text{O}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2$ (NAS)

The effects of Al substitution have been investigated in the system $\text{Na}_2\text{O}\text{--}\text{Al}_2\text{O}_3\text{--}\text{SiO}_2$ (NAS) by direct replacement of the charge-balanced component NaAlO_2 for SiO_2 in the trisilicate (NS_3) composition. Half a mole replacement gives $\text{Na}_{2.5}[\text{Al}_{0.5}\text{Si}_{2.5}\text{O}_7]$

(N_5AS_{10}) and one mole gives $\text{Na}_3[\text{AlSi}_2\text{O}_7]$ (N_3AS_4). The latter composition is the sodic analogue of sodamelilite: $\text{NaCa}[\text{AlSi}_2\text{O}_7]$. FTIR spectra of the series NS_3 , N_5AS_{10} and N_3AS_4 show systematic shifts towards lower frequencies for both high frequency $\nu_{\text{as}}[\text{NBO}]$ and $\nu_{\text{as}}[\text{BO}]$ bands and the mid-range envelope. These changes have been observed in studies of Al-substituted systems by Raman spectroscopy (Mysen *et al* 1981; Seifert *et al* 1982) and were associated with a coupling of Si–O and Al–O stretching vibrations by these authors. McMillan *et al* (1982) have suggested a different interpretation whereby Al^{3+} acts only as a modifying cation in the manner of Ca^{2+} or Na^+ and vibrations maintain a high degree of Si–O character. Since these two models can equally well describe the high frequency Raman spectra, there is at this stage, little to favour either model. The spectra of melilite crystals and glasses however reveal some important features in the interpretation of the structural versus spectroscopic role of Al, relevant to both models (see later).

Compared with NS_3 glass, the N_3AS_4 composition has additional bands appearing in the FTIR spectrum at 1072 cm^{-1} and 880 cm^{-1} (shoulder). These may be compared with similar bands in the Raman spectra of gehlenite (Geh) and Ca-Tschermak's pyroxene (CaTs) composition glasses and crystals observed by Sharma *et al* (1983). Their origin has been attributed by the authors to increased localization of the high frequency stretching modes resulting from $\text{Al} \leftrightarrow \text{Si}$ substitution. On this basis, Sharma *et al* assigned the separate highest frequency bands to $\nu_{\text{as}}[\text{Si–O–Si}]$ and $\nu_{\text{as}}[\text{Si–O–Al}]$ vibrations. A similar interpretation may be made for the 1072 cm^{-1} and 1034 cm^{-1} bands in N_3AS_4 glass. The new shoulder at $\sim 880\text{ cm}^{-1}$ is best assigned to Al–O stretching vibrations (McMillan *et al* 1982).

In the mid-frequency region there is a dramatic shift in the position of the mid-range band envelope from 768 cm^{-1} (NS_3) through 745 cm^{-1} (N_5AS_{10}) to 698 cm^{-1} (N_3AS_4). An IR mid-range envelope centred near 700 cm^{-1} is characteristic of NaAlO_2 or $\text{Ca}_{0.5}\text{AlO}_2$ substitution of the silicate network in numerous aluminosilicate glasses where $\text{Al}/(\text{Al} + \text{Si})$ exceeds about 0.25. For example, jadeite, sodamelilite, albite, nepheline and gehlenite glasses all have mid-range band envelopes located near 700 cm^{-1} . In Al-free systems the mid-range envelope is located at $\sim 800\text{--}750\text{ cm}^{-1}$ (McMillan 1984a). "Cage-like" motions of Al surrounded by a tetrahedral arrangement of oxygen give a calculated "reversal frequency" of 635 cm^{-1} in molecular dynamics simulations (Soules and Busby 1981). Because the mid-range absorption is strongly delocalized in behaviour, expected strong coupling between Si and Al vibrations is consistent with the observed frequency shift of the mid-range band to near 700 cm^{-1} , i.e. intermediate between pure Si and Al "cage-like" vibrations. A mid-range envelope of medium to strong intensity situated near 700 cm^{-1} in aluminosilicate glasses is thus a good indication for the presence of network-substituted AlO_4 polyhedra. This view is consistent with the study of Tarte (1967).

4.3 Comparison of melilite and melilite-analogue glasses and crystals

The IR spectrum of N_3AS_4 glass is in many respects similar to that of crystalline sodamelilite (figure 2) which is isostructural with the other melilite endmembers Ak and Geh (Louisnathan 1970b). Based on X-ray determinations, the melilite structure is best considered as a sheet-like arrangement of $[\text{MT}_2\text{O}_7]^{4-}$ groups (where $\text{M} = \text{Al}^{\text{IV}}$, Mg or Zn; $\text{T} = \text{Al}^{\text{IV}}$ or Si) within which the nature of bonding is largely covalent; the adjacent sheets are held together by Ca^{2+} and Na^+ ions with interlayer bonding

Figure 2. Fourier transform IR spectra ($1500\text{--}400\text{ cm}^{-1}$) for crystalline and vitreous sodamelilite (Sm) and jadeite (Jd). The band at 595 cm^{-1} in crystalline jadeite is associated with AlO_6 polyhedra.

being predominantly ionic (Louisnathan 1969). In sodamelilite Al and Si are ordered on tetrahedral sites and Ca and Na are disordered over the larger, distorted 8-coordination site. Since N_3AS_4 glass is spectroscopically similar to crystalline Sm (figure 2), it is likely that there is considerable Al and Si ordering on tetrahedral sites in this glass.

Raman and IR investigations of the melilite minerals have been carried out by Sharma *et al* (1983), Sharma and Yoder (1979) and Kimata (1979). Results of these studies together with additional FTIR spectroscopic data on melilite composition glasses (this work) have been summarized in tables 1 to 3 where tentative band assignments and correlations are given.

Tables 1-3. IR and Raman spectral correlations for the melilite crystals and glasses.

Band intensity:	vs	very strong.	vibrational modes:	ν_{as}	asymmetric stretch
	s	strong		ν_s	symmetric stretch
	m	medium		δ	deformation
	w	weak			
	vw	very weak	Probable band correlations indicated by		
	br	broad	All glasses quenched from 1 atm unless otherwise stated.		
	vbr	very broad	R - Raman IR - Infrared		
	sh	shoulder			

Table 1. Akermanite $\text{Ca}_2\text{MgSi}_2\text{O}_7$

IR & R $\text{Rb}_2\text{Pb}_2\text{Si}_2\text{O}_7$ linear bridge pyro- silicate crystal (Tarte <i>et al</i> 1973)	IR Hardystonite (Zn-Ak) crystal (Kimata 1980)	IR Ak crystal (Kimata 1980)	R Ak crystal (Sharma and Yoder 1979)	Tentative assignments	IR Ak glass (this work)	R Ak glass (Sharma and Yoder 1979)
			1067 vw	...)		
		1044 sh		...)		
1026 $\nu_{as}[\text{Si}-\text{O}-\text{Si}]$	1010 s.....	1010 s.....	1023 vw	...) $\nu_{as}[\text{Si}-\text{O}-\text{Si}]$	)	
	970 s.....	973 s.....	986 w	...)	)	
913 $\nu_{as}[\text{Si}-\text{O}^-]$	920 vs.....	935 vs		...) ν_{as} and	) br	914 s
889 R $\nu_s[\text{Si}-\text{O}^-]$	885 sh.....	905 sh.....	904 s	...) $\nu_s[\text{Si}-\text{O}^-]$	)	
	838 s.....	851 s		...)	847 sh.....	858 sh
	682 w.....	685 w		$\nu[\text{SiO}_4]?$	...) ν 704 w sh	
668 R $\nu_s[\text{Si}-\text{O}-\text{Si}]$			661 s	$\nu_s[\text{Si}-\text{O}-\text{Si}]$	?.....	683 m
		(642 m 618 s.....		...) $\delta[\text{Si}-\text{O}-\text{Si}]$...)		
		589 m.....	598 w	... $\nu[\text{MgO}_4]$	...) ν 579 sh	
562 $\delta[\text{Si}-\text{O}^-]$	549 sh.....	(559 w 520 sh		...) $\delta[\text{Si}-\text{O}^-]$...)	517 s	533 w
	503 s			$\nu[\text{ZnO}_4]?$		
476) $\delta[\text{Si}-\text{O}^-]$ 452 R)	455 s.....	478 s.....	477 w	...) $\delta[0]$	482 sh	
407 $\delta[\text{Si}-\text{O}-\text{Si}]$			447 w	...)		

Bands due to AlO_4 polyhedra are clearly identified for crystalline Geh by comparison with the gallium substituted analogue $\text{Ca}_2\text{Ga}_2\text{SiO}_7$. They occur at 851, 803 and 685 cm^{-1} and are also represented by bands at 850, 810 cm^{-1} (weak shoulders) and 683 cm^{-1} in crystalline Sm. The $850\text{--}800\text{ cm}^{-1}$ absorptions appear in the "characteristic frequency" range for condensed (i.e. interconnected) AlO_4 polyhedra as defined by Tarte (1967) and are due to stretching vibrations of Al-O-Al linkages as discussed by McMillan *et al* (1982). The $\sim 680\text{ cm}^{-1}$ band is probably a stretching vibration largely involving motion of Al with its tetrahedral co-ordination cage. An analogous motion for Si is tentatively proposed for the bands near 700 cm^{-1} in crystalline Geh, Sm and Ak.

Despite the structural interpretations of Louisnathan (1969, 1970a, b) all the

Table 2. Sodamelilite $\text{NaCaAlSi}_2\text{O}_7$.

IR N_3AS_4 glass (this work)	IR Sm crystal (this work)	R Sm crystal (Sharma and Yoder 1979)	Tentative assignments	IR Sm glass (this work)*	R Sm glass (Sharma and Yoder 1979)
1072 s.....	1070 sh, s		... ν_{as}	)	
1034 s.....	1040 s		... $[\text{Si}-\text{O}-\text{Si}]$	)	(1013)**
		1023 m	... $[\text{Si}-\text{O}-\text{Al}]$	)	(990)**
	(986 s.....	972 sh	... ν_{as} and ν_s	)	980 m
937 vs, br.....	(	930 m	... $[(\text{Si}, \text{Al})-\text{O}^-]$	)	(907)**
	(901 vs.....	894 sh	...)	)	
870 sh.....	850 sh		... $\nu_{[\text{Al}-\text{O}]}$	)	
	810 sh		...)	)	
	(727 m.....	724 sh, m	... $\nu[\text{SiO}_4]?$	)	
698 m.....	(		... $\nu[\text{AlO}_4]$	... 706 m, br	
	(683 m		...)	...)	
		665 sh	... $\delta[\text{Si}-\text{O}-\text{Si}]$		
635 sh.....	640 sh, w.....	648 s	... $\nu_s[\text{Si}-\text{O}-\text{Si}]$	?.....	648 sh
				?	562 sh
	(530 sh, w.....	539 m	... $\delta[\text{Si}-\text{O}-\text{Al}]$	)	
	(	512 vw	)	)	
473 s, br.....	(479 s.....	485 w	)	)	
	(	460 w	) $\delta[0]$	... 468 s, br	490 s
	(434 vs		)	)	
	(	412 w	)	)	

*Run T-1159 quenched from 30 kbar.

**Deconvolutions of 980 cm^{-1} band suggested by Mysen and Virgo (1980).

crystalline melilites exhibit spectral features, associated with the silicon-oxygen stretch bands, that strongly resemble those of pyrosilicate minerals and compounds (i.e. those containing $[\text{Si}_2\text{O}_7]^{6-}$ groups). The $[\text{Si}_2\text{O}_7]$ dimer must therefore be considered as the basic vibrating unit of the melilite minerals rather than the aluminosilicate sheet of Louisnathan. This implies strong localization of Si-O and M-O (M = Al, Mg or Zn) vibrations (i.e. negligible coupling) despite the fact that together they make up the integral $[\text{MSi}_2\text{O}_7]^{3-}$ structural unit of the melilite endmembers. Such an interpretation is similar to the model proposed by McMillan (1984a, b) that argues against significant Si, Al coupling of vibrational modes in aluminosilicate glasses.

As noted by Sharma and Yoder (1979), the IR and Raman spectra of Sm glass do not resemble the spectrum of the crystalline solid. However, the spectrum of N_3AS_4 glass, particularly in the high-frequency region, shows distinct similarity with that of crystalline Sm (figure 1 and 2). The absence in the glass of an intense IR band or band component near 900 cm^{-1} , corresponding to the strong $\nu[\text{NBO}]$ band at this frequency in the crystal, indicates that the vibrating unit in Sm glass cannot be regarded as an $[\text{Si}_2\text{O}_7]$ group but rather must represent a much more polymerized aluminosilicate network structure with little Al, Si ordering on tetrahedral sites. This conclusion is supported by Sharma and Yoder (1979) and Mysen and Virgo (1980); both studies suggest a structure dominated by network aluminosilicate units of the

Table A3. Gehlenite $\text{Ca}_2\text{Al}_2\text{SiO}_7$

IR Gallium subst. Geh crystal (Kimata 1980)	IR Geh crystal (Kimata 1980)	R Geh crystal (Sharma <i>et al</i> 1983)	Tentative assignments	IR Geh glass (this work)	R Geh glass (Sharma <i>et al</i> 1983)
1005 s.....	1022 s.....	1005 vw 998 w	...) ν_{as}) [Si-O-Si]) [Si-O-Al]	... 984 s	... 1004 w, sh
945 vs.....	970 s.....	977 m	...) ν_{s} & ν_{as}		
895 s.....	917 s.....	914 m	...) [Si, Al-O ⁻]...	... 918 s.....	896 s
870 s.....	887 s		...) [Si, Ga-O ⁻]		
	851 s.....	841 w, sh	...) ν [Al-O]	... 860 s	
	803 vs.....	796 m	...	... 818 sh	
718 s.....	717 m 685 m		... ν [SiO ₄]? ... ν [AlO ₄]	...) 690 m, sh	
653 s.....	648 s.....	655 m, sh 626 vs	... δ [Si-O-Si] ... ν_{s} [Si-O-Si]		... 662 sh
583 m 550 m 525 m			...) ν [Ga-O] ...) & ...) ν (GaO ₄)	?	552 s
503 m.....	531 m.....	528 w	... δ [Si-O-Al]		
472 m.....	477 m.....	459 w	...) δ [O]	...) 457 m	
	414 s.....	425 vw	...)		

type $[\text{NaAlSi}_2\text{O}_7]^{2-}$ having $\text{NBO}/\text{T} = 0.667$. The Sm analogue glasses NS_3 and N_3AS_4 both have bulk NBO/T ratios of 0.667 but differ from Sm glass in that their spectra indicate the presence of substantial NBO. This may arise from greater localization of Al-O and Si-O stretching vibrations consistent with greater degree of Al, Si order in N_3AS_4 glass coupled with a much less uniform distribution of structural units (i.e. Q-species) than found in Sm glass.

For Ak glass, IR and Raman spectra are similar to the crystalline phase suggesting that $[\text{Si}_2\text{O}_7]$ pyrosilicate groups are the dominant vibrating unit and in the absence of Al the melt structure is relatively depolymerized.

The Raman spectra of Geh glass and crystals are, in contrast to Ak, significantly different. Sharma *et al* (1983) found the glass to consist of a 3-d aluminosilicate network together with a high proportion of $[\text{SiO}_4]^{4-}$ monomeric units identified by a strong band near 900 cm^{-1} . A bimodal "Q₀-Q₄" dispersion of tetrahedral environments is thus indicated (de Jong *et al* 1981).

4.4 Aluminium co-ordination

Vibrational spectra show that major structural differences occur in isochemical aluminosilicates when a change in Al co-ordination takes place. This difference is illustrated in figure 2 for crystalline and vitreous jadeite. In crystalline jadeite, Al is present as AlO_6 polyhedra while in the glassy state Al occurs in tetrahedral coordination; major changes in the IR spectrum occur in the high frequency region

and at mid-frequencies where a prominent band near 600 cm^{-1} in the crystal is no longer apparent in the glass phase. Other examples that show similar structural changes are $\text{LiAl}^{\text{IV}}\text{Si}_2\text{O}_6$ glass and the crystalline spodumene polymorphs (Sharma and Simons 1981) and vitreous and crystalline CaTs ($\text{CaAl}_2\text{SiO}_6$) (Sharma *et al* 1983).

In both the above studies by Sharma, the structural changes could be readily characterized by Raman spectroscopy, although direct identification of bands due to AlO_4 and AlO_6 polyhedra was not possible. As discussed in §2, IR spectroscopy is expected to be more sensitive to the nature of Al–O polyhedra and Tarte (1967) has suggested frequency ranges for bands indicative of Al–O polyhedra:

	AlO_4	AlO_6
Isolated polyhedra:	800–650	530–400
Condensed polyhedra*:	900–700	680–500
*i.e. containing Al–O–Al linkages		

The ranges quoted by Tarte are broadly consistent with the presence of tetrahedrally-co-ordinated Al in the aluminosilicate glasses investigated in this study although the delocalized nature of the mid-range envelope (i.e. coupling with Si vibrations) does not allow definite identification of AlO_4 in aluminosilicate glasses. Vibrations of AlO_6 groups are probably better approximated as independent (Rao and Elliot 1981) and this has been used by Farmer *et al* (1979) and Serna *et al* (1977) to distinguish octahedrally-co-ordinated Al (identified by strong absorptions at $500\text{--}600\text{ cm}^{-1}$, see §2.4). It is therefore tempting to suggest that the strong band at 595 cm^{-1} in crystalline jadeite (figure 2) which is absent or weak in the glass spectrum, can be assigned to a dominant contribution from AlO_6 vibrations. As might be expected from this prediction, no band exists near 700 cm^{-1} in crystalline jadeite to indicate the presence of AlO_4 but such a band does exist in crystalline and vitreous Sm which both contain tetrahedral Al (table 4, figure 2).

Reference to tabulated IR spectra (Liese 1975; Gadsden 1975) for a variety of silicate minerals, including structurally-related Al-containing and Al-free varieties, strongly supports the hypothesis that strong bands in the $520\text{--}620\text{ cm}^{-1}$ range are indicative of octahedrally-bound Al. While there are a few notable exceptions to the rule (such as the feldspar and scapolite series which have medium to strong IR bands in this region presumably related to their four-membered ring structures) there is a good general agreement for a diverse range of mineral structures and compositions, as summarized in table 4. The natural extension of this rule is to aluminosilicate glasses where direct identification of AlO_6 polyhedra has not been possible with other vibrational spectroscopic techniques. Bands in the $520\text{--}620\text{ cm}^{-1}$ region may thus indicate the presence of AlO_6 polyhedra. Interference by other IR bands in this region may occur due to the presence of Si–O–Si bridge bending vibrations (only expected in pure silica and silica-rich glasses), bands associated with three- or four-membered ring structures (as in the feldspars and scapolites) and absorptions arising from defect centres. The last mentioned case is somewhat controversial and the existence of defect centres in aluminosilicate glasses is now regarded as doubtful (McMillan 1984a).

In aluminosilicate glasses spectral evidence indicates that tetrahedrally-co-ordinated Al is the dominant species. In 1 atm Jd and Ne (nepheline) composition glasses a weak band exists at $\sim 580\text{ cm}^{-1}$ (figure 2) which may indicate the presence of a small amount of non-network, octahedrally-co-ordinated Al, or alternatively four-membered ring structures may be present. Mysen *et al* (1980) found no changes in the silicate

Table 4. Relationship between six-fold Al co-ordination and IR bands in the region 520–620 cm⁻¹.

Mineral	Al co-ordination number	vs or s bands 520–620 cm ⁻¹
Jadeite	6	595
α -spodumene	6	590
Acmite	no Al	absent (505–502)*
Diopside	no Al	absent (513–510)*
Hedenbergite	no Al	absent (515–509)*
Kyanite	6	598–597
Sillimanite	6, 4	545–544
Andalusite	6, 5	535–520
Mullite	6, 4	560–550
Topaz	6	609
Staurolite	6	595–586
Almandine**	6	570–569
Pyrope**	6	575–565
Grossular	6	540–538
Spessartine	6	565–562
Uvarovite	no Al	absent
Andradite	no Al	absent (512–510)*
Gibbsite	6	562–540
Kaolinite	6	545–535
Halloysite	6	545–550
Montmorillonite	6, 4	520
Pyrophyllite	6	542–535
Talc	no Al	absent
Muscovite	6, 4	540
Phlogopite	4	absent
Gehlenite	4	absent
Sodamelilite	4	absent
Zoisite	6	575

Data sources: Liese (1975) and Gadsden (1975).

*closest strong bands in the ~ 500 – 600 cm⁻¹ region.

**Omori (1971) calculates the AlO₆ stretching frequency to be ~ 630 cm⁻¹ for Alm-Pyr garnet in reasonable agreement with the observed strong band at ~ 570 cm⁻¹.

network of Jd glass from 1 atm to 38 kbar and thus find no evidence to suggest that an Al co-ordination change takes place with pressure as originally proposed by Kushiro (1976). These Raman results, however, do not preclude the presence of a small, constant proportion of octahedrally-co-ordinated Al in Jd melt over the pressure range investigated. In hydrous Jd and Sm glasses, enhancement of the 570 cm⁻¹ IR band indicates that measurable AlO₆ is produced by H₂O dissolution (Taylor and Green 1987).

Current techniques for the detection of Al co-ordination environments, including solid-state nuclear magnetic resonance (NMR) (de Jong *et al* 1983), do not appear sensitive enough to distinguish small proportions of Al^{VI} in the presence of Al^{IV}, although at very high pressures gross co-ordination changes are readily identified

(Ohtani *et al* 1985); the question of Al^{VI} existence in lower pressure, anhydrous glasses remains open to further investigation.

5. Summary

The structure of silicate and aluminosilicate glasses has been investigated by IR spectroscopy complemented by data from earlier Raman studies. The IR spectra of glasses are more complex than Raman spectra in the high-frequency region (1200–800 cm⁻¹). The high-frequency IR absorption envelope is composed of a series of bands that arise from both symmetric and antisymmetric stretching of Si–O bonds in non-bridging and bridging positions in the silicate framework. These are well illustrated by glasses in the system Na₂O–SiO₂.

It is shown that glasses of melilite and melilite-analogue (system NAS) composition exhibit a variety of different structural types ranging from those with significant NBO (Ak) to aluminosilicate network structures exhibiting limited (Sm) or substantial (N₃AS₄) Al, Si ordering or which contain a high proportion of other discrete units (Geh). The correlations between spectra (see tables 1–3) allow interpretation of the IR spectra of melilite and related glasses in terms of the basic vibrational units present. In the crystalline melilites and by analogy, in the vitreous phase as well, these units may not always correspond directly with the basic structural units identified by X-ray methods. This is believed mainly due to the effects of increasing band localization which may be correlated with the degree of tetrahedral site ordering. This suggestion has important implications for the structural role of Al as determined by vibrational spectroscopy since glasses of gross structural similarity may exhibit different degrees of Al, Si ordering and hence significantly different vibrational spectra. The results for melilite glasses and crystals suggest that in aluminosilicate glasses such as Sm, the high-frequency bands are best described by the delocalized or Si, Al coupled vibrational model of Mysen and co-workers while in glass structures exhibiting more Al, Si order, such as N₃AS₄, the model of McMillan and co-workers may be more appropriate.

In the glasses studied, the mid-range envelope of moderate IR intensity can be shown to respond in a predictable fashion to NaAlO₂ or Ca_{0.5}AlO₂ substitution of the silicate network. This absorption arises from strongly delocalized vibrational modes associated mainly with the aluminosilicate framework cations Si and Al.

In aluminosilicate minerals and glasses it is shown that IR spectroscopy can be useful in discriminating Al co-ordination environments following the proposal of Tarte (1967). Al in six-fold co-ordination is characterized by absorption bands at 620–520 cm⁻¹ in aluminosilicate minerals and glasses.

Useful future applications of IR spectroscopy may be in the far IR region (500–50 cm⁻¹) where metal-anion complexes, such as those with fluoride (Foley *et al* 1986) or hydroxide, have characteristic vibrations.

Acknowledgements

The author thanks Drs A Finney, R Nordin, S Foley and N Odling for helpful discussions. N Davies and K Harris provided invaluable technical assistance, and

Mrs M Hall (UWA) kindly assisted by typing the manuscript. This research was supported financially by an Australian National Research Fellowship to WRT and by Australian Research Council funds to Prof D H Green. This paper is dedicated to the late Sir C V Raman, on the occasion of his birth centenary.

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