

Structural studies of silicate glasses and melts—applications and limitations of Raman spectroscopy

PAUL McMILLAN

*Department of Chemistry
Arizona State University, Tempe, Arizona 85287*

Abstract

Raman spectroscopic studies of alkali and alkaline earth silicate glasses and melts are reviewed, and the major Raman bands observed for these series are summarized. Vitreous silica shows weak bands near 1200 and 1060 cm^{-1} , a medium intensity band group near 800 cm^{-1} , and a strong polarized band near 430 cm^{-1} . Other silicate compositions show strong bands at 1100–1050 cm^{-1} , 1000–950 cm^{-1} , near 900 cm^{-1} and near 850 cm^{-1} , respectively maximized in relative intensity near the disilicate, metasilicate, pyrosilicate and orthosilicate compositions. Glasses more silica-rich than the orthosilicate also show medium to strong bands in the 700–500 cm^{-1} region. The variation of these bands with composition and their polarization character are discussed, and other weak bands observed in various studies are noted. There is overall agreement as to the most general interpretation of these bands in terms of the silicate glass or melt structure. In general, bands in the 1200–800 cm^{-1} region have been associated with silicon–oxygen stretching vibrations of tetrahedral silicate units. The weak high-frequency bands of silica glass have been assigned to asymmetric stretching within a fully-polymerized tetrahedral silicate network, while the strong polarized bands at 1100–1050 cm^{-1} , 1000–950 cm^{-1} , 900 cm^{-1} and 850 cm^{-1} have been attributed to symmetric stretching vibrations of silicate tetrahedra with respectively one, two, three and four non-bridging oxygens. The bands in the 700–400 cm^{-1} region have been associated with the presence of inter-tetrahedral Si–O–Si linkages. A number of structural models for silicate melts and glasses have been constructed on the basis of these or similar band assignments. These are summarized, and discussed in terms of possible constraints regarding the vibrational interpretations. It is noted that to realize the full potential of Raman spectroscopy in structural studies of silicates in general will require a detailed understanding of their vibrational properties in relation to their structure. A number of vibrational calculations have been carried out for various silicate structures to address this problem. These are briefly summarized, and some limitations of the method are noted. Finally, several recent studies have used silicate melt and glass structural models derived from interpretations of Raman spectra to interpret systematic variations in bulk properties of the glasses and melts. Such systematics are examined for the viscosity and the immiscibility behavior of alkali and alkaline earth silicate series, within the limitations of the Raman spectral interpretations as discussed here.

Introduction

Almost all igneous processes are associated with the presence of a silicate melt phase, or magma. There has been much interest in relating the physical properties of such liquids to their molecular structure, and a number of techniques have been used to gain structural information on molten silicates. One such method has been vibrational spectroscopy, including Raman scattering. Silicate melts are high temperature liquids, which poses some experimental difficulties for Raman spectroscopy. For this reason, most studies have been carried out on glasses quenched from their melts, and the results extrapolated to

the liquid structure. Although some authors doubt the general validity of such extrapolations (e.g., Boettcher et al., 1982), they do seem reasonable for vibrational studies. A number of workers have compared the infrared and Raman spectra of various silicate glasses and their corresponding melts, and found the glass and melt spectra to be similar (e.g., Markin and Sobolev, 1960; Sweet and White, 1969; Sharma et al., 1978a; Piriou and Arashi, 1980; Kashio et al., 1980; Seifert et al., 1981). This similarity was used to suggest that structural interpretations of glass spectra should also be valid for the corresponding melts.

Accepting that Raman spectroscopic studies on silicate

glasses may be used to model the structures of silicate melts, geochemists have combined their results with the large body of data from workers in the glass and solid state sciences. The first Raman studies of simple silicate glasses were carried out shortly after the discovery of the Raman effect in the late 1920's, and have continued to the present day. From the early 1960's, most of these spectra were obtained using laser sources, but it is of interest to note that much of the earlier work with arc sources is comparable in quality to later studies. There are now a considerable number of studies which have used Raman spectroscopy to probe the structures of silicate glasses and melts, which are summarized in Table 1. This article is intended to review these studies for alkali and alkaline earth silicate systems. The initial section discusses in detail the experimental observations for the ensemble of Raman studies of simple silicate glasses and melts. This section is likely to be only of interest to the spectroscopist; the major Raman bands observed as a function of silica content are shown schematically in Figure 1. The following section concerns the interpretation of these spectra in terms of structural models for silicate glasses and melts, beginning with the assignment of observed bands to specific structural features. The most generally accepted assignments are summarized, and the resulting structural models are compared, while the possibility of vibrational mode localization is discussed along with constraints it might place on such models. The next section considers the relation between vibrational spectra and molecular structure in more detail, and critically examines vibrational calculations which have been carried out for silicates. It is noted that until bonding in silicates is better understood, a rigorous correlation between vibrational spectra and structure will not be possible. The final section summarizes the major features of the Raman spectroscopic studies, and discusses applications and current limitations of the method in structural studies of silicate melts and glasses.

Review of general experimental observations

Most of the experimental studies discussed below have examined the Raman spectra of alkali and alkaline earth silicate glasses, although a few have obtained spectra of their melts as noted above. The glass compositions studied have generally been determined by a variety of experimental factors. The alkali silicate systems show no stable liquid immiscibility (Levin et al., 1964; Toropov et al., 1972), and glass series have been prepared continuously from silica to near the metasilicate composition. Glasses with higher alkali content have not yet been studied due to difficulties of preparation and problems of hydrolysis in air. The alkaline earth silicates (except for $\text{SiO}_2\text{-BaO}$) show large two-liquid regions at high silica content and their glass series have usually not been studied to as high silica content as the alkali silicate glasses, although McMillan (1981, 1984) examined CaO-MgO-SiO_2 glasses with compositions within the two-liquid field. However, alkaline earth silicate glasses have been prepared and studied to much lower silica content than the alkali

Table 1. Previous Raman spectroscopic studies of silicate glasses and melts

Pringsheim and Rosen (1928)	Unsuccessful attempt to obtain Raman spectrum of SiO_2 glass.
Hollaender and Williams (1929)	Obtained Raman spectrum of high-silica plate glass.
Gross and Romanova (1929)	Raman spectrum of SiO_2 glass.
Hollaender and Williams (1931)	SiO_2 and high-silica optical glasses.
Bhagavantam (1931)	High-silica optical glasses.
Kujumzelis (1935, 1936)	SiO_2 and high-silica optical glasses.
Langenberg (1937)	SiO_2 glass; commercial glasses.
Vuks and Ioffe (1938)	$\text{SiO}_2\text{-Na}_2\text{O}$ glass series.
Hibben (1939, p. 408-424)	Review article.
Norris (1941)	High-silica optical glasses.
Rank and Douglas (1948)	SiO_2 and high-silica commercial glasses.
Ruess (1949, 1950)	High-silica commercial glasses; review article.
Vuks and Ioffe (1949a,b)	$\text{SiO}_2\text{-Na}_2\text{O}$ glass series; multicomponent high-silica glasses.
Prod'homme (1951, 1954)	SiO_2 glass; high-silica commercial glasses.
Gross and Kolesova (1952, 1953)	$\text{SiO}_2\text{-K}_2\text{O}$, $\text{SiO}_2\text{-Na}_2\text{O}$ and $\text{SiO}_2\text{-Li}_2\text{O}$ glass series.
Krishnan (1953)	SiO_2 glass.
Wilmot (1954)	$\text{SiO}_2\text{-Na}_2\text{O}$ glass series.
Harrand (1954)	SiO_2 glass; polarized.
Bobovich and Tulub (1956, 1957, 1958a-d, 1959); Bobovich et al. (1955)	$\text{SiO}_2\text{-K}_2\text{O}$, $\text{SiO}_2\text{-Na}_2\text{O}$ glass series; other high silica glasses; polarized spectra; vibrational calculations.
Flubacher et al. (1959)	SiO_2 glass; polarized.
Simon (1960)	Review article.
Sidorov (1967)	$\text{Na}_2\text{O-SiO}_2$ glasses doped with variety of components; spectra above 700 cm^{-1} only.
Sidorov and Prudnikova (1968)	$\text{Na}_2\text{O-SiO}_2$ glasses with As, Sb.
Tobin and Baak (1968)	SiO_2 glass; high-silica commercial glasses; polarized spectra.
Hass (1969)	SiO_2 glass; low-frequency (< 800 cm^{-1}) region only; temperature dependence.
Etchepare (1970a,b)	$\text{SiO}_2\text{-Na}_2\text{O}$, $\text{SiO}_2\text{-BaO}$, $\text{SiO}_2\text{-SrO}$ glass series; vibrational calculations.
Etchepare (1970c, 1972)	$\text{CaMgSi}_2\text{O}_6$ glass; polarized.
Stolen et al. (1970)	Neutron-irradiated SiO_2 glass (< 800 cm^{-1} only).
Gaskell (1970)	$\text{Na}_2\text{Si}_2\text{O}_7$ glass; vibrational calculation.
Hass (1970)	$\text{SiO}_2\text{-Na}_2\text{O}$ glass series.
Wong and Angell (1971; 1976, p. 436-451).	Review article.
Sweet et al. (1973); White (1975)	SiO_2 , $\text{Na}_2\text{Si}_2\text{O}_7$ glasses.
Bates et al. (1974)	Neutron-irradiated SiO_2 glass.
Parke (1974)	Review article.
Hagiwara and Oyamada (1974a,b)	$\text{SiO}_2\text{-PbO}$ and $\text{SiO}_2\text{-Na}_2\text{O}$ glasses.
Brawer (1975)	K-, Na- and Li- meta- and disilicate glasses; vibrational calculations.
Brawer and White (1975)	$\text{SiO}_2\text{-K}_2\text{O}$, Na_2O and Li_2O glass series; vibrational calculations.
Smith et al. (1975)	High-silica optical glass.
Iwamoto et al. (1975)	$\text{SiO}_2\text{-K}_2\text{O}$ glass series.
Winterling (1975)	SiO_2 glass; below 600 cm^{-1} ; especially low-frequency region.

Table 1. (cont.)

Walrafen and Stone (1975), Walrafen (1975)	SiO ₂ glass.
Konijnendijk (1975)	Wide range of alkali and alkaline earth glasses, and more complex compositions.
Konijnendijk and Buster (1975)	Various SiO ₂ -M ₂ O-MO glasses.
Galeener and Lucovsky (1976a)	SiO ₂ glass; polarized.
Galeener and Lucovsky (1976b)	Second order spectrum for SiO ₂ glass.
Stolen (1976)	SiO ₂ glass (< 900 cm ⁻¹ only).
Verweij and Konijnendijk (1976); Konijnendijk and Stevels (1976)	SiO ₂ -K ₂ O glass series; other SiO ₂ -M ₂ O-MO glasses.
Kato (1976a,b)	High-silica glasses.
Stolen and Walrafen (1976)	SiO ₂ glass; high-silica SiO ₂ -K ₂ O glass (high-frequency only).
Brawer and White (1977a)	Na-, Ca- and Mg-silicate and aluminosilicate glass series.
Brawer and White (1977b)	Na ₂ Si ₃ O ₇ glass, and other compositions, doped with chromium.
Sidorov et al. (1977)	Various Na ₂ O-TiO ₂ -SiO ₂ glasses.
Konijnendijk and Buster (1977)	SiO ₂ -K ₂ O glass series; other silicate glasses; glasses containing sulphate.
Brawer and White (1978)	Li ₂ Si ₂ O ₅ , Na ₂ Si ₃ O ₇ glasses; polarized; doped with Fe ₂ O ₃ .
Laughlin et al. (1978)	SiO ₂ glass; borosilicate glass; vibrational calculation.
Furukawa et al. (1978)	PbO-SiO ₂ glass series; deconvolutions; polarized spectra.
Worrell and Henshall (1978)	PbO-SiO ₂ glass series; polarized.
Sharma et al. (1978a)	SiO ₂ -Na ₂ O glasses and melts.
Sharma et al. (1978b)	Aluminosilicate glasses; polarized.
Sharma et al. (1979)	CaMgSi ₂ O ₆ glass; polarized; aluminosilicate glasses.
Saissy et al. (1979)	SiO ₂ glass fibers; doped with P ₂ O ₅ and B ₂ O ₃ .
Murray and Greytak (1979)	SiO ₂ glass; polarized.
Seifert et al. (1979)	Na ₂ SiO ₃ glass; high-frequency region only.
Heiman et al. (1979)	SiO ₂ glass; optical glasses; polarized.
Chandrasekhar et al. (1979)	SiO ₂ -TiO ₂ glass series; polarized.
Sharma (1979) and Sharma and Yoder (1979)	CaMgSi ₂ O ₆ , Ca ₂ MgSi ₂ O ₇ and aluminosilicate glasses.
Piriou and Alain (1979)	SiO ₂ -PbO glasses; aluminosilicate glasses; polarized.
Furukawa and White (1979)	Li ₂ Si ₂ O ₅ glass; polarized.
Verweij (1979a,b)	M ₂ SiO ₃ (M = K, Na) and M ₂ Si ₂ O ₅ (M = K, Na, Li) glasses; polarized.
Mysen et al. (1980a,b,c,d; 1981a,b), Virgo et al. (1980) and Mysen and Virgo (1980a,b,c)	Wide range of alkali and alkaline earth silicate, aluminosilicate and other glasses; band deconvolutions.
Piriou and Arashi (1980)	SiO ₂ -PbO glasses; polarized; deconvolutions.
Mikkelsen and Galeener (1980)	SiO ₂ glass; VV polarized only.
Furukawa and White (1980)	SiO ₂ , K ₂ SiO ₃ , Na ₂ Si ₂ O ₅ and Na ₂ SiO ₃ glasses; deconvolution.
Kashio et al. (1980)	SiO ₂ -Na ₂ O and SiO ₂ -CaO glass and melt series.
Sharma et al. (1981)	SiO ₂ glass; polarized.
Shibata et al. (1981)	Various high-silica glasses.
Windisch and Risen (1981)	(Na, Li) ₂ Si ₂ O ₅ glasses.
Tsunawaki et al. (1981)	SiO ₂ -CaO glass series.

Table 1. (cont.)

Furukawa et al. (1981)	SiO ₂ -Na ₂ O glass series; polarized; deconvolutions; vibrational calculation.
McMillan et al. (1981), Piriou and McMillan (1983a)	CaMgSiO ₄ glass; polarized.
Bihuniak and Condrate (1981)	Various high-silica glasses.
Sproson et al. (1981)	SiO ₂ and high-silica optical glass fibers.
Sharma and Simons (1981)	Aluminosilicate glasses; polarized.
Seifert et al. (1981)	SiO ₂ -Na ₂ O and aluminosilicate glasses and melts; temperature-reduced spectra.
Walrafen and Krishnan (1981)	High-pressure SiO ₂ glass.
Galeener and Mikkelsen (1981)	SiO ₂ glass; polarized; oxygen isotopic exchange.
Galeener (1982a,b)	SiO ₂ glass; polarized; temperature reduced.
Mysen et al. (1982a)	SiO ₂ -Na ₂ O, BaO, CaO, (Ca _{0.5} Mg _{0.5})O and MgO glass series; deconvolutions; review article.
Mysen et al. (1982b)	SiO ₂ -CaO glasses; high-frequency region only; deconvolutions.
Seifert et al. (1982)	Aluminosilicate glasses; deconvolutions.
Phillips (1982)	Review article.
Bertoluzza et al. (1982)	Raman spectra of silica gels and glass.
White (1982)	Heat-treated Li ₂ Si ₂ O ₅ and sodium silicate glasses.
McMillan and Piriou (1982, 1983a), McMillan et al. (1982)	Various aluminosilicate glass series; polarized; deconvolution.
McMillan and Piriou (1983b)	SiO ₂ -Na ₂ O and (Ca _{0.5} Mg _{0.5})O glass series; aluminosilicate glasses; review article; polarized.
Piriou and McMillan (1983b)	SiO ₂ , CaSiO ₃ , CaMgSiO ₄ and aluminosilicate glasses; polarized.
Sharma et al. (1983)	Various aluminosilicate glasses; polarized.
Matson et al. (1983)	High-silica SiO ₂ -M ₂ O (M = Li, Na, K, Rb, Cs) glasses; difference spectra.
Müller et al. (1983)	CaO-Al ₂ O ₃ -SiO ₂ glasses.
Galeener et al. (1983)	SiO ₂ and related glasses; also neutron scattering and infrared reflection data.
Galeener and Geissberger (1983)	SiO ₂ glass; silicon isotopic exchange.
McMillan (1984)	CaO-MgO-SiO ₂ glasses: polarized; deconvolutions.

series, extending the composition range to near the orthosilicate composition.

Previous Raman spectroscopic studies on silicate melts and glasses are summarized in Table 1. (For the sake of completeness, this table also includes work on more complex compositions, such as borosilicate and aluminosilicate systems, but which are not discussed in the text.) Within these studies, spectra for similar glass compositions are generally comparable. Some slight differences may be ascribed to compositional errors, such as those induced by alkali oxide loss on heating (e.g., Seifert et al., 1979). Measured positions of well-resolved bands generally agree to within ± 5 cm⁻¹, which is reasonable considering the large band widths involved, while reported positions of poorly-resolved bands may vary more than this. In general, the degree of resolution of individual bands for comparable experimental conditions decreases in the order Cs >

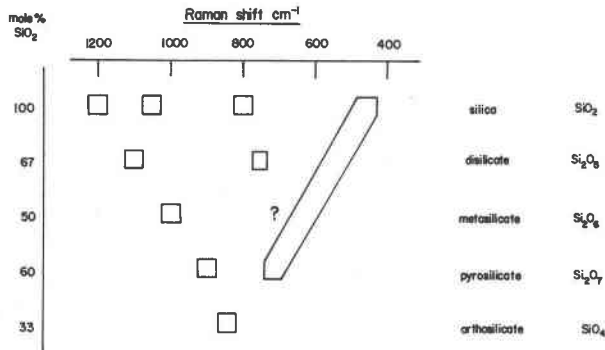


Fig. 1. Schematic of major band groups maximized as a function of silica content in alkali and alkaline earth glass and melt series. The low-frequency (700–400 cm^{-1}) group is shown here as a single continuously varying band. In fact, discrete bands are observed in this region (see text), but their behavior with composition is not yet well characterized.

$\text{Rb} > \text{K} > \text{Na} > \text{Li} > \text{Ca} > \text{Mg}$ for systems studied (e.g., Brawer and White, 1975, 1977a; Brawer, 1975; Mysen et al., 1980a; McMillan, 1981, 1984; Matson et al., 1983).

A number of studies have used deconvolution or curve-fitting techniques to separate such unresolved bands into component sets (e.g., Furukawa et al., 1978; Piriou and Arashi, 1980; Furukawa and White, 1980; Mysen et al., 1980a,b,c,d, 1981a,b, 1982a,b; Mysen and Virgo, 1980a; McMillan, 1981, 1984; Seifert et al., 1982; McMillan et al., 1982). When there are sufficient experimental data and individual band shapes are known, deconvolution methods allow a good solution for component band number, positions and relative intensities within an unresolved envelope. In general, a single pure vibrational absorption band may be approximated by a Lorentzian function centered at the resonant frequency (e.g., Carrington and McLachlan, 1979, p. 9–11). In vitreous systems, there is some distribution of individual geometries which will result in a distribution of vibrational resonant frequencies. At the same time, there will be vibrational coupling with some degree of coherence between vibrating units, which will also affect the observed band shape. The above effects are not yet well understood, and vibrational band shapes for glassy systems are not yet known. In most of the above work on silicate glasses, the component Raman bands have been approximated by Gaussian functions. Although most of these studies have given reasonable agreement with the observed spectra, none of the fits reproduce the experimental spectra exactly. This may be due to a variety of factors: noise in the experimental spectra, deviations of the true component bands from Gaussian shape, weak true component bands not considered in the fit, errors in the chosen component band set, or baseline corrections not accounted for.

In order that the fit be as realistic as possible, a number of constraints have been placed on the various fitting models. In all fits, the major component bands must correspond to unresolved peak maxima and slope changes in the experimental spectra. This constrains the minimum number of major components and their general position, and is more complete when carried out for both parallel (VV) and perpendicular (VH) polarized spectra. Fitting of weaker bands is generally carried out by difference, using statistical techniques to achieve a best fit, or by making further assumptions as to the behavior of the major components.

To summarize the results on the alkali and alkaline earth glass series, it is useful to consider their spectra in three regions: (1) the high-frequency region between 1200 and 800 cm^{-1} ; (2) the low-frequency region between 700 and 400 cm^{-1} , and (3) the mid-range region between 800 and 700 cm^{-1} . The band groups discussed below are schematized in Figure 1.

The high-frequency region

The spectrum of vitreous silica shows two weak, depolarized bands (depolarization ratio $\rho \sim 0.75$: Furukawa et al., 1981) near 1200 and 1060 cm^{-1} . Seifert et al. (1982) and Mysen et al. (1982a) have suggested that the 1200 cm^{-1} band may be split into two components, at 1160 and 1209 cm^{-1} . For compositions between silica and the orthosilicate, the high-frequency region of the glass and melt spectra may be expressed in terms of four bands near 1100–1050 cm^{-1} , 1000–950 cm^{-1} , 900 cm^{-1} , and 850 cm^{-1} (e.g., Virgo et al., 1980; Mysen et al., 1980a, 1982a). These bands appear successively in that order as the silica content is decreased, with the 1100–1050 cm^{-1} band maximized in relative intensity near the disilicate composition, the 1000–950 cm^{-1} band near the metasilicate composition, and the 900 and 850 cm^{-1} bands respectively maximized near the pyrosilicate and orthosilicate compositions (Furukawa et al., 1981; Mysen et al., 1982a; McMillan, 1981, 1984).

The 1100–1050 cm^{-1} band. The band appears on initial addition of M_2O to silica in the alkali silicate glass series (e.g., Hass, 1970; Brawer and White, 1975; Konijnendijk, 1975; Verweij and Konijnendijk, 1976; Konijnendijk and Stevels, 1976; Mysen et al., 1980a, 1982a; Furukawa et al., 1981; Matson et al., 1983), and is a major component in the spectra of high-silica alkaline earth glasses (e.g., Etchepare, 1970a; Virgo et al., 1980; Mysen et al., 1980a, 1982a,b; Mysen and Virgo, 1980; McMillan, 1981, 1984). The band appears near 1100 cm^{-1} for K- and Na-series, near 1080 cm^{-1} for Li-series and near 1060 cm^{-1} for Mg-, Ca-, Sr- and Ba-series, while its width at half height (the "band width") increases from near 50 cm^{-1} for Na- and K-series to near 100 cm^{-1} for Li- and alkaline earth glass series. A few polarized (i.e., where parallel (VV) and perpendicular (VH) spectra have been obtained separately) Raman studies have been carried out for these glasses. The depolarization ratio ρ is defined as $I_{\text{VH}}/I_{\text{VV}}$ (Herzberg, 1945, p. 246–249). Only totally symmetric vibrations of systems with cubic point symmetry are completely polarized, with $\rho = 0$. Antisymmetric vibrations (B, E or F symmetry) are fully depolarized, with $\rho = 0.75$, while all other vibrations have intermediate depolarization ratios. These correspond to symmetric modes of non-cubic point groups, and to non-totally symmetric vibrations of cubic groups. Such vibrations are referred to here as partially polarized. Furukawa and White (1979) suggested that the 1080 cm^{-1} band for $\text{Li}_2\text{Si}_2\text{O}_5$ glass was completely polarized, while Verweij (1979b) found the same band to have a depolarization ratio of 0–0.1 for $\text{Li}_2\text{Si}_2\text{O}_5$, $\text{Na}_2\text{Si}_2\text{O}_5$ and $\text{K}_2\text{Si}_2\text{O}_5$ glasses. McMillan (1984) found the 1056 cm^{-1} band for the $\text{SiO}_2\text{–CaMgSiO}_4$ glass series to have $\rho \sim 0.2$. The 1100–1050 cm^{-1} band decreases rapidly in relative intensity for compositions less silica-rich than the disilicate (Furukawa et al., 1981; McMillan, 1981, 1984), although a contribution may still be present near the orthosilicate composition (McMillan, 1984; also Mysen et al., 1982a), and may show a slight frequency decrease to near 1050 cm^{-1} for the alkali series between the disilicate and metasilicate compositions (e.g., Brawer and White, 1975; Verweij and Konijnendijk, 1976; Mysen et al., 1980a, 1982a; Furukawa et al., 1981). There is no evidence for such a

frequency decrease in the alkaline earth series, but this could be obscured by the poor band resolution.

Some workers have noted additional weak bands near 1100 cm^{-1} at high silica content. First, for compositions between silica and the disilicate in K- and Na-series, the 1100 cm^{-1} band has a shoulder near $1120\text{--}1180\text{ cm}^{-1}$ which appears to have a higher depolarization ratio than the 1100 cm^{-1} band. (Brawer and White, 1975; Iwamoto et al., 1975; Verweij and Konijnendijk, 1976; Konijnendijk and Stevels, 1976; Furukawa and White, 1980; Mysen et al., 1980a, 1982a; Furukawa et al., 1981). Matson et al. (1983) have obtained difference spectra for high-silica glasses $\text{SiO}_2\text{--M}_2\text{O}$ ($M = \text{Li, Na, K, Rb, Cs}$), and observed a shoulder near 1150 cm^{-1} which they found to be polarized. However, this shoulder decreases in relative intensity with decreasing silica content, unlike the major $1100\text{--}1050\text{ cm}^{-1}$ band, and is no longer observed after the disilicate composition. It is possible that this weak $1120\text{--}1180\text{ cm}^{-1}$ band is related to the 1200 cm^{-1} band described earlier for vitreous silica, or to a species similar to that responsible for the major 1100 cm^{-1} band (Matson et al., 1983).

Verweij (1979b) observed a broad depolarized band ($\rho = 0.6\text{--}0.8$) near 1080 cm^{-1} for $\text{K}_2\text{Si}_2\text{O}_5$ and $\text{Na}_2\text{Si}_2\text{O}_5$ glasses, and near 1050 cm^{-1} for $\text{Li}_2\text{Si}_2\text{O}_5$ glass. Brawer and White (1978) suggested that this depolarized band had two components at 1065 and 1045 cm^{-1} , although Furukawa and White (1979) found only a single depolarized band at 1038 cm^{-1} for the same glass. Furukawa et al. (1981) observed a depolarized band near 1080 cm^{-1} between silica and the disilicate composition for the Na-series, whose depolarized band maximum decreased sharply to near 1050 cm^{-1} between the disilicate and metasilicate. It is probable that a depolarized band near 1080 cm^{-1} is associated with the major 1100 cm^{-1} band for K- and Na-series, while a similar depolarized band may be present for Li-series. McMillan (1981, 1984) suggested a weak depolarized ($\rho = 0.5\text{--}0.8$) band at 1154 cm^{-1} for the $\text{SiO}_2\text{--CaMgSiO}_4$ glass series, over a similar composition range to the major 1056 cm^{-1} band.

The 1000–950 cm^{-1} band. In unpolarized spectra of alkali silicate glass series, a band is first observed near 950 cm^{-1} (for Na- and Li-series; near $930\text{--}940\text{ cm}^{-1}$ for K-series) near 20 mole% M_2O . The band remains at these frequencies and increases in relative intensity with increasing M_2O content until just before the metasilicate composition (e.g., Brawer and White, 1975; Iwamoto et al., 1975; Verweij and Konijnendijk, 1976; Mysen et al., 1980a, 1982a). Between 40 and 50 mole% M_2O , and for unpolarized spectra, it appears that the frequency of this band increases sharply to near 980 cm^{-1} (for Na_2SiO_3 glass; 970 cm^{-1} for K_2SiO_3 glass). Previous descriptions of these unpolarized glass spectra have considered that the 950 and 980 cm^{-1} bands are the same band, whose frequency increases sharply just before the metasilicate composition, and whose relative intensity increases smoothly with M_2O content to become maximized at the metasilicate. However, examination of polarized spectra of these glass series shows the interpretation to be more complex (e.g., Brawer and White, 1978; Furukawa and White, 1979; Verweij, 1979a,b; Furukawa et al., 1981). Comparison of VV and VH spectra suggests that the 950 cm^{-1} band has a higher depolarization ratio than the major band near 970 cm^{-1} which appears later in the composition series, and which does not appear in the VH spectra. There are several possible explanations for this apparent problem. First, the major 970 cm^{-1} band may be unrelated to the depolarized 950 cm^{-1} band, and grows rapidly only on approaching the metasilicate

composition. Second, there could be errors in measuring frequencies of the weak bands in the VH spectra, and the 950 cm^{-1} band could in fact correspond to the 970 cm^{-1} VV band. Finally, the 970 and 950 cm^{-1} bands could be due to related but different vibrations, the 970 cm^{-1} band only becoming strongly Raman-active just before the metasilicate composition.

Mysen et al. (1982a) have obtained unpolarized spectra for the series BaO--SiO_2 , where the high-frequency bands are well-resolved. As for the alkali series, they find a weak band near 950 cm^{-1} at 75 mole% silica. However, these authors suggest that the band decreases in frequency (to near 935 cm^{-1}) until near 60 mole% SiO_2 , then increases to near 950 cm^{-1} for the metasilicate where it forms the major band. The behavior of this band for the Ca-, Mg- and (Ca + Mg)-series is less clear due to the poor band resolution in these systems (e.g., Virgo et al., 1980; Mysen and Virgo, 1980a; Mysen et al., 1980a,b, 1982a; Kashio et al., 1980; Tsunawaki et al., 1981; McMillan 1981, 1984). The band appears near $980\text{--}960\text{ cm}^{-1}$ for all these series. Mysen et al. (1982a) suggest that this band does show a frequency change with composition for the Ca-series, while McMillan (1984) found no evidence of significant change for the (Ca + Mg)-series. These differences are probably partly due to the different deconvolution procedures. In fact, it is likely that small frequency changes do occur with composition for all these bands, but these may not yet be well characterized.

McMillan (1981, 1984) found the 972 cm^{-1} band for the (Ca + Mg)-series to be highly polarized ($\rho \sim 0.1$); slightly more polarized than the 1050 cm^{-1} band ($\rho \sim 0.2$) discussed in the previous section.

The 900 cm^{-1} band. A major band near 900 cm^{-1} has only been explicitly observed for the alkaline earth series (e.g., Kashio et al., 1980; Virgo et al., 1980; Mysen et al., 1980a,b,d, 1981a, 1982a,b; Mysen and Virgo, 1980a; McMillan, 1981, 1984; McMillan and Piriou, 1983b). The band is maximized in relative intensity near the pyrosilicate composition (Virgo et al., 1980; Mysen et al., 1980a, 1982a; McMillan, 1981, 1984), and is only resolved for a narrow range of compositions near the pyrosilicate. Its presence in higher silica glass spectra has been deduced from band deconvolutions (e.g., Mysen et al., 1980a, 1982a,b; McMillan, 1981, 1984), and is first observed in this way between the metasilicate and disilicate compositions. It is possible that this 900 cm^{-1} band may be present in spectra of alkali silicate glass series, but unresolved from the major $1000\text{--}950\text{ cm}^{-1}$ band (see Mysen et al., 1982a). McMillan (1984) found the 906 cm^{-1} band for the $\text{SiO}_2\text{--CaMgSiO}_4$ glass series was highly polarized, with a similar depolarization ratio ($\rho \sim 0.1$) to the 972 cm^{-1} band discussed in the previous section. The band width found for the 906 cm^{-1} band ($\sim 80\text{ cm}^{-1}$) was noticeably lower than those for the major 1058 and 972 cm^{-1} band ($\sim 100\text{ cm}^{-1}$) discussed above, but comparable to that of the band near 850 cm^{-1} considered below (McMillan, 1984). The major 906 cm^{-1} band could be associated with a weak depolarized contribution near $1040\text{--}1080\text{ cm}^{-1}$ (McMillan, 1984).

The 850 cm^{-1} band. This band first appears near 40 mole % M_2O in the alkali silicate glass series, near 860 cm^{-1} for Li- and Na-series, and near 830 cm^{-1} for K-glasses (e.g., Brawer and White, 1975; Verweij and Konijnendijk, 1976; Kashio et al., 1980; Mysen et al., 1980a; Furukawa et al., 1981). The band increases in relative intensity with increasing M_2O content but is still weak at the metasilicate, and is highly polarized (Verweij, 1979a; Furukawa et al., 1981). In alkaline earth series, the band is present in the highest silica glasses studied (generally 30–40

mole % MO), and is found near 860 cm^{-1} for Ca-, (Ca + Mg)- and Mg-series (e.g., Kashio et al., 1980; Virgo et al., 1980; Mysen et al., 1980a,b,d, 1981a, 1982a,b; Mysen and Virgo, 1980a; McMillan et al., 1981; McMillan and Piriou, 1983b; McMillan, 1981, 1984), and near 850 cm^{-1} for Ba-series (Mysen et al., 1982a). McMillan (1984) found the 862 cm^{-1} band for the SiO_2 - CaMgSiO_4 series to be completely polarized ($\rho < 0.1$) within experimental error. This 862 cm^{-1} band was probably also associated with a weak, depolarized band near 933 cm^{-1} (McMillan et al., 1981; Piriou and McMillan, 1983a).

The low-frequency region

Vitreous silica shows a strong band at 430 cm^{-1} . This band is asymmetric, partly due to weak bands near 270 and 380 cm^{-1} which correspond to maxima in the depolarized spectrum (Walrafen and Stone, 1975; McMillan et al., 1982), partly to thermal population effects (e.g., Hass, 1969; Leadbetter and Stringfellow, 1974), and is highly polarized. Two weak, sharp peaks which also appear polarized are observed near 500 and 600 cm^{-1} . The origin of these weak peaks is controversial. They were originally attributed to structural defects in vitreous silica associated with broken Si-O-Si bonds (e.g., Stolen et al., 1970; Bates, 1972; Bates et al., 1974; Stolen and Walrafen, 1976) Galeener and Lucovsky (1976a) suggested that the 500 cm^{-1} peak was due to a longitudinal component associated with the major 430 cm^{-1} mode (see later), retaining the broken bond model for the 600 cm^{-1} peak (Lucovsky, 1979). This model has been criticized by Matson et al. (1983). Mikkelsen and Galeener (1980) and Galeener (1982a) proposed the 600 cm^{-1} peak to be related to a specific vibration of small siloxane rings within the glass, while Sharma et al. (1981) applied this argument to the 500 cm^{-1} peak, retaining a broken-bond assignment for the 600 cm^{-1} mode. Matson et al. (1983) considered both broken-bond and ring defect models possible for this latter peak. Galeener (1982b) suggested that both the 500 and 600 cm^{-1} peaks were due to four- and three-membered siloxane rings. Finally, Phillips (1982) has recently proposed a model for defects in vitreous silica involving doubly-bonded silicon-oxygen linkages, but this does not seem to be supported by preliminary *ab initio* molecular calculations (M. O'Keeffe and G. V. Gibbs, pers. comm., 1983; in prep.). These peaks are not discussed further here; it is only noted that they appear characteristic of the Raman spectrum of vitreous silica.

On addition of alkali or alkaline earth oxide, the 430 cm^{-1} band of vitreous silica decreases in relative intensity, disappearing at between 25 mole % (for K-series) and 50 mole % (for Mg-series) metal oxide. This band is replaced by a system of bands at progressively higher frequency with decreasing silica content. These bands are poorly-resolved for all but the series SiO_2 - K_2O (e.g., Iwamoto et al., 1975; Brawer and White, 1975; Konijnendijk and Stevels, 1976; Verweij and Konijnendijk, 1976), which is described first. On initial addition of K_2O to silica (10 mole % K_2O), the sharp 500 cm^{-1} peak of vitreous silica appears to increase in intensity. At 20 mole % K_2O , this band dominates the low-frequency region, and has moved to 520 cm^{-1} . At the same time, a band near 590 cm^{-1} has increased in intensity. By the disilicate composition, these bands are nearly equal in intensity, and the lower frequency band has increased in frequency to near 560 cm^{-1} . On continued addition of K_2O , the 560 cm^{-1} band shows no further frequency change, but decreases in relative intensity and is only a weak shoulder at the metasilicate composition. The 590 cm^{-1} band shows no

frequency change with composition, and is the dominant low-frequency band for K_2SiO_3 glass.

Similar changes with decreasing silica content are observed for the Na- and Li-glass series (e.g., Hass, 1970; Brawer and White, 1975; Konijnendijk, 1975; Mysen et al., 1980a, 1982a, Furukawa et al., 1981). The initial bands in these series also appear near 520 cm^{-1} , but rapidly become unresolved from the increasing band at higher frequency, near 590 cm^{-1} . The 520 cm^{-1} band appears to show a similar frequency increase with M_2O content as for the K-series, but this is partly obscured by the poor band resolution.

Similar bands are observed with increasing MO content in the alkaline earth series (e.g., Etchepare, 1970b; Virgo et al., 1980; Kashio et al., 1980; Mysen et al., 1980a,b, 1982a; Mysen and Virgo, 1980a; Tsunawaki et al., 1981; McMillan, 1981, 1984; McMillan and Piriou, 1983). For the Ba-series near the disilicate, two bands are just resolved near 540 and 600 cm^{-1} (Etchepare, 1970b; Mysen et al., 1982a). As the BaO content is increased, the band system changes to give an unresolved asymmetric band whose frequency maximum increases to near 600 cm^{-1} near the metasilicate composition. The band asymmetry suggests at least one other band at higher frequency. Ca-, Mg- and (Ca + Mg)-series have been prepared to near the orthosilicate composition (e.g., Virgo et al., 1980; Mysen et al., 1980a, 1982a; McMillan et al., 1981; McMillan, 1981, 1984). For higher MO content than the metasilicate, the low-frequency band continues to increase in frequency to near 700 cm^{-1} for the pyrosilicate, and becomes more symmetric. Between the pyrosilicate and the orthosilicate, this band remains near 700 cm^{-1} but decreases in relative intensity.

The polarized Raman studies of Brawer and White (1977b, 1978), Verweij (1979a,b), Furukawa and White (1979) and Furukawa et al. (1981) suggest that the 520 - 560 cm^{-1} and 590 cm^{-1} bands for the alkali series are always highly polarized, although the weak 560 cm^{-1} band near the metasilicate composition in the SiO_2 - K_2O series shows a significant peak in the VH spectrum (Verweij, 1979a). McMillan (1984) found the asymmetric band near 600 cm^{-1} and the band at 700 cm^{-1} for the (Ca + Mg)-series to be highly polarized.

It was suggested above that the bands near 500 and 600 cm^{-1} observed on initial addition of M_2O to vitreous silica might be related to the sharp bands in the silica spectrum at these frequencies; however, this is considered unlikely. For very small additions of Na_2O (Mysen et al., 1982a) or CaO (McMillan, 1984) to silica, the 500 and 600 cm^{-1} bands of silica glass are observed to decrease in intensity along with the silica glass spectrum. The bands which develop on further addition of Na_2O or CaO are then new bands. Also, high-silica SiO_2 -CaO and SiO_2 -MgO glasses show a new band growing near 610 cm^{-1} , as a shoulder on the 600 cm^{-1} peak of vitreous silica, with addition of MO (McMillan, 1981, 1984). The 520 - 560 and 590 - 610 cm^{-1} bands observed in the SiO_2 - M_2O and SiO_2 -MO glass series are then not simply derived from the 500 and 600 cm^{-1} bands of vitreous silica, but are new bands introduced with addition of metal oxide. However, their frequencies are similar to those of the silica bands, which may suggest that they are due to similar vibrations in both silica and the other silicate glasses.

The mid-range region

The spectrum of silica glass shows an asymmetric band near 800 cm^{-1} , with probable components near 790 and 830 cm^{-1} (e.g., Mysen et al., 1982a). Comparison of VV and VH spectra shows that the lower frequency component has a higher

depolarization ratio than the other, although neither are highly polarized (e.g., McMillan, 1984; McMillan et al., 1982). On addition of alkali or alkaline earth oxide, this band moves to lower frequency (to near 770 cm^{-1} at the metasilicate composition), and shows different asymmetry. The band is no longer clearly observed after the metasilicate composition (e.g., Virgo et al., 1980; Mysen et al., 1980a, 1982a; McMillan, 1981, 1984).

Interpretation of spectra

Assignment of observed Raman bands

Most of the Raman spectroscopic studies discussed in the preceding section have assigned the Raman bands summarized above to specific types of vibration of various structural units, and hence developed models for the glass or melt structure. The arguments used in such assignments have mainly been based on observed band positions and symmetry character, examination of systematic changes in spectra with composition, and comparison of corresponding glass and crystal spectra. The assignments discussed below are the most generally accepted in the current literature. Many of the basic concepts were developed early in the history of Raman studies of silicate glasses (e.g., Gross and Kolesova, 1952, 1953; Bobovich and Tulub, 1958a–d, 1959), but most have been modified over the past decade. Most of the Raman studies have primarily considered band assignments related to vibrations of the silicate units, which are generally described in terms of tetrahedral SiO_4 groups in various states of polymerization by corner-sharing of oxygen between tetrahedra (e.g., Liebau, 1980). This is consistent with the results of diffraction and other spectroscopic experiments on vitreous and molten silicates (e.g., Urnes, 1960, 1969; Mozzi and Warren, 1969; Domenici and Pozza, 1970; Narten, 1972; Konnert and Karle, 1973; Wright and Leadbetter, 1976; Waseda and Toguri, 1977; Nukui et al., 1978; Okazaki, 1979; Taylor and Brown, 1979; Misawa et al., 1980; Waseda, 1980, p. 133–158; Greaves et al., 1982), and with the structures of corresponding crystalline phases.

The high-frequency region. It was concluded in the previous section that the high-frequency spectra of alkali and alkaline earth silicate glasses or melts could be described in terms of combinations of four major polarized Raman bands; at $1100\text{--}1050\text{ cm}^{-1}$, $1000\text{--}950\text{ cm}^{-1}$, near 900 cm^{-1} , and near 850 cm^{-1} , each dominant at the disilicate, metasilicate, pyrosilicate and orthosilicate compositions respectively (see Fig. 1). These bands have generally been assigned to symmetric silicon-oxygen stretching motions of silicate units containing SiO_4 tetrahedra with respectively one, two, three and four non-bridging oxygens, denoted here as the groups $\equiv\text{SiO}$, $=\text{SiO}_2$, $-\text{SiO}_3$ and SiO_4 (Fig. 2). This was suggested independently by a number of workers, beginning in the mid-1950's, and has been accepted by most other workers

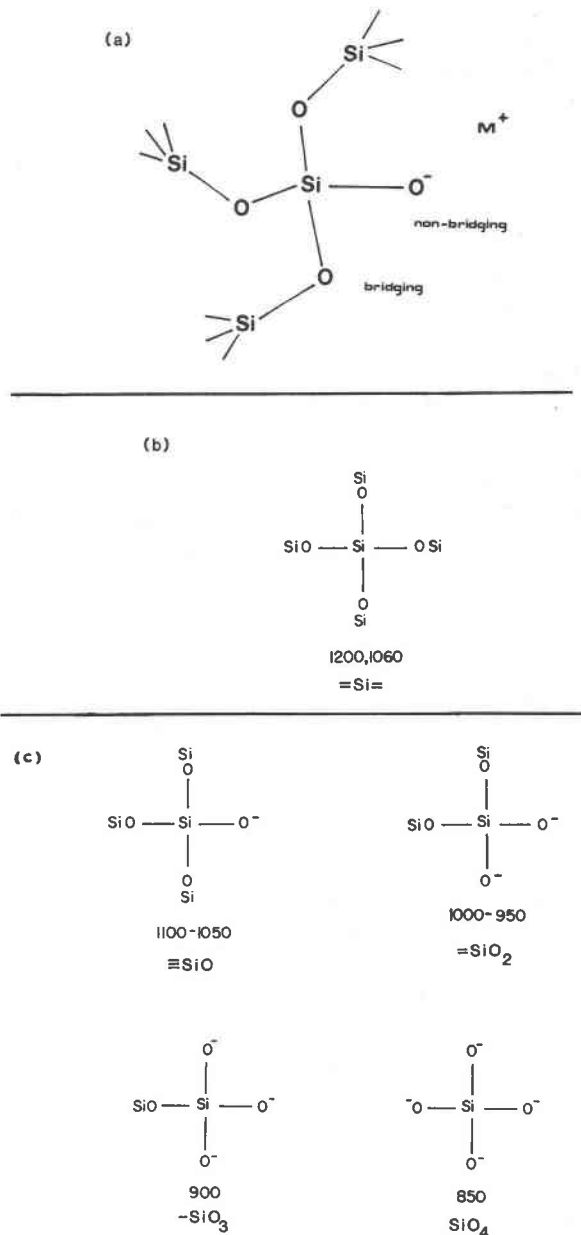


Fig. 2. Silicate structural units. (a) Schematic indicating the nature of bridging and non-bridging oxygen in the present context. M^+ may also refer to 0.5 M^{2+} , as in the alkaline earth series; (b) The weak, depolarized bands at 1200 and 1060 cm^{-1} are thought to correspond to asymmetric silicon-oxygen stretching vibrations within a fully-polymerized tetrahedral network $=\text{Si}=\text{O}$; (c) The four major polarized high-frequency bands are generally assigned to symmetric stretching vibrations of tetrahedral silicate units with one, two, three and four non-bridging oxygens.

in the field (see references in Table 1). These assignments have been rationalized by the following arguments.

The $1200\text{--}800\text{ cm}^{-1}$ region contains the highest frequency first-order Raman bands of silicate melts and

glasses, consistent with silicon-oxygen stretching vibrations of tetrahedral silicate groups (see e.g., Lazarev, 1972, p. 37–72; p. 163–164). The four dominant bands noted above are highly polarized, and that near 850 cm^{-1} may be completely polarized within experimental error. This would be consistent with a symmetric vibration with cubic point symmetry for the 850 cm^{-1} band, and symmetric vibrations of non-cubic symmetry for the $1100\text{--}1050\text{ cm}^{-1}$, $1000\text{--}950\text{ cm}^{-1}$ and 900 cm^{-1} band (e.g., Herzberg, 1945, p. 271). Finally, there is considerable similarity between the spectra of glass or melt and corresponding crystals at the disilicate, metasilicate, pyrosilicate and orthosilicate compositions (e.g., Gaskell, 1970; Etchepare, 1970c, 1972; Braver, 1975; Braver and White, 1975; Konijnendijk and Stevels, 1976; Verweij and Konijnendijk, 1976; Verweij, 1979a,b; Furukawa and White, 1979; Sharma and Yoder, 1979; McMillan et al., 1981; Piriou and McMillan, 1983a). Crystalline disilicates show major Raman bands near 1100 cm^{-1} which have been compared with the $1100\text{--}1050\text{ cm}^{-1}$ glass band maximized near the disilicate composition. Crystalline metasilicates show strong bands near 1000 cm^{-1} , comparable to the $1000\text{--}950\text{ cm}^{-1}$ glass band maximized near the metasilicate composition. Crystalline pyrosilicates and orthosilicates have their major high-frequency bands near 900 cm^{-1} and 850 cm^{-1} respectively, compared with the major glass bands near 900 cm^{-1} and 850 cm^{-1} maximized near the pyrosilicate and orthosilicate compositions.

Alkali disilicate crystals have structures based on infinite sheets of silicate tetrahedra. Each tetrahedron has three oxygens corner-shared with other silicate tetrahedra, known as bridging oxygens. One oxygen per tetrahedron is non-bridging, and is coordinated directly to metal cations (Fig. 2). Alkali and alkaline earth metasilicates are based on a variety of chain or ring structures, where each silicate tetrahedron has two bridging and two non-bridging oxygens. Pyrosilicates have structures in which two tetrahedra share an apex to give silicate dimer units, with one bridging and three non-bridging oxygens per tetrahedron. Finally, orthosilicates have silicate tetrahedra with only non-bridging oxygens (e.g., Wyckoff, 1963, 1968; Bragg et al., 1965; Deer et al., 1971). The similarities in the vibrational spectra of corresponding crystals and glasses were used here to suggest similar features in their molecular structures. (The term "molecular structure" is used to describe static structures within the glass, defined by relative atomic positions. This is distinguished from the "vibrational structure", which refers to atomic displacements during vibrational modes.) Combination of the preceding arguments has led to the band assignments summarized above, on which there is general agreement. However, there remains some uncertainty as to the extent of a structural unit characterized by these vibrational bands. For instance, is the $1100\text{--}1050\text{ cm}^{-1}$ band characteristic of an "infinite" sheet of $\equiv\text{SiO}$ units, as in disilicate crystals, or may it indicate the presence of

discrete $\equiv\text{SiO}$ groups, perhaps isolated from each other by other structural units? This important point is addressed in a later section.

It was noted in the previous section that there are a number of weak, depolarized high-frequency bands which seem associated with the major bands described above. It is likely that these are due to asymmetric stretching vibrations associated with the various silicate groups, although some second-order contribution from combinations of lower frequency bands is possible in this region. It was also noted previously that a band appeared near 940 cm^{-1} for glasses with 30–40 mole % SiO_2 , which increased in intensity with decreasing silica content, to apparently become the dominant $1000\text{--}950\text{ cm}^{-1}$ band near the metasilicate composition. Current band assignments do not yet provide any satisfactory interpretation of the detailed behavior of this band (see earlier, and e.g., Furukawa et al., 1981; p. 3228–3229).

Vitreous silica itself shows two weak, depolarized high-frequency bands at 1200 and 1060 cm^{-1} (or three, at 1060 , 1157 and 1209 cm^{-1} ; Mysen et al., 1982a). Raman spectra of crystalline tetrahedral silica polymorphs show two groups of bands centered near 1050 and 1200 cm^{-1} (Bates, 1972; Etchepare, 1972; McMillan et al., 1982). Diffraction studies on silica glass and melt suggest that their structures are based on some fully-polymerized three-dimensional network of corner-sharing SiO_4 tetrahedra, similar to those of its tetrahedral crystalline polymorphs such as quartz or cristobalite (e.g., Wyckoff, 1963, p. 312–322). The above observations have led most workers to assign the high-frequency bands to non-symmetric silicon-oxygen stretching vibrations within the framework structure. Galeener and Lucovsky (1976a) and Galeener (1982b) suggested that the two sets of high-frequency modes for vitreous silica were due to transverse and longitudinal vibrational components, separated in frequency by the electrostatic field in the glass (see e.g., Sherwood, 1972, p. 3–4, p. 20–22, p. 85–94). Mysen et al. (1980a, 1981b, 1982a) considered instead that the modes indicated the presence of two structural units, differing in average Si–O–Si angle, within the glass. McMillan et al. (1982) discussed these interpretations, and suggested that the two or more high-frequency bands of silica glass could be more simply be assigned to different vibrational modes associated with silicon-oxygen stretching within a single structure. However, a recent hyper-Raman scattering study by Denisov et al. (1978, 1980) seems to support the interpretation of the 1200 and 1060 cm^{-1} bands as a longitudinal-transverse pair (also Matson et al., 1983). The best interpretation of these bands is not yet clear, and must await a better understanding of the dynamics of vitreous silica.

The low-frequency region. All of the classes of crystalline silicates described above, except for the orthosilicates, show major Raman bands in the $700\text{--}400\text{ cm}^{-1}$ region. This observation has been used to suggest that bands in this region are associated with the presence of

bridging oxygens, or Si–O–Si linkages, in the structure (e.g., Lazarev, 1972, p. 64–66). The appearance of these bands in the silicate glass spectra has been generally taken as diagnostic of Si–O–Si linkages within the glass structure, or silicate units more polymerized than the orthosilicate.

In the present silicate glass series, the frequency of the 700–400 cm^{-1} band changes systematically with composition; this could be related to the degree of silicate polymerization. The band occurs at 430 cm^{-1} for silica with only bridging oxygens between $=\text{Si}=\text{Si}=\text{O}$ units, through 520–600 cm^{-1} then 590–650 cm^{-1} for linkages between $\equiv\text{SiO}$ and $=\text{SiO}_2$ units respectively, to near 700 cm^{-1} for $-\text{SiO}_3$ groups (see Fig. 1). A number of studies have shown that the frequencies of bands in this region are sensitive to the Si–O–Si bond angle (e.g., Etchepare, 1970a; Lazarev, 1972, p. 63–72; Scheetz, 1972; Brawer, 1975; Furukawa et al., 1981). If the nature of the vibration responsible for the 700–400 cm^{-1} band remains similar with changing silicate polymerization, it is possible that the systematic decrease in the frequency of this band with increasing silica content may be due to an increase in average Si–O–Si angle with polymerization.

The detailed nature of the vibrations responsible for the 700–400 cm^{-1} bands is not yet well understood. These bands are always highly polarized, suggesting symmetric motions. Lazarev (1972, p. 63–72) used group theory to describe the transition from orthosilicate to pyrosilicate, and concluded that the 700 cm^{-1} band of the pyrosilicate (Si_2O_7) unit was due to a symmetric stretching of the terminal $-\text{SiO}_3$ groups about the bridging oxygen. This is consistent with the $^{28}\text{Si}/^{30}\text{Si}$ substitution experiment of Tarte et al. (1973) for $\text{K}_2\text{Pb}_2\text{Si}_2\text{O}_7$, which has a linear Si–O–Si linkage. The large observed isotope shift for the 669 cm^{-1} Raman band suggests a major component of Si motion in this vibration. However, the isotopic study of Galeener and Mikkelsen (1981) for vitreous silica showed that its 430 cm^{-1} band involves a large displacement of the bridging oxygen. Some workers have suggested that the 700–400 cm^{-1} band group is due to symmetric motion of the bridging oxygen in the plane bisecting the Si–O–Si linkages (e.g., Bates, 1972; McMillan et al., 1982), while other but similar interpretations involving oxygen motion have been suggested (e.g., Bell and Dean, 1970). It is probable that the true nature of these vibrations lies between these two extremes of silicon and oxygen displacement, and that their character changes with changing polymerization of the silicate unit.

The mid-range bands. These bands near 800 cm^{-1} appear weak in the room-temperature spectrum of silica glass, but have a reasonable Raman intensity when the temperature-normalized spectrum is considered (e.g., Leadbetter and Stringfellow, 1974; McMillan et al., 1982). This, coupled with their low infrared activity (e.g., Miller 1968), has been used to suggest a fairly symmetric origin for these bands (Piriou and McMillan, 1983b). The bands have a high depolarization ratio which could be consistent

with symmetric vibrations of a point group with symmetry far from cubic within the isotropic glass. McMillan et al. (1982) have suggested that the bands near 800 cm^{-1} for vitreous SiO_2 are mainly associated with motions of silicon against its tetrahedral oxygen cage, with little associated oxygen displacement, which may involve a silicon motion symmetric about the bridging oxygen (Laughlin and Joannopoulos, 1977; Piriou and McMillan, 1983b). This would be consistent with the small observed isotope shift in the $^{18}\text{O}/^{16}\text{O}$ substitution experiment of Galeener and Mikkelsen (1981), and the large associated $^{28}\text{Si}/^{30}\text{Si}$ shift of Galeener and Geissberger (1983).

The Raman intensity of the band group decreases as the band becomes more asymmetric and moves to lower frequency (to near 770 cm^{-1}) with decreasing silica content and is no longer visible below around 60 mole % silica (e.g., Furukawa et al., 1981; Mysen et al., 1982a). Weak Raman bands are observed in the 700–800 cm^{-1} region for crystalline disilicates and the tetrahedral silica polymorphs, but generally not for less-polymerized silicates (e.g., Etchepare, 1972; Brawer and White, 1975; Verweij and Konijnendijk, 1976; Verweij, 1979a,b; Sharma and Yoder, 1979; Piriou and McMillan, 1983a; McMillan, 1984). If these modes are associated mainly with motion of silicon against its oxygen ‘‘cage’’, it is possible that such vibrations may only be present for highly-polymerized, semi-rigid networks. For less-polymerized silicate units, such modes might transform to or couple with other vibrations of the system with a greater degree of associated oxygen motion.

Many of the above band assignments to detailed vibrational motions are at present highly speculative. Firmer assignments will require further isotopic substitution experiments, and calculation of vibrational properties from the structure and bonding in the glass. A number of such calculations have been carried out for silicate glasses, and give results in general agreement with the major band assignments discussed above. However, such calculations have a number of inherent limitations, and may not yet be used to resolve the true vibrational nature of silicate systems.

Band assignments and structural models for silicate glasses and melts

The vibrational band assignments discussed above have been used to construct a number of structural models for silicate glasses and melts. These models show a number of common features, which are summarized below.

The major high-frequency bands at 1100–1050 cm^{-1} , 1000–950 cm^{-1} , 900 cm^{-1} and 850 cm^{-1} are associated with the presence of $\equiv\text{SiO}$, $=\text{SiO}_2$, $-\text{SiO}_3$ and SiO_4 groups following the notation described in McMillan (1984) (see Fig. 2), and may be used as indicative of the presence of these structural units. The low-frequency bands (700–500 cm^{-1}) are associated with the presence of Si–O–Si linkages in groups more polymerized than SiO_4 .

The fully-polymerized silica network (= Si =) has only weak high frequency bands, but may be characterized by its strong asymmetric band in the 500–400 cm^{-1} region. The groups $\equiv \text{SiO}$, $= \text{SiO}_2$, $-\text{SiO}_3$ and SiO_4 are respectively dominant near the disilicate, metasilicate, pyrosilicate and orthosilicate compositions, consistent with progressive depolymerization of the silicate unit as the silica content is decreased. At compositions other than pure silica, there is coexistence of three or more bands characteristic of different silicate units, consistent with a distribution of polymer species. Mysen et al. (1982a) have attempted to quantify this for a number of silicate systems. Up to this level of structural modelling, there is reasonable agreement between interpretations. The generally-accepted view is that of a fully-polymerized tetrahedral silica network becoming gradually depolymerized on addition of alkali or alkaline earth oxide. At any composition there is some distribution of silicate polymeric species, whose average polymerization decreases with increasing metal oxide content. The character of this distribution is presumably a function of the system and the experimental conditions.

Most of the Raman studies on silicate glasses and melts, especially the earlier work, have not attempted to further specify the nature of these molecular groups. Etchepare (1970c, 1972) compared the spectra of crystalline and glassy diopside ($\text{CaMgSi}_2\text{O}_6$), and suggested that the $= \text{SiO}_2$ units in the glass structure were linked to form "infinite" chains as in the crystal. Brawer and White (1975) discussed alkali disilicate and metasilicate glasses in terms of sheet and chain structures by analogy with their corresponding crystals. These authors envisaged a gradual change in structure with silica content for intermediate compositions via "concentration fluctuations," where adjacent silicate tetrahedra may have different degrees of polymerization. This allows for a continuous overall depolymerization of the glass structure by randomly breaking Si–O–Si linkages with decreasing silica content. This schema may be contrasted with the structural model of Mysen, Virgo and coworkers (e.g., Mysen et al., 1980a, 1982a; Virgo et al., 1980), which also considers the melt structure to consist predominantly of sheet units at the disilicate composition, and chains at the metasilicate. However, these authors considered that the Raman data and other observations were inconsistent with the presence of structures intermediate between sheet and chain in the glass or melt. They suggested instead that, for compositions between the disilicate and metasilicate, sheets and chains coexisted as discrete structural units in mutually varying proportions. These workers also proposed three other silicate structural units; a three-dimensional network unit, and dimer ($\text{Si}_2\text{O}_6^{2-}$) and monomer (SiO_4^{4-}) units. Mysen et al. (1980a) considered that there was no spectroscopic evidence for structures intermediate between the dimer unit and the "infinite" chain, $\text{Si}_2\text{O}_6^{4-}$.

The major difference between the above models arises

from the interpretation of linkages between silicate tetrahedral units in the glass and melt structure. Since all of these models are based on Raman spectroscopic observations, it is important to assess whether Raman spectroscopy of silicate glasses is in fact sensitive to these differences, and whether limiting constraints may be placed on such structural models from Raman data. For this, it is necessary to consider the spatial extent and coherence of the vibrational modes responsible for the major characteristic bands of structural units in the silicate melt and glass.

Vibrational mode localization

A number of observations have led several authors to suggest that certain vibrational modes of silicate glasses and melts are highly localized. The first and most obvious is that, although silicate melts and glasses are known to be macroscopically disordered, they generally have major Raman bands which are well-defined and are often highly polarized. These suggest vibrating units with high symmetry within the glass structure. Extended motions within the disordered network might be expected to give weak, broad and depolarized bands in the Raman spectrum, suggesting that the major polarized bands observed are localized within groups with at least a pseudo-point symmetry. This has been discussed by Brawer (1975), Furukawa and White (1980), and Furukawa et al. (1981) (see also White, 1982).

It was noted earlier that the major Raman band groups of silicate melts and glasses correspond to those of analogue crystalline silicates. The major classes of silicate crystal structures may be distinguished on the basis of the degree of polymerization of their constituent SiO_4 tetrahedral units (e.g., Liebau, 1980). Within any one group of silicates, the major features of their vibrational spectra are remarkably similar; independent of the metal cation, crystal symmetry, unit cell size, or relative arrangement of the silicate tetrahedra. For example, McMillan and Piriou (1983b) compared the Raman spectra of calcium magnesium metasilicates, $(\text{Ca},\text{Mg})\text{SiO}_3$. In these compounds, the metal cation is varied between Ca^{2+} and Mg^{2+} , the unit cells have orthorhombic, monoclinic or triclinic symmetry and contain 10, 20 or 30 atoms in the spectroscopic unit cell, and the silicate units are present as pyroxene or pyroxenoid chains or $\text{Si}_3\text{O}_9^{6-}$ rings (e.g., Wyckoff, 1968, p. 294–296, 301–303, 314–316 and 342–343; Deer et al., 1971, p. 99–119, 140–143). The Raman spectra of all these compounds are similar, with one strong band near 1000 cm^{-1} and a second in the region 650–550 cm^{-1} , similar to the major bands of metasilicate glasses (e.g., McMillan and Piriou, 1983a). This could be interpreted as due to localization of the modes responsible for these major Raman bands within vibrating units common to all these crystal structures. The common features in this case are the presence of SiO_4 tetrahedra with two non-bridging oxygens ($= \text{SiO}_2$ units), and Si–O–Si linkages between such units, suggesting that the modes

may be localized within these groups. Since the spectra of (Ca,Mg)-metasilicate glasses may be equally well compared with any of the above crystal spectra, the glass Raman bands may not be used to distinguish between chain and ring structures in the glasses. In fact, if the interpretation of major band localization is accepted for the crystal spectra, this must also apply to those of the glasses.

A further observation consistent with localization of the vibrations associated with their major bands is provided by the Raman spectra of phase-separated silicate glasses. Furukawa et al. (1981) obtained the spectra of heat-treated Na₂O-SiO₂ glasses with 20 and 15 mole % Na₂O. They found that the 1100 cm⁻¹ band and its associated shoulder near 1165 cm⁻¹ did not change on annealing, which they attributed to a high localization of the vibrations responsible for these modes (see also White, 1982). For the 20 mole % Na₂O sample, the low-frequency band group near 500 cm⁻¹ resolved into bands at 495 and 450 cm⁻¹ characteristic of vitreous silica and another component at 530 cm⁻¹, which Matson et al. (1983) used to suggest a relative *delocalization* for modes near 500 cm⁻¹. McMillan (1981, 1984) prepared samples with bulk compositions within the CaO-MgO-SiO₂ two-liquid field. Normally quenched glasses were opaque and macroscopically unmixed, while fast-quenched samples were transparent and homogeneous on the micron scale. The spectra of both sets were identical, and were simple superpositions of the bands of the limiting unmixed compositions, which McMillan (1981, 1984) discussed as consistent with a high degree of vibrational localization. On the basis of optical transparency, this localization was proposed to be on at least the hundred Ångstrom level. Brawer (1975) and White (1982) have come to similar conclusions. It is also noted that a high degree of localization of the vibrations responsible for these major Raman bands would rationalize the observed correspondence of silicate glass and melt spectra, noted in the Introduction. The localized vibrating units are mainly associated with tetrahedral silicate units, which seem from diffraction studies to be largely unchanged between glass and melt (e.g., Waseda and Toguri, 1977; Nukui et al., 1978).

Finally, the results of several vibrational calculations for silicate glasses imply a certain localization for these major bands. A number of such calculations have only considered small silicate clusters (one or two linked SiO₄ tetrahedra), and successfully reproduced the 1200-800 cm⁻¹ and 700-400 cm⁻¹ bands (e.g., Etchepare, 1970a; Brawer, 1975; Brawer and White, 1975; Furukawa et al., 1981). This suggests that the vibrations responsible for the major bands may be localized within these vibrating units. In addition, Bell and co-workers (e.g., Bell, et al., 1968; Bell and Dean, 1970; Bell, 1976) constructed a random network model for vitreous silica and calculated its vibrational properties. These workers defined a participation ratio which gave information on the localization of selected modes, and found that silicon-oxygen stretching

motions associated with non-bridging surface oxygens were highly localized (Bell et al., 1970).

The above arguments place some limitations on the types of structural model for silicate glasses and melts which may be derived from interpretation of their Raman spectra. The major polarized bands at 1100-1050 cm⁻¹ and 1000-950 cm⁻¹ have been associated with symmetric silicon-oxygen stretching vibrations of groups containing ≡ SiO and = SiO₂ units. It was argued above for metasilicates with = SiO₂ groups (McMillan and Piriou, 1983b) that this vibration is probably highly localized within individual = SiO₂ units. Similar arguments may be made for the symmetric silicon-oxygen stretching vibration of ≡ SiO groups in disilicates. If this is so, then the 1100-1050 cm⁻¹ and 1000-950 cm⁻¹ Raman bands give little or no information as to how individual ≡ SiO and = SiO₂ units are linked to neighboring silicate tetrahedral groups.

The weak, depolarized high-frequency bands of the vitreous silica network (= Si =) have been assigned to antisymmetric silicon-oxygen stretching motions, and must be less localized than the vibrations discussed above. In principle, the behavior of these bands with addition of metal oxide should give information on the depolymerization mechanism of the silica framework. However, these bands are weak, and are usually obscured by the dominant stretching bands of less-polymerized species. Little can be said as yet regarding the -SiO₃ stretching vibrations near 900 cm⁻¹, since there are insufficient Raman studies on crystalline pyrosilicates (with Si₂O₇ dimer groups) and silicates with -SiO₃ units bound to other groups for comparison. These might help decide whether the symmetric -SiO₃ stretching motions are mainly localized within individual -SiO₃ units, or are characteristic of Si₂O₇ dimers.

Information on the coupling of adjacent silicate tetrahedral groups is probably contained in the low-frequency (700-400 cm⁻¹) band group associated with vibrations of the Si-O-Si linkages. Different bands do appear in this region as a function of silicate polymerization, but the frequencies of individual bands also vary with silica content (see previous discussion for the observed low-frequency region of the SiO₂-K₂O glass series). Until these vibrations are better understood in relation to the molecular structures of silicates, it does not seem reasonable to relate specific bands in the 700-400 cm⁻¹ region to Si-O-Si linkages between particular silicate tetrahedral units. It is concluded here that the characteristic high-frequency Raman bands of the ≡ SiO, = SiO₂, SiO₄ and perhaps -SiO₃ units, are to a first approximation, independent of the nature of adjacent silicate groups. The necessary information is presumably present in, but not yet easily extracted from, the bands in the 700-400 cm⁻¹ region. This suggests that models based on Raman studies in terms of extended structural units, such as sheets, chains, rings etc. (e.g., Virgo et al., 1980; Mysen et al., 1980a, 1982a), are only speculative at present. This does

not imply that such models are incorrect, only that our current understanding of the Raman spectra of silicate glasses and melts is not sufficient to firmly establish the long-range structures present in these latter.

Detailed vibrational assignments

The correlation of vibrational with molecular structure

In the studies considered above, Raman spectroscopy has been used to gain information on the structures of silicate glasses and melts. This has been carried out by the assignment of vibrational bands to specific structural features, which have then been used to formulate models for the glass or melt structure. Such an assignment requires an understanding of the atomic displacements involved in each vibrational mode, in order to identify the vibrating unit and relate it to a feature of the structure. The assignments in the previous section were mainly based on the energies ("frequencies") and symmetries of the observed vibrational transitions, and do not give a detailed description of the nature and spatial extent of each mode. This is only possible from a dynamical analysis of the system.

The molecular structure of a system defines the relative positions of its constituent atoms and the interactions between them. If one or more atoms are moved from their equilibrium position, the interatomic forces tend to restore the system to its equilibrium configuration. The atomic displacements executed during this process are described by the equations of motion of the system, whose solutions are its normal modes of vibration (e.g., Nakamoto, 1970, p. 3–75; Lazarev, 1972, p. 1–7; Berry et al., 1980, p. 343–355). The mathematical formulation for the dynamics of discrete molecules and of crystalline lattices are well established (e.g., Herzberg, 1945; Vol'kenshtein et al., 1949; Born and Huang, 1954; Wilson et al., 1955). In general in these treatments, the potential energy of the system is expanded in a Taylor series of the small atomic displacements from their equilibrium positions during vibrational motion. The force constants for the system described the curvature of the potential energy surface near the equilibrium geometry. For certain small molecules, completely general, self-consistent force fields have been obtained from extensive vibrational and rotational analyses. However, for most molecules, including the silicates, the assumed force constants are a function of the particular model used to describe both the interatomic interactions and the vibrational motions. Solution of the equations of motion for the system using appropriate force constants gives the energies of vibrational transitions, and their associated atomic displacements (e.g., Nakamoto, 1970, p. 3–75; Berry et al., 1980, p. 343–355). Treatment of the dynamics of condensed amorphous systems remains a current research problem (e.g., Shuker and Gammon, 1970; Brawer, 1975; Barker and Sievers, 1975; Bell, 1976; Laughlin and Joannopoulos, 1977; Galeener and Sen, 1978; Thorpe and Galeener, 1980a,b). Vibrational calculations have been carried out for silicate glasses and melts using similar methods to those above by considering the amorphous network either as a single large molecule, or by considering small representative units (see references in the following section).

The validity of such vibrational calculations is critically dependent on the force constant model used, and its relevance to the true interatomic potential surface. Realistic force constants may be evaluated if this surface is known analytically; however,

this is not yet the case for silicates (see discussions in O'Keefe and Navrotsky, 1981; Gibbs, 1982). A number of methods are available to construct sets of force constants designed to model interatomic interactions within complex systems (see e.g., Nakamoto, 1970, p. 55–57), a variety of which have been used in the vibrational calculations for silicates discussed below. It is common to compare vibrational spectra calculated using a given force constant set with observed spectra, as a criterion for the applicability of that force constant set. However, it is known that a given observed spectrum may be reproduced using a wide variety of force fields (e.g., Cochran, 1969, p. 10–13; Leigh et al., 1971; Szigeti, 1971; Sherwood, 1972, p. 38). If the chosen force field does not approximate the true potential surface, then calculated atomic displacements may not resemble the motions associated with the true vibrational modes, although the infrared and Raman spectra may have been calculated to within experimental error.

From these considerations, a rigorous correlation of the vibrational properties of silicates with their structures must await a better understanding of their interatomic bonding. A number of the vibrational calculations discussed below have calculated atomic displacements associated with given vibrational modes. These are subject to the limitations noted above, and assignment of vibrational bands to structural features may not safely be taken much further than the general assignments discussed in the previous section. However, examination of a range of vibrational calculations reveals a number of consistent features, which may be used to gain further insight into the vibrational properties of silicates.

Vibrational calculations for silicates

Some of the earlier work was carried out by Saksena (1940, 1942, 1945) for α -quartz, assuming force constants for Si–O stretching and Si–O–Si and O–Si–O bending. Barriol (1946) performed a similar calculation for β -quartz using two force constants; for Si–O and O–O stretching. Matossi (1949) computed the vibrational spectra for a number of silicate fragments, including the Si_2O_7 unit, the Si_3O_9 ring, isolated SiO_4 , a linear Si_2O_6 chain with translational symmetry, and the SiO_2 network as linked SiO_4 units. For all except Si_2O_7 , only Si–O and O–O stretching force constants were considered, while for Si_2O_7 , O–Si–O bending was taken into account. Matossi also distinguished between SiO_b and Si-O_{nb} stretching constants (O_b is a bridging and O_{nb} a non-bridging oxygen; see earlier). Around this time were developed much more efficient techniques for calculating the vibrational spectra of molecules (e.g., Vol'kenshtein et al., 1949; Wilson et al., 1955). Stepanov and Prima (1958a, b) and Prima (1960) used these methods to calculate infrared band positions and intensities for a number of silicate fragments representative of chain, sheet, ring and network silicates. Similar calculations were carried out by Bobovich et al. (1955) and Bobovich and Tulub (1956, 1957). These authors assumed relatively complex force constant sets with Si–O stretching and Si–O–Si and O–Si–O bending, and terms for interaction between these. Further calculations were carried out by Saksena (1961) and Saksena et al. (1963), but with much simpler force constant sets: Si–O stretching (with separated Si-O_b and Si-O_{nb}), and O–Si–O and Si–O–Si bending. Su et al. (1962) applied the method to calculate the vibrational spectra of silicate glasses, based on the vibrations of SiO_4 units. They assumed a complex force field, with Si–O stretching and Si–O–Si and O–Si–O bending terms, inter-term interactions, and

torsional contributions. Wadia and Balloomal (1968) and Bock and Su (1970) performed similar calculations for silica glass, with respectively four (Si–O, O–O, O–Si–O, and Si–O–Si) and three (Si–O, O–Si–O and Si–O–Si) force constants. Gaskell (1967, 1970) and Etchepare (1970a) also carried out a number of calculations for various silicate fragments; Gaskell with simple Si–O, O–Si–O and Si–O–Si force constants, and Etchepare using Si–O, O–O and cross-term interactions. In an extensive series of articles beginning in the 1960's, Bell, Dean and co-workers calculated the vibrational modes for a many-atom random network of vitreous silica (e.g., Bell et al., 1968, 1980; Bell and Dean, 1970; Bell, 1976), using only two (Si–O and O–Si–O) force constants. A large number of calculations have since been carried out for crystalline silicates, using methods similar to those developed by Born and Huang (1954). The largest group is for the crystalline silica polymorphs, especially α -quartz (e.g., Kleinman and Spitzer, 1962; Elcombe, 1967; Mirgorodskii et al., 1970; Bates, 1972; Etchepare et al., 1974; 1978; Striefler and Barsch, 1975; Iishi and Yamaguchi, 1975, 1976; Barron et al., 1976; Iishi, 1978a), while a smaller number have been carried out for other silicates (e.g., Oehler and Gunthard, 1969; Omori, 1971; Lazarev, 1972, p. 240–253; Pavinich et al., 1976; Zulumyan et al., 1976; von Stengel, 1977; Iishi, 1978b; Tomisaka and Iishi, 1980). All of these calculations assumed rather complex force fields, with various two-, three- and higher-body interactions and often inter-term contributions.

Brawer (1975) developed a formalism for calculation of vibrational modes in amorphous systems. A similar approach was suggested by Galeener and Sen (1978). This has been used to calculate the vibrational spectra of a number of alkali silicate glasses (e.g., Brawer, 1975; Brawer and White, 1975; Furukawa et al., 1981), assuming a simple force constant set with Si–O stretching (separated Si–O_b and Si–O_{nb}), and O–Si–O and Si–O–Si bending. Laughlin and Joannopoulos (1977) have used a Bethe cluster approach to calculate the spectrum of vitreous silica, using only Si–O and O–Si–O force constants. Sen and Thorpe (1977) derived a method of calculating the vibrations of disordered networks, which has been further developed by Galeener (1979) and Thorpe and Galeener (1980a,b). These calculations assumed only as a first approximation one central stretching force constant: in the case of vitreous silica, Si–O stretching.

All of the above calculations have included a term for Si–O stretching, with magnitude ranging from around 300 to 700 Nm⁻¹. Gibbs et al. (1981) carried out an *ab initio* molecular orbital calculation for the Si(OH)₄ molecule, for which they derived an Si–O stretching force constant of 665 Nm⁻¹. This is of the same order of magnitude as those used in the vibrational calculations, suggesting that the values used for Si–O stretching may be generally realistic. This is consistent with the fact that most of the calculations have reproduced the high-frequency region of the vibrational spectrum, usually associated with Si–O stretching motions.

O'Keeffe et al. (1980) have pointed out that this Si–O stretching force constant also includes a component from nearest-neighbor O ··· O interactions, since O ··· O distances are changed during Si–O stretching. These interactions have been ignored in a number of the above calculations, and in others, have been estimated to be of the order of 10–80 Nm⁻¹ (e.g., Matossi, 1949; Zulumyan et al., 1976; Iishi, 1978a, b; O'Keeffe et al., 1980). Those calculations which explicitly considered O ··· O interactions tend to be associated with

lower Si–O stretching force constants, suggesting that neglect of O ··· O interactions in the calculation results in over-estimation of the Si–O force constant to compensate.

Most calculations have separated the Si–O stretching force constant into two populations: one associated with Si–O_{nb} and one for Si–O_b, with the Si–O_{nb} force constant some 50–100 Nm⁻¹ larger than the Si–O_b. This separation of the Si–O term has usually been justified by the observed Si–O_{nb} and Si–O_b distances in silicates, with Si–O_{nb} generally (but not always) shorter than Si–O_b (e.g., Ramberg, 1952; Brown et al. 1969; Furukawa et al., 1981). Meagher et al. (1980) calculated Si–O_b stretching force constants of 732 to 878 Nm⁻¹ (as a function of the Si–O–Si angle) for the H₆Si₂O₇ molecule; larger than the value calculated by Gibbs et al. (1981) for Si(OH)₄ (665 Nm⁻¹). This would appear consistent with the assumed relative magnitudes of Si–O_b and Si–O_{nb} stretching force constants. However, O'Keeffe et al. (1980) calculated the Si–O stretching force constant (combined with O ··· O interactions) for H₆Si₂O₇ at 540 Nm⁻¹, less than that for Si(OH)₄.

A number of vibrational calculations for silicates have ignored the terms for M–O stretching (M is the alkali or alkaline earth cation) on the assumption that metal cations do not participate in or affect the vibrations of the silicate unit (e.g., Saksena, 1961; Gaskell, 1970; Etchepare, 1970a; Brawer and White, 1975; Furukawa et al., 1981). This approximation may be valid for certain modes under given circumstances, which will be discussed later. Those calculations which have included M–O interactions have estimated the following stretching force constants: Mg–O 30–90 Mn⁻¹, Ca–O 5–50 Nm⁻¹, K–O 10–14 Nm⁻¹, Na–O 18 Nm⁻¹ and Li–O 40 Nm⁻¹ (Oehler and Gunthard, 1969; Zulumyan et al., 1976; Pavinich et al., 1976; von Stengel, 1977; Iishi, 1978b; Tomisaka and Iishi, 1980). Some calculations have included terms for nearest neighbour non-bonded M ··· M interactions (where M is Si, or an alkali or alkaline earth cation). The Mg ··· Si interaction in forsterite has been estimated at 4–30 Nm⁻¹ (Oehler and Gunthard, 1969; Iishi, 1978b), with Mg ··· Mg at 194 Nm⁻¹ (Oehler and Gunthard, 1969). The latter authors also estimated Ca ··· Si and Ca ··· Ca in γ -Ca₂SiO₄ at 178 and 61 Nm⁻¹ respectively. Si ··· Si non-bonded interactions in quartz have been estimated to contribute 40–120 Nm⁻¹ to the force field (see O'Keeffe et al., 1980), while O'Keeffe et al. (1980) calculated the force constant for Si ··· Si repulsion at near 100 Nm⁻¹ for the H₆Si₂O₇ molecule, with an Si ··· Si separation near 3Å.

Most calculations have also considered O–Si–O, and for polymerized silicates Si–O–Si, angle bending forces. The estimated value for O–Si–O bending has ranged from 20–70 Nm⁻¹ (expressed as $(1/r^2)(\partial^2 E/\partial r^2)$, where r is the Si–O bond length) while the force constant for Si–O–Si bending has been estimated at 2–20 Nm⁻¹. Gibbs et al. (1981) have calculated an O–Si–O bending force constant for the Si(OH)₄ molecule of 100 Nm⁻¹, while O'Keeffe et al. (1980) calculated 8–18 Nm⁻¹ (as a function of the Si–O–Si angle) for the Si–O–Si bending force constant of H₆Si₂O₇. These values calculated from molecular orbital studies are of comparable magnitude to those estimated for the lattice dynamical studies.

A number of general conclusions may be drawn from the above discussion. For studies with similar force constant sets, there is at least an order of magnitude agreement for preferred values of individual force constants. If the force fields derived from molecular orbital calculations on small silicon-oxygen clusters are realistic and transferable to condensed silicate

systems (see O'Keeffe et al., 1980; Gibbs et al., 1980; Gibbs, 1982), then the silicate bending and stretching force constants used in the vibrational calculations appear reasonable. However, most of the calculations neglect one or more of the interaction terms described above (which are already far from a complete list of possible interactions in complex silicates). This must be compensated by an over- or underestimate of those force constants used, or the inclusion of additional interaction terms which are not necessarily real. Individual force constants calculated from molecular orbital studies of small clusters may likewise be poorly estimated, since a detailed analysis of the data is required to separate individual contributing interactions, when this is in fact possible (see O'Keeffe et al., 1980).

In the silicates described here, the short-range interactions seem to be dominated by the Si-O stretching force constant. Although the estimates for this force constant range from 300 to 700 Nm^{-1} , the actual contribution from pure Si-O stretching is probably at the low end of this range when other contributing interactions are identified and subtracted.

The vibrational spectra of silicates in general may be described in terms of the major band groups discussed in the previous section: for all, a high-frequency group from 1200–800 cm^{-1} ; for silicates more polymerized than the orthosilicate, a group from 700–400 cm^{-1} ; and for the disilicate and silica, a mid-range group in the 800–700 cm^{-1} region.

Sen and Thorpe (1977) calculated the vibrational spectrum of SiO_2 considering only the central Si-O stretching force constant, and reproduced both the high- and low-frequency band sets. All of the other vibrational calculations considered above, with dominant Si-O stretching force constants but often considerable differences in other assumed interactions, have also consistently reproduced these regions of silicate spectra in general. These observations seem to suggest that both the 1200–800 cm^{-1} and the 700–400 cm^{-1} bands of silicate vibrational spectra are due to modes dominated by Si-O stretching.

O'Keeffe et al. (1980) have suggested that the force constant for $\text{Si} \cdots \text{Si}$ non-bonded interaction may be rather large, and of the order of the Si-O stretching force constant. Such interactions have been neglected explicitly or assumed small in most silicate calculations; although they may be largely subsumed into an Si-O-Si bending force constant. The effect of ignoring this term may become important for more polymerized silicates, where the number of $\text{Si} \cdots \text{Si}$ interactions becomes comparable to the number of Si-O stretching forces to be considered. This neglect will only be important for modes in which the $\text{Si} \cdots \text{Si}$ distance is varied, but may result in considerable overestimation of other interactions considered, for example, Si-O-Si bending forces.

Motions derived from Si-O stretching

The isolated SiO_4 tetrahedron. The vibrations of a hypothetical isolated tetrahedral SiO_4 group may be described in terms of the totally symmetric stretching mode (ν_1) and the triply-degenerate asymmetric stretch (ν_3) (e.g., Herzberg, 1945, p. 100). These are shown schematically in Figure 3(a). Any deviation from tetrahedral symmetry will result in a mixing or vibrational coupling of ν_1 - and ν_3 -type modes (see Piriou and McMillan, 1983a).

The fully-polymerized SiO_2 network. This may be considered as a network of SiO_4 tetrahedra polymerized by corner-sharing each oxygen between two SiO_4 units. The vibrations derived from Si-O stretching may be simply understood following the model of Sen and Thorpe (1977). These authors developed a

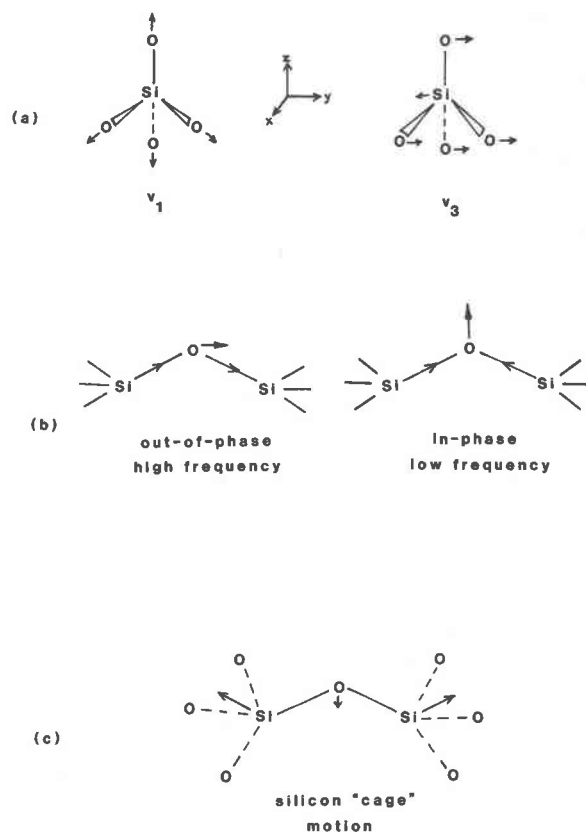


Fig. 3. Schematic of possible types of normal mode in silicates. (a) ν_1 - and ν_3 -type stretching vibrations of the isolated SiO_4 tetrahedron. (b) The in-phase (low-frequency) and out-of-phase (high-frequency) resultant vibrations of two coupled Si-O stretching motions (only Si-O stretching is considered). (c) The type of motion suggested by various vibrational calculations for silica polymorphs to be associated with the Raman bands near 800 cm^{-1} (drawing after Laughlin and Joannopoulos, 1977). No such vibration is calculated when only central Si-O stretching is considered, as in (b).

vibrational model for condensed AX_2 systems where A is tetrahedrally coordinated by X, and X two-fold coordinated by A. They considered only the A-X stretching force, and followed the character of vibrational modes as the X-A-X angle (θ) was varied. Sen and Thorpe found that for θ smaller than some critical angle, the vibrations were best described in terms of ν_1 - and ν_3 -type motions of the isolated AX_4 tetrahedra. For θ larger than the critical angle, the stretching modes of adjacent tetrahedra became strongly coupled. This critical angle for SiO_2 was found to be near 112° . Since the average Si-O-Si angle in silica glass is larger than this, the coupled mode description must be used. The resulting vibrations may be described in terms of stretching motions of adjacent Si-O bonds linked at oxygen: a high-frequency band of modes where the coupled Si-O stretches are out of phase, giving a resultant oxygen motion sub-parallel to the $\text{Si} \cdots \text{Si}$ line, and a low-frequency set of modes where adjacent Si-O stretching is in phase to give a resultant oxygen motion in the plane bisecting the Si-O-Si bond (Sen and Thorpe, 1977). These are shown schematically in Figure 3(b). It is of

interest to compare these simplified vibrations with those calculated using more sophisticated force models for vitreous and crystalline silica polymorphs (e.g., Mirgorodskii et al., 1970; Bates, 1972; Etchepare et al., 1974, 1978; Lucovsky, 1979; Furukawa et al., 1981). In all cases, the atomic displacements calculated for the strong Raman-active modes in the 400–500 cm^{-1} region are similar to those described above for the low-frequency band set, with mainly oxygen displacement in the plane bisecting Si–O–Si, and those for the 1000–1200 cm^{-1} region similar to the above high-frequency bands with oxygen vibrating between silicons in the Si–O–Si bond. This latter motion is generally calculated to involve a larger component of associated silicon displacement.

The central force model of Sen and Thorpe does not predict the silica bands near 800 cm^{-1} , which must require consideration of some other interaction. The models of Bell and co-workers (e.g., Bell et al., 1968, 1980; Bell and Dean, 1970; Bell, 1976) and Laughlin and Joannopoulos (1977), both of which consider only Si–O stretching and O–Si–O bending interactions, do reproduce a band near 800 cm^{-1} . The frequency spectrum from a molecular dynamics calculation with Si–O, O–O and Si–Si interactions also showed a peak near 800 cm^{-1} (Garofalini, 1982). All of these calculations suggested that the 800 cm^{-1} modes involved predominantly silicon motion, consistent with the isotopic substitution experiments of Galeener and Mikkelsen (1981) and Galeener and Geissberger (1983). The calculated atomic displacements for this mode after Laughlin and Joannopoulos (1977) are shown in Figure 3(c). More complex calculations for SiO_2 polymorphs have reproduced similar atomic displacements within Si–O–Si units.

Other silicate compositions. The Sen and Thorpe central force model has since been extended to other cation and anion coordinations (e.g., Galeener and Sen, 1978; Thorpe and Galeener, 1980a, b), while Seifert et al. (1982) and Mysen et al. (1982a) have applied the model to aluminosilicate systems with Si–O–Al linkages. It is possible that the model may be extended to simple silicate systems with both Si–O–Si and Si–O–M linkages, where M is some cation other than silicon, and the oxygen and M coordination may vary.

Within the Si–O–Si linkages of silicates in general, the Si–O–Si angle is larger than the Sen and Thorpe critical angle (see above), hence modes associated with Si–O stretching about an Si–O–Si linkage must be considered in terms of coupled Si–O stretch vibrations as discussed above for silica. For Si–O–M linkages (where M is an alkali or alkaline earth cation, and the oxygen is that usually referred to as “non-bridging”), the character of the mode may be assessed in terms of the relative contributions from M–O and Si–O stretching to the total stretching force on the oxygen along the line of the Si–O bond. It can be shown simply that if Si–O contributes k_{SiO} (the Si–O stretching force constant), each M–O stretch contributes $k_{\text{MO}} \cos^2 \theta$, where k_{MO} is the M–O force constant and θ is the complement of the Si–O–M angle (M. O’Keeffe, pers. comm., 1982). As an example, these contributions may be evaluated for forsterite, Mg_2SiO_4 .

The Si–O–Mg angles in forsterite range from 90° to 124° (Brown, 1980, p. 364). Each oxygen is coordinated to silicon and three magnesium atoms. For $\theta = 90^\circ$, the Mg–O stretching contribution is zero ($\cos^2 90^\circ$). The maximum contribution from each Mg–O would be 0.31 k_{MgO} at 124°, which for three magnesium atoms coordinated to oxygen is 0.93 k_{MgO} , to give a resultant Si–O stretching force constant of $k_{\text{SiO}} + 0.93 k_{\text{MgO}}$. However, k_{SiO} is probably almost an order of magnitude larger

than k_{MgO} (see previous section), so there should be little or no participation of Mg–O stretching in these predominantly Si–O stretching modes. The vibrational calculation of Iishi (1978b) for forsterite supports this prediction, with no contribution from Mg–O stretching appearing in the potential energy change associated with Si–O stretching. It is of interest that this also supports the usual description of the Si–O stretching modes in forsterite in terms of the ν_1 - and ν_3 -motions of isolated SiO_4 tetrahedra, as described above.

In the alkali and alkaline earth silicates, oxygen is generally coordinated by two to four cations (including Si) in Si–O–M linkages, with Si–O–M angles ranging from 90° to around 140° ($M \neq \text{Si}$). In most cases, k_{SiO} is probably larger than k_{MO} (see previous section). Following similar arguments to that for forsterite, Si–O stretching motions in Si–O–M linkages should be largely decoupled from M–O stretching. This was found to be the case for Si–O–Mg and Si–O–Ca in diopside, $\text{CaMgSi}_2\text{O}_6$ (Tomisaka and Iishi, 1980). This would be a partial justification for the common neglect of M–O interactions in simplified silicate vibrational calculations, although M–O stretching may contribute significantly to other vibrations of the silicate unit. The “internal mode approximation” is commonly used to interpret the vibrational spectra of silicates in terms of the vibrations of their constituent silicate units (e.g., Lazarev, 1972, p. 7–26, 46–48; Tarte 1963a,b). The above discussion also justifies this approximation, at least for vibrations derived from Si–O stretching.

In silicate systems with polymerization between the orthosilicate and silica, a given silicate unit may have both Si–O–M and Si–O–Si linkages to a given silicon. As discussed above, silicon–oxygen stretching should result in high- and low-frequency bands from coupled stretching within each Si–O–Si unit, and a high-frequency band from Si–O stretching uncoupled from M–O in each Si–O–M linkage. The degree of coupling between these sets of modes will be a function of the system and the particular vibration. Furukawa et al. (1981) have calculated that the major high-frequency Raman band for an Si_2O_6 (“chain”; = SiO_2) unit involves mainly stretching motion of non-bridging oxygens against silicon with little participation of bridging oxygens, suggesting decoupling of the Si–O–Si and Si–O–(M) (the M cation is in parentheses, since it was not considered explicitly by Furukawa et al., 1981) contributions. The same was true for the calculated major modes of an Si_2O_5 (“sheet”; = SiO_2) unit. However, Tomisaka and Iishi (1980) have carried out a more complete calculation of diopside, $\text{CaMgSi}_2\text{O}_6$, with pyroxene chains of = SiO_2 units. One high-frequency mode is similar of that of Furukawa et al. (1981), with decoupled Si–O–Si and Si–O–M stretching, but another shows large components of both the high-frequency resultant Si–O–Si and the Si–O–M stretching vibrations.

A number of workers have observed that the frequency of the band near 700–600 cm^{-1} for crystalline pyrosilicates (Si_2O_7 groups) increases with decreasing Si–O–Si angle (e.g., Lazarev, 1972, p. 66–72; Scheetz, 1972, p. 75–81). Lazarev (1972) also noted a corresponding decrease in the high-frequency band derived from asymmetric stretching of Si–O–Si. This may be rationalized in terms of the Sen and Thorpe model for the stretching vibrations of the Si–O–Si linkage discussed above. As the Si–O–Si angle becomes narrower, the individual Si–O₆ stretching vibrations become less coupled. This will decrease the high-frequency asymmetric and increase the low-frequency symmetric components of coupled Si–O–Si stretching, to

approach the ν_1 and ν_3 frequencies of isolated SiO_4 units (Sen and Thorpe, 1977).

In silicate crystals and glasses in general, the frequency of the 700–400 cm^{-1} band increased with decreasing silica content, or decreasing polymerization of the silicate unit (Fig. 1). The average Si–O–Si angles do seem to show a general increase from pyrosilicates to the silica polymorphs, which may partially rationalize the behavior of the 700–400 cm^{-1} band following a similar argument to that above for pyrosilicates.

The frequency of the major Raman band in the 1200–800 cm^{-1} region shows a general decrease from silica to the orthosilicate. However, except for the case of silica, this band is probably mostly associated with motions of “non-bridging” oxygens in Si–O–M linkages, not with the high-frequency component of Si–O–Si. It is difficult to relate the lowering of frequency of this band with decreasing polymerization to any specific structural change, since the particular vibrating unit giving rise to the major high-frequency band changes with polymerization of the silicate unit. Then the pseudo-symmetry of the vibrating unit, and the nature and Raman activity of particular vibrational modes, are not the same for silicate tetrahedra in different polymerization states.

Summary

A large body of Raman spectral data has been assembled for alkali and alkaline earth glasses and liquids. Many attempts have been made to relate these spectra to the glass and liquid structure at various levels of modeling. Part of the purpose of the present article has been to critically examine these, and assess the potential applications and limitations of Raman spectroscopy for such structural studies.

First, there is general agreement as to the major observed bands as a function of composition. However, many details of the experimental spectra remain unclear, especially for weaker bands. More work is needed on systems with well-resolved Raman bands, e.g., $\text{SiO}_2\text{--K}_2\text{O}$ and $\text{SiO}_2\text{--BaO}$, to define the frequency behavior with composition and the polarization characteristics of all the bands. These results would be helpful in constraining realistic deconvolutions for systems with less well-resolved bands. For these systems, careful polarized studies noting slope changes on unresolved bands and systematic statistical fitting experiments would be useful.

As noted in the text, there is also agreement as to the general assignment of major band groups to types of structural unit. This is extremely useful, as these bands are then diagnostic of particular units, and this has been used to construct various structural models for the glasses and melts. However, such assignments have been largely phenomenological, and give little indication as to the detailed nature of the vibrational modes. In many cases, this information is necessary to differentiate between possible alternative models. Isotopic substitution experiments on silicate glasses and crystals would help give more detailed vibrational interpretations, but such data are rare at present. In theory, dynamical calculations on silicate structures should directly give the nature of

vibrational modes. However, such calculations rely on models of interatomic interactions in silicate systems which may not yet be assessed, due to our current understanding of chemical bonding. Systematic series of calculations would be useful at the present time, for instance to assess the effect of inclusion or neglect of particular interaction terms on the form of the calculated normal modes for a particular cluster. Until the vibrational properties of silicates are better understood in terms of their structure and bonding, vibrational spectroscopy cannot be rigorously used as a tool for investigating their detailed molecular structure.

The major interest in structural studies of silicate glasses and melts for geological applications has been the rationalization and eventual prediction of properties such as viscosity, density or heat content of a magma as a function of temperature, pressure and composition. In view of the preceding discussion, it remains only speculative to correlate detailed melt and glass structural models derived from Raman spectroscopic studies with variations in bulk properties. However, some general systematic correlations may be made, as discussed below.

It has been noted by many workers that the isothermal viscosity (η) of silicate liquids and glasses decreases by several orders of magnitude as alkali or alkaline earth oxides are added to pure silica (e.g., Heidtkamp and Endell, 1936; Shartsis et al., 1952; Bockris and Lowe, 1954; Bockris et al., 1955; Mackenzie, 1960; Urbain et al., 1982). This decrease has been interpreted in terms of depolymerization of the silica melt or glass network on addition of metal oxide, consistent with the interpretation of Raman spectra of silicate glasses and melts. Urbain et al. (1982) found discontinuities in their curves of $\ln \eta$ versus mole fraction SiO_2 for their $\text{Na}_2\text{O--SiO}_2$ liquids near 0.8 and 0.6 X_{SiO_2} , with a smaller rate of change in viscosity with silica content between 60 and 80 mole % silica. The systems $\text{SiO}_2\text{--K}_2\text{O}$ and $\text{SiO}_2\text{--Li}_2\text{O}$ show similar inflections in their $\ln \eta - X_{\text{SiO}_2}$ curves at slightly different silica contents (Bockris et al., 1955; Mackenzie, 1960). It is of interest that these compositions, near 80–90 mole % and 60 mole % silica, are respectively where fully-polymerized silica network units $=\text{Si}=\text{}$ seem to disappear and where orthosilicate groups SiO_4 first appear, from Raman spectroscopic studies. The viscosity changes could then be interpreted as a large initial change on initial depolymerization of the $=\text{Si}=\text{}$ network, followed by a region of gently decreasing viscosity between 80–90 and 60 mole % silica as units of intermediate but decreasing polymerization are formed, then sharply decreasing viscosity as discrete orthosilicate groups begin to appear in the melt structure. Unfortunately for the above hypothesis, the alkaline earth systems do not show any inflection near 60 mole % silica (Bockris and Lowe, 1954; Bockris et al., 1955; Mackenzie, 1960). At present, more data are needed on the viscosities of simple silicate systems (see Urbain et al., 1982) before realistic structural models may be attempted. Raman spectroscopy may

play an important part in the elaboration of such models. Although the details of flow processes in such associated liquids do not yet seem to be well understood, it is likely that the flow units involved are somewhat larger than the structural groups sampled by our present interpretation of the Raman spectra. It is concluded that both the measurement and interpretation of silicate liquid viscosities, and their correlation with Raman spectroscopic and other structural studies, should remain an active research problem.

Roedder (1979) has recently discussed the current status of liquid immiscibility as a petrological process. It has long been known that liquids in the systems $\text{SiO}_2\text{-MgO}$, CaO and SrO show large miscibility gaps at high silica content (e.g., Greig, 1927), while $\text{SiO}_2\text{-BaO}$ and $\text{SiO}_2\text{-Li}_2\text{O}$, Na_2O and perhaps K_2O show metastable immiscibility in high silica glasses (e.g., Charles, 1966, 1967, 1969; Galakhov and Varshal, 1973; Haller et al., 1974; Hess, 1977). In all cases, the silica-rich liquid is near pure silica (90–100 mole % SiO_2), while the composition of the metal oxide-rich liquid or glass becomes progressively richer in metal oxide in the order $\text{Ba} < \text{Sr} < \text{Ca} < \text{Mg}$ for alkaline earth oxides, and for the alkalis, $\text{K} < \text{Na} < \text{Li}$; with Li between Mg and Ca, Na between Sr and Ba, and K lower than Ba (e.g., Kracek, 1939; Charles, 1967; Galakhov and Varshal, 1973; Hess, 1977). McMillan (1981, 1984) and Matson et al. (1983) have recently derived similar but independent models from Raman spectroscopic studies which rationalize this behavior. This model has been extended to aluminosilicate systems by McMillan et al. (1982), and was used to successfully rationalize and predict systematics in the enthalpies of mixing along the joins $\text{SiO}_2\text{-NaAlO}_2$, $\text{SiO}_2\text{-CaAl}_2\text{O}_4$ (Navrotsky et al., 1982) and $\text{SiO}_2\text{-MgAl}_2\text{O}_4$ (Peraudeau and Navrotsky, in prep.; Navrotsky and Roy, in prep.).

It is concluded that Raman spectroscopy does provide useful information as to the structures of silicate melts and glasses, and if used carefully in conjunction with other techniques, can help us better understand their static and dynamic properties. It is suggested that considerable further work is necessary to fully realize its potential, and to define its useful limits in this type of study.

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