THE STRUCTURE OF Ti SILICATE GLASSES BY MICRO-RAMAN SPECTROSCOPY

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ABSTRACT

Micro-Raman spectra have been obtained for glasses prepared along the TiO_2-SiO_2, $Na_2SiO_3-TiO_2$, and $CaSiO_3-TiO_2$ joins, and for the compounds fresnoite ($Ba_2TiSi_2O_8$), barium titanate (Ba_2TiO_4), rutile and anatase. The spectra do not indicate the presence of 6-fold coordinated titanium ([6]Ti) except where cryptocrystalline anatase is present. Ti is 4-fold coordinated ([4]Ti) in all glass systems investigated at low TiO_2 contents. However, comparison of the spectra of the glasses with spectra of crystalline fresnoite ([5]Ti), glass of fresnoite composition, and $\beta-Ba_2TiO_4$ ([4]Ti) indicates that, at high TiO_2 contents, the alkali-containing glasses have Ti predominantly as [5]Ti. Titanium in the alkaline-earth-containing glasses appears to be a mixture of both [4]Ti and [5]Ti. A structural reorganization of the network occurs in both the alkali- and alkaline-earth-containing glasses at around 10 mol% TiO_2, and this may be associated with the formation of 5-fold coordinated titanium ([5]Ti).

Keywords: micro-Raman, spectroscopy, titanium, glasses, coordination, phase separation, anatase, fresnoite.

SOMMAIRE

Nous avons obtenu des spectres de micro-Raman afin de caractériser des verres préparés dans les systèmes TiO_2-SiO_2, $Na_2SiO_3-TiO_2$ et $CaSiO_3-TiO_2$, ainsi que pour les composés fresnoïte ($Ba_2TiSi_2O_8$), titanate de baryum (Ba_2TiO_4), rutile and anatase. Les spectres n'indiquent pas la présence de titanium à coordinence six ([6]Ti) sauf en présence d'anatase cryptocristalline. Le Ti se trouve en coordinence quatre ([4]Ti) dans toutes les compositions de liquides à faible teneur en TiO_2. Toutefois, une comparaison des spectres de ces échantillons de verre avec ceux de la fresnoïte cristalline ([5]Ti), d'un verre de la composition de fresnoïte, et de $\beta-Ba_2TiO_4$ ([4]Ti) montre qu'à teneurs élevées de TiO_2, les verres contenant des alcalins contiennent le Ti surtout sous forme de [5]Ti. Par contre, dans les verres contenant les éléments alcalino-terreux, le titanium semble être un mélange de [4]Ti et [6]Ti. Une réorganisation structurale de la trame serait entamée dans les deux catégories de systèmes à environ 10% de TiO_2 (base molaire); elle pourrait bien comporter la formation de titanium à coordinence cinq.

Mots-clés: micro-Raman, spectroscopie, titanium, verre, coordinence, séparation de phases, anatase, fresnoïte.

INTRODUCTION

Titanium is a relatively common but low-abundance element found in most igneous rocks, in amounts less than 2 wt% TiO_2 (Mysen 1990). However, the presence of Ti can have a profound influence on the physical and chemical behavior of the natural melts (magmas) from which these rocks are derived. For example, addition of TiO_2 to a silica melt decreases the liquidus temperature and increases the activity of SiO_2 (Kushiro 1975). In addition, quenched synthetic melts containing TiO_2 are some of the most refractory glasses known (they are more refractory than fused quartz) and have an extremely low thermal expansion. Consequently, TiO_2-bearing glasses are used in the manufacture of optical components subjected to temperature extremes. The structural role of Ti^{4+} in both natural and synthetic systems has been investigated by a number of techniques. Solubility experiments suggest that Ti is essentially 4-fold coordinated in TiO_2-bearing Ca–Mg aluminosilicate melts (Wood & Hess 1980). Similarly, vibrational spectroscopy studies of TiO_2-SiO_2 glasses and alkali- and alkaline-earth-containing TiO_2-SiO_2 glasses suggest that Ti is 4-fold coordinated (Furukawa & White 1979, Mysen *et al.* 1980). However, X-ray emission (Hanada & Soga 1980), neutron scattering (Wright *et al.* 1987) and EXAFS/XANES (XAS) studies (Sandstrom *et al.* 1980, Greegor *et al.* 1983, Emili *et al.* 1985) suggest that Ti is both 4- and 6-fold coordinated in silicate glasses. In particular, the studies

of Sandstrom *et al.* (1980) and Greegor *et al.* (1983) suggest that Ti is 6-fold coordinated at low contents of TiO_2 (<~0.05 wt% TiO_2), but 4-fold coordinated between 0.05 and ~9 wt% TiO_2, above which octahedrally coordinated Ti again starts to reappear. The suggestion of a dual coordination for Ti was first proposed by Rao (1963), on the basis of physical properties of $K_2O–TiO_2–SiO_2$ glasses. Recent measurements of density and partial molar volume performed on $Na_2SiO_3–TiO_2$ and $CaSiO_3–TiO_2$ melts (Dingwell 1992a, b) imply that Ti must be 4-fold coordinated in alkali-containing silicate melts, but 6-fold coordinated in alkaline-earth-containing silicate melts.

Clearly, there is disagreement among previous findings. Part of this disagreement may arise from the tendency of geologically oriented investigators to use compositionally complex systems for study. However, most of the ambiguity is probably attributable to the observation that Ti-containing glasses and melts undergo phase separation at ~10.8 wt% TiO_2 (DeVries *et al.* 1954, Evans 1970), such that many studies have actually been performed on immiscible liquids or two-phase glasses. We re-investigated the structure of glasses along the $TiO_2–SiO_2$, $Na_2SiO_3–TiO_2$ and $CaSiO_3–TiO_2$ joins using micro-Raman spectroscopy to resolve the question of Ti coordination.

EXPERIMENTAL

Sample preparation

Glasses along the $TiO_2–SiO_2$ join were prepared by the sol–gel method of Hayashi *et al.* (1983) rather than by the more common flame hydrolysis method. The sol–gel method produces single-phase solid-solution glasses up to 7.4 wt% TiO_2, as opposed to ~11 wt% TiO_2 if the compositions are prepared using flame hydrolysis. Heterogeneous glasses are produced above 7.4 wt% TiO_2. A broad range of compositions were prepared, but several of the gels became opalescent upon final heating as a result of the formation of cryptocrystalline anatase. A clear bubble-free glass was, however, obtained for the following compositions (wt% TiO_2): 0.88, 1.90, 3.62, 5.64, 8.13, 8.50, 12.00, 14.92. Titania contents were verified by electron-microprobe analysis of the final glasses using the Cameca SX50 microprobe system at the University of Toronto.

For the alkali and alkaline-earth series of glasses, mixtures of analytical grade Na_2CO_3, $CaCO_3$, TiO_2 and SiO_2 were prepared at 0.01, 0.03, 0.05, 1.0, 3.5, 7.1, 10.8, 14.7, 27.0 wt% TiO_2, and 0.01, 0.03, 0.05, 1.0, 3.4, 6.8, 10.4, 14.1 and 26.1 wt% TiO_2 along the $Na_2SiO_3–TiO_2$, and $CaSiO_3–TiO_2$ joins, respectively. The powdered mixtures were melted in covered platinum dishes at 1150°C for the Na-containing glasses and 1600°C for the Ca-containing glasses, and

then air-quenched. Results of electron-microprobe analyses of the glasses were within ±1% of nominal values. All compositions resulted in clear, bubble-free glasses, which were examined optically under oil for evidence of phase separation. They appeared to consist of a homogeneous single phase.

Micro-Raman spectroscopy

The coupling of the standard laser Raman system with an optical microscope has enabled micro-Raman spectroscopy, as this combination of instruments has been called, to be applied to a wide range of geological problems. McMillan & Hofmeister (1988) (and references contained therein) provided a good review of the Raman technique and its application to geological problems.

The micro-Raman system uses a standard optical microscope and beam splitter to focus the collimated laser light onto the sample. The scattered light is reflected back up the objective, through the beam splitter and directed into a spectrometer.

This setup has the advantage over the conventional system of allowing one to focus the laser beam down to a very small size (~1–2 μm), as well as to focus the beam within the sample. This enables *in situ* non-destructive analysis of very small or powdered samples. Further, in glass systems such as those in this study, in which unmixing or phase separation may have occurred, particularly on a small scale, the micro-Raman system can be used to investigate possible spatial variations within individual samples.

Figure 1 shows a schematic diagram of the Raman system used in this study. We employed a Lexel 3500 Kr^+ laser operating at ~300 mW and a wavelength of 530.9 nm. The laser light is passed to a tunable excitation filter that removes extraneous plasma lines and other unwanted background before passing the exciting radiation into the spectrometer. Energy resolution is achieved by employing a monochromator that consists of an entrance slit, a diffraction grating and an exit slit.

The monochromator used in this study is a Spex Industries 1877 Triplemate. The Triplemate consists of two sections. The first section is a 0.22-m double monochromator with gratings in a subtraction-dispersion mode. It acts as a variable-wavelength selectable band-pass filter that passes the nondispersed scattered light into a second section of the spectrograph. The second section is a 0.6-m single monochromator that disperses the scattered light over the detector by means of a variable grating.

Finally, a detection system is used to count the number of scattered photons at each frequency (*i.e.*, intensity) exiting the monochromator. All data used in this study were collected using a Charge Coupled Device (CCD) [Princeton Instruments LN/CCD (CSMA)], which is a two-dimensional area detector
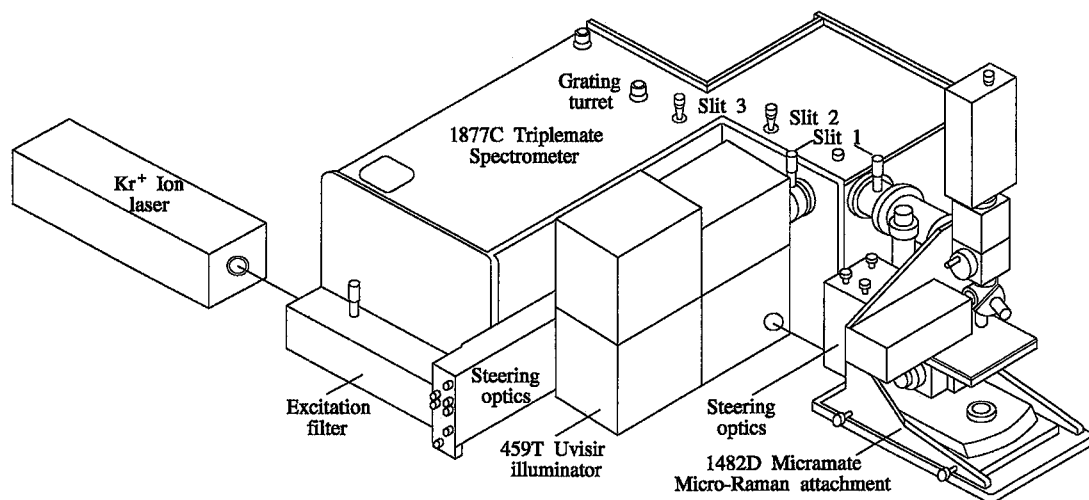
FIG. 1. Schematic diagram of the instrumental setup used in this study. Exciting laser, spectrometer and micro-Raman attachments are indicated.

consisting of a matrix of semiconductor elements. The Spex Triplemate employs a Thompson-type CCD chip with dimensions of 578×384 elements. This type of detector allows the collection of the entire spectrum simultaneously; it offers rapid collection of data and sensitivity. Consequently, high-resolution spectra of relatively weak Raman scatterers such as glasses can be obtained very quickly and easily.

Raman spectra for each composition were obtained by counting an individual spectrum of glass for 30 seconds and then averaging multiple spectra over 1 hour. Instrumental conditions were optimized, for each sample, to minimize scattering from the exciting laser line and to produce the highest signal-to-noise ratio possible. In general, the laser was focussed onto small chips of glass or powdered crystalline material using the highest-magnification objective, which produced a spot size of 1–2 µm. In addition, it was found that defocussing of the laser enhanced the signal-to-noise ratio and eliminated much of the extraneous scattering from the exciting laser line. Polarized spectra were obtained for all samples, but only the parallel-polarized spectra are presented here. Further, an initial spectrum of SiO_2 glass was taken at the beginning of each experimental session. This was done because silicate glasses are relatively weak Raman scatterers, and it can be difficult to distinguish the vibrational bands of a glass from the background during instrument setup. Optimization of instrument conditions on SiO_2 glass prior to collection of a series of spectra from other compositions is therefore desirable. Band positions were found to be accurate to ± 10 cm^{-1} for the broad bands and ± 5 cm^{-1} for the narrower bands.

A series of Raman spectra were also collected for comparison purposes from several Ti-containing minerals in which the coordination of Ti is [4]Ti, [5]Ti, or [6]Ti. Raman spectra were collected for the TiO_2 polymorphs rutile ([6]Ti) and anatase ([6]Ti), as well as β-Ba$_2$TiO$_4$ ([4]Ti), and crystalline fresnoite (Ba$_2$TiSi$_2$O$_8$, [5]Ti) and its vitreous equivalent.

Synthetic fresnoite and β-Ba$_2$TiO$_4$ were prepared from stoichiometric mixtures of the pure compounds $BaCO_3$, TiO_2 and SiO_2, which were ground and mixed, pelletized, and contained in platinum dishes. For the fresnoite composition, two methods of preparation were used. One mixture was sintered at 1350°C for 10.5 h (following Alfors et al. 1965), whereas the other was crystallized from the melt, by cooling from 1500 to 1250°C. The products of both preparations were characterized as pure synthetic fresnoite by powder X-ray diffraction. A glass of fresnoite composition was prepared by melting the starting mixtures at 1500°C and air quenching from 1338°C. β-Ba$_2$TiO$_4$ was heated at 1300°C for 2 h (following Wu & Brown 1973), and confirmed as the pure phase by powder X-ray diffraction. Anatase from Garas, Brazil, and rutile from Minas Gerais, Brazil, were obtained from the mineral collection at The University of Western Ontario. Spectra of the crystalline materials were accumulated over 5 minutes, and peaks are accurate to ± 2 cm^{-1}. All Raman spectra were calibrated using a neon spectrum obtained from a neon discharge lamp.

RESULTS AND DISCUSSION

TiO$_2$–SiO$_2$ glasses

Results for the glasses along the TiO_2–SiO_2 join are shown in Figure 2. The spectra are similar to those documented in previous studies (Kato 1976, Bihuniak
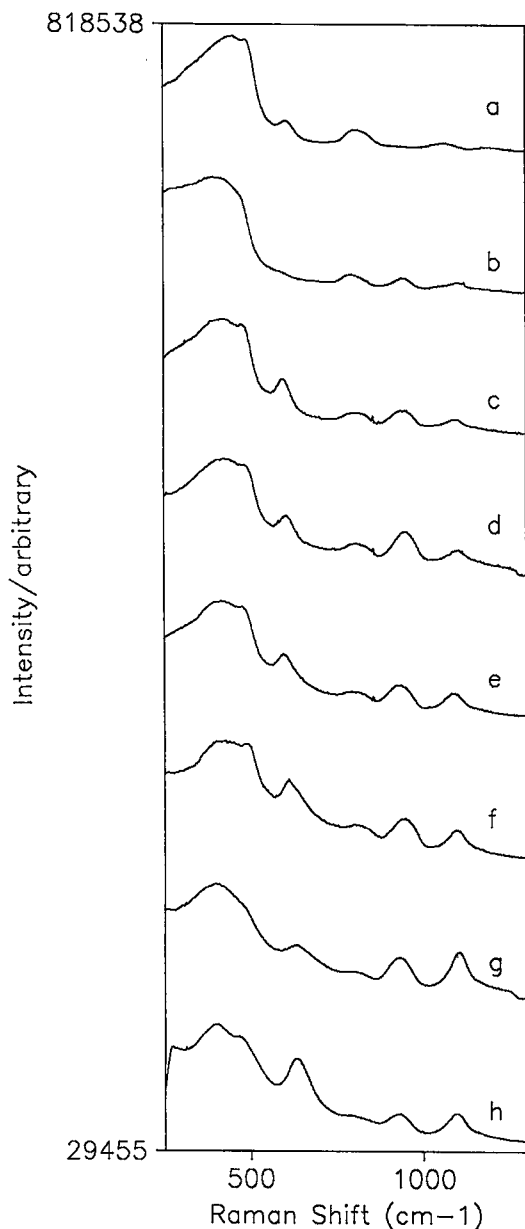
818538

Intensity/arbitrary

29455

500   1000
Raman Shift (cm−1)

FIG. 2. Parallel-polarized Raman spectra for glasses along the TiO$_2$–SiO$_2$ join. a) SiO$_2$, b) 0.88 wt% TiO$_2$, c) 1.9 wt% TiO$_2$, d) 3.62 wt% TiO$_2$, e) 5.64 wt% TiO$_2$, f) 8.50 wt% TiO$_2$, g) 12.00 wt% TiO$_2$, h) 14.92 wt% TiO$_2$.

& Condrate 1981, Chandrasekhar *et al.* 1980, Best & Condrate 1985, Kusabiraki 1987, Beghi *et al.* 1992, Chmel *et al.* 1992, Farrow & Vogel 1992). The Raman spectrum of pure SiO$_2$ glass exhibits peaks at ~449, 490, 606, ~804, ~835, 1062 and ~1195 cm^{-1}. The

low-frequency vibration at ~449 cm^{-1} is due to symmetrical stretching of bridging oxygen (BO) atoms (*cf.* Henderson *et al.* 1985). The bands at 490 and 606 cm^{-1} are due to BO vibrations associated with 4- and 3-membered siloxane rings, whereas the features at ~800, 1062 and 1195 cm^{-1} are due to silicate cage or Si–O–Si bending, and asymmetrical BO vibrations, respectively, which have longitudinal and transverse optical (LO/TO) splittings [*cf.* McMillan (1984a) for a comprehensive discussion of band assignments].

With the addition of Ti to pure SiO$_2$ glass, the SiO$_2$ vibrational bands shift to lower frequency. This shift is attributed to the substitution of Ti for Si within the glass network and is similar to the shift seen with the addition of Ge (Henderson *et al.* 1985). It is indicative of random substitution of Ti for Si within the glass network. We did not observe a systematic decrease in intensity of the 490 and 606 cm^{-1} bands of pure SiO$_2$ glass with addition of TiO$_2$ (Chandrasekhar *et al.* 1980). The 606 cm^{-1} band appears to weaken with the addition of 0.88 wt% TiO$_2$ (Fig. 2b), but this may be attributed to the rather poor spectrum we obtained from this sample.

Two intense bands at ~945 and ~1100 cm^{-1} reflect the addition of TiO$_2$. The intensity of the band at 945 cm^{-1} exhibits a linear dependence on TiO$_2$ concentration (Knight *et al.* 1989). The two bands have been assigned to the E and A$_1$ vibrational modes of the SiO$_4$ tetrahedron, which occur as the site symmetry of SiO$_4$ is reduced from T_d to C_3V (Bihuniak & Condrate 1981). Alternatively, Kato (1976) attributed the bands to vibrations involving Si and nonbridging oxygen (NBO) atoms that occur as Ti is added, whereas Knight *et al.* (1989) suggested that they result from Ti-enriched clusters within the glass network.

Interpretation of these bands is problematic because similar bands are observed in Ti-free glasses and in glasses with other dopants. Sodium silicate glasses containing no Ti exhibit two vibrational bands, at 945 and 1100 cm^{-1}, which can be assigned to NBO vibrations associated with Q^2 and Q^3 species, respectively (*cf.* Henderson & Fleet 1991). Similar vibrational bands are observed in B-, F-, and Ge-bearing silicate glasses. It would seem likely that these vibrational bands are not directly related to the dopant species but rather to a response of the silicate network to the addition of the dopant. Given the close similarity of the bands with those observed for sodium silicate glasses, we interpret the observed bands in the TiO$_2$–SiO$_2$ glasses as being due to the formation of SiO$_4$ tetrahedra with two atoms (945 cm^{-1}) and one atom (1100 cm^{-1}) of nonbridging oxygen (Q^2 and Q^3 species, respectively; *cf.* Henderson & Fleet 1991). This interpretation suggests that the addition of Ti to fully polymerized SiO$_2$ glasses, although its distribution is random, does result in the formation of Q^2 and Q^3 tetrahedra, and some depolymerization of the network. However, one cannot rule out the possibility

that these bands are due to Ti–O vibrations associated with Q^2 and Q^3 species, particularly if the vibrations resulted predominantly from motion of oxygen atoms with little contribution from the movement of cations.

Best & Condrate (1985) have observed a band at 665 cm^{-1} that they attributed to the formation of 6-fold coordinated Ti ([6]Ti). However, this band was observed only in the glasses whose TiO_2 content exceeds 11.2 mol%. This is the region in which phase separation of TiO_2–SiO_2 glasses occurs (Evans 1970). The spectra in Figure 2 for compositions with <7.4 wt% TiO_2 have no vibrational bands at ~665 cm^{-1}. This suggests that no [6]Ti occurs in the homogeneous glass region. However, above about 8 wt% TiO_2, phase separation and formation of crypto-crystalline anatase ([6]Ti) (Best & Condrate 1985) do occur in our glasses, as observed by a broadening and increase in intensity of a shoulder on the high-wavenumber side of the 606 cm^{-1} band of pure SiO_2 glass (see Fig. 2f). Figure 2h, for the bulk composition with the highest TiO_2 content, has three bands at ~400, 465 and 634 cm^{-1}, which are slightly sharper than equivalent bands in glasses containing less Ti. These bands are indicative of anatase. This is most clearly seen in Figure 3, where cryptocrystalline anatase precipitated when the gel was heated. Comparison with the vibrational spectrum of crystalline anatase (Fig. 4) shows that the three relatively sharp bands observed in the "glass" are the same as those for pure anatase. Figure 4 also shows the spectra for rutile; vibrational bands of rutile are absent in all glass spectra, consistent with the findings of Best & Condrate (1985).

Alkali-containing Ti-silicate glasses

Results for the glasses along the Na_2SiO_3–TiO_2 join are shown in Figure 5. The results are similar to those described in the limited study of Mysen et al. (1980) for comparable compositions. At low TiO_2 contents, three bands are observed, at 608, 843 and 965 cm^{-1}. A shoulder also is observed to the high-wavenumber side of the 965 cm^{-1} band (Fig. 5). The same bands are observed for pure Na_2SiO_3 glasses (Brawer & White 1975). With the addition of up to 3.5 wt% TiO_2, there is an increase in intensity of the 843 cm^{-1} band and of the high-wavenumber shoulder. The strong band at 965 cm^{-1} gradually shifts to lower wavenumbers, and the low-frequency band at 608 cm^{-1} remains essentially unchanged. By 7.1 wt% TiO_2, the 843 cm^{-1} band has become the dominant peak and has shifted to slightly higher wavenumbers, along with the low-frequency 608 cm^{-1} band. The high-wavenumber shoulder also has increased in intensity relative to the band originally at 965 cm^{-1}. Beyond 7.1 wt% TiO_2, all bands rapidly decrease in intensity, except for the main 843 cm^{-1} band (now at 851 cm^{-1}). At 27.0 wt% TiO_2, there is little evidence for the band that was at 965 cm^{-1} other than a slight asymmetry to the high-wavenumber side of the main band, now at 858 cm^{-1}. A high-wavenumber shoulder remains at ~1030 cm^{-1}, but the low-frequency band, originally at 608 cm^{-1}, has completely disappeared. However, three very weak bands are observed in the same region, at 568, 640 and 702 cm^{-1}.

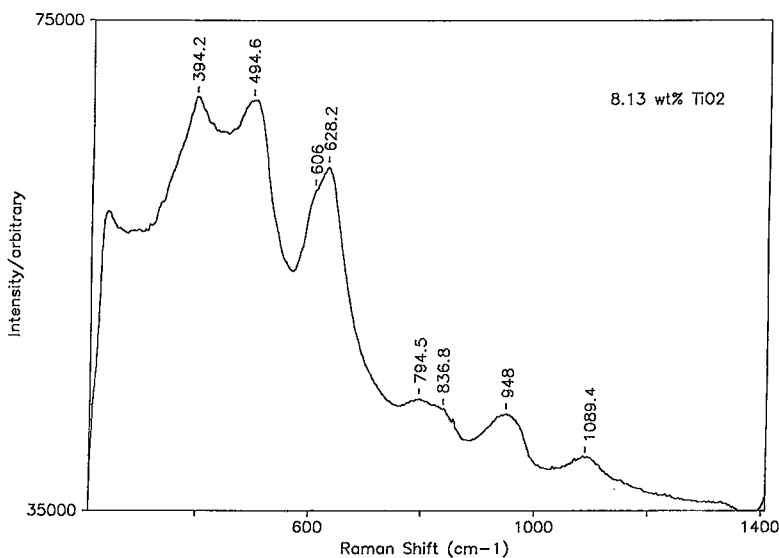The band at 965 cm^{-1} and its shoulder to the high-

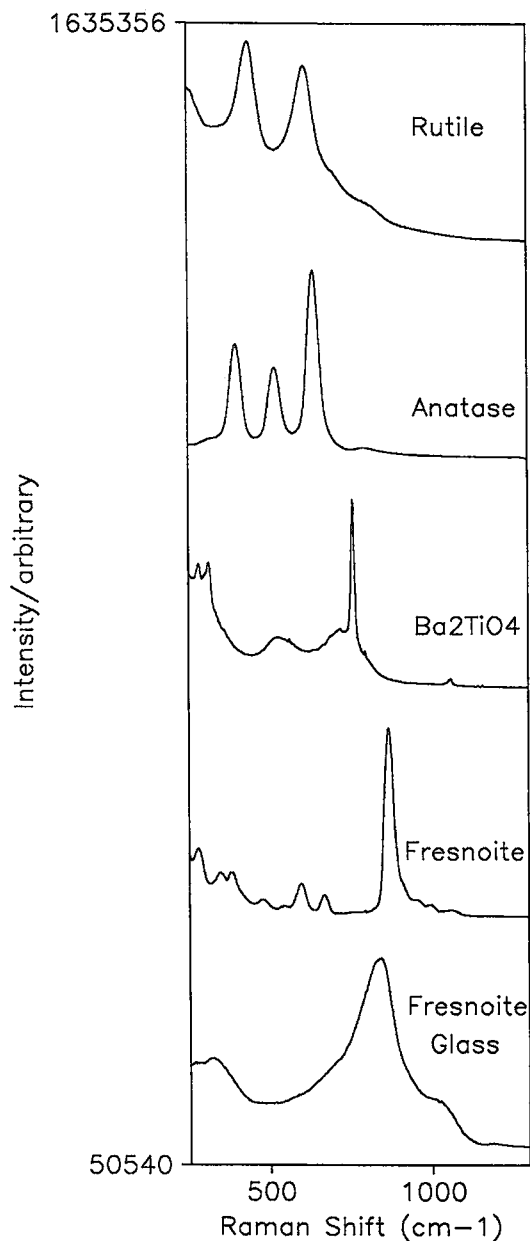FIG. 3. Parallel-polarized Raman spectrum of a glass with 8.13 wt% TiO_2 and crypto-crystalline anatase present.

FIG. 4. Parallel-polarized Raman spectra of TiO₂ polymorphs, β-Ba₂TiO₄, crystalline fresnoite (Ba₂TiSi₂O₈) and a glass of fresnoite composition: a) rutile, b) anatase, c) β-Ba₂TiO₄, d) crystalline fresnoite, e) glass of fresnoite composition.

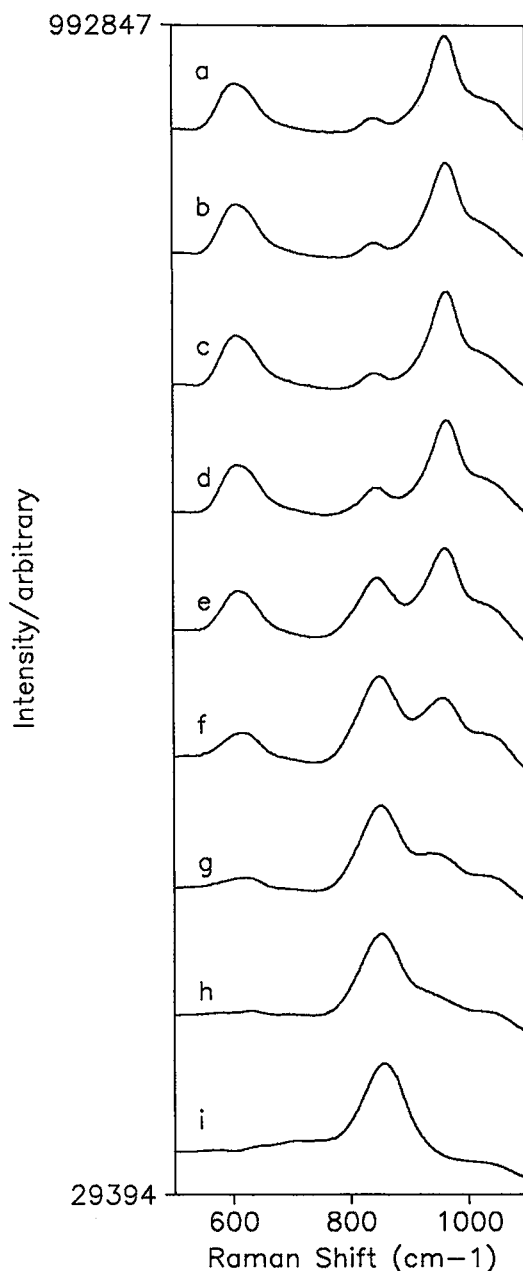FIG. 5. Parallel-polarized Raman spectra of glasses along the Na₂SiO₃–TiO₂ join: a) 0.01 wt% TiO₂, b) 0.03 wt% TiO₂, c) 0.05 wt% TiO₂, d) 1.0 wt% TiO₂, e) 3.5 wt% TiO₂, f) 7.1 wt% TiO₂, g) 10.8 wt% TiO₂, h) 14.7 wt% TiO₂, and i) 27.0 wt% TiO₂.

wavenumber side can be assigned to Si–NBO vibrations associated with Q^2 and Q^3 tetrahedra, respectively (*cf*. Henderson & Fleet 1991, McMillan *et al*. 1993). The low-frequency band at 608 cm⁻¹ has been assigned to Si–BO vibrations associated with small 3-membered siloxane rings within the glass (Henderson & Fleet 1991). The dependence of the 843 cm⁻¹ band upon TiO₂ content clearly indicates that

this particular vibrational band is associated with Ti–O vibrations. A similar band is observed in Li-bearing Ti-silicate glasses (Furukawa & White 1979) and in Na_2TiO_3 glass (Mysen et al. 1980). These authors assigned this band to Ti–O symmetrical stretching vibrations associated with Ti_2O_6 anionic units within the glass. A band is observed at ~850 cm^{-1} in alkali-rich alkali silicate glasses [cf. McMillan (1984a) and references therein] that has been assigned to NBO vibrations associated with isolated (Q^0) SiO_4 tetrahedra (McMillan 1984b). Whereas some of the intensity of the 843 cm^{-1} band may be attributable to Q^0 tetrahedra, its very strong dependence on Ti content appears to indicate a major Ti–O component. The Raman spectrum of Na_2TiO_3 glass, containing no Si, exhibits a strong band at around 880 cm^{-1} (Mysen et al. 1980). We therefore assign the 843 cm^{-1} band observed in our spectra to Ti–O vibrations. Whether the Ti–O vibrations are associated with a mixed Ti–Si structure, as suggested by Furukawa & White (1979), or to isolated TiO_4 tetrahedra, must remain speculative until a detailed vibrational analysis of mixed TiO_4–SiO_4 systems is available.

Furukawa & White (1979) observed that discrete TiO_6 vibrations in crystalline compounds occur at wavenumbers less than 650 cm^{-1}, whereas discrete TiO_4 vibrations occur at around 750 cm^{-1}. The high-frequency vibrational bands for rutile and anatase ([6]Ti) are at 613, and 638 cm^{-1}, whereas for Ba_2TiO_4 ([4]Ti) it is at 767 cm^{-1}. Note that the strongest vibrational band for anatase occurs at ~143 cm^{-1} and is outside the spectral range covered by our experimental

setup. Titanium can also have a coordination of [5]Ti. Fresnoite consists of $[Si_2O_7]^{6-}$ groups linked by common corners to TiO_5 tetragonal pyramids (Moore & Louisnathan 1969). The main vibrational band in the Raman spectrum occurs at 867 cm^{-1}.

Comparison of the Na_2SiO_3–TiO_2 glass spectra with the spectra obtained from crystalline Ti analogues (Fig. 4) indicates that Ti is not 6-fold-coordinated in these glasses. The main vibrational band in the glasses is at 843 cm^{-1} and is clearly closer to the position of the [4]Ti band than the [6]Ti vibrations at lower wavenumbers. This would suggest that Ti is predominantly [4]Ti in the glasses. However, there is a close correspondence at higher TiO_2 contents between the band at 843 cm^{-1} and the main vibrational band observed in crystalline fresnoite and its vitrified equivalent (Fig. 6). In addition, the shape of the vibrational envelope in the 27 wt% TiO_2 glass is essentially the same as that observed for glass of fresnoite composition. The similarities in band shape and position would suggest that at higher TiO_2 contents, a significant portion of the Ti is 5-coordinate ([5]Ti). This implies that while Ti initially enters the glass network as [4]Ti, the continued addition of Ti results in the formation of [5]Ti. Preliminary Ti EXAFS/XANES data on $Na_2O·TiO_2·2SiO_2$ and $Na_2O·TiO_2·4SiO_2$ glasses essentially confirm our findings concerning the presence and behavior of [5]Ti (F. Farges, pers. comm). Similarly, Yarker et al. (1986) have proposed that [5]Ti occurs in $K_2O·TiO_2·2SiO_2$ glasses based on neutron diffraction and EXAFS studies.

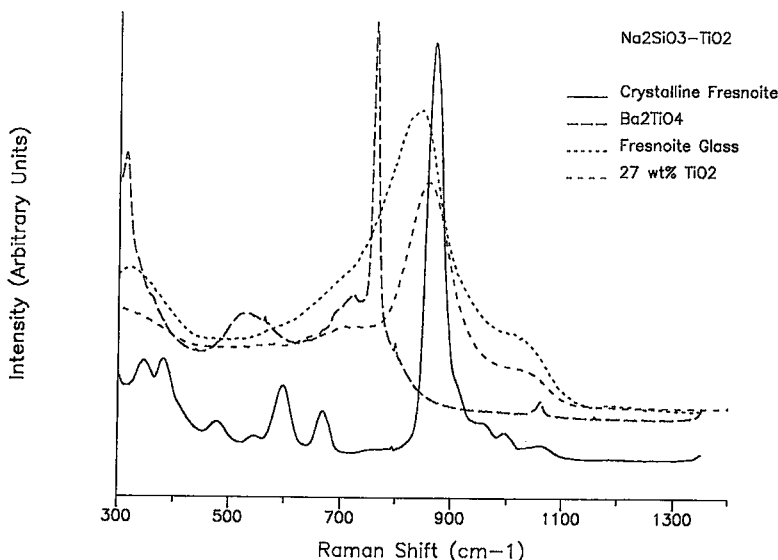The spectra also show evidence for a structural

FIG. 6. Parallel-polarized Raman spectra of β-Ba_2TiO_4, crystalline fresnoite, a glass of fresnoite composition, and the Na_2SiO_3–TiO_2 glass containing 27 wt% TiO_2.

change in glasses with more than 7.1 wt% (~ 10.5 mol%) TiO_2. Spectra of glasses with less than 7.1 wt% TiO_2 clearly exhibit the low-frequency 608 cm^{-1} band assigned to Si–BO vibrations associated with 3-membered siloxane rings. In addition, the band shifts to lower wavenumbers as Ti is added, up to 7.1 wt% TiO_2. However, beyond 7.1 wt% TiO_2, the 608 cm^{-1} band rapidly decreases along with the high-frequency Q^2 and Q^3 NBO vibrations. This would suggest that Ti substitutes randomly for Si up to 7.1 wt% TiO_2 and could indicate that beyond this value, the coordination of Ti changes, perhaps from [4]Ti to [5]Ti. A change in coordination of Ti would drastically affect the vibrational modes of the silicate network, and may well alter the site symmetry for Si–O vibrations sufficiently to make them relatively weak or possibly Raman inactive.

Alkaline-earth-containing Ti-silicate glasses

The spectra of alkaline-earth-containing silicate glasses (Fig. 7) are more complex than their alkali counterparts. At low TiO_2 contents, two relatively sharp bands are observed at 637 and 1094 cm^{-1}, with three broader bands at ~700, 855 and 958 cm^{-1}. With the addition of TiO_2 up to 6.85 wt%, all bands, with the exception of the one at 1094 cm^{-1}, increase in intensity. The 1094 cm^{-1} band rapidly decreases in intensity. The band at 855 cm^{-1} shifts to lower wavenumbers, becomes asymmetrical and is the dominant vibrational feature by 6.85 wt% TiO_2 (9.7 mol%). The higher-frequency bands at 957 and 1092 cm^{-1} also shift to lower wavenumbers as Ti is added. Beyond 6.85 wt% TiO_2, there is a rapid decrease in the intensity of all bands other than the main 855 cm^{-1} band that is now at 838 cm^{-1}. This behavior is similar to that of the alkali-containing glasses. By 26.1 wt% TiO_2, the main band at 814 cm^{-1} is markedly asymmetrical to the low-wavenumber side, and only weak remnants of the bands observed at low TiO_2 contents are visible. Band assignments are similar to the spectra of the Na-bearing compositions. The two high-frequency bands at 1094 and 958 cm^{-1} can be assigned to NBO vibrations associated with Q^3 and Q^2 tetrahedra, respectively. The low-frequency BO band at 637 cm^{-1} is associated with 3-membered siloxane rings. The band at 855 cm^{-1} is assigned to Ti–O vibrations.

Like the alkali-containing glasses, comparison of the spectra with crystalline Ti analogues (Fig. 4) suggests that no [6]Ti is present in the $CaSiO_3$–TiO_2 glasses. Similarly, at low TiO_2 contents, the spectra indicate that Ti is predominantly in 4-fold-coordination; the main vibrational band at 855 cm^{-1} is closer to the position of the [4]Ti band than the [6]Ti vibrations at lower wavenumbers. At high TiO_2 contents, the main vibrational band at 814 cm^{-1} is not comparable, unlike the alkali-containing glasses, in position or in shape to the main band observed for crystalline fresnoite and its
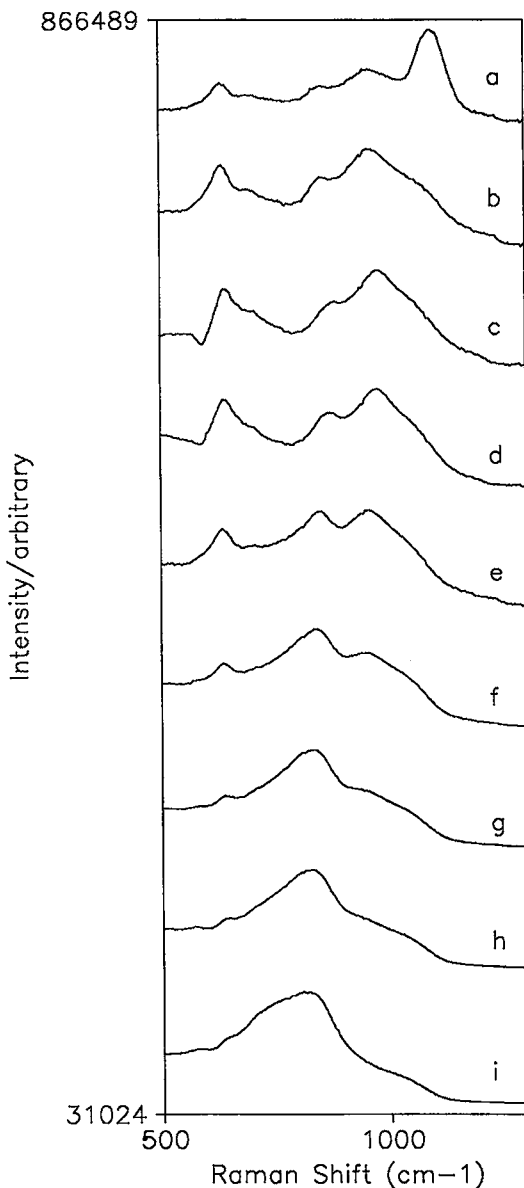

FIG. 7. Parallel-polarized Raman spectra of glasses along the $CaSiO_3$–TiO_2 join: a) 0.01 wt% TiO_2, b) 0.03 wt% TiO_2, c) 0.05 wt% TiO_2, d) 1.0 wt% TiO_2, e) 3.4 wt% TiO_2, f) 6.8 wt% TiO_2, g) 10.4 wt% TiO_2, h) 14.1 wt% TiO_2, and i) 26.1 wt% TiO_2.

vitreous equivalent (Fig. 8). The band at 814 cm^{-1} is, however, midway between the main band for β-Ba_2TiO_4 ([4]Ti) and that of crystalline fresnoite ([5]Ti). We speculate that this may indicate that some of the Ti atoms are in 5-fold-coordination in these high-TiO_2 glasses. This implies that there is more of a
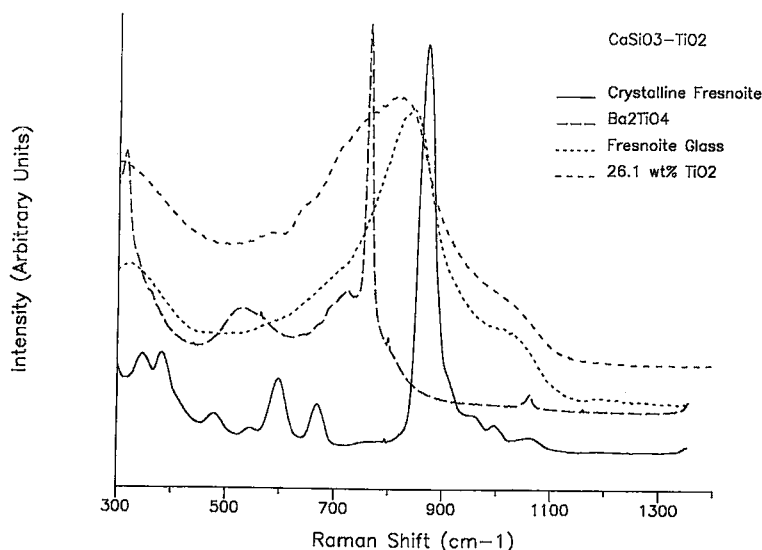
FIG. 8. Parallel-polarized Raman spectra of β-Ba_2TiO_4, crystalline fresnoite, a glass of fresnoite composition, and the $CaSiO_3$–TiO_2 glass containing 26.1 wt% TiO_2.

mixture of both [4]Ti and [5]Ti in the Ca-bearing glasses than in the Na-bearing glasses, where [5]Ti seems to dominate at the higher TiO_2 contents. A structural change, or at least a change in site symmetry similar to that observed in the alkali-bearing glasses at 7.1 wt% TiO_2 (10.5 mol%), is indicated at around 6.85 wt% TiO_2 (9.7 mol%).

CONCLUSIONS

The Raman spectra of glasses along the TiO_2–SiO_2 join indicate that [6]Ti is observed only where phase separation occurs and cryptocrystalline anatase is formed. The presence of anatase is first indicated by broadening of the 606 cm^{-1} band of SiO_2 on the high-wavenumber side, followed by the evolution of three Raman bands characteristic of anatase at 397, 517, and 638 cm^{-1}. Titanium is 4-fold-coordinated in the homogeneous glasses.

Glasses along the Na_2SiO_3–TiO_2 join appear to be homogeneous, and the Raman spectra exhibit no indication of [6]Ti. Titanium is 4-fold-coordinated ([4]Ti) at low TiO_2 contents, but is predominantly 5-fold-coordinated ([5]Ti) at high TiO_2 contents. A structural change is inferred in the glasses at 7.1 wt% (~10.5 mol%) TiO_2. This change is observed as a decrease in intensity of the vibrational bands associated with the silicate network, which may indicate a change in the SiO_4 site symmetry associated with the formation of the [5]Ti.

The spectra of glasses in the system $CaSiO_3$–TiO_2 behave in a similar manner to the alkali silicate glasses upon the addition of TiO_2. The spectra do not indicate the presence of [6]Ti, and titanium is 4-fold-coordinated at low TiO_2 contents. At high TiO_2 contents, the presence of [5]Ti is indicated but, unlike the case of the alkali silicate glasses, a significant proportion of Ti remains 4-fold-coordinated.

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