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The vibrational spectra of $MgO–Al_2O_3–SiO_2$ glasses containing TiO_2

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The infrared spectra from a series of $MgO–Al_2O_3–SiO_2$ glasses containing TiO_2 are consistent with the existence of a phase-separated structure consisting of a high silica phase and a high modifier phase of metasilicate composition. The invariance of the spectra throughout the range of pre-crystallization heat treatments and compositions precludes the possibility of significant changes in the average number of non-bridged oxygen ions per silica tetrahedron either during "nucleation" treatments or upon the addition of TiO_2 to the base glass. The Raman spectra from the same series of glasses consist of two main high-frequency bands, at 1000 and 910 cm^{-1} which change markedly in relative intensity as TiO_2 is added to the base glass, and several subsidiary bands at lower frequencies. It is suggested that the high-frequency bands arise from two dissimilar metasilicate-type structures which are the pre-cursors of the major crystalline phases which precipitate upon devitrification of the glasses, namely cordierite in the low titania glasses (rings of $[SiO_4]^{2-}$ tetrahedra), and a pyroxene similar to enstatite in the high titania glasses (chains of $[SiO_4]^{2-}$ tetrahedra).

1. Introduction

The highly refractory glass–ceramics based on cordierite ($2MgO·2Al_2O_3·5SiO_2$) have physical properties, notably the good resistance to thermal shock [1–3] combined with the excellent dielectric characteristics of this system at both high temperatures and frequencies, which have led to many commercial applications of this ceramic system. Without added TiO_2, cordierite glasses do not produce mechanically strong and fine-grained ceramics, i.e. the observed phase separation within many glasses of the cordierite composition [4] is not of itself sufficient to produce useful glass–ceramics. In two recent papers [5, 6], the authors have described a series of systematic studies upon a group of glasses and their resulting ceramics with compositions based upon cordierite, and with added TiO_2 in the range 0 to 10 wt%. ESR spectroscopic techniques were used to study the glasses during compositional changes, and pre-crystallization ("nucleation") and crystallization heat treatments.

As regards the glass systems it was found that, after irradiation with ^{60}Co γ-rays, cordierite glasses with added TiO_2 displayed two dominant ESR resonances arising from (a) Ti^{3+} ions and (b) holes trapped at non-bridging oxygen ions singly bonded to $[SiO_4]^-$ tetrahedra. The Ti^{3+} ions appeared to be in D_{4h} octahedral sites with the evident distributions between the principal g-values arising from an isotropic randomness at the titanium sites. However, the g-parameter distributions of the hole resonance, and their changes during the addition of TiO_2 indicated the development of silicate structures in the glasses which are the precursors of the major low-temperature crystalline phases. The invariance of the hole and electron resonance lines with pre-crystallization heat treatments indicated that neither the titanium-associated structures or the basic silicate structure of the glass were changed by such treatments.

With reference to the glass–ceramics, which were formed from the "as-melted" or

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TABLE I Compositions of glasses examined

Reference number	Melt classification and nominal composition	Analytical data (wt %)			
		SiO_2	Al_2O_3	MgO	TiO_2
Melt 1	Base glass (BG)	60	20	20	0
Melt 2	BG + 0.2% TiO_2	59.88	19.96	19.96	0.20
Melt 3	BG + 1% TiO_2	59.41	19.80	19.80	0.99
Melt 4	BG + 5% TiO_2	57.14	19.05	19.05	4.76
Melt 5	BG + 10% TiO_2	54.55	18.18	18.18	9.09

"pre-crystallization" heat-treated glasses by a 24 h heat-treatment at 1000° C, the ESR spectra observed arise from two principle sites; Ti^{4+} ions radiochemically reduced to Ti^{3+}, and holes trapped at the π-type orbitals of oxygen ions bridging between SiO_4 and AlO_4 units. The Ti^{3+} line, although very similar to its form in the parent glasses, was in general a composite of two distinct lineshapes, each of which is associated with one of the two major crystalline phases, cordierite or enstatite. The hole centre has a characteristic hyperfine interaction similar to that of the boron oxygen hole centre of borate glasses.

In this paper we describe infared absorption and Raman scattering studies which provide structural information complementary to the ESR investigations.

2. Experimental details

2.1. Glass preparation and compositions

The glass batches were prepared from fine powders of SiO_2, Al_2O_3, MgO and TiO_2. The base glass components, i.e. SiO_2, Al_2O_3 and MgO were all of 4N purity, the 100 ppm of impurities being largely refractory oxides similar to the melt components. Total iron group impurities were less than 10 ppm. The TiO_2 which was added to the base glass was of "specpure" quality with less than 1 ppm of any individual paramagnetic impurity. In all, five glass compositions were founded, four containing TiO_2, and a base glass without added titania. The melt compositions were given in Table I.

Melt batches of 100 g were founded at 1600° C, within Pt–Pt 10% Rh crucibles, for a period of 50 h. Periodic stirring *in situ* prevented fractioning of the melts into layers of varying composition, and seed-free homogeneous melts resulted. Homogeneity was confirmed by test specimens, which after careful annealing, showed only slight birefringence due to residual stresses when viewed in a "strain" viewer, there being no indication of composition-induced birefringence.

The annealing temperature (T_g) of the base glass was found by differential thermal analysis to be at 790 to 800° C, and since it has been established that optimum "nucleation" temperatures are some 20 to 50° C above the annealing temperature the samples studied here were heat-treated for 3 h at either 750, 800 or 850° C.

2.2. Infrared absorption

The glasses and ceramics were finely ground and prepared as KBr discs by a standard die-pressing technique. Room temperature absorption spectra between 2.5 and 40 μm, (4000 to 250 cm^{-1}), were measured on a Perkin–Elmer model 475 double beam spectrometer.

2.3. Raman scattering

A Varian–Carey model 82 Raman spectrometer, in conjunction with a Spectra Physics model 164 Argon-ion laser operating at 514.5 nm, were used to record Raman spectra from the as-produced and pre-crystallization heat-treated glasses. For these measurements rectangular glass blocks were founded and two "ends" and one "face" polished to 0.25 μm Al_2O_3 leaving final specimen dimensions of 8 mm × 7 mm × 6 mm. The exciting laser beam was directed through the specimen between the polished ends and a multiple pass arrangement used to intensify the scattered signal. The radiation was incident along the x-axis and polarized in the z-direction. The scattered radiation was collected along the y-axis, i.e. at 90° to the incident beam, the scattered intensity being the sum of radiation polarized in the z and x directions. All spectra were recorded at room temperature with a bandwidth of 10 cm^{-1}.

3. Results

3.1. Infrared absorption spectra

Fig. 1 is a composite diagram of the infrared absorption spectra from glasses 1, 3 and 5, both with and without pre-crystallization heat

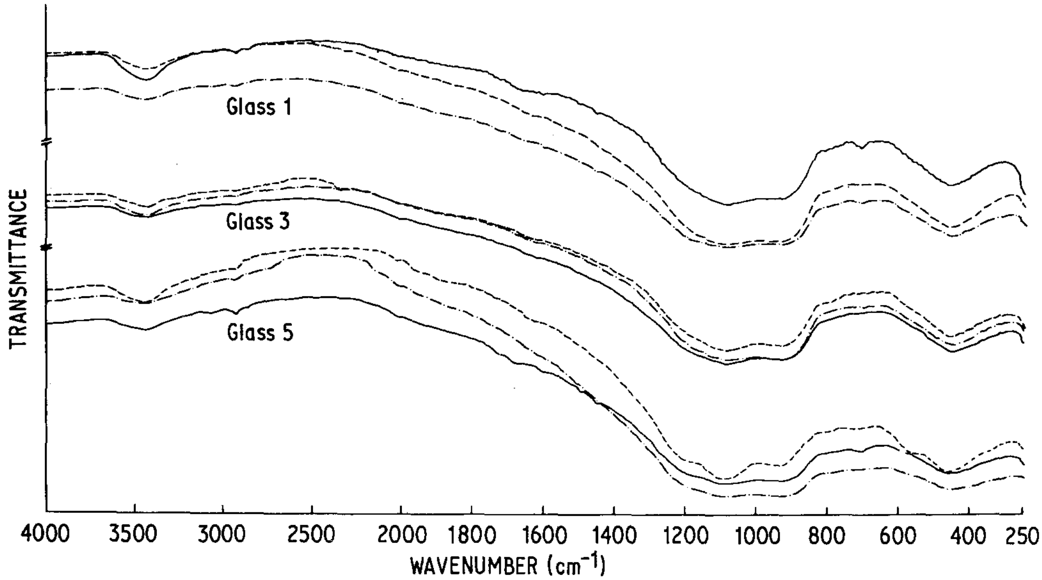

Figure 1 Infrared spectra of glasses: (a) no heat treatment —; (b) 750° C for $2\frac{1}{2}$ h — · —; (c) 850° C for $2\frac{1}{2}$ h — — —.

treatments. The absorption peaks are broad and ill-defined but it is clear that no substantial changes in the spectra have resulted from the addition of TiO_2 to the base glass composition, or indeed within any particular composition due to pre-crystallization heat treatments. The main "high" and "low" frequency peaks occur at 1080 and 450 cm^{-1} with shoulders on these peaks at ~ 1200, ~930 and ~ 550 cm^{-1}. The absorption on all traces at ~3500 cm^{-1} is due to O–H "group" vibrations [7].

3.2. Raman scattering spectra

The spectra from melts, 1, 3, 4 and 5 are given in Fig. 2. These show that there are clear differences in the spectra from the different glasses, although within a composition, the pre-crystallization heat treatments leave the spectra unaltered. The analysis of these spectra into their component Gaussian bands is shown in Figs. 3 to 6. Essentially (except for melt 4, which has at least three strong bands), the glassy Raman spectra between 300 and 1300 cm^{-1} resolve into two main bands plus two or three minor bands. The most striking change in the spectra as titania is added to the base glass is the shift to lower frequencies of the main high-frequency band, and the smaller but definite shift, in the same direction, of the low-frequency peak. The minor bands remain largely unchanged during the compositional and main peak changes, although there is an increase in the relative intensity of the ~ 730 cm^{-1} band as the titania content increases.

4. Discussion

4.1. Infrared spectra

The vibrational spectra of α and β quartz have been successfully computed [8, 9] and, assuming a disordered quartz structure, i.e. a distribution of bond angles and strengths around those found in quartz, as a model of vitreous silica [10], the main features of the glassy spectrum have been derived [11–13]. Multicomponent glasses, however, contain silica tetrahedra with one, two, three, or four non-bonding oxygens (nbo), i.e. their basic structural units may be the $[SiO_4]$, $[SiO_4]^{2-}$, $[SiO_4]^{3-}$, or the $[SiO_4]^{4-}$ groups. Theoretical studies [13] have shown that these units incorporated into a crystalline or vitreous material will have characteristic "group" frequencies [7]. Thus the existence of these silicate groups in a glass, can, in principle, be inferred by a comparison of the vibrational spectrum of the glass, and the vibrational spectra of crystalline silicates known to contain specific groups. This approach has been successfully employed by Konijnendijk [14] in identifying borate groups in borate and borosilicate glasses.

Most crystalline silica polymorphs, fused silica, and many commercial high silica glasses such as Vycor, have been studied and the main infrared bands catalogued, [9, 13–16]. The framework

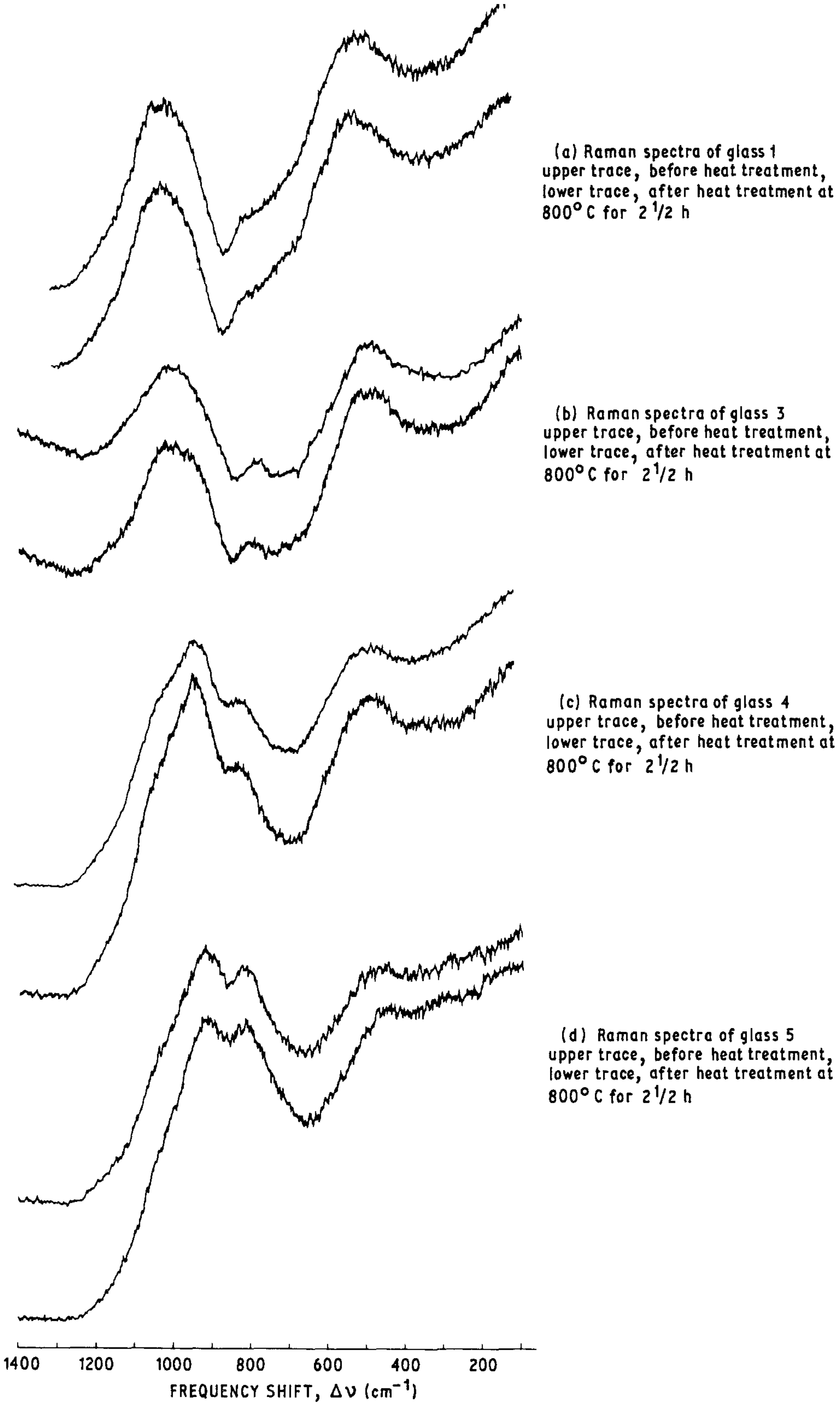

Figure 2 Experimental Raman spectra.

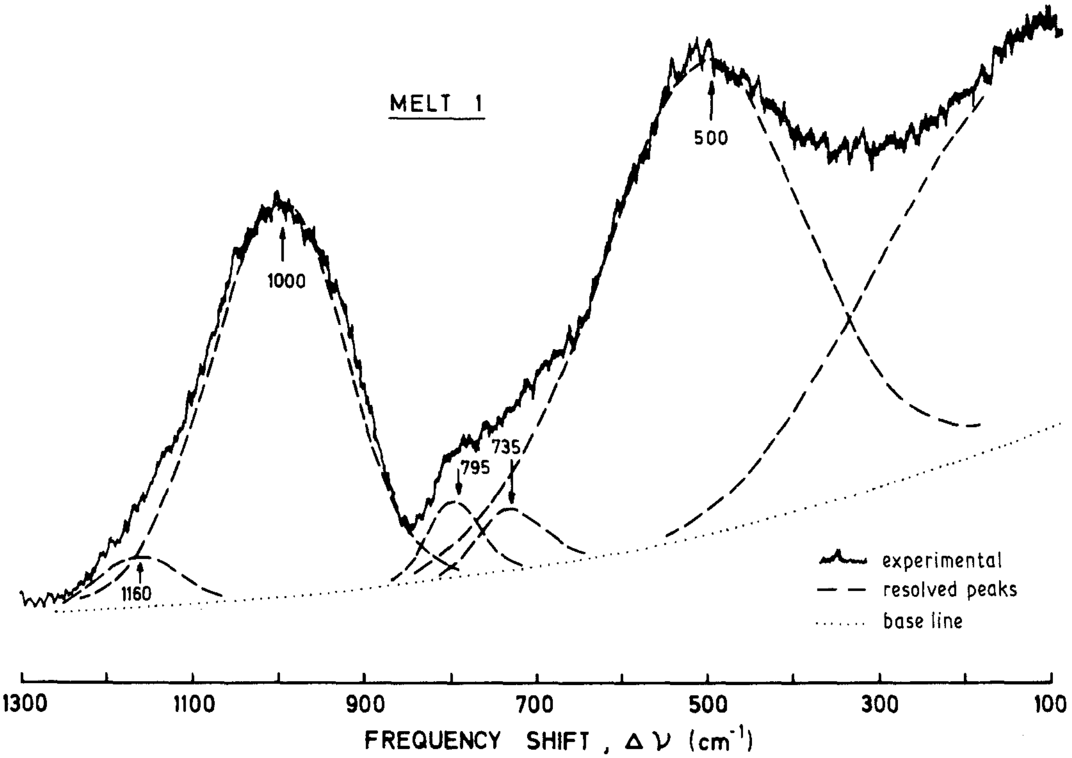

Figure 3 Analysis of Raman spectra (melt 1).

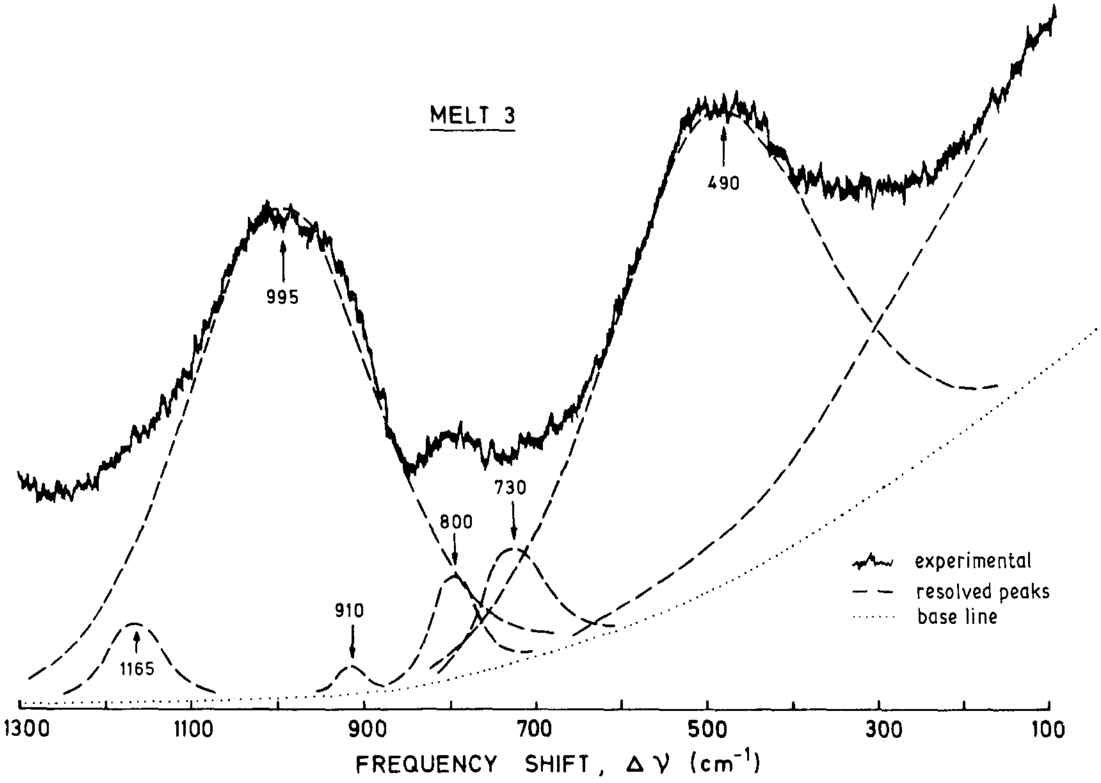

Figure 4 Analysis of Raman spectra (melt 3).

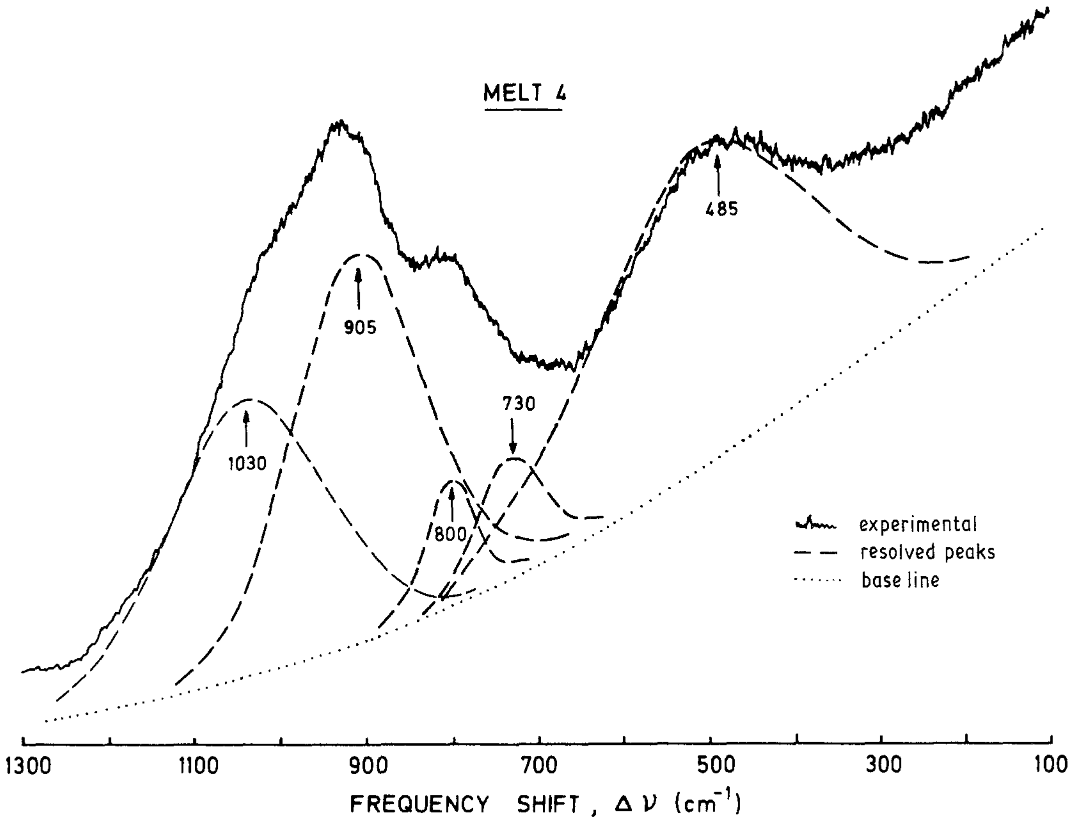

Figure 5 Analysis of Raman spectra (melt 4).

[SiO_4] tetrahedron has its main bands (in both glasses and crystals), in the 1070 to 1090 cm^{-1} and 440 to 480 cm^{-1} regions. The silicate glasses do mirror the "shift" to lower frequencies which is observed in the main high-frequency crystalline silicate bands when the number of nbos increase. Essentially, bands at frequencies lower than the 1070 to 1080 cm^{-1} main peak of the framework tetrahedron, become more intense, e.g. in most crystalline metasilicates ([SiO_4]$^{2-}$ units), there are three main high-frequency bands in the 850 to 1080 cm^{-1} region, all of comparable intensity [14, 17].

The multiple high-frequency peaks of the crystalline silicates broaden to one or two main peaks in the glassy silicate spectra. At low concentrations of nbos a peak at ~ 950 cm^{-1}, taken by many authors to be indicative of the Si–O terminal stretching mode [18–20] appears as a shoulder on the intense 1050 to 1080 cm^{-1} vitreous silica peak. As the glass modifiers increase to the metasilicate ratio, these peaks assume approximately equal intensities [14, 18, 20]. In some systems the above peaks merge to a single broad peak at ~ 980 cm^{-1}.

In most binary silicate glasses and crystals of disilicate and metasilicate compositions, the infrared absorption in the region of 1200 cm^{-1} is very weak. Exceptions occur when the glass phases separate into high silica and high alkali regions [21]; it is suggested then that the high-frequency part of the spectrum, and in particular the high-frequency shoulder at ~ 1200 cm^{-1} on the main ~ 1060 cm^{-1} peak, is due to the high-silica region, and the band in the region of ~ 950 cm^{-1} is due to the high-alkali phase. This explanation may be applied here, the ~ 1200 and 930 cm^{-1} could be characteristic of a high-silica region and a region of disilicate or metasilicate composition. The 1080 cm^{-1} band would be common to each of these glass phases.

The constancy of our experimental spectra throughout the compositional range must be interpreted as a corresponding constancy in the nature of the silicate units within the glass; if there were significant changes in the number of non-bridged oxygen atoms per silica tetrahedron these would be reflected in significant intensity changes in the high-frequency bands.

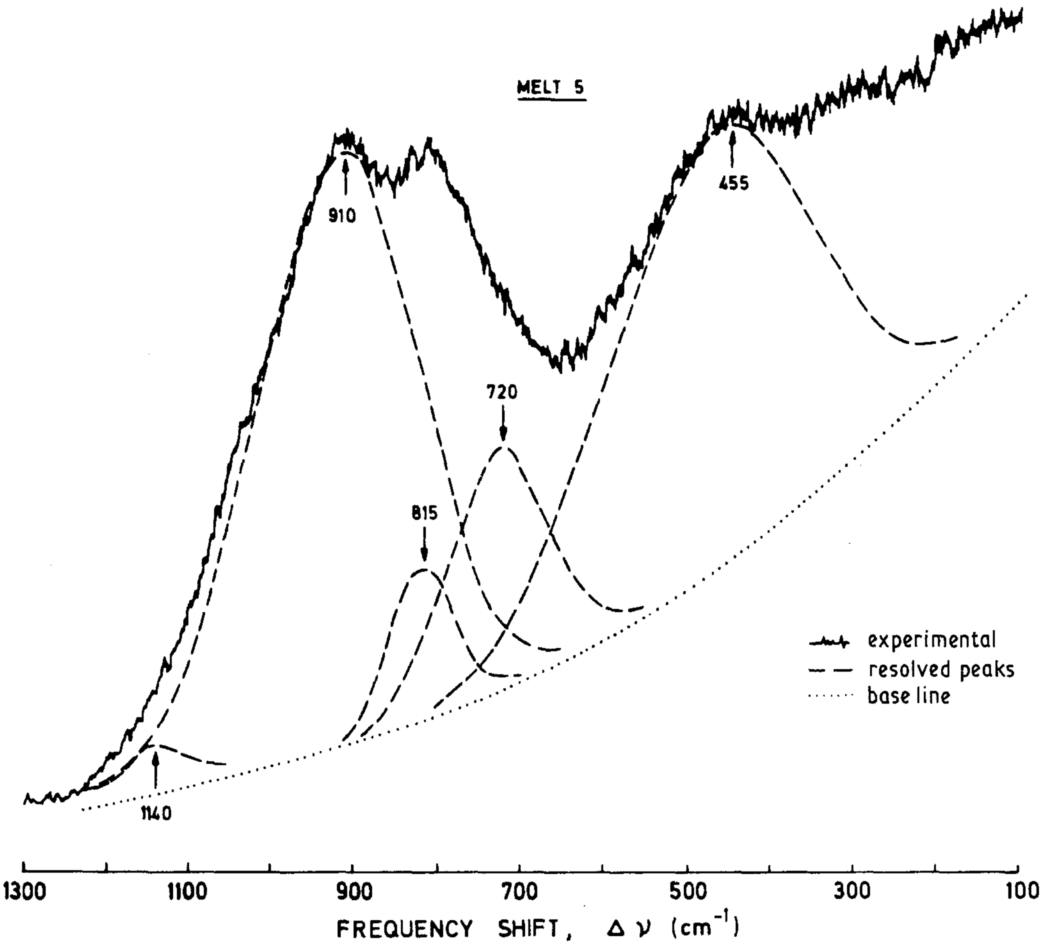

Figure 6 Analysis of Raman spectra (melt 5).

4.2. The Raman spectra

High-silica crystalline compounds and glasses, e.g. quartz and vitreous silica, have only weak Raman lines in the 800 to 1200 cm^{-1} wave number region, i.e. the Si–O–Si antisymmetric stretch which produces the strong infared peak at 1080 cm^{-1} and the shoulder at 1180 cm^{-1}, is only a weak Raman scattering mode [9]. The Si–O–Si bending vibration is the strongest Raman mode [9], producing a broad peak in the region of 400 cm^{-1} with a sharp shoulder/peak at 490 cm^{-1}, and in high-silica glasses, these peaks dominate the Raman spectrum [13, 22]. In addition, in these glasses, there are medium-weak peaks at 800 and 600 cm^{-1}.

As glass modifiers, i.e. potassium, sodium etc, are added to a high silica glass, a strong Raman band at 1080 to 1100 cm^{-1} appears, and increases in intensity as the modifier content is increased [14]. This band is assigned to an Si–O^- stretching mode within a $[SiO_4]^-$ disilicate unit [13, 21, 22], and it dominates the high-frequency region as the modifiers are increased up to approximately the disilicate composition; all published spectra from crystalline and glassy disilicates have a characteristic band at ~ 1100 cm^{-1} [13, 22–24].

As the modifier content is increased beyond the disilicate ratio, a band at 950 to 980 cm^{-1} grows in intensity [14, 21, 22]. This band is assigned to the Si–O^- stretching vibration within a $[SiO_4]^{2-}$ unit, i.e. a metasilicate tetrahedon [22, 23]. The cataloguing of spectra from a series of pyroxene minerals [14, 24–26] has shown that almost all have a characteristic high-frequency peak in the 970 to 1010 cm^{-1} region. Studies of metasilicate ratio glasses have shown an intense Raman peak in this region (usually a slight downward shift of frequency of some 20 to 30 cm^{-1} occurs, bringing the glass peaks into the region 950 to 990 cm^{-1}) [14, 22, 25].

The melt 1 glasses have their main high-frequency peak in the metasilicate wavenumber region. The broad low-frequency peak at 500 cm^{-1} may well be a composite of two bands. The infrared spectra are consistent with the presence of a high-silica glass phase, which would be expected to produce a strong broad peak at ~ 440 cm^{-1}. Combined with the metasilicate peak at ~ 590 cm^{-1}, these bands may merge to give the observed maximum at 500 cm^{-1}. Certainly this effect is present in the spectra of Brawer and White [22] where their lithium-silicate glasses, known to phase separate, produce broad peaks at 555 and 470 cm^{-1}. The peaks are only just resolved in their spectra and we assume here that this resolution has been lost in the spectra from our glasses. Some additional support of this interpretation is afforded by the weak bands at 1160 and 795 cm^{-1}, which are compatible with the presence of a high or vitreous silica glass phase.

As TiO_2 is added to the base glass composition, the principal effect upon the Raman spectrum is growth of a band at 910 cm^{-1} and the concomitant decay of the 1000 cm^{-1} band, until at the composition of melt 4 (5% TiO_2), the bands are of comparable intensity, and in the melt 5 (10% TiO_2) glasses the 910 cm^{-1} band dominates the high-frequency region. During this process the minor bands remain largely unchanged, although the ~ 750 cm^{-1} band appears to increase in relative intensity, and the broad low-frequency peak shifts some 40 to 50 cm^{-1} to lower wavenumbers.

If the observed frequency shift of the high-frequency peak were ascribable to a change in the average number of non-bridging oxygens per silica tetrahedron, then one should expect similar band changes in the infrared specra of the glasses, and certainly such major changes are absent from these spectra. We consider, therefore, the effect of configurational changes within the metasilicate groups of a metasilicate glass phase.

In considering simple pyroxene chain structures and, in particular, the vibrational modes which are allowed for various arrangements of the $[SiO_4]^{2-}$ tetrahedra, it is found that modes which involve phase relationships between the vibrations of atoms in adjacent tetrahedra, are quite sensitive to changes in the translational symmetry of the chain, although characteristic "group" vibrations exist for all arrangements, corresponding to atomic motions within a single tetrahedron. The infrared bands are determined primarily by the short-range dipolar forces of nearest neighbour interactions [24] and, whilst sensitive to changes in the co-ordination cations, these bands are largely constant for a specific $[SiO_4]$ group, i.e. for silica tetrahedra with none, one, two three or four non-bridging oxygens per tetrahedron. The Raman intensities and frequencies are sensitive to changes in the translational order of a specific $[SiO_4]$ group [24], and a plausible explanation of the constancy in the infrared bands with simultaneous changes in the high-frequency Raman peaks, is that the glasses all contain a phase whose structural groups are essentially similar, but that the arrangement of these groups relative to one another, is changing as TiO_2 is added to the base glass composition. The high-frequency peaks in the Raman and infrared spectra of our glasses indicate that the most probable common group is the $[SiO_4]^{2-}$ tetrahedron, and we now consider possible configurations.

Data presented by Fabel *et al.* [25] contain Raman spectra from a series of polycrystalline pyroxenes including ($MgSiO_3$), diopside ($CaMgSi_2O_6$), and spodumene ($LiAlSi_2O_6$). The principal high-frequency peaks of enstatite and diopside are displaced by only 10 cm^{-1} relative to one another, but compared with these minerals, the spodumene peak is displaced some 60 cm^{-1} to higher wavenumbers. Spodumene is similar in structure to diopside except for the replacement of the large calcium and magnesium ions by the smaller, higher field strength lithium and aluminium ions. The result is a closer packing of the SiO_4 tetrahedra and a smaller unit cell [27]. In our glass specimens, therefore, we could expect a shift of the Raman peaks to lower frequencies if aluminium ions co-ordinating $[SiO_4]^{2-}$ tetrahedra were removed from that sphere of co-ordination. Such frequency shifts are essentially due to changes in the force constant of the Si–O bond, and as such we should expect to see similar changes in the infrared spectra. Allowing for the poor resolution of the infrared spectra, the large 90 cm^{-1} frequency shift of the high-frequency Raman peak does not appear in these spectra and mechanism additional to changes in the cation co-ordination must be responsible for the Raman spectra effects.

The principal low-temperature phases which crystallize from the low- and high-titania glasses are cordierite and an enstatite-like phase, respectively [6]. Enstatite is a chain silicate [27], consisting of infinite chains of $[SiO_4]^{2-}$ metasilicate units. Cordierite, however, is classified [27] as a ring or cyclosilicate. The cordierite structure is essentially one of six-membered SiO_4 rings connected laterially and vertically by aluminium and magnesium ions. Within the silicate rings half of the SiO_4 tetrahedra are associated with MgO_6 octahedra and may be considered metasilicate $[SiO_4]^{2-}$ units, and half are associated with AlO_4 tetrahedra and are, therefore, more properly disilicate units $[SiO_4]^{-}$. The silicate rings are arranged in "sheets" with the rings of each sheet arranged vertically above one another in long "columns".

The main high-frequency scattering peak from the low titania glasses is at rather higher frequencies than the high-frequency peaks from the crystalline metasilicates and glasses of the metasilicate composition, but well below the high-frequency peaks of the crystalline and glass disilicates. Thus the ring-type silicate structure with its equal proportion of metasilicate and pseudo-disilicate units, would seem to fit well the observed scattering frequency. The growth and ultimate dominance of a peak at lower frequencies as TiO_2 is added to the glass may be interpreted in terms of a breaking of the silicate rings into short chains of $[SiO_4]^{2-}$ tetrahedra. The fact that the latter peak falls outside of the range reported for other metasilicate glasses and pyroxene minerals, may be accounted for by the short chains which would result from the breaking of the six-membered rings of silica tetrahedra. Calculations (e.g. [28] of the terminal stretch of the metasilicate unit, using a limited number of tetrahedral units, have predicted the value to be 960 cm^{-1} for the chains of a K_2SiO_3 glass in close agreement with the observed data [22].

Turning now to the other changes in the Raman spectra upon the addition of TiO_2 and, in particular, the shift to lower frequencies of the main low-frequency peak, we note that particularly if the glass has a phase-separated structure, this change may have a number of possible origins. An increase in the amount of the silica-rich phase, (relative to other glass phases), or a decrease in the metasilicate phase, would produce such a displacement. An additional possibility is afforded by Brawer and White [22]. These authors have calculated the change in frequency of the strongest Raman bands of a disilicate sheet structure when the Si–O–Si intertetrahedral angle bond angle is increased from 130° to 180° (the most probable bond angle [29] for vitreous silica is 144°). They conclude that the high-frequency stretching modes are largely insensitive to bond angle changes, but that the low-frequency bending mode moves to lower frequencies as the bond angle increases. A change in the bond angle would be expected during a cyclosilicate to chain silicate configurational change.

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