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Structure and crystallization behaviour of Li_2O-Fe_2O_3-SiO_2 glasses

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Iron-containing lithium disilicate glasses, other silicate and borate glasses, and crystallized lithium disilicate glasses have been studied by Raman spectroscopy, luminescence spectroscopy and X-ray diffraction. In the as-quenched glasses the presence of iron leads to a strong Raman band at 950 cm^{-1} and to a broad Raman scattering continuum below 500 cm^{-1}. There is also an emission due to trivalent iron at about 14 000 cm^{-1}. Lithium metasilicate has been identified in all crystallized glasses with more than 1% Fe_2O_3. It was possible to crystallize some of the glasses by irradiating them with intense blue laser light, and Raman spectra of various stages of photocrystallization have been obtained. By comparing the Raman spectra of the crystallized glasses with those of as-quenched glasses it is deduced that the trivalent iron has its own distinct local environment in the glass.

1. Introduction

The manner in which iron is incorporated into oxide glasses and the behaviour of iron-containing oxide glasses with heat treatment has been a subject of considerable interest. Fe-containing glasses have been studied by optical spectroscopy [1, 2], Mössbauer spectroscopy [3, 4], EPR [5, 6] and various magnetic techniques [7, 8]. The ferrous–ferric equilibrium has been studied by a number of workers [1, 9–11]. The interpretation of these measurements has been hampered by the extremely rich and complex behaviour of iron in glasses.

In this paper we report a study of iron-containing lithium disilicate glass and several other silicate and borate glasses by Raman and luminescence spectroscopy. It is our purpose to determine something about the nature of the trivalent iron sites in the as-melted glasses. Our method is to examine the products of crystallization and to relate this information back to information about the glass. We study the early crystallization products, so our crystallization times are generally between a few seconds and 1 hour.

We have found that a convincing argument can be made that all the trivalent iron does not enter the glass as a simple isotopic substituent for Li or Si. Rather, a significant fraction of the trivalent iron deforms the local glass structure to form a range of structurally distinct sites.

The information determined by Raman spectroscopy from iron-containing silicate glasses is likely to be complementary to that obtained by magnetic techniques. The iron oxides that precipitate out when the glass is heat treated are not very strong Raman scatterers (they are also very difficult to detect by X-ray diffraction.) However, these precipitates are expected to dominate the magnetic properties of the material. On the other hand, the silicate structures in the glasses and crystallized glasses will dominate the Raman spectra, and these are what are observed in this study. Moreover, silicate phases can be detected by X-ray diffraction if present in concentrations greater than about 1 wt %.

The use of lithium disilicate as the host glass has several advantages. This glass is very easy to crystallize, it does not phase separate, it has only

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one stable equilibrium phase, and appears to have a very weak tendency to form metastable crystalline phases. The simplicity of crystallization of the host glass makes it easier to study the complexities introduced by iron. Raman spectra of lithium and other alkali silicate glasses were reported earlier [12] with an interpretation of the structure of the glasses.

2. Experimental

2.1. Procedures

Glasses were prepared from reagent grade silica, lithium or sodium carbonates and ferric oxide (red, anhydrous). The powders were melted in air in a platinum crucible in an electric resistance furnace at 1250 to 1300° C for about 24h. For Raman and luminescence spectra, rods about 1 to 3 mm diameter were drawn from the melt. Raman and luminescence spectra were measured on a Spex model 1401 double-grating spectrometer with a cooled RCA 31034 photomultiplier and photon-counting electronics. The excitation source

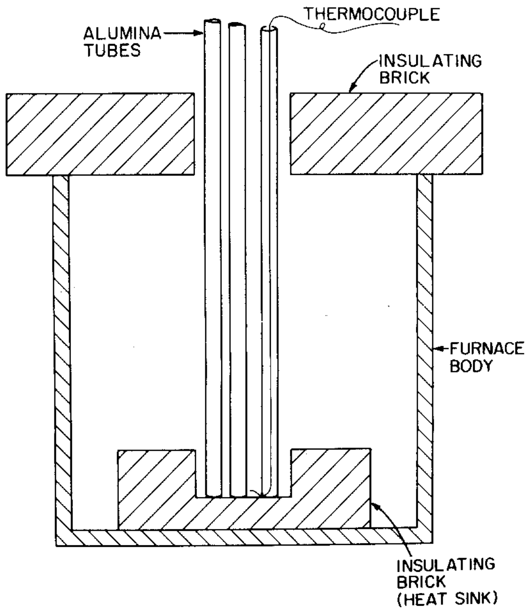

Figure 1 Arrangement used to heat-treat glass rods, as described in text.

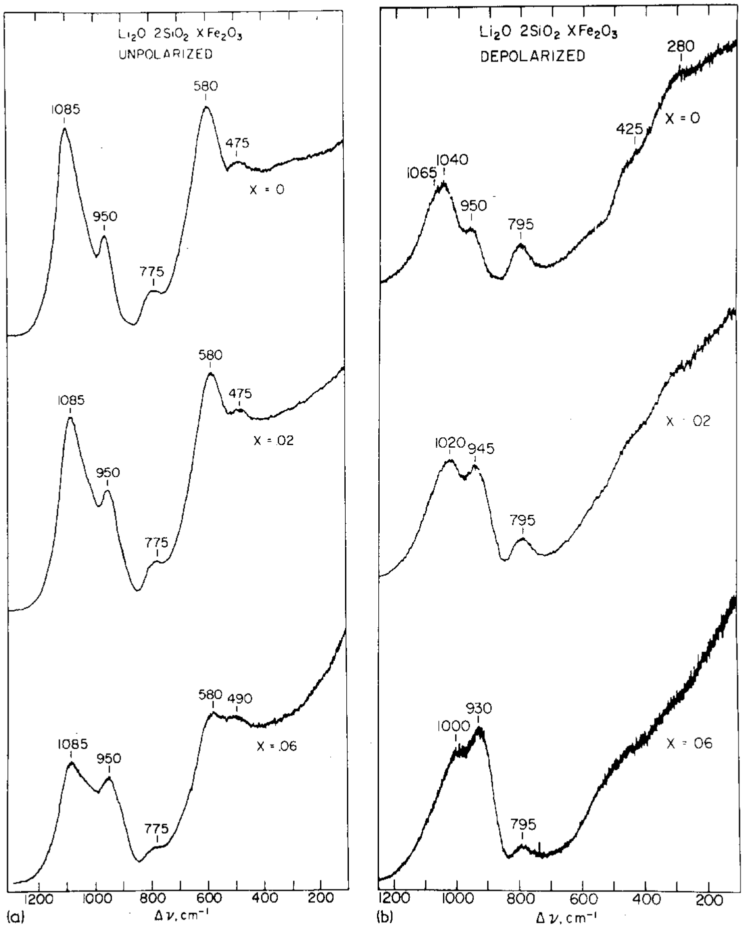

Figure 2 Raman spectra of as-quenched iron-containing lithium disilicate glass. (a) Unpolarized and (b) depolarized.

was a Spectra Physics model 164 Argon ion laser at 4 W total power. Absorption spectra were measured on a Cary model 14 recording spectrophotometer.

Five glass compositions, $Li_2O \cdot 2SiO_2 \cdot xFe_2O_3$, with $x = 0, 0.001, 0.01, 0.02$ and 0.06, are reported in this study. These glasses will be referred to as the 0%, 1/10%, 1%, 2% and 6% glasses respectively. For the 6% glass, chemical analysis showed that 23% of the total iron was in the ferrous state.

In order to study the early stages of crystallization, the glasses were heat treated for times as short as five seconds. In order to do this, the arrangement of Fig. 1 was used. Alumina tubes cemented at the bottom and inside diameter of $\frac{1}{8}$ in. were set in the furnace and the whole arrangement was allowed to come to thermal equilibrium. Then the glass rods were dropped into the alumina tubes, one glass rod about 1 to 2 cm long per tube. After the desired heating times the tubes were removed from the furnace and inverted so the glass rods fell out. Since crystallization of lithium disilicate glass is so rapid, especially at higher temperatures, the rods usually did not flow or bend during heat treatment. For glasses which crystallize sluggishly this technique is less effective, especially at temperatures above the transformation temperature.

2.2. Appearance of as-drawn and crystallized glasses

The as-drawn 0% and 1/10% glass rods were clear, the 1% glass rods had a trace of green and the 6% rods were medium olive green. No crystallization of the as-drawn rods was detected by Raman spectroscopy, X-ray diffraction, or with the polarizing microscope.

All iron-containing glasses changed colour upon heating. The 1/10% glass turned yellow, the 1% glass turned brown and had dark and light brown bands on the surface. The 6% glass rods turned black and had a metallic sheen on the surface. Most of the rods, when heated for long times, became hollow inside. (See Rindone [13] for a discussion of the reasons for this.) At 900 °C the change in colour was instantaneous. No such colour change was observed in the glass melt upon cooling.

A large number of crystallized rods were examined in cross-section with an optical microscope using reflected light. The crystals of all the 0% and 1/10% rods were in the form of axial dendrites.

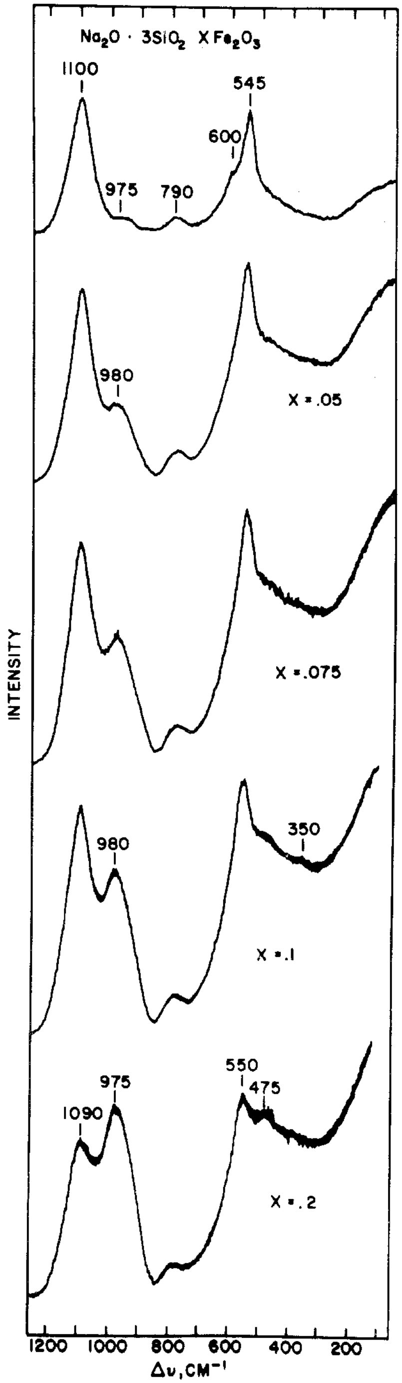

Figure 3 Raman spectra of as-quenched iron-containing sodium trisilicate glass.

For the 1% rods, no dendrites were found. The rods generally consisted of the following three features: a hole, approximately (but not exactly) in the centre of the rod; a central area consisting of irregularly shaped, highly reflecting crystallites embedded in a dark brown or black smooth matrix; and an outside layer, light brown and smooth, about 1 to 3% of the rod diameter in width. No consistent variation of morphology with changes in heat treatment temperature or time was observed.

The 6% glasses were similar to the 1% glasses, but were nearly black rather than brown. Sometimes a dendrite structure could be made out in the 6% glass.

In general, then, the rods were heterogeneous and appeared to have a thin surface layer.

3. Results

3.1. Raman spectra of glasses

The Raman spectra of lithium disilicate glass, of a 2% glass, and of the 6% glass are shown in Fig. 2. It is seen that the presence of iron leads to a strong band at 950 cm^{-1} as well as to a continuum below 500 cm^{-1}. The whole glass spectrum is highly polarized, so that the depolarized spectra are about an order of magnitude weaker than the polarized spectra. Note that for the 2% glass the 950 cm^{-1} band due to the iron is easier to see in the depolarized spectrum.

In Fig. 3 the Raman spectra of sodium trisilicate glass containing various amounts of ferric oxide are shown. It is seen that qualitatively the spectra are similar to those of lithium disilicate, although the band associated with iron occurs at about 980 cm^{-1}. As in the case of lithium silicate, there is a strong low-frequency continuum associated with addition of iron to the glass. Identical results were obtained with the glass series $0.5Na_2O \cdot 0.5CaO \cdot 3SiO_2 \cdot xFe_2O_3$.

The effect of iron on the spectra of the glass $BaO.4B_2O_3$ is the introduction of some additional scattering intensity at 1325 cm^{-1}, the spectral region associated with B–O stretching motions (Fig. 4). The spectrum is for most part unaffected by the introduction of iron oxide. Results for the alkali borates are similar.

These spectra were measured using the 19 435, the 20 492, and the 21 839 cm^{-1} lines of the argon laser. They are independent of excitation frequency.

Adding 1% ferric oxide to silicate glass appears to enhance the Raman intensity by almost an order of magnitude. By this we mean that if we run a spectrum of rods of the 0% and 1% glasses (either sodium or lithium silicates) under identical conditions, the iron-containing glass appears to Raman scatter much more strongly. This is only a qualitative observation and no attempt has been made to quantify the difference.

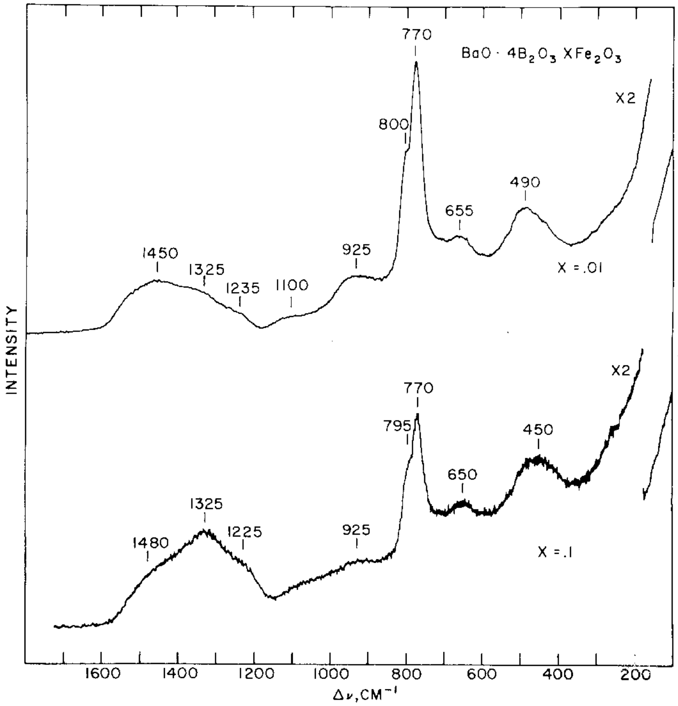

Figure 4 Unpolarized Raman spectra of iron-containing borate glass.

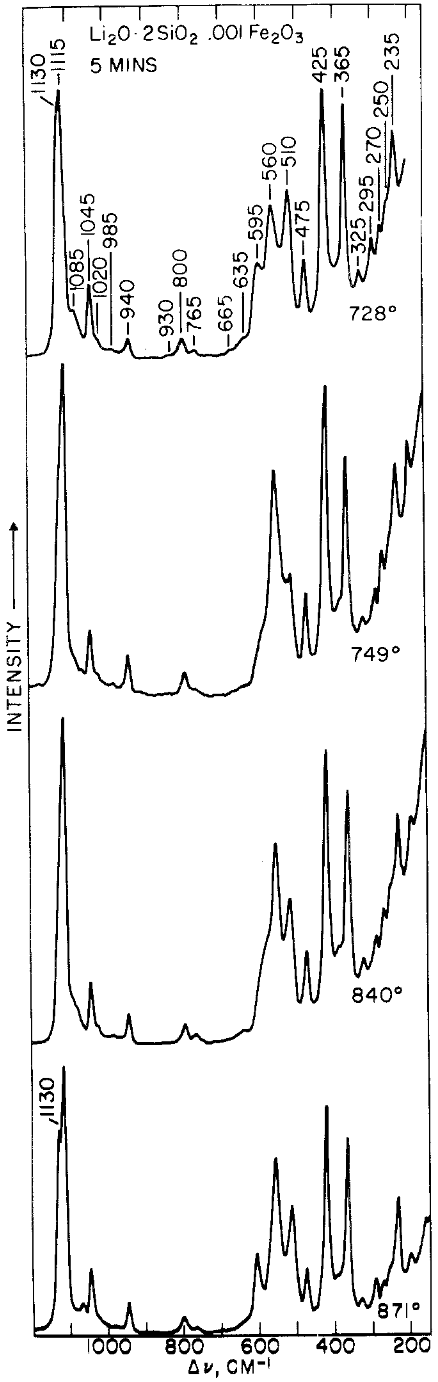

Figure 5 Raman spectra of crystallized 1/10% glass given heat treatments as marked.

3.2. Raman spectra of crystallized 1/10% glasses

The process of crystallization of lithium disilicate is quite well understood, although perhaps the Raman spectrum of the crystallized glass is not as well known. Lithium disilicate has space group Ccc2. The crystal consists of parallel Si_2O_5 sheets with the lithium ions residing in tetrahedral coordination between the sheets. No polymorphs of lithium disilicate have been reported.

Raman spectra of the 1/10% glass crystallized at various temperatures and times are shown in Fig. 5. These spectra are the same as the 0% glass. It is seen that the spectra are nearly independent of temperature and time of heat treatment except for subtle changes.

An unexpected result is the splitting of the $1110\,cm^{-1}$ band at higher temperatures of heat treatment. Usually the $1110\,cm^{-1}$ band has a high-frequency shoulder which is not resolved in the spectra. This splitting is not observed in glasses heated for long periods of time. The splitting must be regarded as significant and is an indication of a metastable phase.

As far as rates of crystallization are concerned, at 635 °C it required 5 to 10 min to produce enough crystallization in the glass to be detectable in the Raman spectra. In the case of lithium disilicate, the crystals show up in the X-ray pattern a few minutes before they are seen in the Raman spectra. (This is not true for all glass compositions.) At 750 °C and above crystallization of enough of the glass so that no glass spectrum was observed took place in less than a minute. This does not necessarily mean that the rod was entirely crystallized. Rather, the Raman intensity at the maximum of the $1110\,cm^{-1}$ band is more than an order of magnitude greater in the crystals than in the glass, so if 10% of the glass were crystallized the Raman spectrum would be dominated by the spectrum of the crystalline phase.

3.3. Raman spectra of crystallized 1% glasses

Raman spectra of the 1% glass given various heat treatments are shown in Fig. 6. Comparison of the spectra with the spectra of the 1/10% glasses (cf. Fig. 5) shows that lithium disilicate is the predominant crystalline phase. However, there are differences between the spectra of the 1% and 1/10% glasses. The most important difference is the growth of a band at $985\,cm^{-1}$ in the 1% glasses heated above 750 °C. This band never appears for glasses heated below 650 °C (at least for times less than 24 h). Above 750 °C the rate at which the $985\,cm^{-1}$ band increases in intensity goes up with

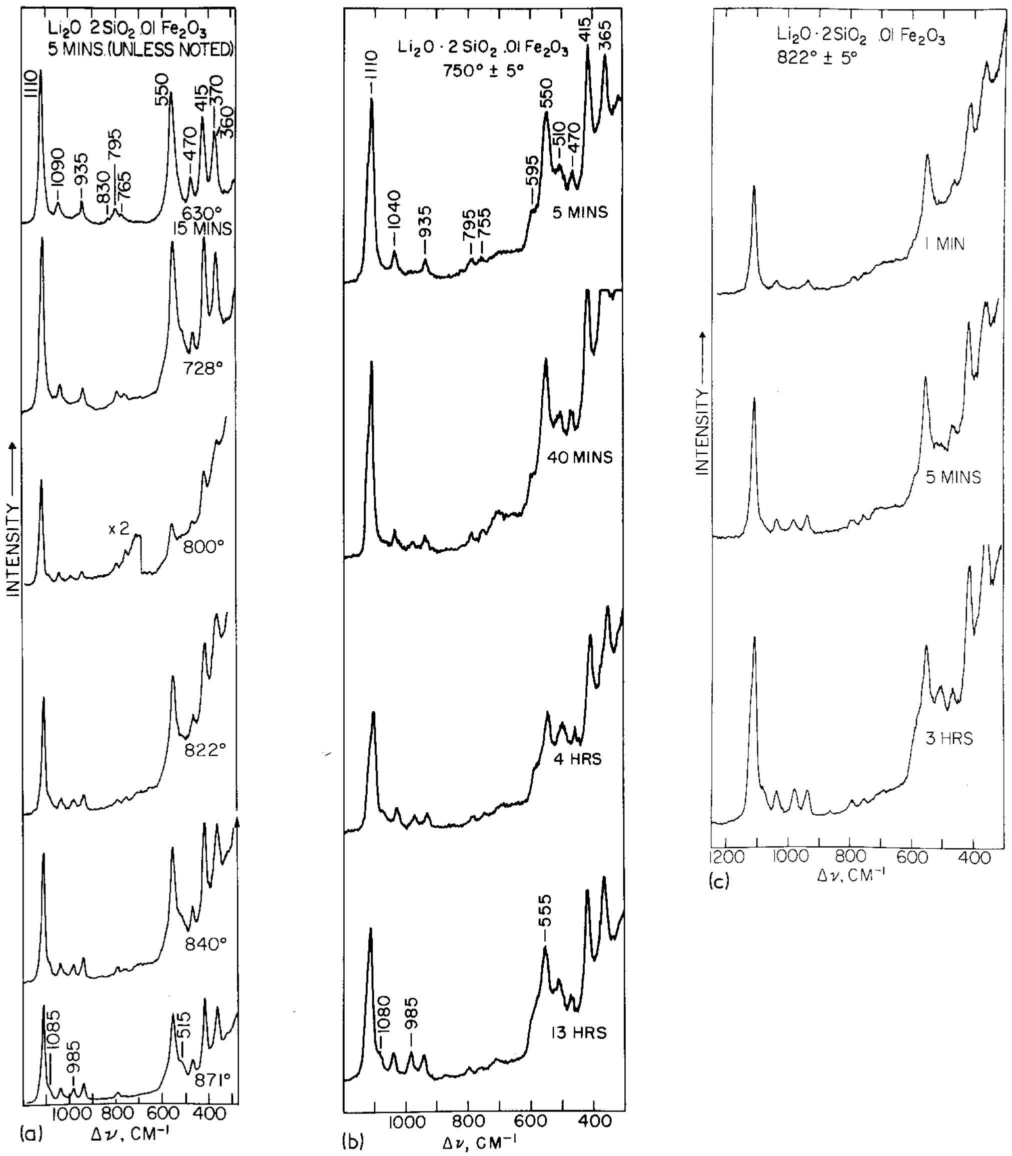

Figure 6 Raman spectra of 1% glasses given various heat treatments. (a) 5 minutes at various temperatures and 15 minutes at 630° C; (b) 750° C for various times; (c) 822° C for various times.

temperature, as clearly shown in Fig. 6. At 900 ° C the 985 cm^{-1} band appears in less than 5 seconds.

The presence of this band is indicative of the crystallization of a small amount of an additional phase besides the disilicate. This phase is almost certainly lithium metasilicate. The Raman spectrum of lithium metasilicate is shown in Fig. 7, and is seen to have its strongest band at 985 cm^{-1}, just where the extra band appears in the 1% glass. It will also be seen that lithium metasilicate is found by X-ray diffraction in the crystallized 6% glasses, although no phase other than lithium disilicate was detected in the X-ray powder patterns of representative crystallized 1% glasses.

The other difference between the spectra of 1% and 1/10% crystallized glasses is that in the 1% glass heated for short times the region between 500 and 600 cm^{-1} has only one strong band at 550 cm^{-1} with several weak and unresolved shoulders, while the 1/10% glass has three well resolved bands there. After long times, an additional band develops in the 1% glass at about 500 cm^{-1}.

3.4. Raman spectrum and X-ray pattern of crystallized 6% glass

As noted previously, the 6% glasses turn black upon heating. There were severe difficulties in de-

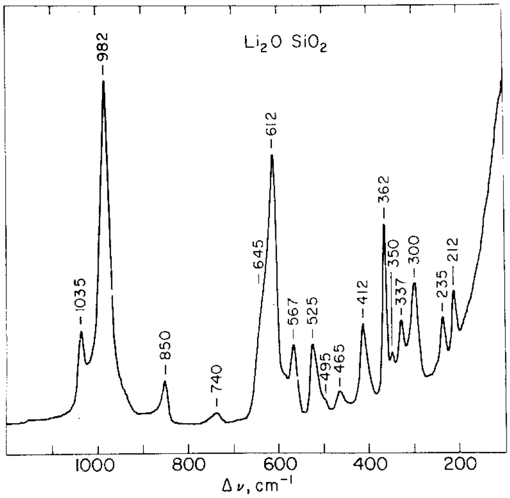

Figure 7 Raman spectrum of crystalline lithium metasilicate.

termining the Raman spectra of these glasses. It was essential that the light beam not scatter off the edge of the heat-treated rod and into the monochrometer. If this happened, the directly reflected light (the rods had a metallic sheen on the surface), which could not be completely eliminated, produced an intense low-frequency continuum and a large number of artifacts in the spectrum. (Interestingly enough, it was found that the intensity of this scattered light was time dependent, and it decreased somewhat in intensity after about 30 seconds. This was found to be due to a superimposed luminescence which was presumably bleached by the laser beam.) In any event, it was necessary that the laser beam pass through the bulk of the rod. Since the rods were black, not much Raman scattered light excited to the monochrometer. If the light intensity was increased to compensate for these losses, the glass photocrystallized further, and in a characteristic manner. A study of the photocrystallization will be described later.

It was possible to record spectra only for short heat-treatment times, and some of these are shown in Fig. 8. Consider first Fig. 8a. As seen, at lower temperatures lithium disilicate appears (compare Figs. 5 and 6). The broad band between 750 and 815 cm^{-1} is probably due to an iron oxide phase since strong bands in this region have been reported for magnetite and lithium ferrite [14, 15]. As the temperature is raised, an additional band at 980 cm^{-1} appears. The appearance of this band is reminiscent of the extra 985 cm^{-1} band in the spectrum of crystallized 1% glasses, and indicates the presence of lithium metasilicate. In addition there are weak features at 935 and 1025 cm^{-1}.

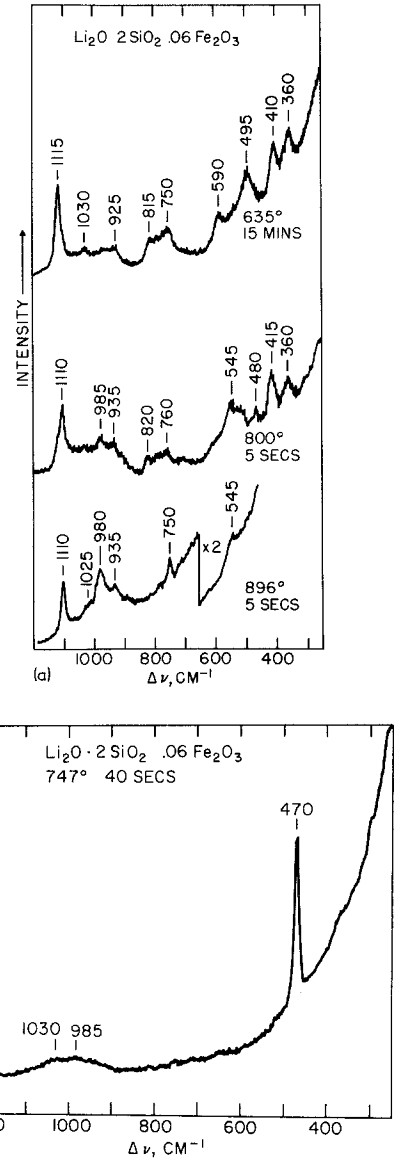

Figure 8 Raman spectra of heat-treated 6% glass.

In a number of cases, spectra like that of Fig. 8b were obtained with one very strong band at 470 cm^{-1} and a weak band centred about 1000 cm^{-1}. The strong band is probably due to SiO$_2$ [16] (quartz or cristobalite) and is probably due to surface crystallization of the rod.

The X-ray powder patterns of the 6% glasses were also run. For glasses crystallized below 650° C (for less than a day) only lithium disilicate was detected. Above 700° C lithium metasilicate was detected as well. Typical X-ray patterns are shown in Fig. 9. Also shown in Fig. 9 is the X-ray

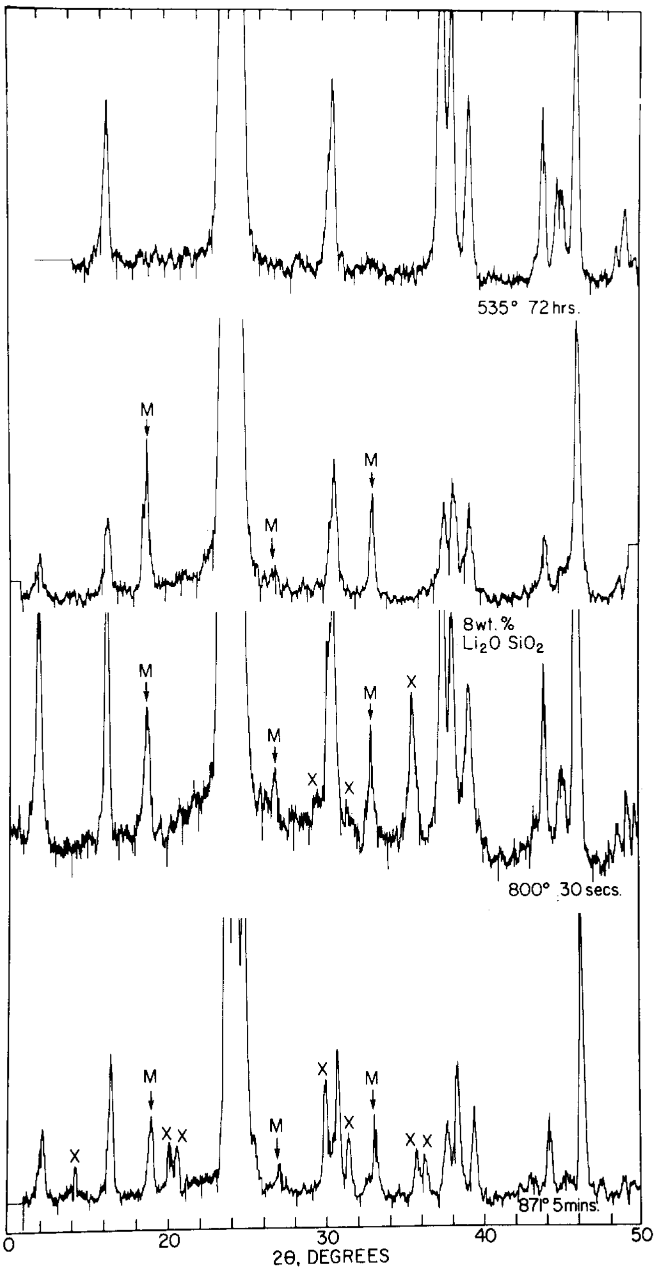

Figure 9 X-ray powder diffraction patterns of heat-treated 6% glasses. The second pattern from the top is a mechanical mixture of 8 wt% lithium metasilicate and 92 wt% lithium disilicate, the disilicate formed from a glass by heating at about 700° C for 10 min. The peaks corresponding to the metasilicate are marked by M. The points marked (X) denote unidentified phases.

pattern of a mechanical mixture of 8 wt % lithium metasilicate crystal and 92 wt % crystallized lithium disilicate glass. It is clear that identification of lithium metasilicate in crystallized 6% glasses is unambiguous. In the more thoroughly crystallized glasses, the peak intensities are commensurate with a few weight per cent metasilicate.

It is difficult to determine the relative amounts of lithium metasilicate and disilicate from the powder patterns. The reason is that, besides preferred orientation effects, the X-ray patterns of lithium disilicate heated for short times seems to depend somewhat on the thermal treatment. This is clearly seen in Fig. 9. By comparing the intensities of the metasilicate X-ray lines with the disilicate X-ray lines at $\sim$12° and 16° it was found that in general the rate of crystallization increased with increasing temperature. At 750° C about an hour was required to form appreciable amounts of metasilicate, at 800° C metasilicate was formed in several minutes and at 900° C the metasilicate was formed instantaneously. This behaviour is qualitatively the same as the rate of growth of the 985 cm^{-1} Raman band in the 1%

glass. There were exceptions to this behaviour. In one case a rod heated for one minute at 740° C yielded what seemed to be a relatively large amount of metasilicate.

As seen in Fig. 9, there is at least one other phase in addition to lithium metasilicate and disilicate. The unidentified X-ray lines in the glass heated at 871° C for 5 min are at 2θ values of 14.2, 20.1, 20.6, 30.0, 31.4, 35.75 and 36.2 degrees. Some of these lines (but not all of them) generally appear in the X-ray patterns of all 6% glasses heated above 800° C. The problem with identifying the phases is that many iron oxides and lithium ferrites have X-ray lines present in the 2θ regions where we have observed them. In addition, uncatalogued metastable phases may also be present.

3.5. Photocrystallization of 6% glass

It was observed that the 6% glass could be crystallized by irradiation with intense laser light, and so a number of spectra of various stages of photocrystallization were obtained. It was considerably easier to obtain Raman spectra from photocrystallized glasses than it was to obtain them from heat-treated 6% glasses, as there was much less reflection of the laser beam into the monochrometer.

The procedure for photocrystallization was as follows: A rod about 1 to 3 mm diameter was placed in the usual rod holder for Raman scattering measurements. The laser beam was focused so it passed through the centre of the rod. Then the laser power was turned up to 1 to 1.5 W and the interference filter removed. The rod was left this way for times from 10 seconds to a few

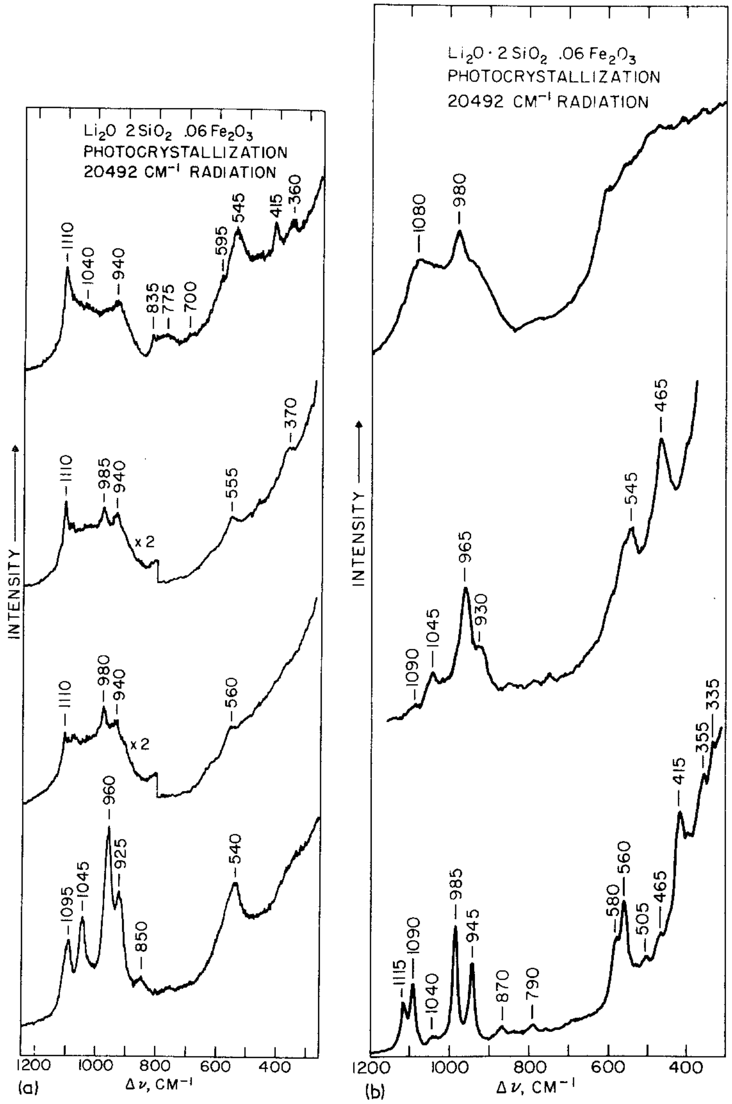

Figure 10 Various stages in photocrystallization of 6% glasses, as described in the text. The earlier spectra are on top and the later ones on bottom. (a) A series in which lithium disilicate was observed first. (b) A series for which no lithium disilicate was observed.

minutes. Then the power was lowered to about 400 mW, the interference filter replaced and a spectrum run. No photocrystallization took place below 400 mW power; in fact, there was a threshold power between 800 and 1000 mW, depending on the rod, below which no photocrystallization occurred. Rods that were very thin (less than 0.5 mm diameter) were burned in two by the laser beam. All the rods were supported 0.25 cm on either side of the irradiated region so as not to bend during irradiation. The rods became hot enough to flow. The irradiated regions of the rod were black while the as-drawn rods were medium olive green. Only rods, and not large pieces, of glass could be photocrystallized in this manner. The 1% glass could not be photocrystallized, nor could iron-containing soda–lime–silica glasses.

Several of the spectra obtained during various stages of photocrystallization of different rods are shown in Fig. 10. These figures show approximately the different stages of photocrystallization that were determined, the later stages being toward the bottom of the figure. It required about 10 to 15 min to go from the glass to the bottom spectrum of each figure.

Different rods and different sections of the same rod gave different spectra. Sometimes the early stages of crystallization gave lithium disilicate, as shown in the top two spectra of Fig. 10a. During successive exposure to the beam bands in the neighbourhood of 900 to 1000 cm^{-1} would grow smaller or even disappear and the disilicate would re-emerge. This is probably due to flowing of the glass during the irradiation.

On the other hand, as shown in Fig. 10b sometimes we did not observe the disilicate spectrum at all, but rather only bands in the neighbourhood of 950 cm^{-1} (in addition to lower-frequency bands) were observed.

It was always observed that after long periods of irradiation (10 to 20 min) spectra similar to the bottom ones of Figs. 10a and b were obtained. Note that these spectra have their strongest bands in the neighbourhood of 900 to 1000 cm^{-1}. These spectra are different from that of lithium disilicate and indicate a completely different and unrelated phase. It is probable that the phases giving rise to these spectra are composed of silicate chains, qualitatively similar to the alkali metasilicate structure (see the spectrum of lithium metasilicate Fig. 7). The spectra of crystalline sodium and potassium metasilicates [12] have their dominant high-frequency Raman bands at 973 and 963 cm^{-1} respectively. Generally chain silicates have their dominant high-frequency Raman band in the neighbourhood of 950 to 1000 cm^{-1}.

It was also possible to photocrystallize rods after heat treatment. For example, after heating at 650 to 750° C for 1 to 15 min, one would find a spectrum like the top spectrum of Fig. 8a, which, as discussed before, contains crystalline lithium disilicate and probably an iron oxide phase. Under photocrystallization the spectrum of the rod would be altered to one like the bottom ones of Figs. 10a and b, and completely different from the

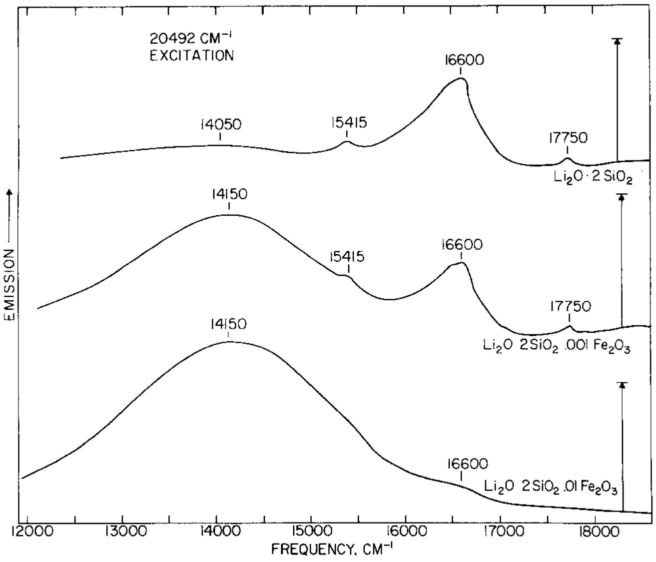

Figure 11 Laser-excited luminescence emission of as-quenched glasses.

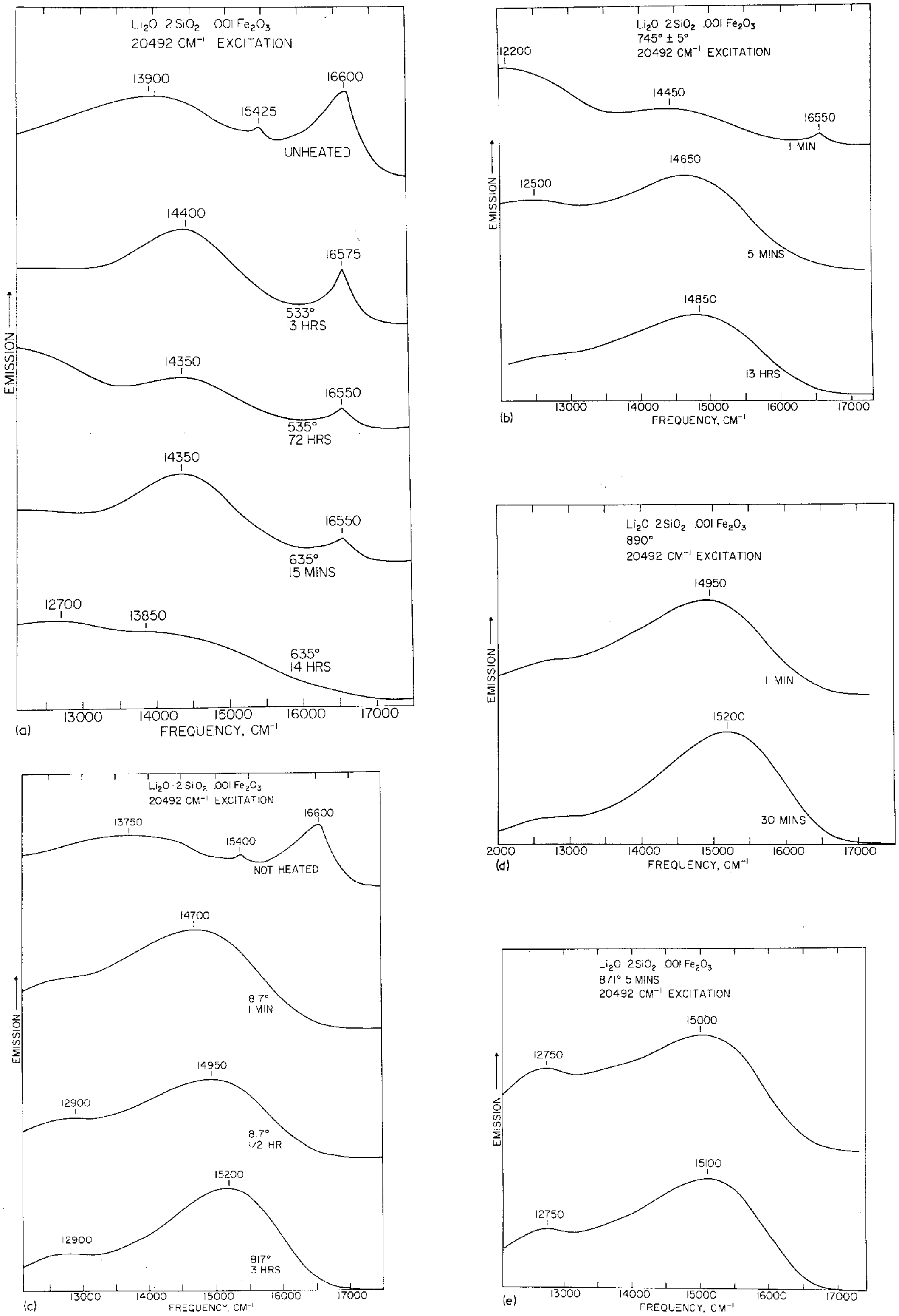

Figure 12 Laser-excited luminescence emission of heat-treated 1/10% glasses. (a) Heated below 700° C for various times; (b) 745° C for various times; (c) 817° C for various times; (d) 890° C for various times; (e) two different rods heated at 871° C for 5 minutes to show variation of emission with sample. The top spectrum of (a) is a different rod from the 1/10% glass of Fig. 11, showing sample dependence of emission of as-quenched glasses.

disilicate. This would occur via an intermediate stage during which no Raman spectrum could be obtained at all.

Finally, a glass rod was photocrystallized in the beam in a number of spots so that its Raman spectra were like those of the bottom of Figs. 10a and b. Then the rod was ground and X-rayed. The pattern showed predominantly lithium disilicate present with a trace of metasilicate. This is remarkable in view of the fact that the Raman spectra show a phase completely different from the disilicate.

3.6. Luminescence of the 1/10% glasses

The laser excited luminescence (20 492 cm^{-1} excitation) of the unheated 0%, 1/10% and 1% glasses are shown in Fig. 11 and of heat-treated 1/10% glasses in Fig. 12. The emission is exceedingly weak, being comparable to the intensity of the 1100 cm^{-1} Raman line of the glasses. The emission of the unheated 1/10% glass has sharp features at 15 425 and 16 600 cm^{-1} and a broad band between 13 900 and 14 200 cm^{-1}. The precise spectrum depends somewhat on the sample. In Figs. 12a and c the emission of two different rods of 1/10% glass are shown, and they differ somewhat in the intensity and position of the broad band. This broad band at about 14 000 cm^{-1} is due to trivalent iron as is clear from Fig. 11. We have observed a similar emission in iron-containing sodium silicates and sodium borates. Ferrous iron does not emit at the frequencies shown in Figs. 11 and 12. The sharp features in the 1/10% glass emission are also present in the nominally pure glass (cf. Fig. 11) and are due to either an intrinsic colour centre or impurities in the glass. We have found that they appear in all silicate glasses in varying degrees.

When the glass is crystallized an additional broad band appears in the neighbourhood of 12 500 cm^{-1}. Below about 700° C this low-frequency emission eventually becomes stronger than the band at 14 000 cm^{-1}. At temperatures above 750° C this broad band appears very rapidly (Figs. 12b and c) and then gradually decreases in intensity relative to the higher-frequency band at 14 500 to 15 000 cm^{-1}. At higher temperatures (Fig. 12d) the 12 500 cm^{-1} band is quite weak relative to the higher-frequency emission for all heating times.

Furthermore, with increased heating times and/or heating temperatures the band at 14 000 cm^{-1} shifts to a much higher frequency and also becomes much more intense relative to the intensity of the 1100 cm^{-1} Raman band of the crystallized glass. This means that the absolute intensity of the 14 500 cm^{-1} broad band increases monotonically with increasing heating times and temperatures. Finally, Fig. 12e shows two different rods given the same heat treatment at 871° C for 5 min, and demonstrate that the emission spectra are somewhat sample dependent.

3.7. Summary of crystallization behaviour

Some definite trends have been observed in the crystallization behaviour of the 1% and 6% glasses, even though some of the details seem to be sample dependent. These trends are summarized below.

For heat-treated 1% and 6% glasses, only lithium disilicate is crystallized below 650° C for times less than 1 day. At temperatures above 750° C, lithium metasilicate and lithium disilicate phases are detected as well as iron oxide phases. The rate of crystallization of the metasilicate phase is much slower than the rate for disilicate crystals, and the rate increases with increasing temperature. Even the photocrystallization of the 6% glass shows the general trend that the disilicate phase appears early (if it appears at all), and the chain-structure phases appear later on.

There is a parallel behaviour for the luminescence of trivalent iron in the 1/10% glasses, where only lithium disilicate is observed to crystallize. Below 650° C only the iron emission at 12 500 cm^{-1} band appears nearly instantaneously (as does the disilicate crystal phase). The growth in intensity and increase in frequency of the higher frequency band at 14 500 to 15 200 cm^{-1} occurs much less rapidly than the crystallization of the disilicate phase, but the rate increases with temperature.

A variety of what seems to be chain-structure silicate phases appears in the 6% glass during photocrystallization. Although the photocrystallized glasses are predominantly lithium disilicate according to X-ray diffraction, very little disilicate appears in the Raman spectrum and the chain structures yield a very strong Raman intensity.

Finally, the morphology of the crystalline phases in the heat-treated rods is affected by the presence of iron. The radial dendritic growths always found in the 0% and 1/10% glasses were never observed in the 1% glasses and rarely observed in the 6% glasses.

4. Discussion

Let us now discuss how these results can be used to deduce information about the environment of Fe^{3+} in lithium disilicate glass and other glasses. Note first that the previous spectroscopic study [12] as well as X-ray diffraction studies clearly show that iron-free binary alkali silicate glasses have well defined structural features. In the case of lithium disilicate glass, each Si is tetrahedrally surrounded by oxygens and each SiO_4 tetrahedron has on the average only one non-bridging oxygen, although there are fluctuations. Thus the short-range order in the glass is similar to that of crystalline lithium disilicate, and this similarity is reflected in a similarity of the Raman spectra of crystalline and glassy lithium disilicate (cf. Figs. 2 and 5).

Returning to the iron-containing glasses, it has been found that the addition of ferric oxide to silicate glass is correlated with a strong, well defined Raman band between 950 and 980 cm^{-1} and with a low frequency continuum (see Figs. 2 and 3). The intensity of this band increases relative to the intensity of the 1100 cm^{-1} band of the $(Si_2O_5)_n$ sheets (which may be used as an internal standard) as the iron concentration increases. The depolarized spectra show that this band is present in a glass with 2% iron oxide. On the other hand, for borate glasses there are only small changes in the spectra upon addition of iron (cf. Fig. 4). It was also observed that the Raman spectra of the glasses $Na_2O \cdot 3SiO_2 \cdot 0.1Al_2O_3$ and $Na_2O \cdot 3SiO_2 \cdot 0.1B_2O_3$ are very similar to the spectrum of undoped sodium trisilicate. In particular, there are no additional outstanding features in these glasses at any frequency. (These spectra are not included here).

These results suggest that in iron-containing silicate glass (and, in particular, in lithium disilicate) the iron is associated with a distinctive range of structures or sites, whose vibrations lead to the observed spectral features. It is important to keep in mind that we can make statements only about those iron groupings which give rise to the 950 cm^{-1} band. The remainder of the iron is invisible as far as the Raman spectra are concerned.

There are several things that the iron can do in the glass. It can substitute for silicon or lithium such that the local structure of the host glass is largely unchanged by the substitution. That is, the neighbourhoods of the iron atoms have the same statistical properties as neighbourhoods of Li or Si atoms (depending on how the iron substitutes). Such a substitution can be called an *isomorphous substitution,* since the iron atom differs from a Li or Si atom, where appropriate, by its different mass and force constants but not be the nature of its environment.

On the other hand, the iron can cause a structural rearrangement so that in the neighbourhoods of the iron atoms the local glass structure is different from what it is in the neighbourhood of Li or Si atoms.

As an example, if the iron substitutes for Li, and if SiO_4 tetrahedra adjacent to the iron atoms always have two non-bridging oxygens while in the host glass each SiO_4 tetrahedron has on the average only 1, a gross rearrangement has been made.

For the first part of this discussion we show that it is possible to eliminate as the source of the 950 cm^{-1} band the isomorphous substitution of iron for Si or Li (or both).

The argument is as follows: Let us assume the opposite, that the iron is simply an isomorphous substituent for Si, Li or both. Then the 950 cm^{-1} band in iron-containing lithium disilicate glass must be due to an antisymmetric Fe–O–Si vibration. There will be no symmetry restrictions on the Raman activity of this vibration. Moreover, the frequency is the same magnitude as the antisymmetric vibrations of oxygen-bridged tetrahedral Fe^{3+}–Si binuclear complexes [17]. When the glass is crystallized to lithium disilicate, the iron will be incorporated into the crystal as an isomorphous substituent. Then the vibrations of such iron-containing disilicate crystals must give rise to a very strong, sharp Raman band in the neighbourhood of 950 cm^{-1} (assuming no valence change of the iron on crystallization). The reason is that the strong, high-frequency Raman active vibrations of the glass are very similar to the vibrations of crystals of similar short-range order. This has been discussed by Brawer [18] for a theoretical model and by Brawer and White [12] in reference to the Raman spectra of silicate glasses. There is no question but that a strong Raman band in the spectrum of a glass implies rigorously that in a crystal of similar short-range order a similar, very strong and sharp Raman band would exist. Since the vibration is localized about a defect – in this case iron – the selection rules of a perfect crystal would not apply.

Now the results for crystallization of the 1%

and 6% glasses clearly show that when lithium disilicate crystallizes there is no extra band in the frequency interval 950 to 1000 cm^{-1} that is correlated with the disilicate crystal spectra. In fact, at temperatures below 650° C no extra band is seen at all between 950 and 1000 cm^{-1}, even when the glass is very well crystallized. Rather, in those cases where bands in the spectra are seen between 950 and 1000 cm^{-1} the bands are due to completely separate chain-structure phases which make their appearance a long time after a large amount of disilicate is crystallized. This is supported by the observation that much of the iron in the higher iron concentration glasses phase-separates into other oxide phases on crystallization.

It is argued, then, that the iron atoms in sites which give rise to the 950 cm^{-1} band are not simply substituted for Li or Si in the structure of the host glass. Rather, the iron is associated with regions which have a different local structure from the host glass. The extra bands at 950 to 1000 cm^{-1} are then due to the vibrations of the "defect" regions. We do not mean to say that no iron substitutes for Li or Si in either the host glass or the disilicate crystals, but only that such iron atoms do not contribute appreciably to the 950 cm^{-1} band of the iron-containing glass. The iron-rich regions are the precursor to the iron oxide phases and the iron-depleted regions are the precursor to the dominant lithium disilicate phase.

It is, of course, enormously tempting to assume that these iron-containing regions must in some way be chain-like because the strong Raman band of chain silicates lies in the 950 to 1000 cm^{-1} region, just where the extra band is in the doped glasses. However, another interpretation is possible. It is found that for the binary alkali silicates between the disilicate and metasilicate compositions a Raman band at 950 cm^{-1} is observed in addition to the one at 1100 cm^{-1}. This extra band is due to the fact that there are two non-bridging oxygens (NBOs) on some SiO_4 tetrahedra and the band increases in intensity relative to the 1100 cm^{-1} band with an increase of alkali concentration. For the iron-containing glasses, it is possible that the trivalent iron requires two NBOs on nearby SiO_4 tetrahedra and this give rise to the 950 cm^{-1} band. Such a structure would agree with our deductions that the iron occupies a distinctive site.

For the above two models, the vibrations giving rise to the 950 cm^{-1} band are due to the silicate structure of the glass. However, if the vibration is an Fe–O–Si vibration, then it is not likely that the structure of the site can be inferred at all from the Raman spectra.

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