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Phase separation in Li_2O–SiO_2 glasses with additions of V_2O_5, MnO_2 and Cr_2O_3

J. MA. RINCÓN
Instituto de Cerámica y Vidrio, CSIC, Arganda del Rey, Madrid, Spain
C. J. R. GONZÁLEZ-OLIVER
Battelle-Geneva Research Centre, Geneva, Switzerland
P. F. JAMES
Department of Ceramics, Glasses and Polymers, University of Sheffield, UK

A number of lithium silicate glasses, inside and just outside the miscibility gap, containing low percentages of V_2O_5, MnO_2 and Cr_2O_3 were examined by electron microscopy techniques. Upon heat treatment in the range 450 to 550° C these glasses exhibited phase separation preceding extensive crystallization. The Li_2O contents (mol %) of the base glass compositions were: 26 (C-I), 30 (C-II), 34 (C-III) and 37 (C-IV). The V_2O_5 and MnO_2 additions were 1 mol % and the Cr_2O_3 addition was 0.1 mol %. Globular or sectorized domains were obtained for compositions C-I to C-III containing V_2O_5, for formulations C-II to C-IV containing Cr_2O_3 and for glass C-I containing MnO_2. In nearly every case a much finer liquid-phase separation of droplet type was also detected. The results indicate that V_2O_5 and MnO_2 widen the Li_2O–SiO_2 miscibility gap and that the Cr_2O_3 may cause fine-scale crystallization.

1. Introduction

The microstructure of heat-treated Li_2O–SiO_2 glasses has been extensively studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Thus, the early and final stages of crystallization [1, 2], as well as amorphous phase separation, in lithium silicate glasses have been analysed [3, 4]. Specific or less common morphologies have also been obtained in related glasses. For instance, in partially crystallized Na_2O–Li_2O–SiO_2 glasses sectorized phases or phases containing protuberances have been observed [5]. Similar structures were detected in the Li_2O–SiO_2 and Na_2O–CaO–MgO–Al_2O_3–SiO_2 [6, 7] systems and more recently also in Li_2O–CdO–SiO_2 compositions [8, 9].

Here some preliminary observations of the microstructure of Li_2O–SiO_2 glasses containg V_2O_5, MnO_2 and Cr_2O_3 were made using SEM, TEM of replicas and TEM of thin foils. This study is a part of a more general investigation of glass-ceramics for nuclear reactor applications.

2. Experimental details

The glasses were prepared from the following analytical grade reagents: SiO_2, Li_2CO_3, V_2O_5, MnO_2 and Cr_2O_3 [9]. The batches were dry mixed and melted in Pt-Rh crucibles at 1300° C for 2 h with a total stirring time (with a platinum blade) of 1 h. After melting, the molten glasses were cast into brass moulds. The nominal compositions of the glasses are listed in Table I. The Li_2O content ranged (in wt %) from 14.9 for C-I to 23.4 for C-IV. Chemical analysis indicated maximum Li_2O losses in the range from 0.5 to 2 mol % [9]. Nearly every glass was opalescent in appearance after the above casting procedure. The cast glasses were heat treated for 2 h at 450 or 550° C and examined by powder X-ray diffraction (XRD) for evidence of crystallinity.

Thin glass sections for TEM were prepared by first grinding and polishing each glass specimen, using SiC and diamond, to a thickness of approximately 15 μm. The foil was then cemented to a copper grid and placed on a rotating plate in the vacuum chamber of an Edwards IBMA 2 ion-beam thinning apparatus. The glass sample was bombarded with 5 kV argon ions until a small hole appeared. Carbon replicas were prepared of fractured and etched surfaces (15 sec in 2% HF solution) and examined in either a Siemens 51 or a Philips TEM-300 transmission electron

TABLE I Nominal compositions of glasses studied

Code	Base glass (mol %)		Additions to base glass (mol %)		
	SiO_2	Li_2O	V_2O_5	MnO_2	Cr_2O_3
C-I (V_2O_5)	74	26	1	–	–
C-I (MnO_2)	74	26	–	1	–
C-I (Cr_2O_3)	74	26	–	–	0.1
C-II (V_2O_5)	70	30	1	–	–
C-II (MnO_2)	70	30	–	1	–
C-II (Cr_2O_3)	70	30	–	–	0.1
C-III (V_2O_5)	66	34	1	–	–
C-III (MnO_2)	66	34	–	1	–
C-III (Cr_2O_3)	66	34	–	–	0.1
C-IV (V_2O_5)	63	38	1	–	–
C-IV (MnO_2)	63	38	–	1	–
C-IV (Cr_2O_3)	63	38	–	–	0.1

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microscope. The thin foils were studied in an Hitachi HU 11A electron microscope at 100 kV and the SEM observations were performed in an Etec-Autoscan apparatus using fractured and etched surfaces.

3. Results and discussion

The heat treatments at 450 and 550° C for 2 h were chosen to minimize crystallization of the specimens and to produce extensive liquid–liquid phase separation. Compositions C-I and C-II (with additions) showed appreciable crystallization of lithium disilicate at 600 and 650° C. They were nearly fully crystallized [9] showing also a small percentage of cristobalite crystalline and quartz. Composition C-III showed little crystallization at 550° C (3 to 5% crystal content) and much more at 600° C (main phases: lithium disilicate (LS_2) and lithium metasilicate (LS)) and for glasses C-IV there was appreciable crystallization at 550° C (LS_2, LS and SiO_2).

Fig. 1 shows typical micrographs of C-I (V_2O_5) heat treated at 550° C for 2 h. It should be noted that specimens either for replication or for SEM were lightly etched with dilute HF in order to increase the contrast. Large domains were clearly detected in the replica and scanning electron micrographs consisting of globular features typically about 2 μm × 10 μm in size. A much finer droplet microstructure was also visible.

This is probably the same as the fine droplets observed by TEM in the ion-beam thinned samples and may be attributed to glass in glass-phase separation. However, the larger globular features were not detected in the thin foils although circular dark contrast regions of about 1 μm in maximum dimensions were observed. At this point it is suggested that both the fine droplet microstructure as well as the larger globular domains appear to be related to phase-separation effects as the heat-treated glasses (with the exception of C-IV (Cr_2O_3) showed little evidence of crystallinity from XRD.

The fine microstructure is common to both chemically etched specimens (observed by SEM and/or replica TEM) and to ion-beam foils examined by TEM. In the case of the thin foils, special care was taken to minimize electron-beam damage by examining several samples at liquid nitrogen temperatures and by using a range of accelerating voltages and electron-beam intensities. It should be emphasized that for similarly melted glasses with compositions outside the immiscibility gap, and heated to similar temperatures, no globular structures could be detected for the chemically etched samples using either SEM (fracture surface) or TEM (replicas). It is possible that the globular domains correspond to variations in composition that are small compared with the compositional changes for the finer droplet microstructure. Thus it was more difficult to observe them by means of TEM of thin foils. Although not shown here, very similar microstructures were also observed for the glass C-I (MnO_2) heated to 550° C for 2 h.

For the series of heat-treated glasses C-II, globular domains were detected for V_2O_5 and Cr_2O_3 additions but not for MnO_2 addition. It is worth noting that these C-II glasses contained from 1 to 2 wt % lithium disilicate which was the only crystal phase present in the amorphous matrix detected by XRD.

Transmission electron micrographs for the series of ion-beam thinned glasses C-III are shown in Figs 2 to 4. The globular microstructure is observed for the V_2O_5 and Cr_2O_3 additions and the three glasses contained from 3 to 5 wt % lithium disilicate, the only phase detected by X-ray diffraction. There was also clear evidence for fine-scale phase separation in all the glasses.

The results for C-IV (Cr_2O_3) are presented in Fig. 5. The ion-beam thinned specimen showed clearly defined large circular dark regions containing another phase concentrated at their boundaries. Typical selected-area diffraction patterns consisted of at least two

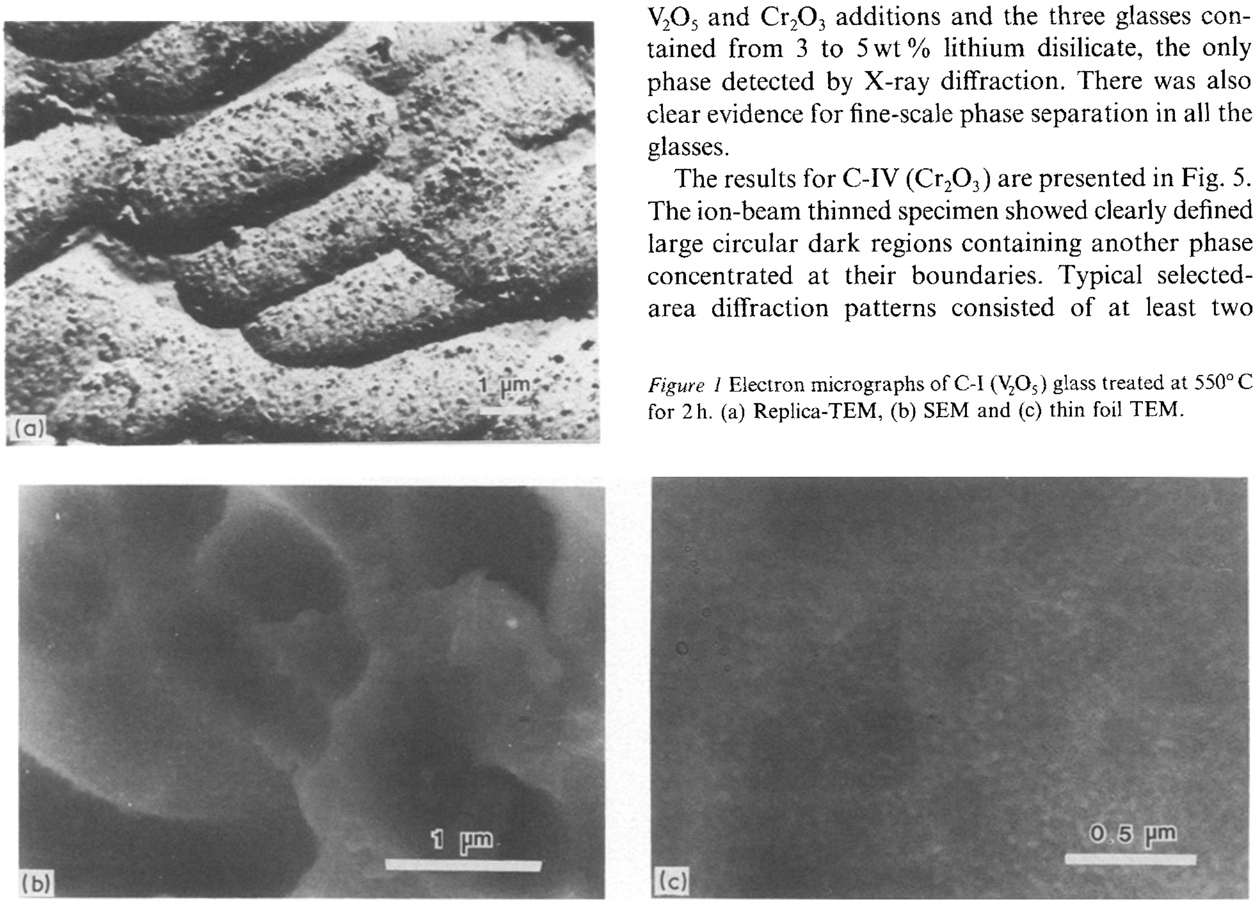

Figure 1 Electron micrographs of C-I (V_2O_5) glass treated at 550° C for 2 h. (a) Replica-TEM, (b) SEM and (c) thin foil TEM.

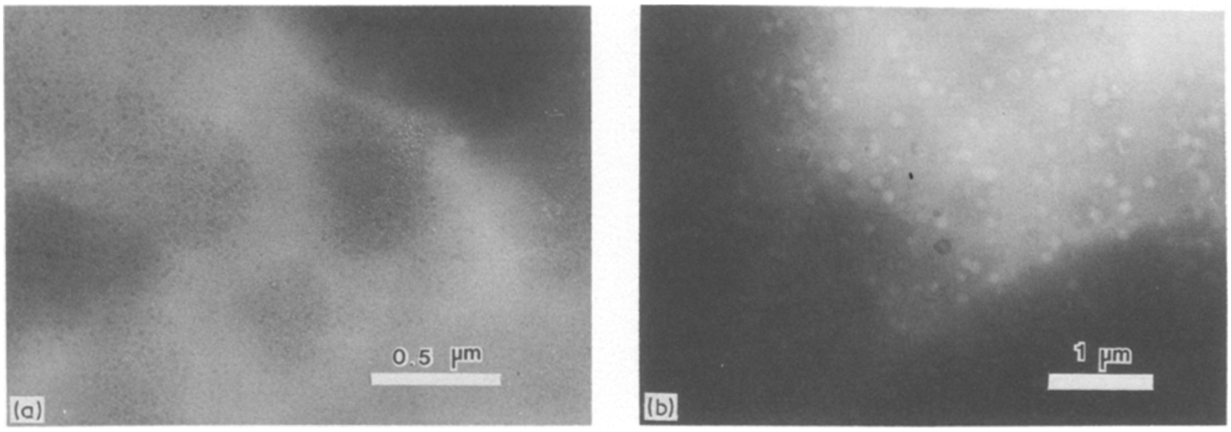

Figure 2 Transmission electron micrographs (thin foil) of C-III (V_2O_5) glass heat treated (a) at 450° C for 2 h, and (b) at 550° C for 2 h.

well-defined rings indicating the presence of lithium metasilicate (Fig. 5b).

The globular or sectorized domains are observed mainly in etched samples of compositions C-I to C-III containing V_2O_5, for compositions C-II to C-IV having Cr_2O_3 as an addition, and for glass C-I containing MnO_2. The micrographs taken from corresponding ion-beam thinned samples do not show exactly the same globular features as the TEM replicas. However, for the thin foil case, the dark circular regions might correspond to the same globular features. One may speculate that these dark regions are related to a change in composition producing a change in image contrast. However, it should be remarked that image formation in amorphous materials is not well understood and only the occurrence of micelles or paracrystals in the size range 5 to 10 nm in SiO_2 glass [10] or microdomains in some amorphous materials observed in dark-field illumination, has been demonstrated [11, 12].

There appears to be better agreement between the different techniques with regard to the fine scale phase separation. The mean radii of the droplets were obtained directly from the electron micrographs of the thin foils and the results are given in Table II.

In the case of the V_2O_5 and MnO_2 additions, the XRD and selected-area electron diffraction evidence indicated that the fine droplets were amorphous. However, for composition C-IV (Cr_2O_3), appreciable crystallization has occurred suggesting that the droplets were probably fine crystals.

Amorphous phase separation in the binary Li_2O–SiO_2 system has been well characterized in previous work [4] and glasses containing less than 66.7 mol % Li_2O are not expected to show immiscibility at any temperature. Hence in the present work the presence of amorphous droplets in the V_2O_5 containing glass C-III (66% SiO_2) may be explained in terms of a widening of the miscibility gap at 550° C as a result of the V_2O_5 addition.

The increase in size of the droplets from composition C-I to C-III (i.e. from 74 to 66 mol % SiO_2) may be attributed to two effects. Firstly, the nucleation rate of silica-rich droplets decreases as the miscibility boundary for 550° C is approached, leading to precipitation on a smaller number of available nuclei and, consequently, larger sized droplets are produced. Secondly, the glass viscosity would be expected to decrease with decrease in silica content in the glass leading to an increase in growth rate. However, it should also be noted that the volume fraction of the silica-rich phase would itself decrease with the decrease in the overall silica content in the glass [4].

Similar results were observed for the MnO_2

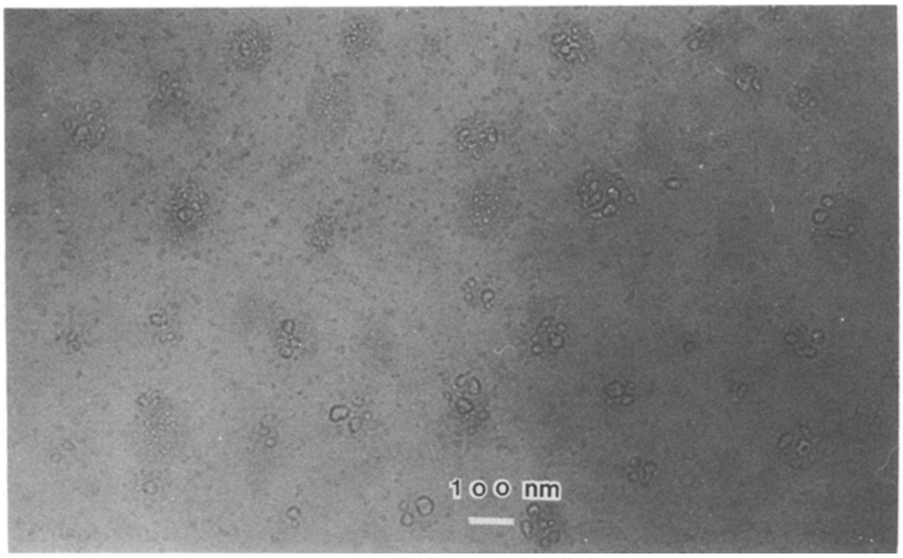

Figure 3 Transmission electron micrograph (thin foil) of C-III (MnO_2) glass heat treated at 550° C for 2 h.

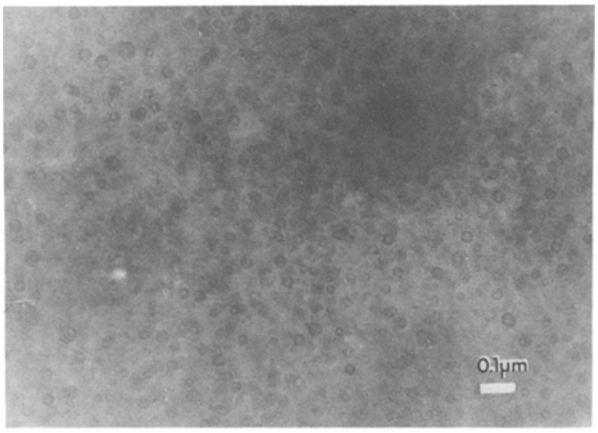

Figure 4 Transmission electron micrograph (thin foil) of C-III (Cr_2O_3) glass heat treated at 550° C for 2 h.

additions. The presence of fine droplets in C-III (MnO_2) containing 66% SiO_2 also indicates a widening of the immiscibility gap. The larger droplet sizes than in the case of the V_2O_5 additions could be the result of a difference in diffusion rates resulting in a higher growth rate of the droplets, although other possible explanations exist in terms of differences in the nucleation rates or volume fractions of phase precipitated.

Fine droplets were also observed in the glasses C-II to C-IV containing Cr_2O_3. The fine droplets in C-II (70% SiO_2) are expected because the corresponding base glass without Cr_2O_3 shows phase separation [4, 5]. However, the presence of droplets in the Cr_2O_3 containing glasses with lower silica contents (C-III and C-IV) is difficult to understand because the level of Cr_2O_3 (0.1 mol %) addition seems unlikely to widen the miscibility gap sufficiently. However, the "droplets" in these glasses, particularly C-IV (Cr_2O_3) containing 62 mol % Si_2O_3 may be very fine crystals. XRD and selected-area electron diffraction evidence suggests that they are probably crystals of lithium metasilicate. Thus Cr_2O_3 may be acting as a crystal nucleation catalyst in these glasses, although further work is required to confirm this interpretation.

TABLE II Mean droplet radius (nm) obtained from transmission electron micrographs of ion-beam thinned foils

Addition	C-I	C-II	C-III	C-IV
V_2O_5	20*	30* 20.5†	48*	–
MnO_2	34*	73.5*	47*	–
Cr_2O_3	–	13*	19*	58†

* Glasses heat treated at 550° C for 2 h.
† Glasses heat treated at 450° C for 2 h.

4. Conclusions

Lithium silicate glasses, inside and just outside the immiscibility gap, containing V_2O_5, MnO_2 or Cr_2O_3 were heat treated for 2 h at 450 or 550° C and examined by SEM and TEM. The glasses, generally exhibited little crystallization but there was clear evidence of various microstructures arising from amorphous phase separation. Two distinct forms of phase separation on quite different scales were found. One type took the form of a coarse globular or sectorized domain morphology. A much finer amorphous phase separation in the form of droplets was also observed.

Preliminary observations suggest that V_2O_5 and MnO_2 additions widen the miscibility gap at 550° C for the base Li_2O–SiO_2 system so that fine-scale amorphous phase separation is observed even for compositions with 66 mol % SiO_2. Fine droplets were also observed in the glasses containing 0.1 mol % Cr_2O_3 which may be attributed to fine-scale crystallization.

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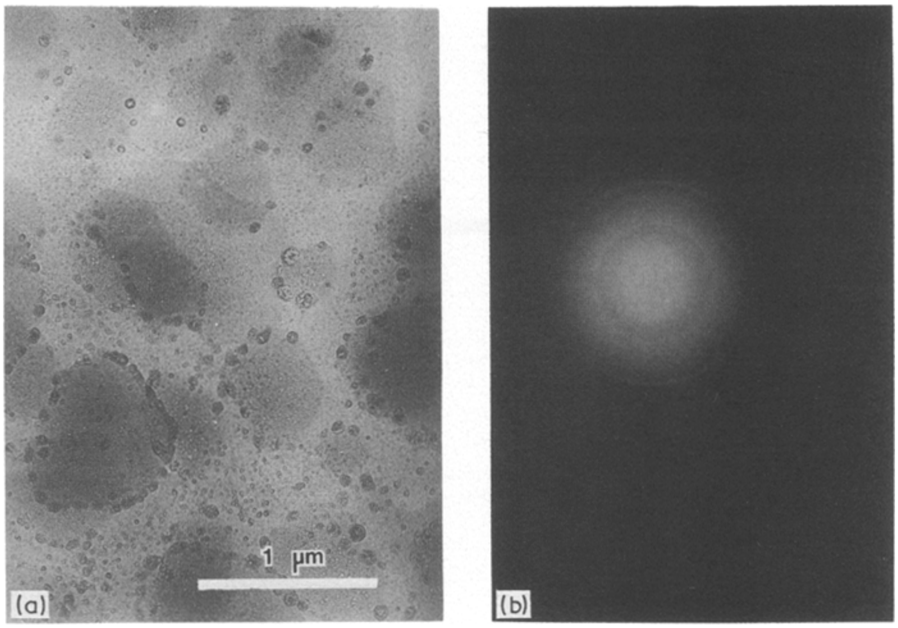

Figure 5 (a) Transmission electron micrograph (thin foil, bright field) and (b) selected-area diffraction pattern of C-IV (Cr_2O_3) glass heat treated at 450° C for 2 h.

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