JOURNAL OF MATERIALS SCIENCE 30 (1995) 995–999

Structural and microstructural study of glasses in the Li_2O–TiO_2–SiO_2 system

M. A. VILLEGAS, A. de PABLOS, J. M. FERRNÁNDEZ NAVARRO
Instituto de Cerámica y Vidrio, C.S.I.C., Arganda del Rey, Madrid, Spain

Glasses from the Li_2O–TiO_2–SiO_2 system with TiO_2 content ranging between 5 and 20 mol % were prepared. The glasses studied have an opal appearance and when their microstructure is studied through transmission electron microscopy, a strong phase separation in droplet form is observed, with the size of the droplets depending on the TiO_2 and the Li_2O content. X-ray diffraction showed that these glasses are non-crystalline and identified the crystalline phases which take place after the corresponding thermal treatment to enhance liquid immiscibility. A structural study of the samples prepared was carried out through infrared spectroscopy. Titanium oxide is incorporated into glasses as a network modifier, so that titanium atoms place themselves in octahedral positions [TiO_6]. This is attributed to the presence of Li_2O which breaks up the glass network, favouring the hexacoordination of titanium atoms.

1. Introduction

The glasses in the TiO_2–SiO_2 binary system have aroused a great deal of scientific interest thanks to their low expansion coefficients [1], which means that they can be used for lenses in equipment for astronomical observation. To be more precise, with contents of 7–8% of TiO_2 weight, glasses can be obtained with expansion coefficients near to zero which become negative [2] when the percentage of TiO_2 reaches a weight of 15%.

Moreover, titanium oxide is used as a nucleating agent in glasses and glass-ceramic materials [3], especially in systems with Li_2O, since it shortens the induction period of crystalline nucleii and increases their growth rate. Porous glass-ceramic materials prepared from silicotitanate are thermally and chemically very stable, thanks to the presence of dispersed crystallites of anatase and rutile [4]. Some silicotitanate glasses with crystalline phases of sphene, perovskite, etc. have been used to immobilize nuclear wastes thanks to their strong alkaline resistance and relative ease of manufacture [5, 6].

TiO_2 also provokes the phase separation of glasses [7] and increases their refractive index [8] and their hardness and toughness [9, 10]. All of this emphasizes the interest in knowing how titanium is structurally incorporated into glasses, since the characteristic behaviour of glasses depends on this.

2. Experimental procedures

The composition of the glasses prepared from the Li_2O–TiO_2–SiO_2 system can be seen in Table I and Fig. 1. In all cases 75% of Li_2O was incorporated in the form of Li_2CO_3 Merck (analytical reagent) and the remaining 25% added was in the form of $LiNO_3$ Merck (analytical reagent).

The nitrate was used as an oxidizing agent in order to shift the redox equilibrium $Ti^{3+} \rightleftarrows Ti^{4+}$ to the highest state of oxidation. Titania was added in the form of TiO_2 pure Fluka and SiO_2 as quartz sand. The homogenized batch was melted in a platinum/rhodium crucible at temperatures of 1450–1550 °C in an electric furnace. Each sample was melted at least twice for between 1.5 and 2 h. After the first melting, the glasses were crushed to improve their final homogeneity. They were poured into brass moulds and allowed to cool to room temperature to prevent devitrification or to reduce immiscibility. All the samples showed an opal appearance.

The phase separation of the samples was studied with a transmission electron microscope (TEM), Philips model EM 300, using carbon replicas obtained from a recent fracture of the samples treated with HF (10 vol %) for 30 s. Besides the TEM observations carried out with the tempered glasses, replicas of sample 6, treated at 600, 650, 700 and 750 °C for 5 h in order to accentuate their phase separation and/or devitrification, were prepared. The crystalline phases formed during the cooling of some of the glasses or after the corresponding thermal treatment were identified by means of X-ray diffraction (XRD) with Siemens D5000 equipment. The infrared (IR) absorption spectra were obtained with Nicolet FT-IR equipment between 400 and 4000 cm^{-1} using the anhydrous KBr pellets technique.

3. Results and discussion

The ternary system Li_2O–TiO_2–SiO_2 presents a wide area of liquid immiscibility where optically dense

0022–2461

TABLE I Composition of the glasses

Sample no.	% Li_2O		% TiO_2		% SiO_2	
	mol	wt	mol	wt	mol	wt
1	10	5.1	10	13.5	80	81.4
2	15	7.8	10	13.9	75	78.3
3	15	7.7	15	20.5	70	71.8
4	15	7.5	20	26.9	65	65.6
5	20	10.8	5	7.3	75	81.9
6	20	10.6	10	14.3	70	75.1
7	20	10.5	15	21.0	65	68.5
8	20	10.3	20	27.6	60	62.1

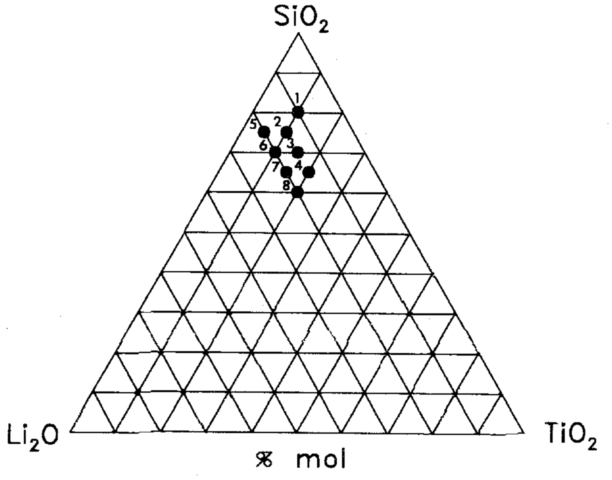

Figure 1 Location of the compositions studied in the ternary system Li_2O–TiO_2–SiO_2.

opaque glasses are obtained, such as those prepared in this study. Their opacity is due to the fact that they present a strong phase separation. The immiscibility area in this system is found between a weight of 0 and 27% of Li_2O [11]. It is common knowledge that the presence of liquid immiscibility in glasses causes important changes in many of their properties. In binary silicotitanate glasses it has been proved [12] that the lack of continuity observed in certain properties (density, refraction index and thermal expansion coefficient) depending on the TiO_2 content is due to the precipitation of a second phase rich in TiO_2 in the glass network.

All of the glasses prepared are essentially non-crystalline, as was shown by XRD, with the exception of sample 4, where two crystalline phases were detected in small proportions: rutile (TiO_2) and anosovite (Ti_3O_5). Fig. 2 shows TEM micrographs for some of the glasses prepared. These reveal the presence of a phase separation of the droplet type; the size of the droplets increases with the percentage of Li_2O and TiO_2. In Fig. 2c the aspect of the crystals detected by XRD upon the separated ground of glass 4 can be observed.

Fig. 3 shows the evolution of the phase separation of glass 6 according to the temperature at which it was treated. The drops gradually grow and form 750 °C large flat crystals start to appear. By means of XRD lithium disilicate ($Li_2O \cdot 2SiO_2$) is found in glasses treated at over 750 °C. The incipient crystallization of lithium disilicate is detected in samples treated at 700 °C for 5 h.

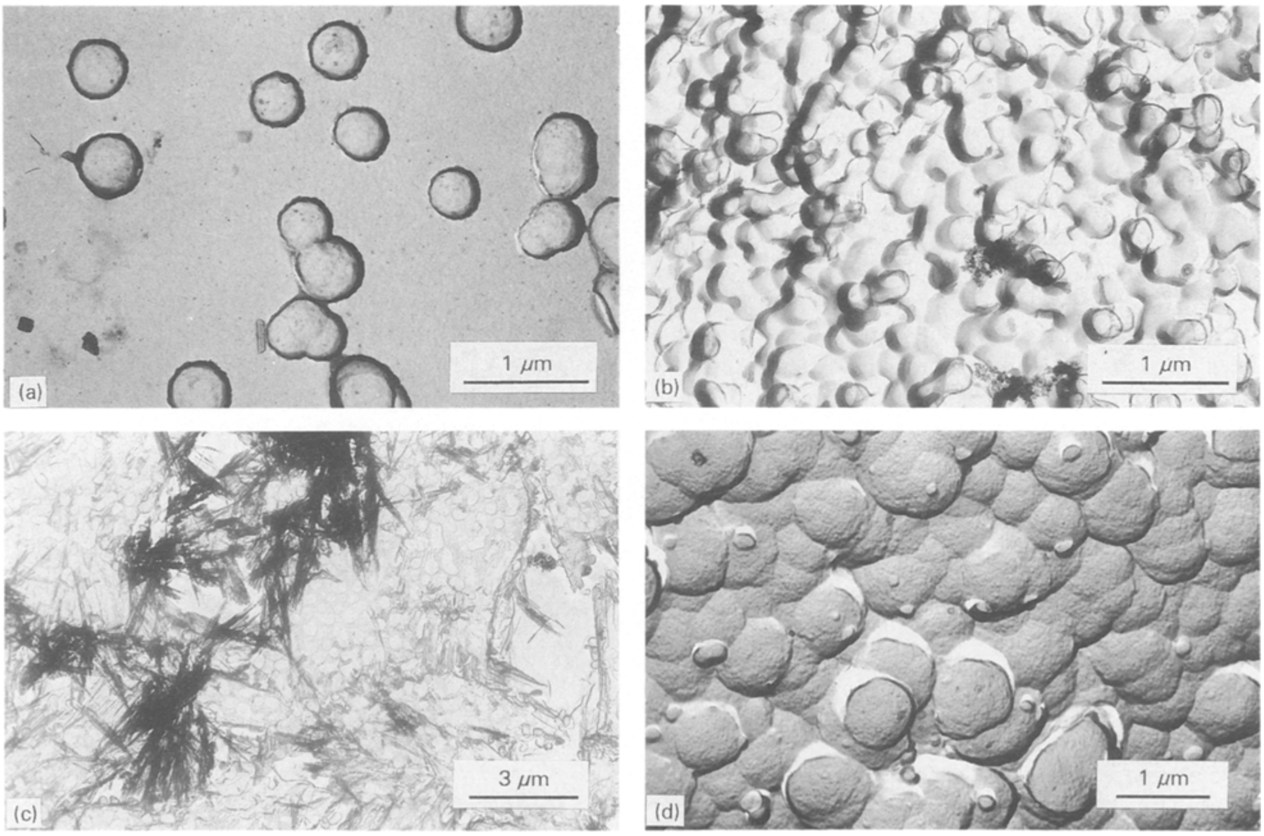

Figure 2 TEM micrographs of some of the prepared glasses: (a) glass 1, (b) glass 2, (c) glass 4, (d) glass 7.

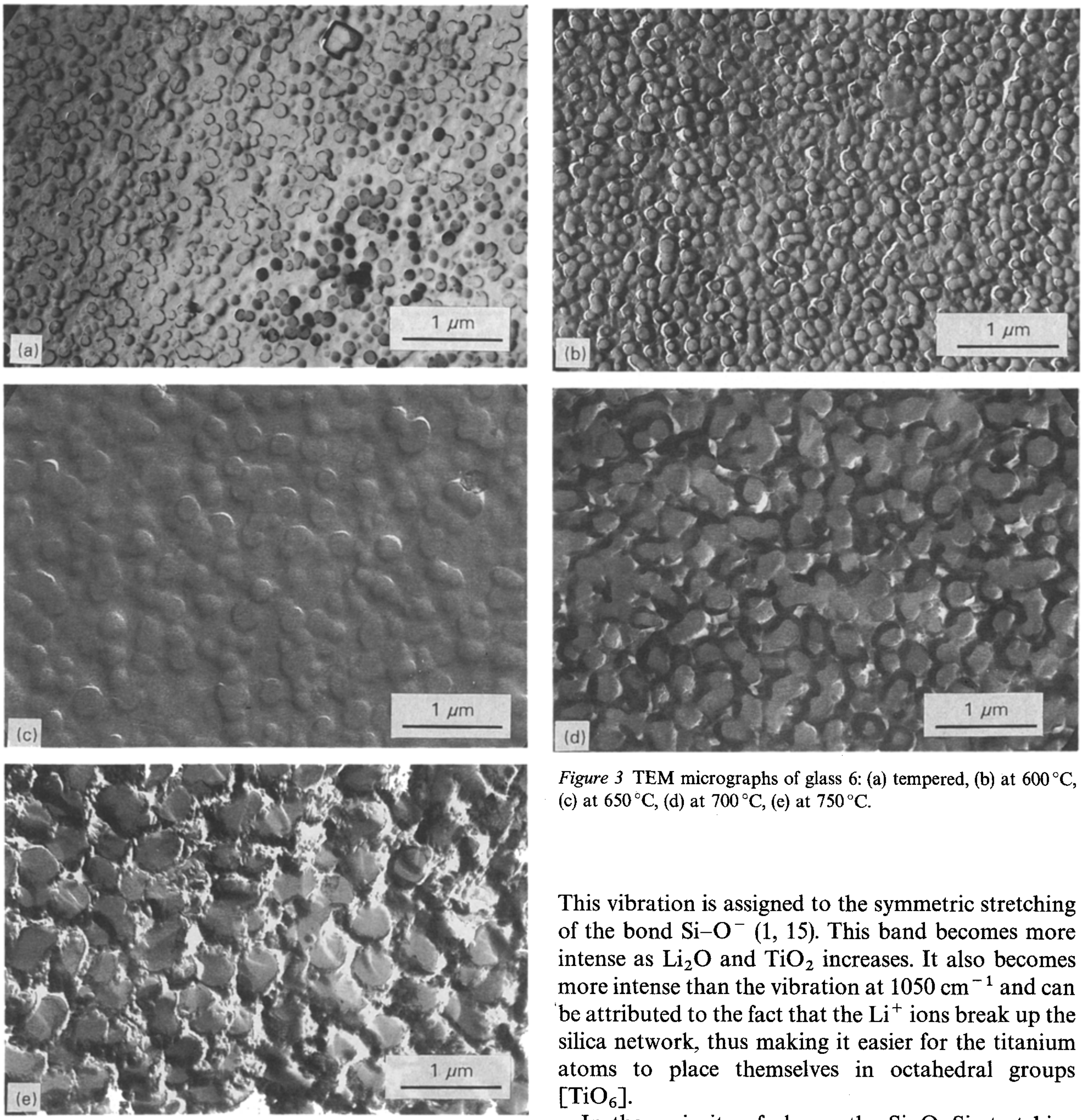

Figure 3 TEM micrographs of glass 6: (a) tempered, (b) at 600 °C, (c) at 650 °C, (d) at 700 °C, (e) at 750 °C.

In the IR absorption spectra of glasses in the Li_2O–TiO_2–SiO_2 system (Figs 4 and 5), a band appears between 1400 and 1430 cm^{-1} which decreases as the proportion of silicon dioxide increases and the TiO_2 and Li_2O content diminishes (glasses 8, 3 and 1). In sodium silicate glasses [13] it has been proved that the intensity of the said band also diminishes as the silicon dioxide content increases.

The band situated at 1100 cm^{-1} corresponding to the asymmetric stretching vibration Si–O–Si in pure silica (2, 10, 13, 14) splits into two bands around 1165 and 1086 cm^{-1} (glasses 1, 2, 3, 5 and 6), 1121 and 1060 cm^{-1} (glasses 7 and 8) and 1098 and 1042 cm^{-1} (glass 4). This is due to the network weakening as a result of the addition of TiO_2. The split takes place at lower frequencies as the percentage of TiO_2 in the glasses increases.

When Li_2O and TiO_2 are added to the glass network, bands appear at between 900 and 950 cm^{-1}. This vibration is assigned to the symmetric stretching of the bond $Si–O^-$ (1, 15). This band becomes more intense as Li_2O and TiO_2 increases. It also becomes more intense than the vibration at 1050 cm^{-1} and can be attributed to the fact that the Li^+ ions break up the silica network, thus making it easier for the titanium atoms to place themselves in octahedral groups $[TiO_6]$.

In the majority of glasses the Si–O–Si stretching vibration of the bridges between silica tetrahedra around 800 cm^{-1} [16] appears as a doublet (795–813 and 780–782 cm^{-1}) which is typical in the IR spectrum of alpha-quartz [13]. When the glass structure is more disorganized, the intensity of the doublet diminishes and it changes into a single band, as can be seen in the spectra of glasses 4, 7 and 8, with greater TiO_2 and Li_2O content.

Between 661 and 695 cm^{-1} the Ti–O–Ti symmetric stretching vibration is assigned to octahedral groups $[TiO_6]$ [2, 17]. The bands which appear at 555, 595 and the shoulders between 507 and 516 cm^{-1} [1,18] are also attributed to the same type of vibrations of condensed groups $[TiO_6]$.

Lastly, the bending vibration corresponding to the bonds Si–O–Si and O–Si–O (9, 10, 13, 14, 16) appears between 456 and 480 cm^{-1}. This band is not displaced when different proportions of Li_2O are added [13].

In glasses containing TiO_2, according to the most generally accepted ideas, titanium atoms may adopt co-ordination numbers four and six, depending on the

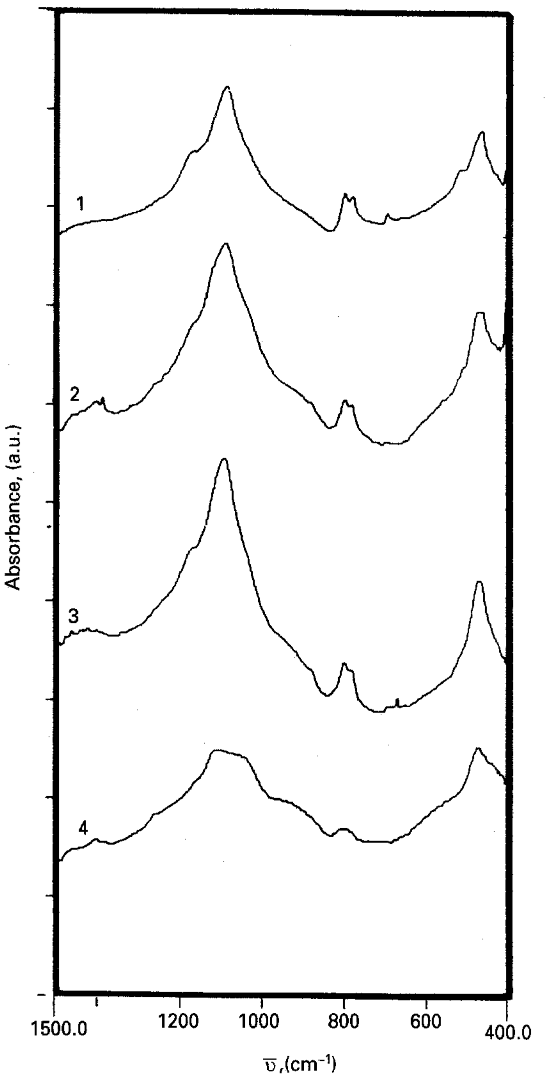

Figure 4 Infrared absorption spectra of glasses 1, 2, 3 and 4.

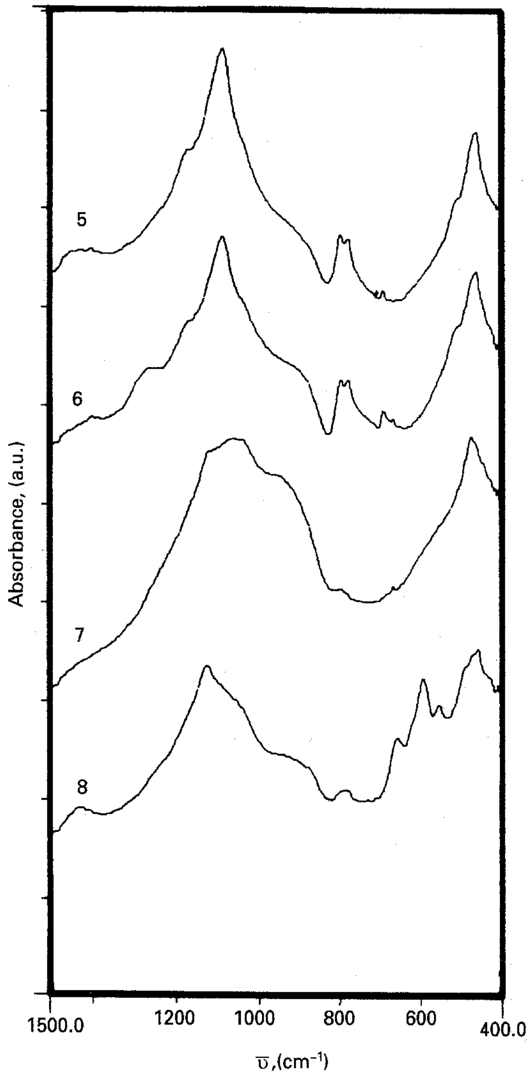

Figure 5 Infrared absorption spectra of glasses 5, 6, 7 and 8.

quantity and type of alkaline oxide present. Silicotitanate glasses may contain titanium atoms both in the cationic parts of their structure (titanium polyhedra linked to each other and to silica tetrahedra by the axes) and in the anionic part (titanium polyhedra link up with each other and with silica tetrahedra through their vertices). Thus, the structural function of the titanium atoms is associated with the type of bond of the polyhedra, rather than with their co-ordination number [19]. When the titanium octahedra are connected by their vertices, the oxygen shares its charge with two titanium atoms, which results in an excessive negative charge for the octahedra (network-forming positions). However, if the titanium octahedra are connected by the axes, they can stand an excessive positive charge (network-modifying positions). In titanate glasses with large cations, the octahedra [TiO_6] are connected by the vertices (titanium atoms as network formers), while in those with small cations, the titanium polyhedra can be connected in two different ways (titanium atoms as network formers and modifiers).

As bands attributable to Ti–O stretching in tetrahedral positions [TiO_4] between 700 and 800 cm^{-1} [17, 18] are not observed, it can be affirmed that the majority of the titanium atoms in the glasses studied are situated in octahedral positions as network modifiers. The presence of small alkaline ions, such as the Li^+, are responsible for the formation of a discontinuous glass network which enhances the positioning of the octahedra [TiO_6].

4. Conclusions

In glasses in the Li_2O–TiO_2–SiO_2 system, the majority of the titanium oxide moves into octahedral groups [TiO_6], acting as a network modifier. This is attributed to the type of discontinuous glass network favoured by the Li^+ ions present. The glasses prepared show a strong phase separation with a droplet size that increases with the TiO_2 and Li_2O content. The prepared glasses devitrify when subjected to thermal treatment at 700 °C, producing lithium disilicate.

Acknowledgements

The authors thank A. Tomás for his support in the experimental part, and the CICYT for financing the MAT 89-727 project.

References

1. C. F. SMITH, Jr, R. A. CONDRATE, Sr and W. E. VOTAVA, *Appl. Spectrosc.* **29** (1975) 79.
2. G. A. PAVLOVA, *Fiz. Khim. Stekla* **8** (1982) 395.
3. P. W. MCMILLAN, in "Glass Ceramics", edited by J. P. Roberts and P. Popper (Academic Press, London, 1964) p. 61.
4. T. KOKUBU and M. YAMANE, *J. Mat. Sci.* **22** (1987) 2583.
5. P. J. HAYWARD and E. V. CECCHETTO, in "The Scientific Basis for Nuclear Waste Management", edited by S. V. Topp (Elsevier Science Publishing Co. Inc., New York, 1982) p. 91.
6. P. J. HAYWARD, E. R. VANCE, C. D. CANN and C. DOEM, *J. Am. Ceram. Soc.* **74** (1989) 579.
7. P. D. LABARBE, J. S. LIN and A. F. WRIGHT, *Phys. Chem. Glasses* **29** (1988) 91.
8. R. C. DE VRIES, R. ROY and E. F. OSBORN, *J. Am. Ceram. Soc.* **38** (1955) 158.
9. S. T. GULATI, Mat. Res. Soc. Symp. Proc. MRS Fall Meeting, 1991, Boston, MA, edited by M. M. Broer, G. H. Sigel, Jr, R. Th. Kersten and H. Kawazoe **244** (1992) 67.
10. M. A. VILLEGAS, A. DE PABLOS and J. M. FERNÁNDEZ NAVARRO. *Glass Technol.* submitted.
11. A. DURÁN and J. M. RINCÓN, in "Separación de fases en vidrios" (Sociedad Española de Cerámica y Vidrio, Madrid, 1982) p. 85.
12. P. C. SCHULTZ, *J. Am. Ceram. Soc.* **59** (1976) 214.
13. R. HANNA and G. J. SU, *J. Am. Ceram. Soc.* **47** (1964) 597.
14. R. HANNA, *J. Am. Ceram. Soc.* **48** (1965) 595.
15. M. M. MORSI and A. W. A. EL-SHENNAWI, *Phys. Chem. Glasses* **25** (1975) 64.
16. M. H. MANGHNANI, J. R. FERRARO and J. L. BASILE, *Appl. Spectrosc.* **28** (1974) 256.
17. H. MARFELS, *Glastechn. Ber.* **42** (1969) 161.
18. P. TARTE, *Silicates Industriels* **28** (1963) 345.
19. E. I. ABDRASHITOVA, *J. Non-Cryst. Solids* **38–39** (1980) 75.

Received 30 September 1993
and accepted 27 July 1994