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Metastable liquid immiscibility and Vycor-type glass in phosphate-silicate systems

Part 2 *Substitution of Li^+ and R^{2+} for Na^+ in glass of $Na_2O–P_2O_5–SiO_2$ system*

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Substitution of Li^+, Mg^{2+}, Sr^{2+}, Ba^{2+} and Zn^{2+} for 50 or 100% of Na^+ in glass with composition $3Na_2O \cdot 7P_2O_5 \cdot 10SiO_2$ resulted in liquid immiscibility in some of the new glasses. Glasses containing SrO and BaO were studied more thoroughly, and a high-silica porous glass was obtained from $3SrO \cdot 7P_2O_5 \cdot 10SiO_2$ glass by heat treatment at 500 to 700° C and subsequent leaching with 3N HCl. However, this porous glass proved incapable of sintering into a bulk glassy body, because of its high rate of cystallization.

1. Introduction

In Part 1 [1], it was described how high-silica glass containing 91% SiO_2 was obtained from low-silica glass (no. 21) in the $Na_2O–P_2O_5–SiO_2$ system by means of phase separation, leaching and sintering. Partial or complete substitution of ions with higher field strength for the Na^+ ions may make for increased liquid immiscibility and increased SiO_2 content in the Vycor-type glass thus obtained. These substitutions are described in the present part.

2. Experimental procedure

Procedures were the same as in Part 1 [1], except that additional analytical reagents were used for preparation of glasses – Li_2CO_3, $SrCO_3$ and $BaCO_3$ of Baker and Adamson, MgO and ZnO of Merck – and the interval of primary heat treatments was wider – 400 to 750° C. Viscosities were determined by the beam-bending method alone, at a constant temperature specific to each glass. Glass 21 in the $Na_2O–P_2O_5–SiO_2$ system was used as a basis for substitution (complete, or 50 mol %) of various cations for the Na^+ ions. The compositions are given in Table I. All new glasses were preliminarily melted in 30 ml fused silica or Vycor crucibles. Four glasses (SrNa, Sr, BaNa and Ba) were selected for more detailed study, because of the stronger visible opalescence in them after the heat treatments; they were melted twice in the 350 ml crucibles (see Part 1).

3. Results and discussion

Chemical analysis of four of the new glasses showed significantly lesser amounts of SrO and BaO compared with the design compositions (Table I). The LiNa, SrNa, SrBa and Ba glasses were opalescent after melting; the others were transparent.

The results of heat treatments (isothermal soaking for 24 h) of these glasses at 400 to 750° C are given in Fig. 1. No visible opalescence was observed in the Mg and Zn glasses; the others showed various degrees of opalescence, but X-ray diffraction examination failed to reveal any crystalline phase in them, except for the Sr glass after the 750° C treatment.

3.1. SrNa glass

SEMs of this glass are given in Figs. 2a to e. The original glass has a non-homogeneous structure. Exposure at 500 to 750° C caused development of a definite droplet structure, but the amount of the droplet phase decreased with increasing temperature, the decrease being very steep between 700

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TABLE I Compositions of glasses

Designation	Calculated Compositions (mol/wt %)					Chemical analysis* (wt %)			
	SiO_2	P_2O_5	Na_2O	M_xO		SiO_2	P_2O_5	Na_2O	M_xO
				Kind	Amount				
21	50/33.75	35/55.8	15/10.45	–	–				
LiNa	50/34.7	35/57.35	7.5/5.35	Li_2O	7.5/2.6				
Li	50/35.7	35/59.0	–	Li_2O	15/5.3				
Mg	50/35.05	35/57.9	–	MgO	15/7.05				
SrNa	50/32.6	35/53.9	7.5/5.05	SrO	7.5/8.45	34.9	52.6	4.9	7.6
Sr	50/31.55	35/52.15	–	SrO	15/16.3	34.3	53.8	–	11.9
BaNa	50/31.35	35/51.8	7.5/4.85	BaO	7.5/12.0	34.0	50.5	4.8	10.7
Ba	50/29.25	35/48.35	–	BaO	15/22.4	32.7	48.3	–	19.0
Zn	50/33.55	35/55.5	–	ZnO	15/10.95				

*Because of high water absorption, the powdered glasses showed significant loss on ignition (up to 10%); data reduced to moisture-free basis.

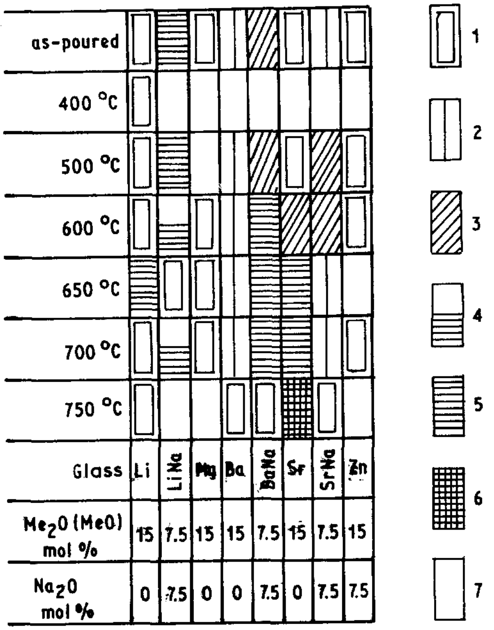

Figure 1 External appearance of glasses after heat treatments (heating rate about 200° C h^{-1}, soaking at the indicated temperatures for 24 h, cooling outside the furnace): (1) transparent glass; (2) weak opalescence; (3) opalescence; (4) transparent on removal from the furnace and opalescent on cooling in air; (5) heavy ("milky") opalescence; (6) a crystalline layer on part of the surface; (7) not studied.

and 750° C. This phase consisted of convex particles (established by comparison of direction of the electron beam and the location of shadows), hence the matrix here was chemically unstable, i.e. low-silica.

The viscosities measured at 425° C are given in Fig. 3 (curve 1). While the 500° C variant showed no significant change compared with the original glass, the 600, 650 and 700° C variants showed a definite decrease in viscosity – confirming the conclusion of a low-silica matrix. In the 750° C variant the decrease was smaller, in agreement with the micrograph (Fig. 2e)*. The specimen treated successively at 750 and 700° C, for 24 h each, showed the same viscosity as the 700° C variant.

While the original glass was fairly stable to 3 N HCl at 50° C, the heat-treated specimens developed, after 24 h leaching, white layers which were very weak mechanically. Chemical analyses of these layers for three specimens are given in Table II. It is seen that the residues after leaching in all these specimens were high-silica and low-phosphate and the Na_2O and SrO contents were low. However, increase of the treatment temperature resulted in significant reduction of the silica content and increase in the P_2O_5 and SrO contents. In this the glass differs from the soda glass 21 of Part 1, where the composition of the high-silica phase

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*Because of danger of fracture, air-quenching of the specimens for the viscosity measurements was avoided, and they were cooled together with the furnace; the small SEM specimens were cooled quickly outside it. In spite of the difference in the cooling technique, there is good agreement between viscosity and SEM data, apparently because the cooling time of the former specimens was relatively small (30 to 45 min to 300° C) compared with the duration of the isothermal treatment (24 h).

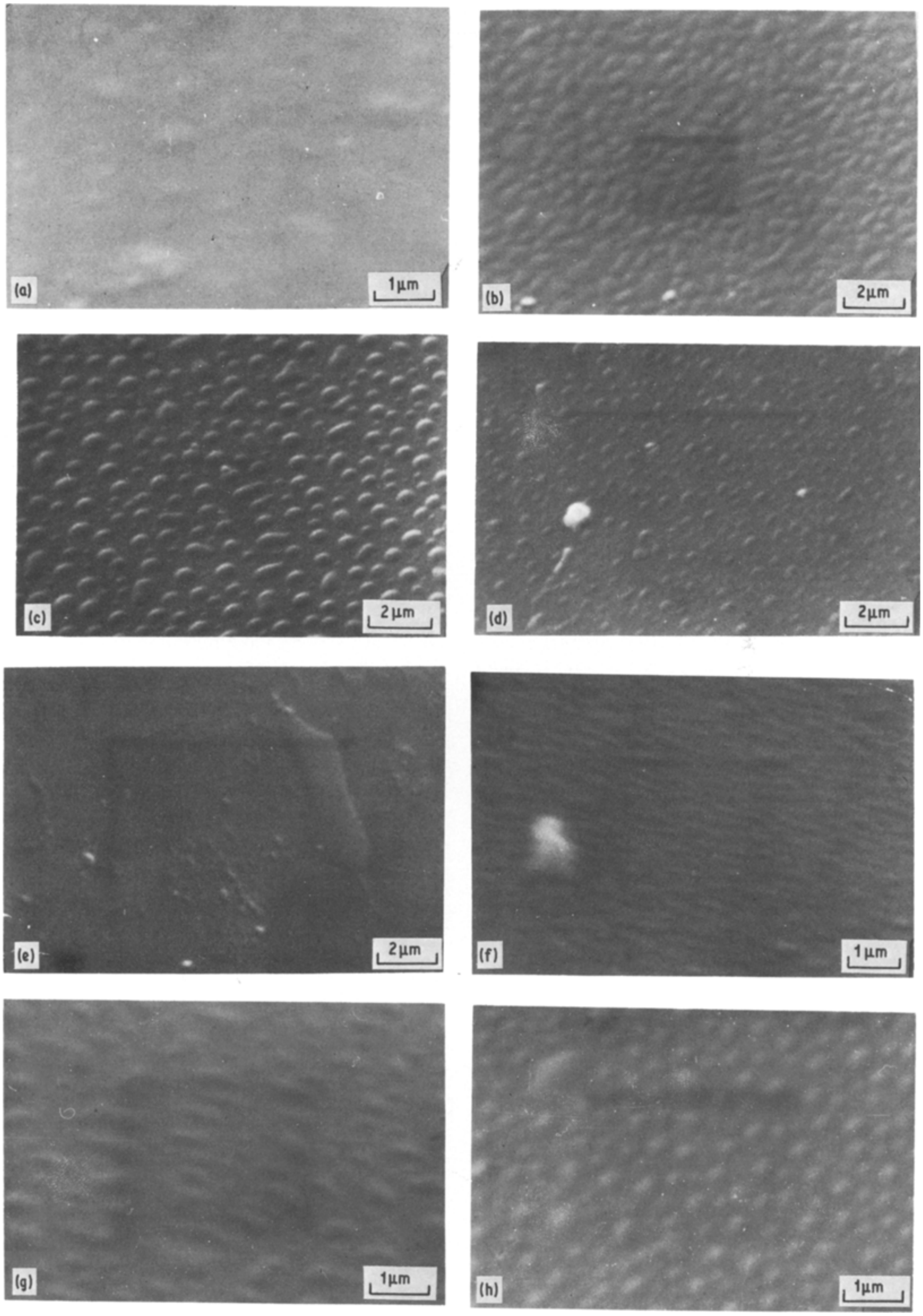

Figure 2 SEM of glasses SrNa and Sr; (a) to (e) SrNa: (a) as-poured, untreated, (b) 500° C, (c) 600° C, (d) 700° C, (e) 750° C; (f) to (j) Sr: (f) as-poured, untreated, (g) 500° C, (h) 600° C, (i), (j) 700° C (at two magnifications). Soaking for 24 h, cooling outside the furnace.

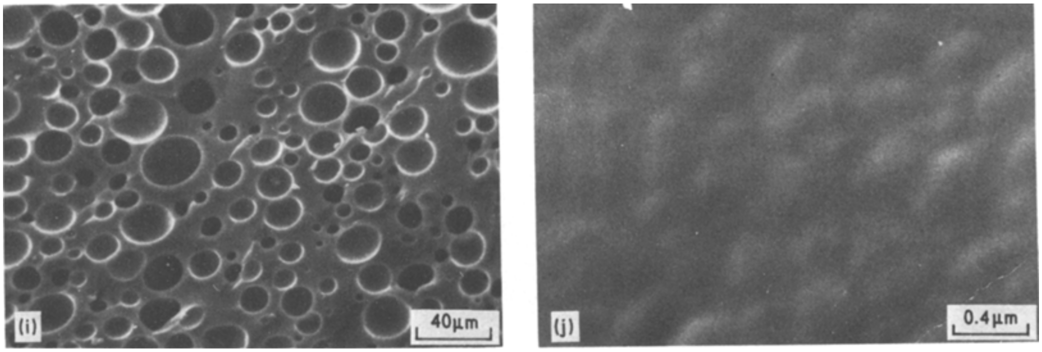

Figure 2 continued.

was almost independent of the treatment temperature. This may be due to the difference in shape of the immiscibility "dome" between the Na_2O–P_2O_5–SiO_2 and Na_2O–SrO–P_2O_5–SiO_2 systems. When the dome tends to symmetry (apparently the latter case), the compositions of both separated phases are strongly temperature-dependent. When one branch tends to verticality (apparently the high-silica side in the former case, or that of the binary Na_2O–SiO_2 system – see Fig. 1 in Part 1), one of the phases is again strongly temperature-dependent, while the other may maintain a fairly constant composition over a wide temperature interval.

Firing at 1100° C for 1 h (the 650° C variant – also at 900° C and 1200° C) failed to produce any sintering but did make for significant formation of cristobalite, as observed in those Na_2O–P_2O_5–SiO_2 glasses where the high-silica glassy residues were obtained from the droplet phase rather than from the matrix (Part 1).

3.2. Sr glass

Heat treatment of this glass involved interesting colour effects. The 500° C variant became pale yellow after 24 h (while retaining its transparency), and bright orange after 48 h. The latter was also the case with the 600° C variant at 24 h (without crystallization, according to X-ray diffraction). The 650° C variant became opaque and pink at 24 h. The 700° C variant initially (24 h) became opaque and white, with an abundance of small

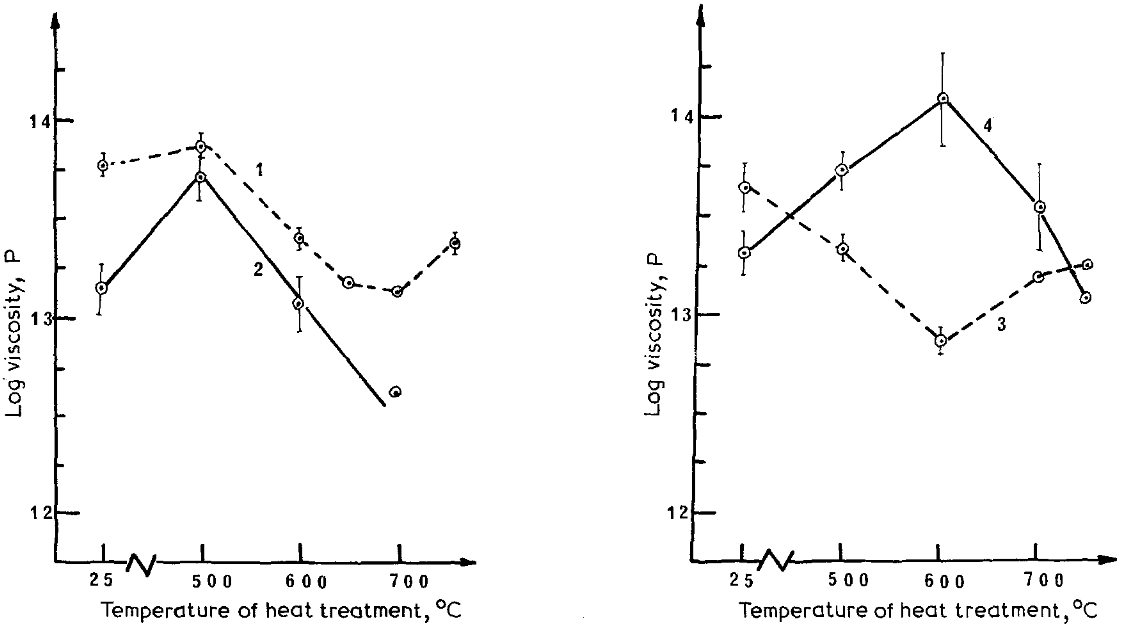

Figure 3 Dependence of viscosity on temperature of heat treatment for 24 h; (1) glass SrNa, viscosities at 425° C; (2) glass Sr, viscosities at 520° C; (3) glass BaNa, viscosities at 425° C; (4) glass Ba, viscosities at 485° C.

TABLE II Chemical analyses (in wt %) of glassy residues after heat treatments (for 24 h) and leaching (3 N HCl, 50° C, 24 h)*

Designation of original glass	Temperature of heat treatment (° C)	SiO_2	P_2O_5	Na_2O	SrO	BaO
	500	95.9	3.5	0.3	0.3	–
SrNa	600	88.6	10.1	0.3	1.0	–
	700	85.9	12.0	0.4	1.7	–
	500	95.25	3.5	–	1.25	–
Sr	600	94.4	4.05	–	1.55	–
	700	93.65	4.4	–	1.95	–
	500	98.2	1.15	0.35	–	0.3
BaNa	600	85.6	10.3	0.65	–	3.45
	700	87.85	6.25	0.35	–	5.55
	500	52.4	36.7	–	–	10.9
Ba	600	83.6	6.9	–	–	9.5
	700	70.2	7.7	–	–	22.1

*Data reduced to moisture-free basis.

bubbles, but in storage it turned pink and subsequently brown. While the 500 to 750° C variants did not undergo crystallization, the 750° C variant showed crystallization, beginning at the surface, after 24 h. These colour effects call for separate study.

SEMs of the glass are given in Fig. 2f to j. The original inhomogeneity of the glass is seen to be enhanced by heat treatment. The bubbles in the 700° C variant are clearly visible at low magnification (Fig. 2i), while high magnification reveals the phase-separated structure (Fig. 2j).

The viscosities, measured at 520° C, are given in Fig. 3 (curve 2). The chemical analyses of all leached specimens lie close together, with around 94% SiO_2 (Table II). Colours were destroyed by the leaching (indicating that they are due to the strontia–phosphate phases) but the HCl solution remained uncoloured, the 700° C variant improved its transparency. The original glass, as well as the 500° C–24 h variant, showed cracks after leaching; the others (including the 500° C–48 h) remained intact.

The 500 and 600° C variants crumbled after firing at 1100° C for 1 h; the 650 and 700° C ones became dense, chalk-like and weak. This crumbling effect is due to α–β transformation of the cristobalite formed in significant amounts.

3.3. BaNa glass

SEM pictures are given in Fig. 4a to d. While the original inhomogeneity of the glass is seen to have been enhanced by the 600 and 700° C treatments, the 750° C variant showed no visible opalescence and no inhomogeneities were observed in the micrograph (Fig. 4d). The viscosity of this glass at 425° C showed a minimum for the 600° C variant (Fig. 3) and increased again as inhomogeneity was reduced (at 750° C). Apparently the high-silica phase formed a droplet structure.

The 500° C variant leached slowly, depositing a white layer on the surface; the 600, 650 and 700° C variants leached in the bulk. In all cases the white, chalk-like leaching products were very weak and readily formed needles. The residue was extremely high in silica (98%) in the 500° C variant, but in the higher temperature variants the SiO_2 content was reduced (Table II).

As in the preceding leached glasses, in which the high-silica phase did not form the matrix, firing at 1100° C for 1 h resulted in crystallization and no sintering was observed. The main crystalline phase was cristobalite; the small peaks at 4.22, 3.87 and 3.48 Å are possibly related to α-tridymite.

3.4. Ba glass

The SEM pictures show that while the original glass and the 500 and 600° C variants were inhomogeneous, the 700 and 750° C variants were relatively homogeneous (Fig. 4e to i). The viscosity at 485° C (Fig. 3) had a maximum for the 600° C variant, hence it was the high-viscosity phase that formed the matrix. Apparently it was again high-silica, as the leaching residue contained 83.6% SiO_2 (Table II). The 500 and 700° C variants showed lower viscosity after the heat treatment. because of smaller

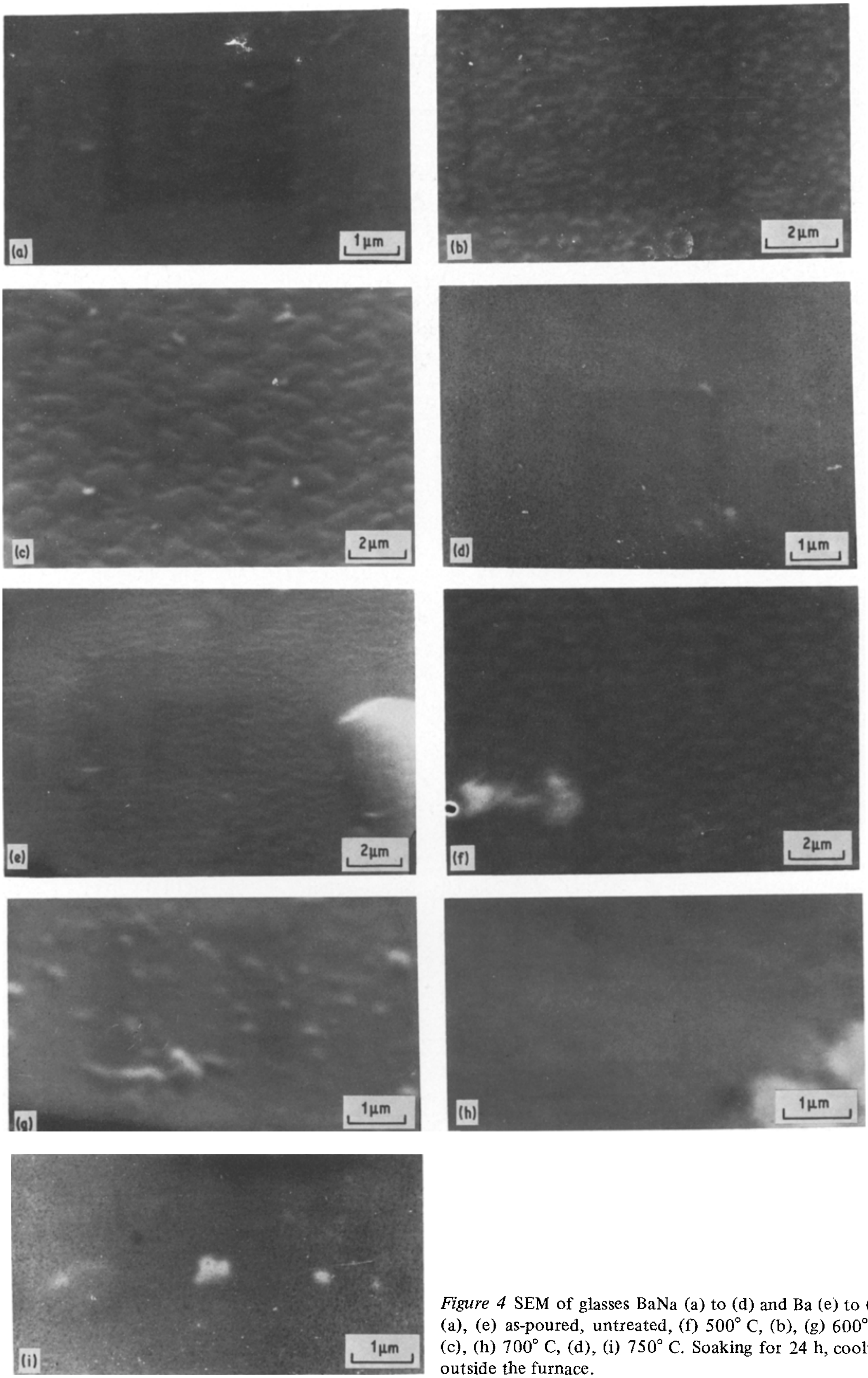

Figure 4 SEM of glasses BaNa (a) to (d) and Ba (e) to (i): (a), (e) as-poured, untreated, (f) 500° C, (b), (g) 600° C, (c), (h) 700° C, (d), (i) 750° C. Soaking for 24 h, cooling outside the furnace.

degree of liquid immiscibility*, and their silica content after leaching was correspondingly lower.

The leached layers in the 500, 600 and 650° C variants were white; in the 700° C variant the layer was transparent. All layers were very weak mechanically. Firing at 1100° C for 1 h produced sintering only in the leached 500° C variant which contained as little as 52% SiO_2. All variants crystallized in the course of firing, after which nearly identical X-ray diffraction graphs were obtained for the 500, 600, 650 and 700° C variants, showing α-cristobalite, possibly α-tridymite and other unidentified phases. The strongest X-ray diffraction peaks are at 4.22, 4.02, 3.95, 3.87, 3.15, 3.04, 2.80 Å.

4. Conclusions

(1) Metastable phase separation was observed in $3R_xO \cdot 7P_2O_5 \cdot 10SiO_2$ glasses, where $R_xO = Li_2O$, SrO and BaO or their equimolar mixtures with Na_2O.

(2) Substitution of SrO for Na_2O in glass 21 of Part 1 ($3Na_2O \cdot 7P_2O_5 \cdot 10SiO_2$) resulted in an increased SiO_2 content in the residual high-silica glassy matrix, up to 95%. However, the strong tendency of this glass to crystallization prevented sintering. Further study of the SrO glasses, and of the variations in their compositions, will be needed with a view to reducing the crystallization effect.

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Reference

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*This is the only case in which the difference in cooling between the SEM and viscosity specimens is apparent: according to the SEM, the 700° C variant is rather homogeneous, while the viscosity and leaching experiments showed separation in it.