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

Part 1 Na_2O–P_2O_5–SiO_2 system

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Glass formation and metastable liquid immiscibility in Na_2O–P_2O_5–SiO_2 glasses were studied. Phase separation in some of these glasses resulted in formation of an interconnected two-phase amorphous structure, similar to that in glasses of the Na_2O–B_2O_3–SiO_2 system used for production of Vycor glass. Leaching of the high-phosphate phase yielded a high-silica (over 90% SiO_2) skeleton, which could be sintered to a bulk glass.

1. Introduction

Very little work on liquid immiscibility in phosphate–silicate systems has been published. A hypothetical region of stable immiscibility in the Na_2O–P_2O_5–SiO_2 system was outlined by Turkdogan and Maddocks [1]. Wide regions of stable immiscibility were found in the ternary systems MgO–P_2O_5–SiO_2 [2, 3] and CaO–P_2O_5–SiO_2 [3], but these have not been studied in detail. No studies of metastable phase separation in phosphate–silicate systems are known to the authors.

Considerations of field strength lead to the assumption that phase separation should occur in the phosphate–silicate systems. Glasses containing two strong cations (i.e. cations with high field strength $Z/(r + 1.40)^2$, where 1.40 is the ionic radius of oxygen) are usually incapable of building a homogeneous structure and tend to phase separation. The Ti^{4+} ion has a field strength of 0.92, and the Si^{4+} ion = 1.22; this results in a very wide region of stable phase separation in the binary TiO_2–SiO_2 system: between 15 and 91 mol% TiO_2 [4]. The P^{5+} ion, possessing even a higher field strength (1.65), should certainly be expected to favour phase separation in glasses containing silica.

By contrast, Levin [5] criticizes this concept and believes, on the basis of the high strength of the P–O bond, that "immiscibility, if found in phosphoric oxide systems, should be the exception. . . . Immiscibility would not be expected, of course, with the other network formers". Accordingly an experimental study of the immiscibility in phosphate–silicate systems would have theoretical significance.

Another point of interest is related to the spatial distribution of liquid phases after separation in these glasses. Interconnected structures obtained through metastable immiscibility in the Na_2O–B_2O_3–SiO_2 system permit production of porous and sintered high-silica glasses (Vycor) [6–8]. If a similar structure could be induced in phosphate–silicate glasses, the chemical instability would favour leaching of a phosphate constituent, leaving a silica-rich skeleton which could be sintered to form a high-silica (i.e. Vycor-type) product. The main object of the present work was, therefore, to study glass formation and phase separation of the part of the Na_2O–P_2O_5–SiO_2 system close to the SiO_2 corner, with a view to such a product. Phosphate–silicate glasses containing Li_2O, MgO, SrO, BaO and ZnO were also studied on a smaller scale, and will be described in Part 2.

Regions of glass formation in the P_2O_5–SiO_2

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and Na_2O–P_2O_5–SiO_2 systems have been studied by several workers [9–11]. According to Syritskaya in [9], a glass-forming region in the binary system is located between 27 and 50 mol% P_2O_5; glasses were melted in silica crucibles at 1500° C. Vaivad *et al.* [10] found this region to be wider in the binary as well as in the ternary system, but it may be a result of melting in alumina crucibles. All workers noted that it is difficult to obtain glasses in the central part of the ternary system.

A survey of methods of study of liquid immiscibility is given in [4]. Electrical and rheological properties are very sensitive to changes in phase distribution. In the present work liquid immiscibility was studied with the aid of viscosity measurements in the interval of 10^{10} to 10^{14}P. Owing to the large differences in this respect between high-silica and high-phosphate glasses, the viscosity of the specimen after phase separation should be determined mostly through the phase forming the continuous matrix and only to a small extent through the droplet-forming one. In the case of an interconnected structure, the viscosity should be determined mainly through the highly viscous phase [4, 12].

2. Experimental procedure

2.1. Glass preparation

Glasses in the P_2O_5–SiO_2 and Na_2O–P_2O_5–SiO_2 systems were prepared from the following materials: Belgian sand "Sibelco" (99.8% SiO_2, 0.1% Al_2O_3), $(NH_4)_2HPO_4$ A.R., "Merck" (99%), and Na_2CO_3 A.R., "Merck" (99.5%). Batches, calculated for 50 to 300 g glass, were mixed by hand and melted in fused silica or Vycor crucibles (30 or 350 ml) in a rotating hearth electric furnace, with loading at 800 to 1000° C (two to three portions at 0.5 h intervals) and heating to 1450 to 1580° C. The melts were then poured onto a cold metal plate. Glasses melted in the larger crucibles were then ground in a porcelain mortar to 35 mesh, remelted, poured again onto a heated metal plate and annealed by slow cooling from 400° C in an electrical muffle furnace.

2.2. Thermal and chemical treatment

The specimens, after thermal treatment (up to 700° C) in a Gallenkamp muffle furnace, were leached in 3 N HCL at 50° C, rinsed with distilled water and dried at 100° C in a drying oven. This was followed by sintering at 900 to 1200° C.

2.3. Viscosity and thermal expansion measurements

As the fibre elongation method proved unsuitable for the viscosity measurements due to the poor chemical stability of the glasses, the beam-bending method was resorted to instead. The apparatus was similar to that described by Hagy [13], except that the support stand and loading rod were of fused silica. Rectangular beams, 60 × (2 to 4) × (2 to 4) mm^3 were prepared by cutting the poured and annealed glass plate with a diamond saw cooled with oil, so that contact of the glass with water was avoided. The cut specimens were then ground with a view to a better-defined geometry.

Two methods were used to study the immiscibility. The first and main method consisted in measuring the viscosity at constant temperature (near T_g of the original glass) before and after heat treatment at 500, 600 or 700° C. In the second method, the dilatometric deformation point, M_g, (which corresponds approximately to a viscosity of 10^{11} P) was determined before and after the heat treatment. A vertical dilatometer, with an LVDT as elongation indicator, was employed for these determinations, as well as for measurement of linear coefficients of thermal expansion.

2.4. Examination of structure

Crystalline phases were identified by X-ray diffraction (XRD), Cu$K\alpha$, with a Ni filter. The microstructure was examined by SEM (Cambridge, S-600 stereoscan). Freshly fractured specimens were etched in 3 N HCl for 10 sec, rinsed with de-ionized water, dried in vacuum (30 mm Hg, 80° C) for 48 h, and coated with carbon and gold. The etching technique was chosen after a series of preliminary experiments with water, HF and HCl; vacuum drying was dictated by the chemical instability of the glasses.

3. Results

3.1. Glass-forming region in the Na_2O–P_2O_5–SiO_2 system

The calculated compositions of the melted glasses are shown in Fig. 1. The true compositions may be somewhat different, due to volatilization of P_2O_5. Compositions determined by chemical analysis of glasses nos. 17, 21 and 25, together with their calculated counterparts, are shown in Table I. The system of compositions was built around glass 1, which is an analogue of that used in the Na_2O–B_2O_3–SiO_2 system for a Vycor glass:

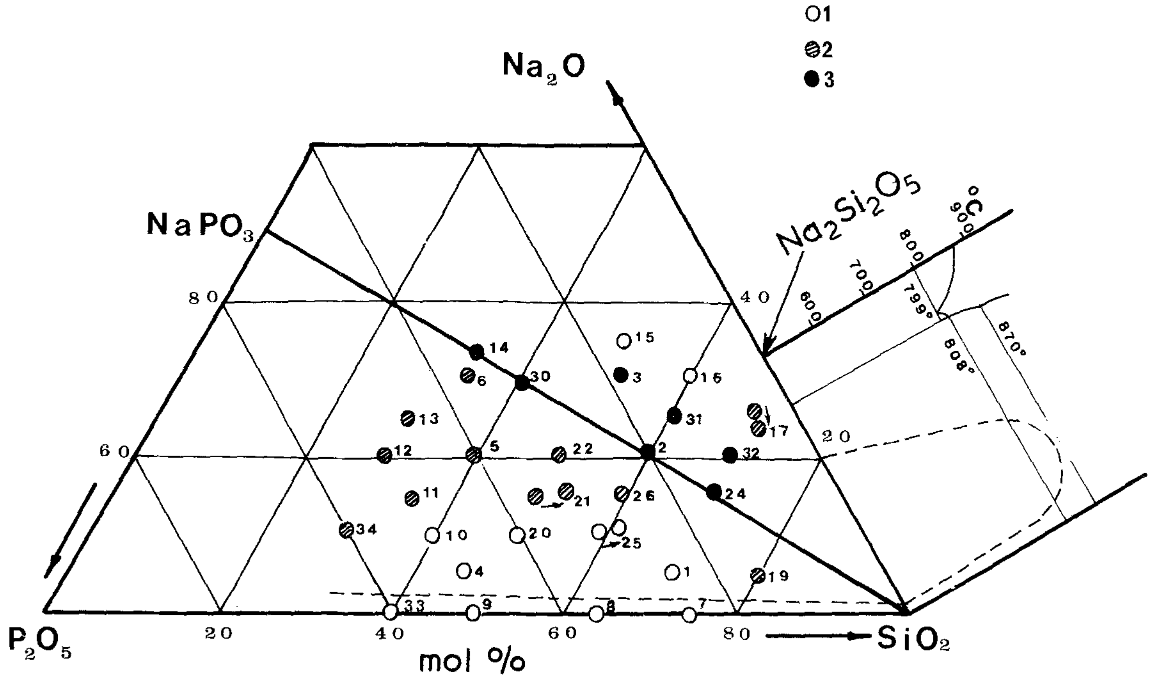

Figure 1 Glass compositions in the Na_2O–P_2O_5–SiO_2 system (calculated compositions given; shifts from calculated to analytical compositions for glasses 17, 21 and 25 indicated by arrows). (1) Glasses transparent after melting; (2) glasses translucent after melting; (3) glasses not obtained below 1580° C. Dashed lines represent boundaries of metastable liquid immiscibility. Part of equilibrium phase diagram of Na_2O–SiO_2 system according to [17], binodal curve of immiscibility in this system according to [4, 20–23].

Glass for Vycor (mol %):
$7\,Na_2O \cdot 23B_2O_3 \cdot 70\,SiO_2$

Glass 1 (mol %): $7\,Na_2O \cdot 23P_2O_5 \cdot 70\,SiO_2$.

As may be seen from Fig. 1, quite transparent glasses were obtained in the P_2O_5–SiO_2 system between 40 and 80 mol % SiO_2, and SEM examination of these glasses (as-poured) did not show a non-homogeneous structure. This result is in good agreement with data by Vaivad *et al.* [10], although Syritskaya [9] reported a narrower region of glass formation in this binary system. The corresponding region in the ternary system, observed in the present work, is also broader than that in Syritskaya's work; this may be attributed to the higher melting temperature used here (1580 compared with 1500° C in Syritskaya's work).

The visual appearance of the glasses poured onto a cold metal plate is also shown in Fig. 1. XRD examination of some of the opalescent glasses, nos. 5, 13, 17, 20, 21 and 25, failed to detect a crystalline phase, so that this opalescence could be attributed to liquid immiscibility. No glasses, or even melts, were obtained (up to 1580° C) on the SiO_2–$NaPO_3$ tie-line or close to it. Some glasses (nos. 7, 19, 15 and 16) proved too viscous for pouring.

Most of the glasses were heat-treated at 500,

TABLE I Compositions of selected glasses

	Calculated compositions (Mol/wt %)			Chemical analysis (wt %)		
	SiO_2	P_2O_5	Na_2O	SiO_2	P_2O_5	Na_2O
17	70/65.05	5/11.0	25/23.95	66.2	10.2	23.6
21	50/33.75	35/55.8	15/10.45	38.0	50.3	11.7
25	60/42.5	30/50.2	10/ 7.3	44.8	45.4	9.8
NaBSi	70/67.4	23/25.65 B_2O_3	7/ 6.95			

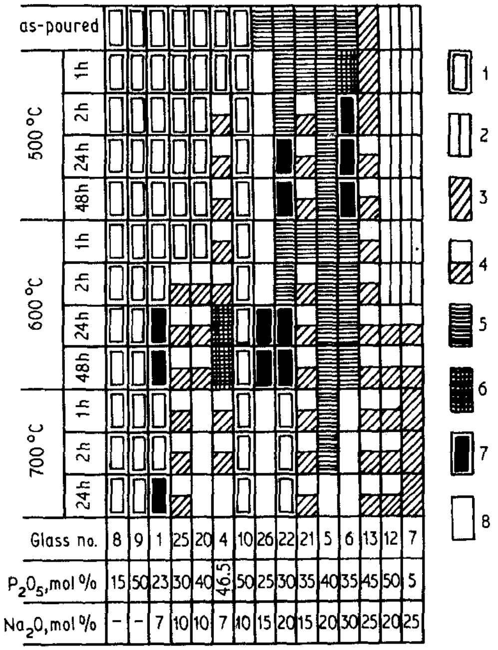

Figure 2 External appearance of some of the glasses after heat treatments: (1) transparent, (2) weak opalescence, (3) opalescence, (4) transparent on removal from furnace and opalescent upon cooling in air, (5) heavy ("milky") opalescence, (6) crystalline layer on part of surface, (7) thick crystalline surface layer, (8) not studied.

600 and 700° C for 1, 2, 24 and 48 h. The rate of heating was approximately 200° C h^{-1} and cooling was done in air outside the furnace. Results are shown in Fig. 2. Two of the binary glasses (nos. 8 and 9) showed no visible opalescence or crystallization under these conditions; by contrast, onset or enhancement of opalescence was observed in the ternary glasses exposed to these temperatures. Glasses 1 and 10 are exceptions: the first showed surface crystallization, and the second exhibited no visible changes. Some of the opalescent glasses below the SiO_2–$NaPO_3$ tie-line showed only surface crystallization, so that it may be concluded that a process other than crystallization is responsible for their opalescence – apparently liquid immiscibility. Some of the glasses, opalescent or transparent after melting, were quite transparent on removal from the heat-treatment furnace, but became rather strongly opalescent during cooling, even if thrown into cold water.

Since glass 1 (an analogue of the soda–borate–silicate glass) did not show noticeable opalescence before crystallization, three other glasses were selected for detailed study: no. 21 with opalescence after melting; no. 25 with opalescence only after heat treatments at 600 to 700° C; and no. 17, also

TABLE II Phase transformations in glass 17 under heat treatments and leaching

Low-temperature heat treatment			Crystalline phases according to XRD [15–18]		
Temperature (° C)	Time (h)	External appearance	After low temp. heat treatment	After leaching for 24 h	After sintering at 900–1100° C
500	24	Slight opalescence	Weak peaks at 4.25 Å (α–tridymite?) and 2.61 Å	A weak peak at 4.25 Å only	n.d.*
600	1	Slight opalescence		n.d.	n.d.
600	24	"Milky" opalescence	α–cristobalite α–tridymite?(medium peaks at 4.25 Å and 3.79 Å†), α_{III}–$Na_2O{\cdot}2SiO_2$, unidentified peaks at 3.19 Å and 2.61 Å	mainly α–cristobalite α–tridymite? (medium peaks at 4.25 Å and 3.79 Å†), a peak at 3.19 Å	
700	24	"Milky" opalescence	α–cristobalite, α–tridymite? (the same 2 peaks), peakes at 3.19 Å and 2.61 Å	n.d.	As 600° C, 24 h
680 + + 530 [14]‡	25 75	"Milky" opalescence			

*Not determined.

†The 3.79 Å peak belongs to both α–trigymite [15] and α_{III}–$Na_2O{\cdot}2SiO_2$ [17], reduced after leaching.

‡Rate of heating about 200° C h^{-1}, slow cooling in the furnace.

opalescent after melting but located on the other side of the SiO_2–$NaPO_3$ tie-line.

3.2. Phase transformations, leaching and sintering in glasses 17, 21 and 25

The glasses were melted twice as described above. A $7Na_2O \cdot 23B_2O_3 \cdot 70SiO_2$ ("NaBSi") glass was also melted. The compositons of these glasses are given in Table I.

3.2.1. Glass 17

Small pieces and rods for viscosity measurements were heat-treated at 500, 600 or 700° C for 24 h with slow cooling. XRD examination showed crystallization at these temperatures as described in Table II. The SEM pictures are given in Fig. 3. A microheterogeneous structure is already seen in the untreated glass, and is enhanced after the treatments at 500 and 700° C; well developed crystals, less than 1 μm in size, are seen in the picture for the latter variant. By contrast, the crystallization pattern of the 600° C variant (picture taken at low magnification because of the large sizes of the crystal branches) is of a rather different nature – an unexpected observation, seeing that the XRD diagrams for the 600 and 700° C specimens showed approximately the same amounts of crystal phases. Dilatometric curves (Fig. 4) show good agreement with the XRD data indicating the cristobolite α–β transformation for the 600 and 700° C variants.

The dependences of viscosity at 435° C and of M_g on the temperature of heat treatment are shown in Fig. 5. While the 500 and 600° C variants showed a sharp increase in viscosity (too high to be measured), the increase in the 700° C variant

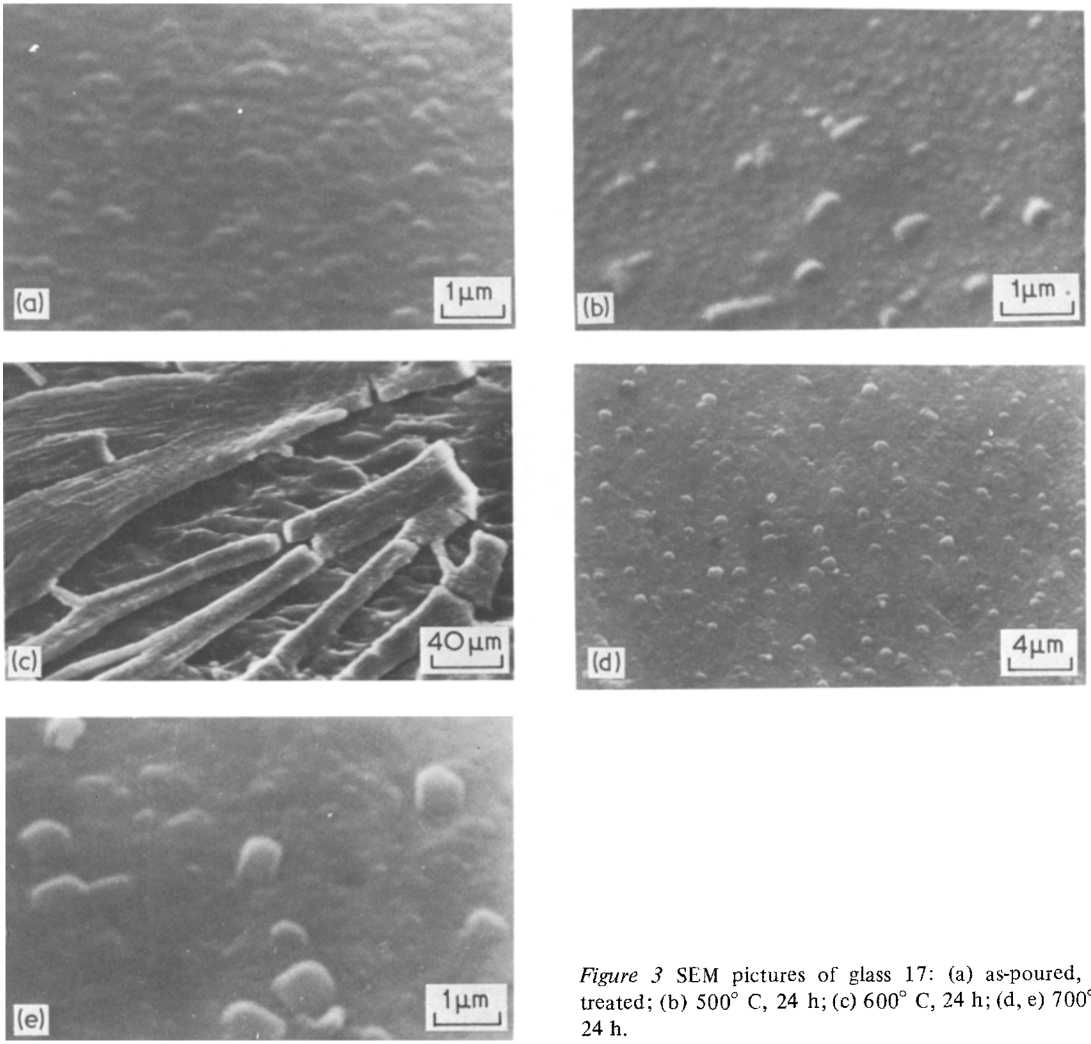

Figure 3 SEM pictures of glass 17: (a) as-poured, untreated; (b) 500° C, 24 h; (c) 600° C, 24 h; (d, e) 700° C, 24 h.

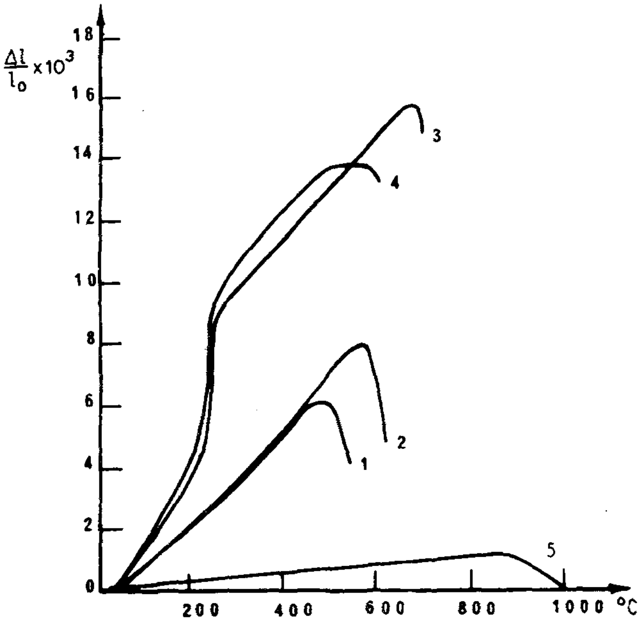

Figure 4 Curves of linear thermal expansion: curves 1–4, glass 17: (1) untreated; (2) 500° C, 24 h; (3) 600° C, 24 h; (4) 700° C, 24 h; curve 5, glass 21, 600° C, 24 h, leaching, sintering at 1100° C for 30 min.

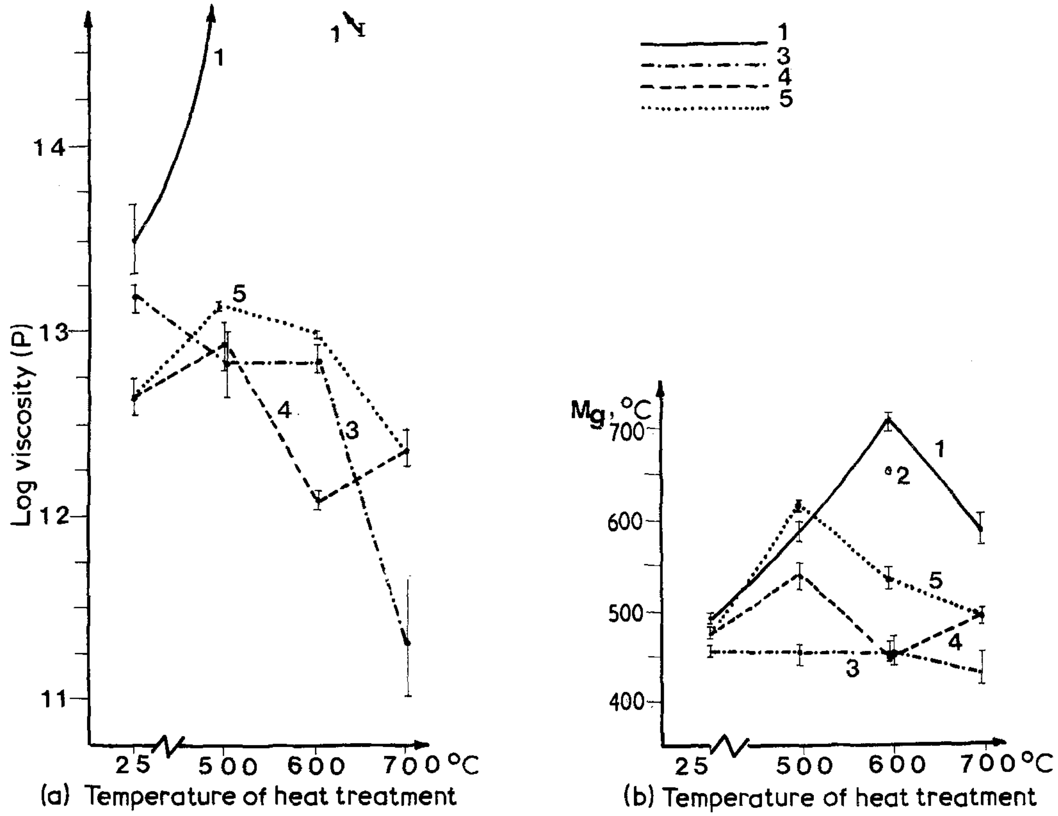

Figure 5 Dependence of viscosity η at constant temperatures (a) and of dilatometric point of deformation M_g (b) on temperature of heat treatment: (1) glass 17, treatments for 24 h, viscosities at 435° C; (2) glass 17, treatment for 1 h; (3) glass 21, treatments for 24 h, viscosities at 400° C; (4, 5) glass 25, treatments for 24 h (curve 4) and for 48 h (curve 5), viscosities at 400° C.

was less, although the degree of crystallization according to XRD and SEM was higher in this variant than in its 500° C counterpart (see Fig. 3).

Leaching of an untreated specimen in 3 N HCl at 50° C showed relatively uniform dissolution, with development of a transparent cracked layer on the surface. By contrast, the heat-treated specimens acquired on leaching a white layer of reaction products at a rate of about 0.5 to 1 mm in 24 h, had significant changes in phase composition (Table II). When the NaBSi and no. 17 glasses were subjected to additional heat treatment, similar to that used for production of porous glass from the former [14], (680 + 530° C, Table II), the NaBSi specimen remained glassy while no. 17 crystallized. As for the layer of reaction products after 24 h leaching, it was firmly anchored and had a glassy appearance in the first glass, but detachable and with a chalky appearance in the second. The reacted layers on the thermally and chemically treated specimens of glass 17 did not show any noticeable sintering at 900, 1000 and 1100° C (slow heating; the same specimens were soaked for 2 h at each of these temperatures; a separate treatment consisted of heating up to 1100° C and soaking for 0.5 h). This is attributable to a high degree of crystallization of no. 17. The leached specimens of this glass showed more than 90% SiO_2, mainly as cristobalite.

The leached NaBSi glass was successfully sintered by heating to 960° C, but its final composition differed from that of Vycor glass: it contained only 88.9% SiO2, as against 96% in Vycor. The compositions of the leached and sintered products are given in Table III.

TABLE III Composition (wt %) of leached and sintered products made of glasses 17, 21 and 25 (according to chemical analysis). Leaching for 72 h between 1st and 2nd heat treatments

Glass no.	Heat treatments*	SiO_2	P_2O_5	Na_2O
17	600° C, 24 h, 900 – 1100° C	97.2	1.1	1.0
	According to [14] and 1000° C, 2h	94.5	1.85	2.0
21	600° C, 24 h, 900 – 1100° C	91.0	8.3	0.5
	700° C, 24 h, 900 – 1100° C	91.2	8.0	0.7
	According to [14] and 1000° C, 2 h	90.0	n.d.†	1.4
25	700° C, 24 h, 900 – 1100° C	93.3	5.3	0.5
Na–B–Si	According to [14] and 960° C	88.9	11.6 B_2O_3	0.6

*For details, see text.
†Not determined.

3.2.2. *Glass 21*

No crystalline phases were observed by XRD in this glass after melting and cooling, or after heat treatments at 500, 600 and 700° C for 24 h. SEM pictures are given in Fig. 6. While the untreated glass shows a microheterogeneous structure, an interconnected one was observed in the 500° C variant. Both coarsening and the degree of separation increase with temperature, and at 700° C one of the phases forms droplets; apparently this is a high-silica phase, as the viscosity of this glass (at 400° C) is somewhat reduced in the 500 and 600° C variants and drastically so in the 700° C variant (Fig. 5a). M_g shows an analogous, although less pronounced, pattern (Fig. 5b). Specimens of the untreated glass were completely disintegrated by 3 N HCl (24 h at 50° C). On the other hand, the 500 and 600° C variants maintained their form after leaching, with a white, dense and uniform appearance. The leached specimens, previously treated at 700° C, crumbled readily, although they were stronger than the leached untreated glass. Similar results were observed after the more complex heat treatment at 680 + 530° C, as described above. The specimens lost 40 to 45% of their weight during the first 24 h of leaching.

Chemical analyses show about the same high-silica content for all leached (72 h) products made of no. 21, irrespective of the temperature of heat treatment (Table III).

Sintering schedules were the same as those for no. 17. Subsequent soaking at 900, 1000 and 1100° C (for 2 h) resulted in sintering of the 500 and 600° C variants to form transparent bulk glass with a surface layer of α-cristobalite. The same result was obtained on soaking for 0.5 h at 1100° C, and the cristobalite content of the surface film (by XRD) was low. The 700 and 680 + 530° C variants sintered into a non-uniform white mass with a significant cristobalite content. SEM pictures of the 600 and 700° C variants after sintering (Fig. 6e, f) show marked uniformity at

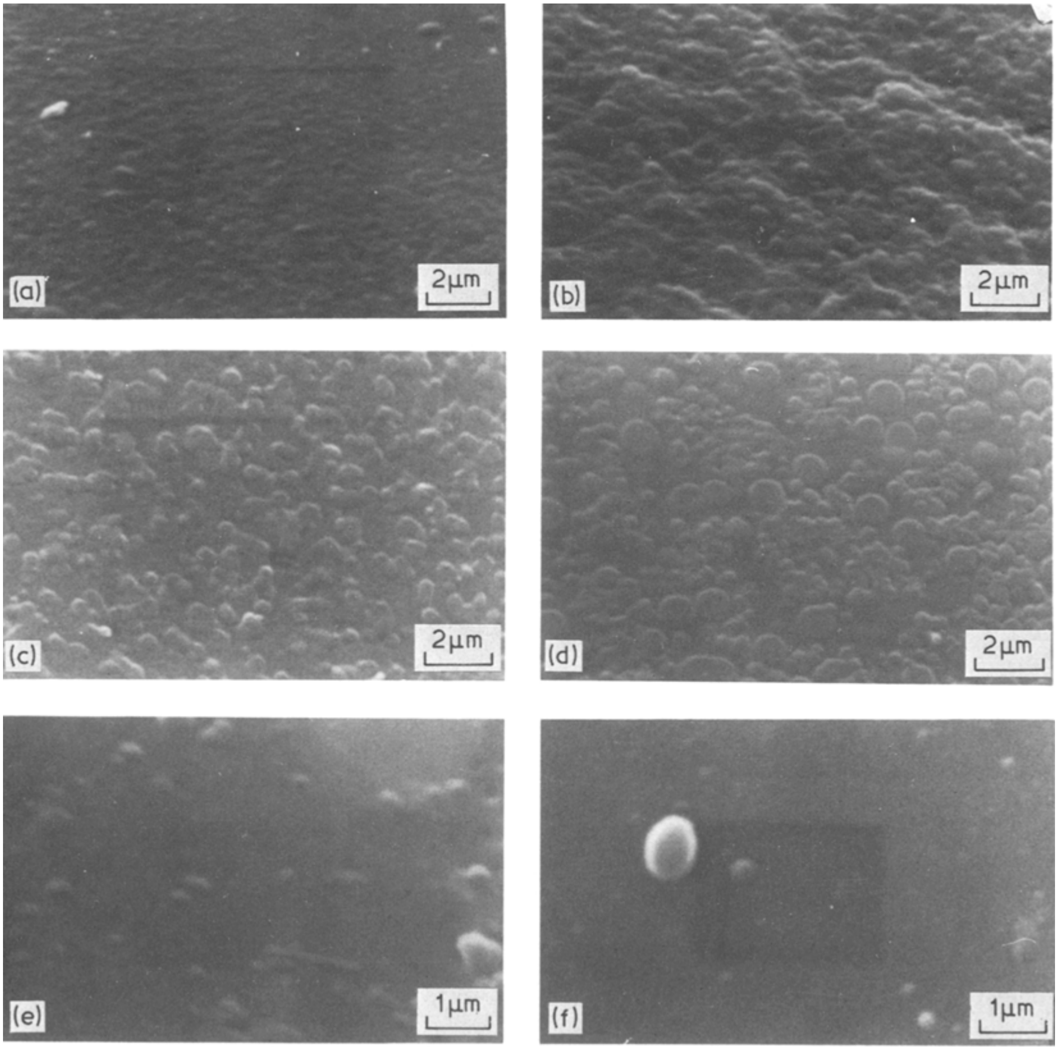

Figure 6 SEMs of glass 21: (a) as-poured, untreated; (b) 500° C, 24 h; (c) 600° C, 24 h; (d) 700° C, 24 h; (e) 600° C, 24 h, leaching and sintering at 1100° C for 30 min; (f) 700° C, 24 h, leaching and sintering at 1100° C for 30 min.

the level of resolution of several hundredths of a micron.

The thermal expansion curve for the sintered 600° C specimen is given in Fig. 4. There is no break in the curve, indicating the presence of cristobalite (compare the curves for no. 17 in the same figure) and the linear coefficient of thermal expansion is as low as $\alpha_{25-400^\circ C} = 16 \times 10^{-7}\,{}^\circ C^{-1}$; the corresponding calculated value for the chemical composition given in Table III, according to Appen [19], is $\alpha^{\text{calc.}}_{20-400^\circ C} = 15 \times 10^{-7}\,{}^\circ C^{-1}$. (Values of $\alpha \times 10^{7}\,{}^\circ C^{-1}$ at 20 to 400° C for the untreated no. 21 are: experimental 117, calculated 127). Bulk density of this sintered specimen is 2.11 g cm^{-1}, while the calculated density for this composition (based on data by Winkelman and Schott, in the absence of data for P_2O_5 in Appen's work) is 2.3 g cm^{-3}; if this value is taken as the theoretical density, the degree of sintering is about 92%. It is thus seen that high-silica glass is obtainable from no. 21, although further work is needed to improve its properties.

3.2.3. Glass 25

No crystalline phases were detected by XRD in the untreated glass and after treatments at 500, 600 and 700° C for 48 h. SEM pictures are shown in Fig. 7. The original as-melted glass has a droplet structure; after the 500° C treatment a more chemically resistance phase apparently forms the

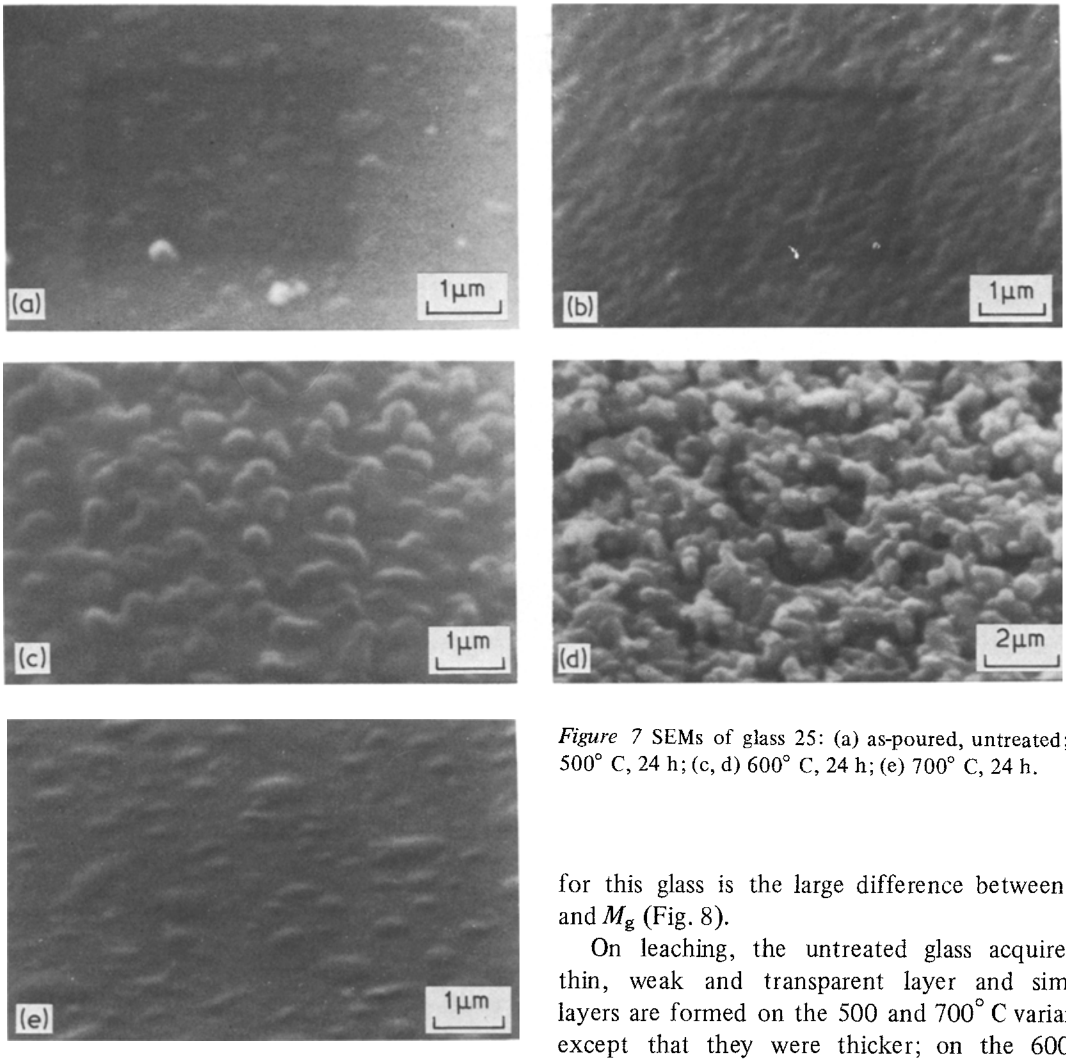

Figure 7 SEMs of glass 25: (a) as-poured, untreated; (b) 500° C, 24 h; (c, d) 600° C, 24 h; (e) 700° C, 24 h.

matrix, while the structure following the 600° C treatment seems to be interconnected, and that after 700° C – again of the droplet type. It is worth noting that this glass treated at 600 or 700° C is transparent when taken out of the furnace, but becomes opalescent upon cooling (see Fig. 2), so that the SEM pictures are not really representative of the indicated temperatures, since considerable structural changes take place upon cooling.

Both viscosity and M_g increase considerably after treatment at 500° C for 24 h and 48 h (Fig. 5), although the glass is quite transparent even after 48 h. The viscosity after soaking at 600° C for 24 h is lower, and after 48 h higher, than that of the untreated glass. In the 700° C variant the viscosity remains close to that of untreated glass. An interesting feature of the 500° C treatment for this glass is the large difference between T_g and M_g (Fig. 8).

On leaching, the untreated glass acquires a thin, weak and transparent layer and similar layers are formed on the 500 and 700° C variants, except that they were thicker; on the 600° C variant the layer was rather thick, weak and white. Weight loss in the heat-treated specimens during the first 24 h leaching was about 50%. The layer on the 700° C variant readily disintegrated into powder (unlike the other two); its silica content on leaching was about 93% (Table III). Although amorphous, all these specimens did not lead themselves to sintering at 900 to 1100° C, apparently due to the high rate of their crystallization into cristobalite.

4. Discussion

4.1. Liquid immiscibility

The findings of this work do not confirm Levin's opinion [5] that liquid immiscibility can occur in phosphate systems as an exception, although this opinion refers to binary systems and immiscibility has actually not been observed in the binary P_2O_5–SiO_2 system. The approximate boundary

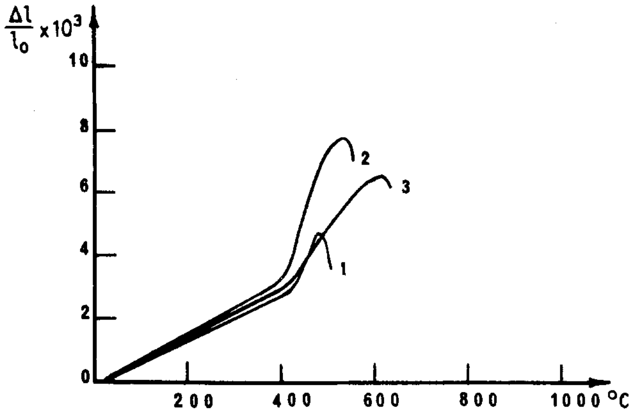

Figure 8 Curves of linear thermal expansion of glass 25: (1) untreated; (2) 500° C, 24 h; (3) 500° C, 48 h.

of a metastable immiscibility region in the ternary system, shown in Fig. 1 by a dashed line and based on results of the heat treatments (see Fig. 2), is readily extended to the high-silica boundary of the immiscibility zone in the Na_2O–SiO_2 system [4, 20–23].

Let us compare this situation with that in the B_2O_3–SiO_2 and Na_2O–B_2O_3–SiO_2 systems. In the binary system, metastable immiscibility is detected only with difficulty: Charles and Wagstaff [24] treated such glasses for this purpose for 2 to 4 weeks in a gradient furnace, but Mazurin and Streltsina [4] failed to reproduce their result. By contrast, in the ternary system, a wide field of metastable immiscibility is a well-established fact [4]. Apparently, introduction of the Na^+ ions into the binary system, resulting in formation of $[BO_4]$ tetrahedra, greatly facilitates and enhances phase separation. In this context the following explanation is offered by Zhdanov and Koromaldi [4, 25]. Boron–oxygen triangles in an alkali-free borosilicate glass form long thin chains within the silicon–oxygen matrix without noticeable increase in the free energy of the system; addition of sodium oxide causes formation of boron–oxygen tetrahedra which are readily joined with the triangles. This results in breaks in the chains and facilitates phase separation.

Partial analogy in behaviour may be suggested for the P_2O_5–SiO_2 and NaO–P_2O_5–SiO_2 systems. Although the phosphorus ion can only be four-co-ordinated, there is some similarity between the $[BO_3]$ triangle and $[PO_4]$ tetrahedron since one of the four P–O bonds in the latter is double so that only three free bonds are available for junction with other tetrahedra [26]. Addition of Na^+ ions to phosphate–silicate glasses must result in breaking of the long phosphate chains, with the resulting facilitation of immiscibility. Immiscibility is not ruled out in the binary P_2O_5–SiO_2 system, but its detection necessitates careful study like that of Charles and Wagstaff [24] for the B_2O_3–SiO_2 system. Rindone and Ryder [27] detected immiscibility in the Na_2O–P_2O_5 system which was catalysed by small admixtures of platinum. Vesifeld and Rabinovich [28] found that opalescene in soda-lime–silica glasses with P_2O_5 additions resulted from liquid–liquid phase separation, with subsequent crystallization of phosphates from the second glassy phase.

Several glasses obtained after melting as transparent (nos. 4, 20, 25) or opalescent (nos. 12, 13, 21) showed absence of visible opalescence immediately after heat treatment at 500 to 700° C (mostly at 700° C) but developed it on rapid cooling in air or in cold water. It may be proposed that their immiscibility mechanism is of spinodal nature, with a steep approach to equilibrium [4]. The so-called "transparent" glasses in Fig. 1 may, in fact, be non-homogeneous, as is seen in the SEM picture for the untreated no. 25 (Fig. 7a). It seems that temperatures of 600 and 700° C are above-critical for these glasses, and spinodal decomposition takes place at lower temperatures. Its character, however, differs for the melts (at 1500 to 1550° C) and for the specimens exposed to the low temperatures. Glasses quenched from 1500° C develop smaller amounts of a second phase and can have a transparent appearance (nos. 4, 20 and 25), but after exposure at 600 to 700° C (for glass 20, at 600° C only) they develop larger amounts of this phase on cooling and are opalescent. The transparent glasses 20 and 25 remain transparent when heated only to 500° C, apparently for kinetic reasons, but the microstructure and viscosity of the 500° C variant of no. 25 (Fig. 7b) differ from those of the untreated glass; the 600° C variants (24 h) of both glasses maintain their opalescence after additional treatment at 500° C for 24 to 48 h.

Viscosity data for glass 21 (Fig. 5) show that the viscosity of the 500 and 600° C variants is determined by the high-silica phase, as expected for an interconnected structure or a high-silica matrix; the finding that one phase can be leached out and the residue sintered to a solid glass indicates that the structure is, in fact, interconnected. By contrast, the leached 700° C variant exhibited a high-silica phase of spherical particles, and was incapable of sintering prior to significant crystallization. It appears that in this glass the separated phases had different spatial distributions according to the treatment temperature, but the composition of the high-silica phase was practically unaffected by it (Table III).

The failure to obtain Vycor-type glass from no. 25 is rather difficult to account for. The SEM pictures (Fig. 7) as well as the viscosity data (Fig. 5) show that a variety of spatial distributions of the phases is obtainable here as well, and that leaching leaves a high-silica residue (Table II). Apparently the surface structure of the latter favours crystallization which inhibits sintering. The dependence of crystallization on morphology was also clearly seen for no. 21, where widely differing amounts of cristobalite were obtained on sintering of the 600 and 700° C leached specimens, in spite of their very close compositions (Table III).

It should be noted that the optimal region for Vycor-type glass in phosphate–silicate systems has not yet been located, and the fact that the leached and sintered specimens of no. 21 tend to crack indicates that this composition is not ideal for the purpose. This is apparently the same phenomenon as in the Na_2O–B_2O_3–SiO_2 system, where the glasses in the zone of maximum phase separation swell on leaching and subsequently burst [29], and the good parent compositions for Vycor glass fall outside that zone.

4.2. Phase transformations in glass 17

This glass, located in a part of the system remote from nos. 21 and 25, yielded the highest silica content in the leached product, which was crystalline. Two alternative mechanisms of phase transformation may be considered for this glass: (1) crystallization without prior phase separation, (2) crystallization preceded by liquid–liquid phase separation.

The first mechanism, if valid, should account for the increase in viscosity. However, if the weak peak at 4.25 Å in the 500° C variant is actually related to tridymite, the residual glassy matrix must be enriched in Na_2O, and the large increase in viscosity of this variant compared with the untreated glass, or with the well-crystallized 700° C variant, remains unexplained. The extreme dissimilarity in crystal morphology between the 600 and 700° C variants (Fig. 3) is also difficult to understand, seeing that their XRD graphs show rather small qualitative and quantitative differences.

The second mechanism is supported by the non-uniform structure of the untreated glass (Fig. 3a). Apparently the high-silica matrix in conjunction with the high degree of crystallization of both the droplets and matrix in the 500 and 600° C variants, makes for a drastic increase in viscosity. At 700° C the phase distribution seems to be different (Fig. 3d and e). If a high-silica phase is precipitated in droplet form and then crystallizes, the resulting viscosity may be higher than that of the untreated glass, but lower than those of the 500 and 600° C variants because of interaction of a low-silicate glass, with relatively low viscosity, and a large amount of crystalline inclusions. This mechanism may also account for the absence, in this variant, of crystallization of sodium disilicate, which probably precipitates more readily from droplets (600° C) than from the matrix (700° C).

The above considerations point in favour of the mechanism of liquid immiscibility in no. 17, whose location near the zone of metastable immiscibility in the binary $Na_2O \cdot 2SiO_2$–SiO_2 system in seen in Fig. 1.

5. Conclusions

(1) Metastable liquid immiscibility was observed in glasses over a large part of the Na_2O–P_2O_5–SiO_2 system.

(2) Separation of these glasses into high-silica and high-phosphate glassy phases permits production of a high-silica glass, similar to that in the Na_2O–B_2O_3–SiO_2 system, through leaching with HCl. A low thermal expansion ($\alpha_{20-400°C} = 16 \times 10^{-7}\,°C^{-1}$) glass containing more than 90% SiO_2 was obtained from one of the glasses in the Na_2O–P_2O_5–SiO_2 system.

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