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Alkali resistant non-silicate porous glass-like material

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Substitution of the end-member oxides in the ternary sodium borosilicate system has been studied. Replacing SiO_2 with a combination of alkali resistant oxides, Th, Zr, Ce with or without Y_2O_3, was found to produce glasses which, after heat treatment, decomposed into two immiscible microphases, one of which was water soluble. The structure of the leached material or material sintered after leaching (ThO_2, ZrO_2, CeO_2, Y_2O_3 or ThO_2, ZrO_2, CeO_2) was predominantly glass-like. Some Na_2O and B_2O_3 may be expected to remain unleached in the pores as has been observed in silica-based material. However, no evidence of this in crystalline form was found during X-ray diffraction analysis. The specific surface areas of the materials so formed ranged between 58 and 315 $m^2\ g^{-1}$, having calculated pore radii of between 0.8 and 13.6 nm. Alkali resistance of up to 1.96×10^{-2} mg dm^{-2} and water resistance between 5 and 16.18 mg $Na_2O\ g^{-1}$ were measured.

1. Introduction

Substitution of the end-member of oxides in the ternary borosilicate systems resulting in phase separable glasses and a porous silica structure was reviewed by Res *et al.* [1]. In this system the replacement of SiO_2 by combinations of selected oxides (Ce, Nb, La, Ta, Ti) including aluminium as a contaminant from Al_2O_3 crucible corrosion led, after heat treatment (phase separation) and leaching, to porous ceramics [1–4].

The present work concentrates on sodium borate glasses containing as a third ingredient a combination of alkali resistant oxides. The oxides selected were ThO_2, ZrO_2, CeO_2 and Y_2O_3, which were combined as mixtures in the melt with Na_2O and B_2O_3.

These melts were expected to yield porous glass-like materials with some alkali and water resistance after undergoing suitable heat treatment and leaching. The selected oxides have already been applied as components in research and industrial glasses.

2. Glass preparation

The glasses were prepared from chemically pure reagents, H_3BO_3*, Na_2CO_3*, CeO_2*, Y_2O_3†, and standard quality ZrO_2‡ and ThO_2§. Batches of 50 g glass samples were melted in platinum/rhodium or Al_2O_3 crucibles in air at temperatures between 1400° C and 1420° C (four to five hours). The glasses were cast in iron moulds, annealed and heat treated. Two heat treatment programmes were followed depending on the Y_2O_3 content of melt; those samples containing Y_2O_3 received two hours soaking at 600° C followed by two hours at 650° C, the other samples received a further two hours soaking at 700° C.

After the respective heat treatments the samples were leached in boiling distilled water; those resulting from melts in Al_2O_3 crucibles

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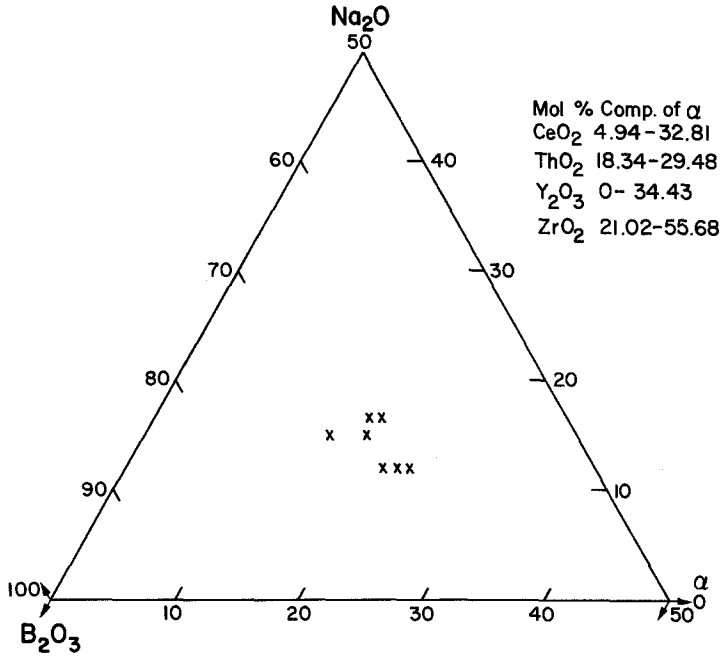

Figure 1 ThO_2, ZrO_2, CeO_2, Y_2O_3–Na_2O–B_2O_3 starting glass composition (mol% see Fig. 1 and Table I) as recalculated from the original batch.

receiving 72 h leaching treatment whilst those from melts in platinum/rhodium crucibles were treated for 24 h.

Portions of the samples were sintered at 1520° C for 30 min. Surface area, void volume, chemical resistance, X-ray and SEM–EDX analysis were then carried out on the samples.

3. Measurements

Surface areas were determined by a nitrogen adsorption method, void volume by critical moisture content point (the state when surface moisture has evaporated and evaporation rate changes due to pore moisture evaporation being influenced by capillary forces) determination and the average pore radii were calculated using a method described by Res *et al.* [1].

A SEM–EDX technique was used to establish the degree of phase separation as well as the morphology of the porous materials. The EDX analyses furthermore gave a qualitative analysis of the chemical composition of the materials. The character of the glassy or crystalline structure was determined by a Rigaku X-ray diffraction system.

Chemical resistance of the leached samples was determined according to DIN 52 322 [5] for alkali resistance and DIN 12111 [6] for water resistance. The measured values were calculated for the whole surface area in the case of the alkali resistance, and the results for the water resistance are given according to DIN 12111 as alkali loss in mg Na_2O per gram of sample.

4. Results

From the number of materials investigated a few, representative of a cross-section of the results obtained, are presented in Fig. 1 and Tables I and II. The samples contain 15.32 to 22.03 mol% of the oxides CeO_2, ThO_2, Y_2O_3 and ZrO_2 shown as α in Fig. 1, while the composition of glasses in

TABLE I Starting compositions calculated from batch with appearance of glasses as annealed

Sample no.	Crucible	Oxide (mol%)						Reflected light appearance
		ThO_2	ZrO_2	CeO_2	B_2O_3	Na_2O	Y_2O_3	
169	Pt/Rh	5.30	3.78	2.71	66.97	15.05	6.13	Brownish amber
173	Pt/Rh	4.65	9.97	1.59	68.00	11.76	4.03	Brownish amber
280	Al	3.91	8.39	5.51	66.21	15.98	–	Brownish amber
281	Pt/Rh	3.91	8.39	5.51	66.21	15.98	–	Brownish amber
282	Al	3.23	8.29	5.94	66.05	16.49	–	Brownish amber
283	Pt/Rh	3.23	8.29	5.94	66.05	16.49	–	Brownish

TABLE II Results of tests made on glasses and appearance of heat treated and leached samples

Qualitative EDX analyses	Sample no.	Crucible type	Void volume ($ml\,g^{-1}$)	B.E.T. surface area ($m^2\,g^{-1}$)	Mean pore radius (nm)	Heat treatment (°C:h)	Alkali resistance* ($mg\,dm^{-2}$)	H_2O resistance†		Appearance of glasses as-leached
								Na_2O ($mg\,g^{-1}$)	($ml\,g^{-1}$)	
Y Zr Ce Th	169	Pt/Rh	0.064	161	0.8	600:2 650:2	1.4×10^{-2}	16.18	52.2	Greyish opaque brittle
Y Zr Ce Th	173	Pt/Rh	0.104	115.3	1.8	600:2 650:2	7.3×10^{-2}	–	–	Cream opaque brittle
Al Zr Ce Th	280	Al	0.1306	181.8	1.4	600:2 650:2 700:2	3.2×10^{-2}	13.2	42.7	Cream opaque brittle
Zr Ce Th	281	Pt/Rh	0.395	58	13.6	600:2 650:2 700:2	9.77×10^{-2}	5.0	16.0	Cream opaque brittle
Al Zr Ce Th	282	Al	0.155	314.7	1.0	600:2 650:2 700:2	1.96×10^{-2}	–	–	Cream opaque brittle
Zr Ce Th	283	Pt/Rh	0.274	186.0	2.9	600:2 650:2 700:2	sample	crumbled	–	Cream opaque brittle

*DIN 52322 [5] (alkali resistance calculated on whole specific surface area).
†DIN 12111 [6].

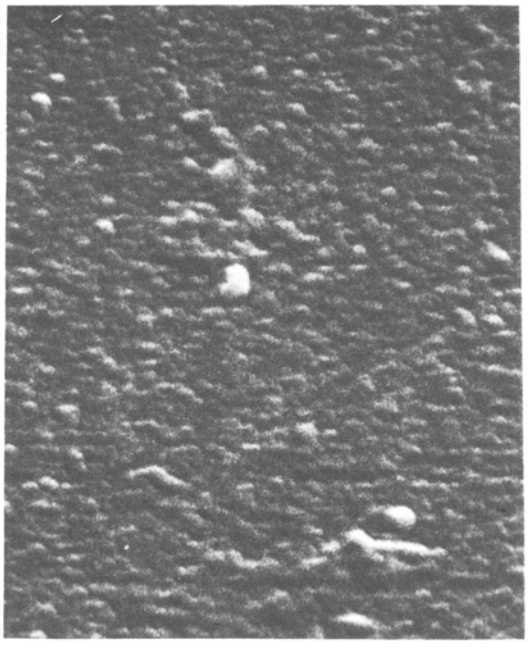

Figure 2 Early stage of spinodal decomposition (× 16 200).

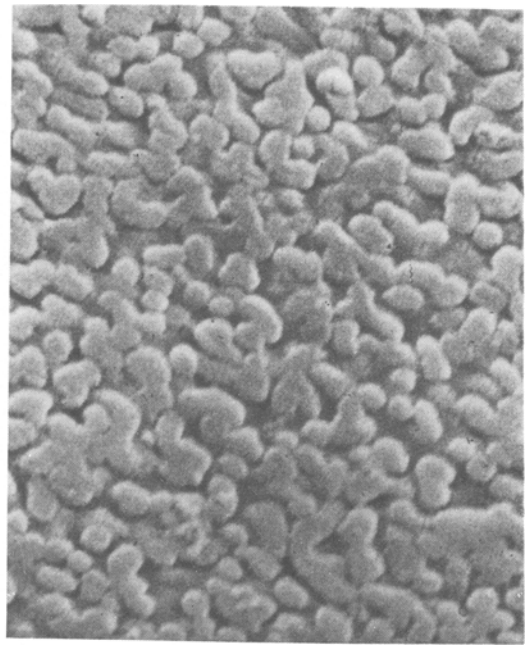

Figure 3 Progressed stage of spinodal decomposition (× 14 500).

mol% is given in Table I. The $Na_2O:B_2O_3$ ratio is in the region of the position of the boron anomaly line for the sodium borosilicate system. By analogy with this system, this is the region in which porous glasses would be expected.

The appearance of the samples before heat treatment, in general, was brownish amber in reflected light changing to creamish white and opaque after heat treatment. The leachability in boiling distilled water of phase separable glass can be explained by the microheterogeneity of the samples and by the findings of Turner and Winks [7], who reported a high leachability of sodium lime borosilicate glass if SiO_2 was replaced by B_2O_3 above 30%.

Secondary electron micrographs of the quenched glasses were compared with the findings of Vogel [8], which were of a sodium borosilicate type. The same characteristics, namely clear glasses with droplet-like phases, were observed (Fig. 2). After one stage of heat treatment at 650°C or 700°C for two hours the samples which showed unevenly distributed surface crystallization were abandoned.

A multi-stage heat treatment was experimentally established. Compared with the findings of Gauthier and Gombert [9], heat treatment at 600°C for two hours results in an early stage of spinodal decomposition while the combined following second step of 650°C for two hours or a further step of treatment at 700°C for two hours resulted in a coarsening process increasing the size of the particles (Fig. 3) or leading to nucleation (Fig. 4).

Typical structures of melts from Al_2O_3 and platinum/rhodium crucibles are illustrated in Figs. 5 and 6 respectively. The secondary electron image (Fig. 5) from the SEM presents the appearance of a freshly cracked surface of leached sample No. 280 (Al_2O_3 crucible melt), whilst Fig. 6 shows the freshly cracked surface of leached sample No. 169 (platinum/rhodium crucible melt).

Fig. 7 illustrates the habit modification for leached sample No. 169 resulting from sintering for 30 min at 1520°C. A glass-like state results containing waves of cracks common in glass which are comparable to Jebsen-Marwedel's [10] radiant cracks.

Typical void volume, surface areas, average pore radii, heat treatment and chemical resistance figures are given in Table II. EDX analysis showed the presence of aluminium in samples Nos. 280 and 282 which were melted in an Al_2O_3 crucible whereas samples Nos. 169, 173, 281 and 283 prepared in platinum/rhodium crucibles showed no aluminium to be present in the resulting materials.

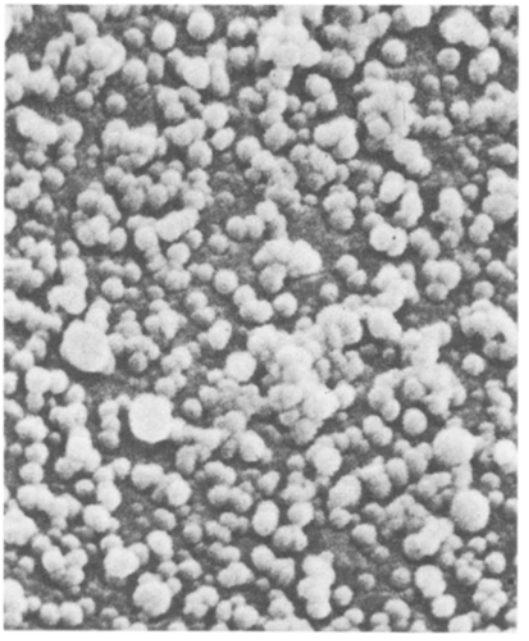

Figure 4 Progressed stage of spinodal decomposition – coarsening and/or nucleation (× 14 500).

Figure 6 A freshly cracked surface of leached sample 169 (platinum/rhodium crucible melt) (× 580).

All the leached samples were creamy opaque and brittle.

X-ray powder diffraction analyses were carried out using a Rigaku diffractometer system. Samples 169 and 173 were examined in the leached and sintered states and samples 280, 281, 282 and 283 were examined only in the leached state to give representative results. Samples 169 and 173 were glassy in both conditions, whereas the remaining samples showed crystalline features. Broad peaks

Figure 5 A freshly cracked surface of leached sample 280 (Al_2O_3 crucible melt) (× 580).

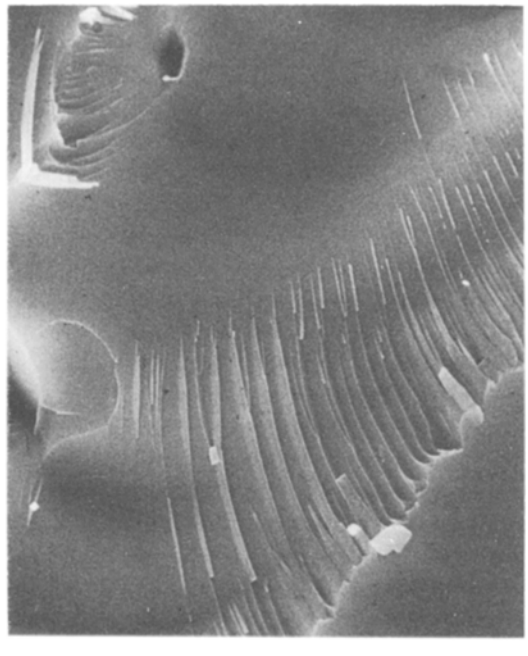

Figure 7 Leached sample 169 sintered for 30 min at 1520° C (× 2320).

were seen for Nos. 281 and 283 indexing to a cubic unit cell of 0.524 nm with the same peaks being considerably sharper in samples 280 and 282. This could mean that the alumina crucible induces better crystallization, perhaps by providing more nucleation sites than the platinum/rhodium one. Similar crystallization behaviour has been noted before by Res *et al.* [11] and is likely to indicate the presence of a solid solution of ceria and/or other oxides in zirconia. Such solid solutions have been characterized by Duwez and Odell [12] with similar unit cell dimensions. No evidence of crystalline sodium borate phases are detected.

5. Discussion

A series of sodium borate cerium, thorium, yttrium, zirconium oxide glasses showed similar phase separation, leachability and porosity to those achieved in the well-known ternary sodium borosilicate system. The identification of a solid solution in the leached samples is tentative. Duwez and Odell [12] studied the crystalline phases of the ceria–zirconia system and showed that complete miscibility was obtained with a cubic structure with a ceria content of more than 20%. Although their studies were on material fired at 2000° C their tentative phase diagram indicates the solid solutions to be formed at lower temperatures also. It is thus possible that solid solutions of the relevant oxides in zirconia will exist.

The results indicate that a glass-like state can be achieved with non-network forming or intermediate oxides of cerium, thorium, zirconium and yttrium when a sodium borate matrix containing them is phase separated. The glass-like state appears also in the leached and sintered modifications. This can be compared with compositions of the Morey–Eastmann Kodak Glasses reported by Weyl and Marboe [13], where melts of the oxides of hafnium, lanthanum, niobium, tantalum, thorium, titanium, yttrium and zirconium mainly with a B_2O_3 content of 10 to 33.4 wt% resulted in clear glasses.

As in the silica-based porous glasses, for the present glass-like materials approximately 4% sodium borate is expected to remain in the pores of the skeleton after leaching. This would support the glass forming and sintering processes. The more pronounced crystallinity in the leached and then sintered glass-like materials indicates that the sintering time and temperature (30 min at 1520° C) approach the crystallization conditions.

The observation by Vogel [14] that binary borate and silicate melts of the III, IV, and V groups of the periodic table show a strong tendency towards microphase separation is confirmed in the case of the present multiple oxide systems. In the present system a coarsening process occurs after heat treatment and the soluble phase can be leached out, resulting in porous glass-like materials with some crystalline content.

A surface area of pores of up to 315 $m^2 g^{-1}$ and a mean pore radius of between 0.8 and 13.6 nm are comparable with silica-based porous glasses. The alkali resistance of the newly developed materials of up to 1.96×10^{-2} mg dm^{-2} is superior to that of quartz glass (approximately 50 mg dm^{-2}), while the water resistance between 5.0 and 16.18 mg $Na_2O\,g^{-1}$ is comparable with that of a SiO_2 69.3%; B_2O_3 22.6% and Na_2O 8.1% glass (21.7 mg) reported by Volf [15].

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