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A lanthanum titanium porous glass ceramic

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Studies on the substitution of the end-member oxides in the ternary sodium borosilicate system have included work on the replacement of SiO_2 with combinations of La_2O_3 and TiO_2 which after heat treatment resulted in leachable sodium borate and insoluble La_2O_3–TiO_2 ceramic phases. Sensitivity to impurities during this phase decomposition is illustrated by the differences in physical properties, chemical resistance properties and structures of the insoluble phase when results obtained from melts from Pt/Rh or Al_2O_3 crucibles are compared. These materials exhibit after leaching interconnected pores with surface area of up to 217 $m^2 g^{-1}$ and pore radii ranging between 1.2 and 10.25 nm with noteworthy alkali resistance of up to 0.08×10^{-2} mg dm^{-2} Na_2O mg calculated on the whole surface area of the samples.

1. Introduction

The substitution of the end-member oxides in the ternary sodium borosilicate system for porous glass preparation has been presented by Res *et al.* [1, 2]. The reasoning expressed in these papers proved the possibility of SiO_2 replacement by non-network forming oxides of elements. It also supported the conclusion reached by Rabinovich *et al.* [3] concerning new phase separable glass compositions (in replacement of B_2O_3 by P_2O_5 in the classical Na_2O–B_2O_3–SiO_2 phase separable glass). The reported glass forming of La–Ti oxides by Shishido *et al.* [4] was taken into consideration. Another basis considered was Vogel's [5] phase separation condition for a wide spectrum of binary borate and silicate melts which tend to segregate or exhibit a marked trend towards microphase separation; thus it was concluded, that melts of sodium borate glasses containing selected oxides other than SiO_2 could be phase separated.

The present work concerns sodium borate glasses containing La_2O_3–TiO_2. After heat treatment and leaching the system was expected to yield a La_2O_3–TiO_2-rich skeleton.

The replacement of SiO_2 in the sodium borosilicate system with $La_2O_3 \cdot TiO_2$ was considered from the findings of Shishido *et al.* [4] where glassy states were reported for Ln–Ti oxides (Ln = lanthanides) that had been rapidly quenched. In the $Ln_2O_3 \cdot xTiO_2$ system a glassy state for Ln_2O_3 has been observed in the range $1 < x < 7$ [4].

2. Experimental details

2.1. Glass preparations

The glasses were prepared from chemically pure grade reagents, H_3BO_3, Na_2CO_3, TiO_2 (Merck) and La_2O_3 (BDH).

50 g batches of glass were melted in Pt/Rh or Al_2O_3 crucibles. The melts were made in an electrically heated furnace fitted with SiC elements, and under atmospheric conditions. Melting temperatures were between 1350 and 1400° C and melting times were less than 4 h. The glasses were cast in iron moulds, annealed and heat treated. Different heat treatments were made for different samples depending on composition and crucible selection. For heat treatment and subsequent leaching, 3 mm thick slices of the samples were used. After heat treatment the sodium borate-rich phase was leached out in boiling distilled water (pH < 7). The leaching times were 72 and 24 h for the Al_2O_3 and Pt/Rh crucible melts respectively. After leaching the samples were washed in distilled water and dried at 100° C.

Examples of pore characteristics, compositions and properties of glasses are illustrated in Table I.

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TABLE I Compositions, heat treatments, crucible selection, appearance and properties of some selected samples

Sample	Starting composition* (wt %)				Alkali resistance (mg dm^{-2})	Water resistance (mg Na$_2$O g^{-1})	Crucible	HT	Leach (h)	Void volume (ml g^{-1})	Surface area (m^{2}g^{-1})	Pore radius (nm)	Appearance	Qualitative EDX
	La$_2$O$_3$	TiO$_2$	B$_2$O$_3$	Na$_2$O										
56	20.65	23.06	49.02	7.27	–	9.9	Pt/Rh	600/2	24	0.128	99.29	2.48	Compact	La Ti
								650/2					White	
								700/2					Opaque	
								730/2						
254	20.0	15.0	56.0	9.0	–		Al$_2$O$_3$	650/2	72	0.0629	83.9	1.5	Compact	La Ti Al
								700/2					White	
								750/2					Opaque	
								700/2					Compact	
						9.4		750/2		0.1435	127.3	2.25	Brittle	
								800/2					White, Opaque	
255	20.0	15.0	56.0	9.0	0.08 × 10^{-2}	12.4	Pt/Rh	600/2	24	0.268	83.9	6.39	Brittle	La Ti
								650/2					White	
								700/2					Opaque	
256	17.48	19.52	53.0	10.0	1.2 × 10^{-2}	17.79	Al$_2$O$_3$	650/2	72	0.122	146.9	1.86	Compact	La Ti Al
								700/2					White	
								750/2					Opaque	
								700/2		0.134	146.9	1.82	Compact	
								750/2					White	
					1.67 × 10^{-2}	17.8		800/2					Opaque	
258	16.53	18.46	50.01	15.0	1.23 × 10^{-2}	25.6	Al$_2$O$_3$	650/2	72	0.131	217	1.21	Compact	La Ti Al
								700/2					White	
								750/2					Opaque	
								700/2					Compact	
								750/2		0.175	203	1.73	White	
					1.24 × 10^{-2}	22.3		800/2					Opaque	
200	20.0	20.0	50.0	10.0	–	–	Pt/Rh	600/3	34	0.269	52.5	10.25	Chalky, soft	La Ti
													Opaque	
1	20.0	2.5	65.0	12.5	no further processing done									
2	12.5	7.5	65.0	15.0										

*Glass compositions calculated from batch.

2.2. Evaluation of samples

2.2.1. Visual observation

The state of as-quenched samples was evaluated by naked eye or by magnifying glass observation.

2.2.2. Pore characteristics

The void volume of the porous material was determined by measuring the volume of water retained in the pores of the sample at the critical moisture content point under ambient conditions [6].

The surface area of the sample was determined by a method which relies on the nitrogen adsorption of the sample using the BET [7] apparatus and equation.

It was assumed that the pores were cylindrical in shape and from the results obtained from the above two evaluations a value for a mean pore radius was obtained for comparative purposes.

Pore size distribution curves were not used in this work.

2.2.3. Chemical resistance properties

The materials were tested for chemical resistance in accordance with modified DIN 53322 [8] and DIN 12111 [9] specifications for alkali and water resistance respectively and the latter calculated in mg Na_2O for 1 g sample (DGG modification).

2.2.4. Electron microscopy

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were carried out on samples of all experimental stages namely melted, heat treated and leached.

2.2.5 X-ray analysis

X-ray diffraction analysis was done on leached and sintered samples prepared in Al_2O_3 and Pt/Rh crucibles with a Philips PW1010 diffractometer.

3. Results

The effects of crucible choice and the resultant impurities on pore size is shown in Table I. It also presents a cross-section of the results obtained from selected samples: starting composition calculated from batch, chemical resistance, crucible used for the melt, heat treatments, leaching times, void volume, surface areas (assuming cylindrical shaped pores) and average pore radii are given. The samples were glassy, opaque glassy or crystalline, the latter two were white. The composition range showed a Na_2O and B_2O_3 ratio in the region of the boron anomaly line for the sodium borosilicate system. By analogy this is the region in which porous glasses may be expected. The calculated starting compositions of the phase separable Na_2O–B_2O_3–La_2O_3–TiO_2 (mol %) glasses are illustrated in Fig. 1.

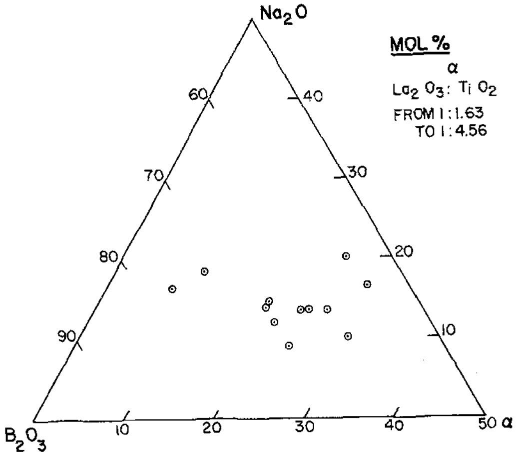

Figure 1 La_2O_3–TiO_2–B_2O_3–Na_2O glass compositions (Table I) as recalculated from original batch (mol %).

3.1. Visual observation

One glass of 20.0 wt % La_2O_3, 2.5 wt % TiO_2, 65.0 wt % B_2O_3 and 12.5 wt % Na_2O composition was clear-transparent (Pt/Rh crucible melt) Table I, no. 1. Glass no. 56 was crystalline, while all remaining glasses were evaluated as opaque glasses.

3.2. Pore characteristics

Void volume was determined by critical moisture content method covered a range of 0.069 ml g^{-1} (Al_2O_3 crucible) to 0.269 ml g^{-1} (Pt/Rh crucible).

Surface areas measured by the nitrogen adsorption method varied between 52.5 and 217 $m^2 g^{-1}$. Calculated mean pore radii (assuming cylindrical pores) were between 1.21 and 10.25 nm.

Melts contained in Al_2O_3 crucibles exhibit higher surface areas and generally lower mean pore radii than that from Pt/Rh crucible melts,

3.3. Chemical resistance properties

The porous materials had water resistance values between 9.4 and 25.6 mg in Na_2O per 1 g samples.

Alkali resitance values in mg dm^{-2} of the whole surface area of the porous sample were measured in the range 0.08×10^{-2} to 1.67×10^{-2}.

3.4. SEM and EDX

The detection of microphase segregation in glass

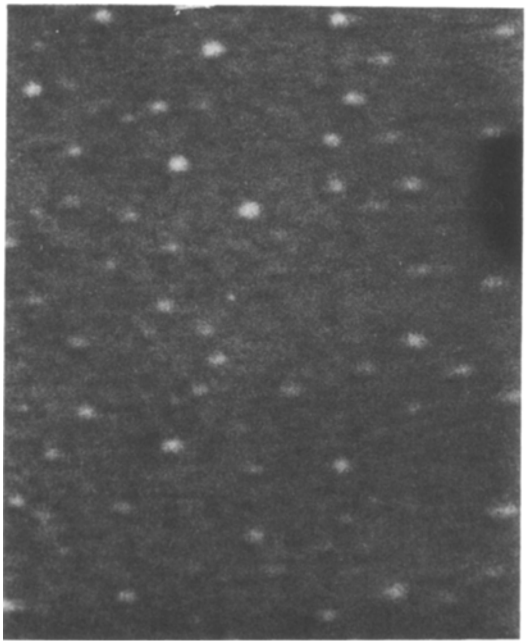

Figure 2 SEM micrograph of fracture surface of a quenched experimental glass no. 1. Droplet-like microheterogeneities present. Magnification (23 000 X).

Figure 4 SEM micrograph of fracture surface of heat-treated glass 255, nucleation crystallization. Magnification (30 000 X).

using electron microscope techniques has been discussed in some detail by Vogel [5].

Secondary electron micrographs of as quenched, heat treated and leached samples explain the structure of the examined clear and opaque glasses and of the crystalline material. In Fig. 2 an experimental low TiO_2 containing clear glass (no. 1 from Table I) shows the presence of droplet-like heterogeneities comparable to that reported by Rabinovich *et al.* [3]. When the content of TiO_2 and $TiO_2 \cdot xLa_2O_3$ was increased, the opaque glassy material (no. 255) on quenching exhibited coarsening and/or nucleation patterns as seen in Fig. 3. After heat treatment of the sample crystallization occurred (Fig. 4). The pronounced crystalline structure remains in sample no. 256 after leaching (Fig. 5). For comparison the resulting structure of heat treated and leached sample no. 256 melted in an Al_2O_3 crucible is shown in Fig. 6. A state of coarsening and tendency to nucleation is observed. Differences in characteristics of surface areas and mean pore radii suggest that due to bigger holes and bigger crystallites in the materials from Pt/Rh crucible melts, generally, the void volume values are higher and the surface areas lower than in the closer packed nuclei in materials from the Al_2O_3 crucible melts (see Figs. 5 and 6).

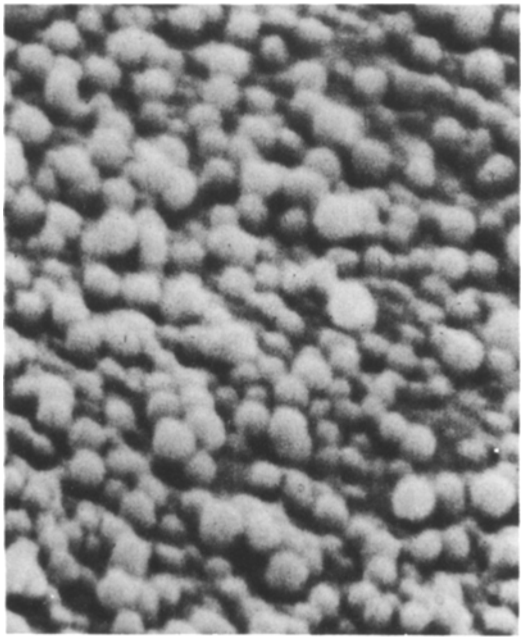

Figure 3 SEM micrograph of fracture surface of opaque glass. Coarsening and nucleation. Magnification (24 000 X).

3.5. X-ray diffraction analysis

The X-ray analysis were performed on samples 200 and 256 which had the mole ratios of $La_2O_3:TiO_2 = 1:4,55(200)$ and $1:4.08(256)$.

Sample no. 200 melted in a Pt/Rh crucible

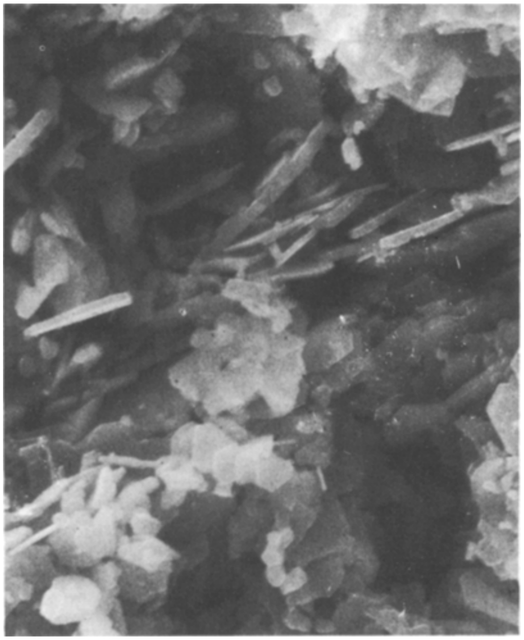

Figure 5 SEM micrograph of fracture surface of leached sample 255, crystallization pronounced. Magnification (30 000×).

showed unreacted TiO_2 in form of rutile as the major crystalline phase present. The second major crystalline phase observed was metastable hexagonal phase as described by Shishido *et al.* [4] for compositions of La_2O_3–TiO_2 with molar ratio 1:4.5 and by Limar *et al.* [10] as hexatitanate. Beside these two major components, small amounts of unreacted La_2O_3 and $La_2O_3 \cdot TiO_2$ compound were observed. To prove the presence of the metastable hexagonal phase, the leached sample was sintered for 5 min at 1350° C. Again the major resulting phase was TiO_2 (rutile), but the peaks of the stable compound $2La_2O_3 \cdot 9TiO_2$ were apparent. This is in agreement with the findings of Shishido *et al.* [4] and McChesney and Sauer [11].

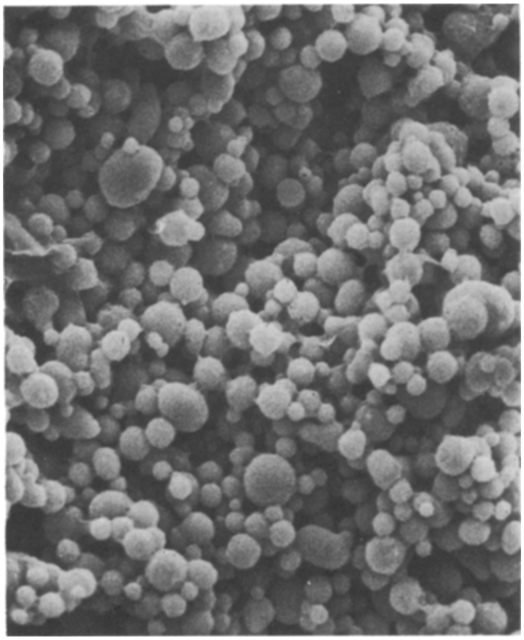

Figure 6 SEM micrograph of fracture surface of leached sample 256 (Al_2O_3 crucible). Coarsening and/or nucleation. Magnification (30 000×).

Sample no. 256, which was melted in an Al_2O_3 crucible does not show the formation of the metastable hexagonal phase. The diffraction pattern shows unreacted TiO_2 and La_2O_3 as the major crystalline phase with minor amounts of $La_2O_3 \cdot TiO_2$ and free alumina. Sintered samples again showed TiO_2 as the major crystalline phase, with minor formation of $2La_2O_3 \cdot 9TiO_2$ compounds [12].

4. Discussion

A series of Na–La–Ti–Al–B–oxide glasses showed phase separation, leachability and porosity after quenching and/or heat treatment, similar to the effects achieved in the ternary sodium borosilicate system. The porous glass ceramic with Al_2O_3 as a contaminant from the crucible showed a rather pronounced coarsening and nucleation.

Melts made in a Pt/Rh crucible showed well-developed crystals which affected the pore size and surface area of the sample.

The results indicate that at melting temperatures the interaction of La_2O_3 and TiO_2 leads to the formation of titanates in the leached sample in a small portion only. The major phase remains an unreacted TiO_2 in form of rutile. In the system investigated, microphase separation and crystallization occurs in the as-quenched and/or heat treated samples and the phase separated melts can be leached resulting in porous glass–ceramics with surface areas of up to $217\,m^2\,g^{-1}$ and pore radii ranging between 1.2 and 10.25 nm. The alkali and water resistance according to DIN specifications is shown for some of the samples studied; whereby the alkali resistance of 0.08×10^{-2} to $1.67 \times 10^{-2}\,mg\,dm^{-2}$ $Na_2O/1$ g (total surface area) is noteworthy.

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