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Al_2O_3–Ta_2O_5-rich glass–ceramic with interconnected pores and its sintering

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Substitution of SiO_2 in the ternary sodium borosilicate system with Al_2O_3 plus Ta_2O_5 was found to produce glass which decomposed into microphases and/or crystallized after heat treatment. At least one of the phases present was water soluble. The structure of the material was glassy with the presence of a small crystalline content. Crystalline forms found during powder X-ray diffraction analysis of heat treated, leached and then sintered materials were orthorhombic $NaTaO_3$ plus $AlBO_3$, orthorhombic $NaTaO_3$ and orthorhombic $Na_2O \cdot 4Ta_2O_5$ plus rhombic $9Al_2O_3 \cdot 2B_2O_3$, respectively. The specific surface areas of the leached materials ranged between 96 and $304\,m^2\,g^{-1}$, while the mean pore radii of interconnected pores were calculated to be between 2.0 and 8.4 nm. A sintering rate of between 1520 and 1580° C for 5 min were estimated from void volume and bulk density measurements.

1. Introduction

The development of porous glassy silica from phase-separated and leached sodium–borosilicate glasses has been reviewed by Res *et al.* [1]. Na_2O–B_2O–SiO_2 glasses can be heat treated and separated into two phases, one almost pure SiO_2 which is insoluble in water and the other a Na_2O–B_2O_3-rich phase which is water soluble. The latter may be leached out leaving a porous silica glass skeleton with interconnected pores.

In recent work, replacements for silica were reported where two to four heat and/or alkali-resistant oxides of Ce, Nb, La, Ta, Ti, Th, Y and Zr were introduced into a Na_2O–B_2O_3 matrix and melted. According to Res *et al.* [1–5], the resulting phase separated and leached materials showed higher heat and/or alkali resistance compared to the porous SiO_2. The presence of Al_2O_3 was found to influence pore characteristics, i.e. the surface area was improved and the material's crystallization [6] was depressed in all processing steps.

The influence of Al_2O_3 on the pore characteristics and the crystallization of the materials reported in [1–4] was only analysed qualitatively. The introduction of quantitative chemical analysis in the experimental studies of further porous material developments showed that a surprisingly large amount of Al_2O_3 was dissolved in the basic glass from crucible erosion. Hart *et al.* [7] found up to 30 mass % Al_2O_3 in the as-quenched Na_2O–B_2O_3–Sc_2O_3 melt. In the system Na_2O–B_2O_3–Ga_2O_3 the presence of up to 12 mass % Al_2O_3 from crucible erosion was detected by Res *et al.* [8]. Similar results were reported by Res *et al.* [9] for Na_2O–B_2O_3–HfO_2 glass and by Hart *et al.* [10] for Na_2O–B_2O_3–ZrO_2 glasses, where amounts of Al_2O_3 between 40 and 50 mass % in as-leached samples were analysed if the batches were melted in Al_2O_3 crucibles. Clark *et al.* [11], who achieved clear glasses in the Na_2O–B_2O_3–Al_2O_3 system containing approximately 35 mass % Al_2O_3, started a comprehensive study of the influence of Al_2O_3 on porosity characteristics and on crystallization of the leached and then sintered Al_2O_3-rich materials.

Systematic work is in progress to replaced SiO_2 in the Na_2O–B_2O_3–SiO_2 system with two oxides from the elements Al, Ce, Ga, Ge, Er, Hf, La, Ta, Nb, Nd, Sc, Th, Ti, Y and Zr. After melting the glasses, phase separation by heat treatment is induced and the expected soluble phase is leached out, leaving a porous material containing mainly two of the selected oxides. In this work the possibility of replacing SiO_2 by Al_2O_3–Ta_2O_5 in the Na_2O–B_2O_3–SiO_2 system was examined in order to produce a porous glass ceramic. The replacement of SiO_2 was carried out by Al_2O_3 plus Ta_2O_5 in mass % ratios of 3 : 1, 2 : 1, 1 : 1, 1 : 2 and 1 : 3 Al_2O_3–Ta_2O_5 with the intention of producing an Al_2O_3–Ta_2O_5-rich material with interconnected pores after phase separation and leaching of the Al_2O_3–B_2O_3–Na_2O–Ta_2O_5 glasses.

Some results with Ta_2O_5 containing glasses reported by White *et al.* [4], Bednarik *et al.* [12] and Res *et al.* [13], gave reason to combine Ta_2O_5 with Al_2O_3 as a replacement for silica. A higher heat resistance than that of porous SiO_2 is expected in the Al_2O_3–Ta_2O_5-rich resulting material.

2. Experimental details

2.1. Glass preparation

50 g batches were prepared from chemically pure grade H_3BO_3, Na_2CO_3, Al_2O_3 and Ta_2O_5. They were melted in Pt/Rh crucibles in air at a temperature of 1400° C in an electrically heated furnace equipped with SiC elements. Melting times were 4 h. Part of the melt was cast in iron moulds and then annealed, while part of the melt was quenched on a cold steel plate. The annealed samples were then phase separated by heat treatment at 550° C for 24 h. These samples were

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TABLE I Glass compositions calculated from batch, appearance of as-quenched and as-leached samples and porosity characterization

Sample No.	Composition calculated from batch (mass %)		Al_2O_3–Ta_2O_5 ratio		Appearance of as-quenched samples	Appearance of as-leached samples	Consistency after leaching	Void volume (ml g^{-1})	BET surface area ($m^2 g^{-1}$)	Mean pore radii (nm)
			mass %	mol %						
1	Al_2O_3 Ta_2O_5 B_2O_3 Na_2O	26.25 8.75 50 15	3:1	13:1	Clear glass with yellow shade. Very slight surface layer-opaque.	White opaque	Crumbled	0.3855	95.97	8.034
2	Al_2O_3 Ta_2O_5 B_2O_3 Na_2O	23.33 11.67 50 15	2:1	8.66:1	Clear glass	White opaque	Crumbled	0.3958	259.32	3.053
3	Al_2O_3 Ta_2O_5 B_2O_3 Na_2O	17.5 17.5 50 15	1:1	4.33:1	Clear glass	Glass-like opalescent	Crumbled	0.3029	303.95	1.993
4	Al_2O_3 Ta_2O_5 B_2O_3 Na_2O	11.67 23.33 50 15	1:2	2.17:1	Clear glass and minor opaque phases	Opaque	Crumbled	0.2087	156.65	2.665
5	Al_2O_3 Ta_2O_5 B_2O_3 Na_2O	8.75 26.25 50 15	1:3	1.44:1	Clear glass and minor opaque phases	Opaque	Crumbled	0.4811	114.23	8.423

Heat treatment: All samples 550° C for 24 h.
Leaching time: All samples 24 h.

leached in distilled boiling water (24 h). After the main part of the sodium borate-rich phase was leached out, the samples were rinsed with fresh distilled water and dried at 100° C. A representative porous sample was sintered.

2.2. Characterization of glasses

Pore characterization was established by BET nitrogen absorption–desorption and void volume measurements. Scanning electron microscope, SEM, techniques, X-ray powder diffraction, wet chemical characterize the material at different processing steps. Details of the methods have been given in [3, 4, 7].

3. Results

3.1. Characterization of resulting materials

Table I is a summary of the starting compositions, Al_2O_3 : Ta_2O_5 ratios (mass and mol %), of the visual appearance of as-quenched and as-leached samples, their consistency and pore characteristics. The as-quenched Samples 1 to 5 were predominantly glassy. Some minor opacity appeared in Samples 1, 4 and 5. After heat treatment and leaching, Samples 1, 2, 4 and 5 were opaque, while Sample 3 remained glass-like with opalescence. It was noted that all leached samples were brittle and crumbled.

3.2. Scanning electron microscopy

The microstructure of as-quenched Sample 3 is shown in the secondary electron micrograph in Fig. 1. Droplet-like micro-heterogeneities, which are similar to those reported earlier [5, 10], can be seen. After heat treatment of Sample 3, phase separation started as is shown in Fig. 2. Samples 2 and 3 were leached for 72 h after heat treatment. The resulting fractograph structures were crystalline for Sample 2 and glass-like for Sample 3, as shown in Fig. 3. A similar glass-like structure as Fig. 3b was reported in [14]. Leached Sample 3 was subsequently sintered at 1580° C for 5 min. The micrograph of the resulting crystalline structure can be seen in Fig. 4. Compared to Fig. 3b, crystal growth from the glass-like material is apparent.

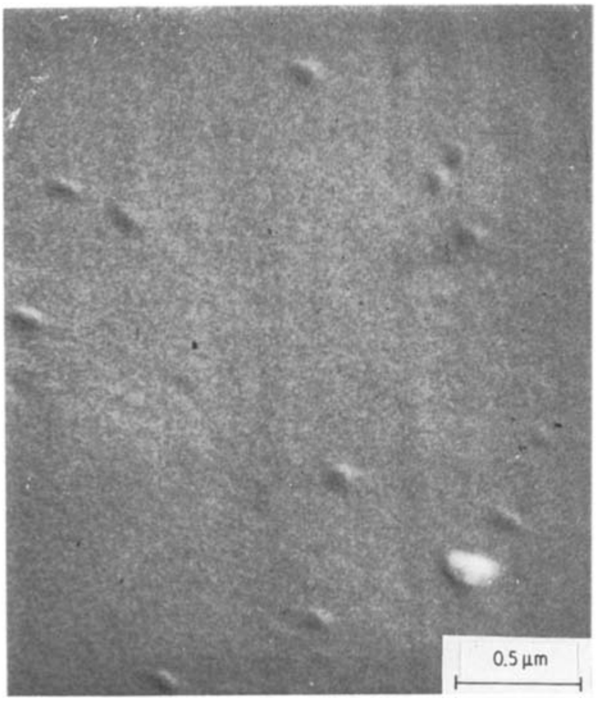

Figure 1 Scanning electron fractograph of clear as-quenched Glass 3 showing droplet-like micro-heterogeneities.

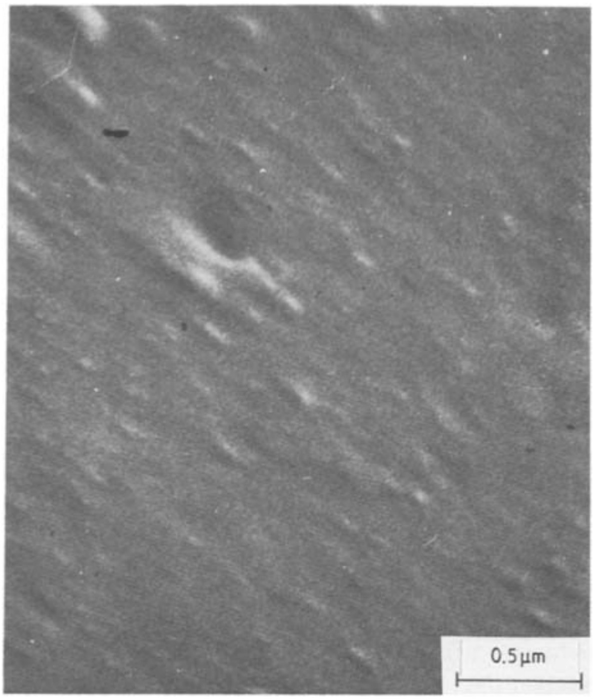

Figure 2 Scanning electron fractograph of heat treated Glass 3 (microheterogeneities and start of phase separation).

3.3. Wet chemical analysis

Wet chemical analysis was carried out on Sample 3 after leaching for 72 h in boiling distilled water. The results, compared to the starting composition, are given in Table II. The high B_2O_3 and Na_2O content remaining in the porous skeleton is remarkable. During leaching an enrichment of the "skeleton-forming" oxides (Al_2O_3 and Ta_2O_5) occurred.

TABLE II Chemical composition (of Sample 3) in mass % before and after leaching

	Composition calculated from batch	Composition after heat treatment and leaching 72 h
Al_2O_3	17.5	21.0
Ta_2O_5	17.5	43.4
B_2O_3	50	28.4
Na_2O	15	8.5

3.4. X-ray analysis

Powder X-ray diffraction studies were conducted on as-quenched, heat treated, leached and sintered Sample 3. Sample 3 was selected due to its visually observed glassy appearance in the as-quenched state and the highest surface area measured in Samples 1 to 5. The X-ray analysis revealed glassy and crystalline structures, depending on the sample treatment. As-quenched Sample 3 showed no significant crystalline peaks, only the characteristic pattern typical of a glassy state. After heat-treatment, Sample 3 showed the presence of two crystalline phases with strong peaks, identified as $NaTaO_3$ (stronger) and $AlBO_3$ compounds. However, after leaching the $AlBO_3$ compound was not detected, only the orthorhombic $NaTaO_3$ peaks were registered. Stronger crystallization was observed after firing the leached Sample 3 for 5 min at 1580° C. Two crystalline phases, orthorhombic $Na_2O \cdot 4Ta_2O_5$ and rhombic $9Al_2O_3 \cdot 2B_2O_3$, were then detected.

3.5. Heat treatment for densification

Specimens from heat treated and leached Sample 3 were fired at 1120, 1220, 1320, 1420, 1520 and 1580° C for 5 min. After each sintering step the samples were tested for remaining pore volume and after crushing to a grain size of 0.5 to 1 mm for bulk density. The results are shown in Fig. 5.

4. Discussion

A series of Na_2O–Al_2O_3–Ta_2O_5–B_2O_3 glasses showed,

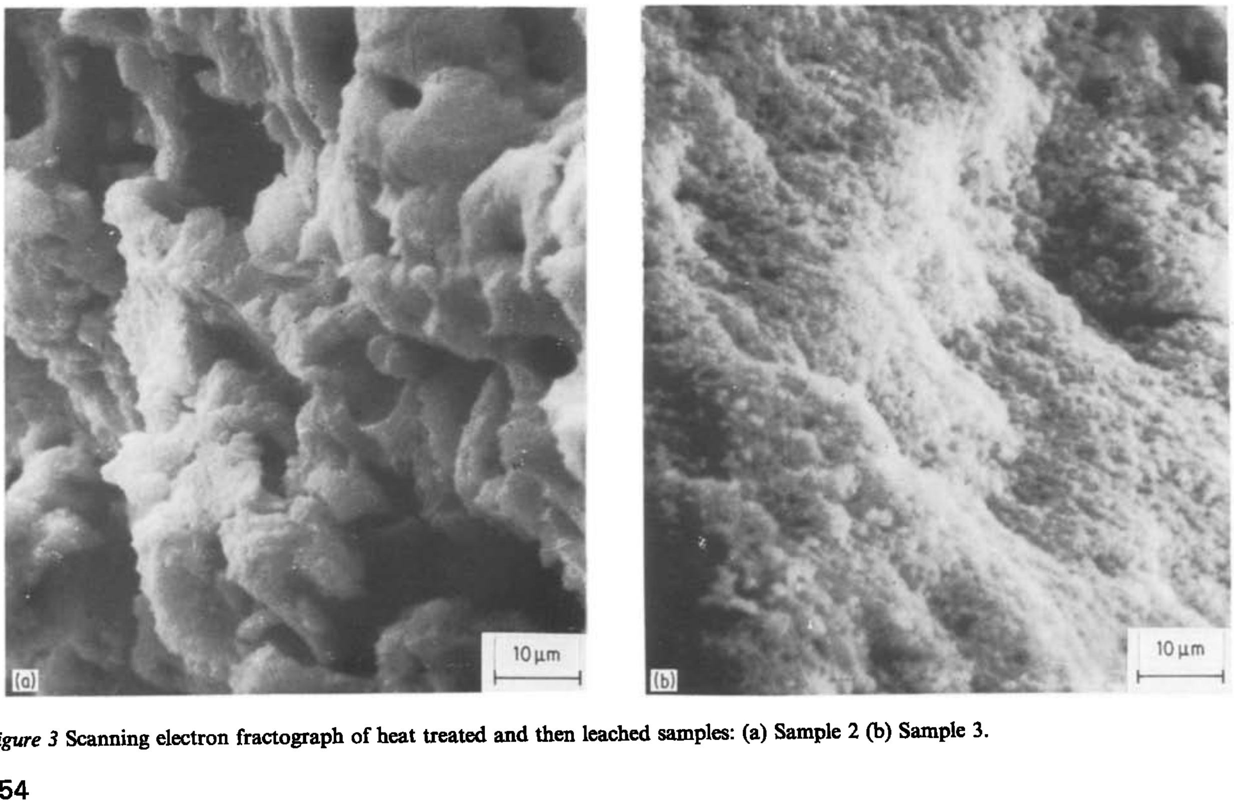

Figure 3 Scanning electron fractograph of heat treated and then leached samples: (a) Sample 2 (b) Sample 3.

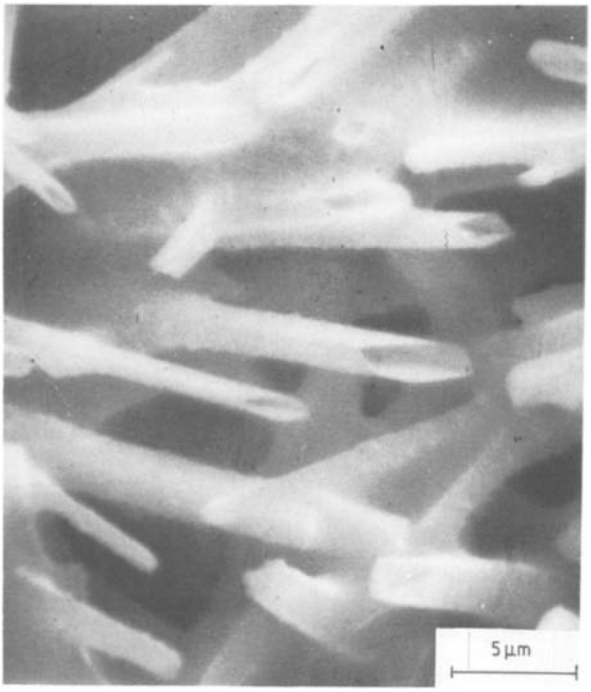

Figure 4 Scanning electron fractograph of heat treated, leached and then sintered at 1580° C for 5 min, Sample 3. Strong crystallization present.

after heat treatment, phase separation and/or crystallization, leachability and high surface areas of interconnected pores, similar to that achieved in the ternary sodium–borosilicate system. The resulting melts were predominantly glassy in the as-quenched state. Scanning electron microscopy studies revealed the presence of droplet-like micro-heterogeneities in clear glasses. In these glasses no cords, threads or striae were observed. In heat-treated samples orthorhombic $NaTaO_3$ and $AlBO_3$ compounds were detected and after leaching, only the presence of orthorhombic $NaTaO_3$ was recorded. The greatest crystallization was observed after the leached sample was sintered for 5 min at 1580° C. The resulting crystalline compounds present in sintered Sample 3 were orthorhombic $Na_2O \cdot 4Ta_2O_5$ and rhombic $9Al_2O_3 \cdot 2B_2O_3$.

Comparison of the batch composition with that determined after heat-treatment and leaching indicates an enrichment of the skeleton-forming Al_2O_3–Ta_2O_5. The change in $Al_2O_3 : Ta_2O_5$ ratio of 1 : 1 to 1 : 2 is especially noteworthy. The rather high sodium and boron content remaining after extensive leaching can be partially explained by the presence of various crystalline and amorphous phases containing sodium and/or boron.

Some of the sodium and boron appears to be tied up in the crystalline compounds, $NaTaO_3$ and $AlBO_3$, after heat treatment with the aluminium borate phase being leachable, thus accounting for the abovementioned decrease in relevant ratio.

On sintering the orthorhombic $NaTaO_3$ phase transformed to another orthorhombic phase $Na_2O \cdot 4Ta_2O_5$ and a new aluminium borate phase $9Al_2O_3 \cdot 2B_2O_3$ was formed probably by crystallization from the amorphous matrix.

Surface areas of between 96 and $304\,m^2\,g^{-1}$ and mean pore radii of 2.0 to 8.4 nm are comparable to those of other systems [1–5, 7–14]. Because of the small amount of leached and/or sintered material available in this study (approximately $0.5\,cm^3$ of each sample) the results of bulk density and void volume measurements could only be evaluated qualitatively. The results show, however, the trend of densification of the porous material with decreasing pore volume and increasing bulk density with increasing firing temperatures. The results in Fig. 5 indicate a far better heat resistance of approximately 1580° C for 5 min, than that reported for porous SiO_2 glass [5].

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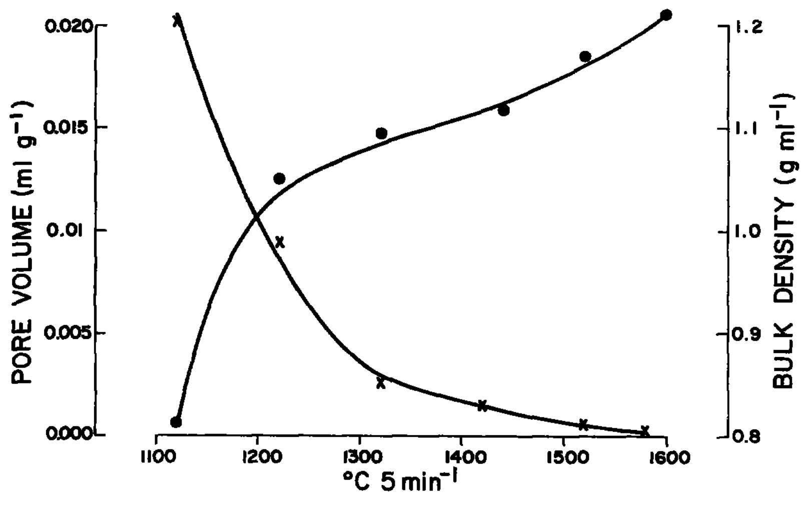

Figure 5 (×) Pore volume and (○) bulk density after sintering steps for Sample 3. (Previously heat treated and leached for 72 h. The results are qualitative.)

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