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Transformation of Na_2O–HfO_2–B_2O_3 glass into a material having interconnected pores

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Substitution of SiO_2 in the ternary sodium borosilicate system with HfO_2 was found to produce glasses, which after heat treatment decomposed into immiscible microphases, one of which was water soluble. The structure of the leached material after heat treatment was either glassy (mainly in the presence of Al_2O_3) or crystalline. Crystalline forms found during X-ray diffraction analysis of heat treated and leached material (melted in Pt/Rh crucibles) were monoclinic HfO_2. Monoclinic HfO_2 was also found in heat treated, leached and then fired materials melted in Pt/Rh or Al_2O_3 crucibles, in the latter an additional $9Al_2O_3 \cdot 2B_2O_3$ phase was detected. The higher solubility of HfO_2 in a Na_2O–B_2O_3 matrix than that of ZrO_2 (30 wt% against 15 wt%) resulting in clear glasses is of interest. The specific surface areas of the leached materials ranged between 41.3 and 290 $m^2 g^{-1}$, while the mean radii of interconnected pores were calculated to be 1.2 and 15.2 nm. A firing temperature between 1450 and 1500° C is estimated from void volume and bulk density measurements.

1. Introduction

A review of porous silica development was reported by Res *et al.* [1]. Sodium borosilicate glasses can be separated into two phases, only a SiO_2 rich and the other a Na_2O–B_2O_3 phase. The latter may be leached out, leaving a porous SiO_2 skeleton. During forty years of development different compositional changes have been reported: Na_2O was replaced by K_2O, Li_2O or alkaline earth oxides. The substitution of B_2O_3 with P_2O_5 and the total and/or partial replacement of SiO_2 by GeO_2 and Al_2O_3 or $AlPO_4$ are mentioned in [1]. Oxides of cobalt, molybdenum, nickel, vanadium, tungsten and zirconium were used as minor components in the preparation of porous SiO_2 glass. Recent work investigated the replacement of SiO_2 in Na_2O–B_2O_3–SiO_2 glasses by heat and/or alkali resistant oxides which are usually characterized as intermediate or modifying constituents. Combinations of two or more oxides of aluminium, cerium, hafnium, lanthanum, niobium, tantalum, thorium, titanium, yttrium and zirconium were introduced into a Na_2O–B_2O_3 matrix and melted. The melts after casting were phase separated by a suitable heat treatment, leached and sintered. The resulting porous glass ceramics or glass-like materials showed a higher alkali and/or heat resistance than porous SiO_2 [1–8]. Alumina in the melts was found to influence porosity and pore size. The presence of B_2O_3 in the porous skeleton of some of the new materials was also established. Following on Vogel's work [9] which reported phase separation in binary B_2O_3 or SiO_2 containing systems, a research programme has been initiated to replace SiO_2 in the Na_2O–B_2O_3–SiO_2 system by single oxides. Hart *et al.* [10] and Clark *et al.* [11] prepared porous skeletons consisting of hexagonal $ScBO_3$ and $2Al_2O_3 \cdot B_2O_3$, respectively.

Res *et al.* [12, 13] reported on the development of a porous β-Ga_2O_3 and of a porous mixed structure of the aragonite type containing cubic CeO_2 plus cerium metaborate.

The present work investigates sodium–borate glasses containing HfO_2 as a third component. After heat treatment to achieve phase separation and/or crystallization and subsequent leching a HfO_2-rich porous skeleton was expected. A glass-like porous material containing HfO_2 in combination with CeO_2, La_2O_3, ThO_2, Y_2O_3 and ZrO_2 has already been reported [7]. In order to study the influence of alumina on the resulting material some batches contained Al_2O_3 purposely introduced from crucible erosion.

2. Experimental procedure

2.1. Glass preparation

The glasses were prepared for chemically pure reagents H_3BO_3 and Na_2CO_3 (E. Merck A.G., Darmstadt, West Germany) and HfO_2 (99.7%) (Koch-Light Laboratories Ltd., Colnbrooks, Berkshire, UK). Batches of 25 and 100 g were melted in Pt/Rh as well as in Al_2O_3 crucibles in air at 1400° C for 3 to 4 h. The melts were cast in iron moulds and annealed. Phase separation was induced by heat treatment. The relevant programmes are included in Table I.

The phase separated samples were leached in boiling distilled water for 24 to 72 h depending on sample composition and crucible type. Selected leached samples were fired at 1380, 1440 or 1500° C for 30 min.

2.2. Characterization of glasses

Various techniques for characterization of porous glasses and glass-ceramics have been outlined in previous papers and will not be dealt with further.

The methods used in the present work for material

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TABLE I Treatment and characterization of leached samples

Sample No.	Chemical composition calculated from batch wt %			Crucible type	Heat treatment		Leaching (h)	Appearance of as leached samples	Void volume (ml g^{-1})	BET surface area ($m^2 g^{-1}$)	Mean pore radius (nm)
					(°C)	(h)					
	Na_2O	B_2O_3	HfO_2								
1	14.93	58.71	26.36	Pt/Rh (a)	600	3	6	white	0.3727	49.0	15.2
				(b)	500	3*			0.456	147.6	6.2
					550	3	24				
2	15	60	25	Pt/Rh	475	2*	2	white	–	41.3	–
					525	2					
					550	2					
					575	2					
					600	2					
					625	2					
3	10	75	15	Al_2O_3	500	2*	72	white, very slightly yellowish	0.3473	249.39	2.78
					550	2					
					600	2					
					625	2					
4	14.93	58.71	26.36	Al_2O_3	600	2	72	white, very slightly yellowish	0.1768	290	1.2
5	13.11	57.23	29.66	Al_2O_3	600	2*	72	white, very slightly yellowish	0.163	261.4	1.3
					650	2					
					700	2					
					750	2					

*Heating rate between temperature steps was 4° C min^{-1}.

characterization include pore volume measurements [1], scanning electron microscopy [2], X-ray diffraction analysis [5], Brunauer, Emmett and Teller (BET) nitrogen absorption and desorption [8], qualitative bulk density measurements [10] and sintering experiments [12]. A wet chemical analysis was also performed on selected samples.

3. Results

3.1. Characterization of resulting materials

The starting glass compositions calculated from the batch of as quenched samples are shown in Fig. 1. The term "other formations" means opaque, slightly or fully crystallized samples.

The characterization of selected samples is given in Table I. This table includes starting compositions calculated from batch, crucible type, heat treatment programmes, leaching times, appearance of as leached samples, their void volumes, surface areas and mean pore radii.

The compositions in Fig. 1 covered a region of 5 to 20 wt % Na_2O, 45 to 85 wt % B_2O_3 and 10 to 35 wt % HfO_2. The general appearance of samples 1 to 3 prior to heat treatment was either colourless or with a slightly green coloration. Under visual observation of as quenched or annealed samples no cords, threads or striae were seen in the clear glasses. Samples 4 and 5 were slightly opaque. After heat treatment of these samples opaque white materials with a slightly greyish tint resulted. Samples 1 and 2 were opaque white after leaching while samples 3 to 5 took on a slightly yellow tint.

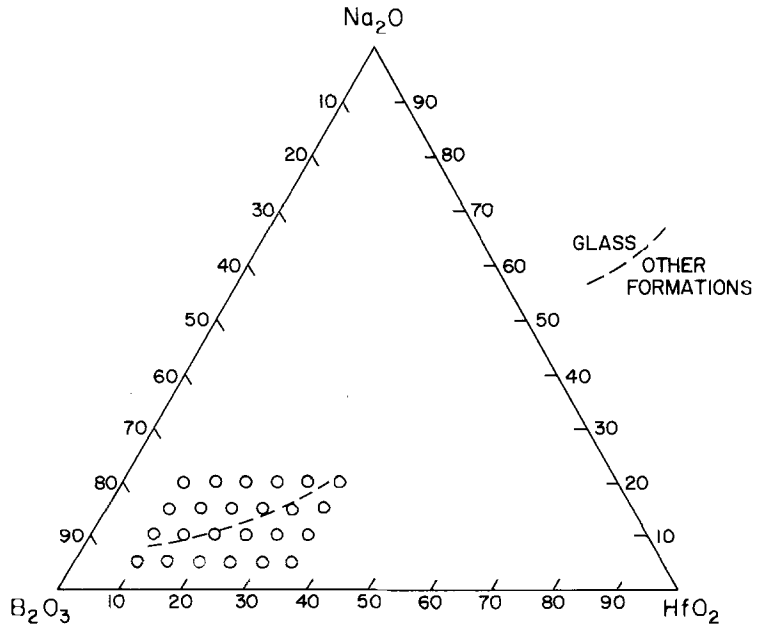


Figure 1 Starting compositions (wt %) and clear glass region of as quenched Na_2O–B_2O_3–HfO_2 melts.

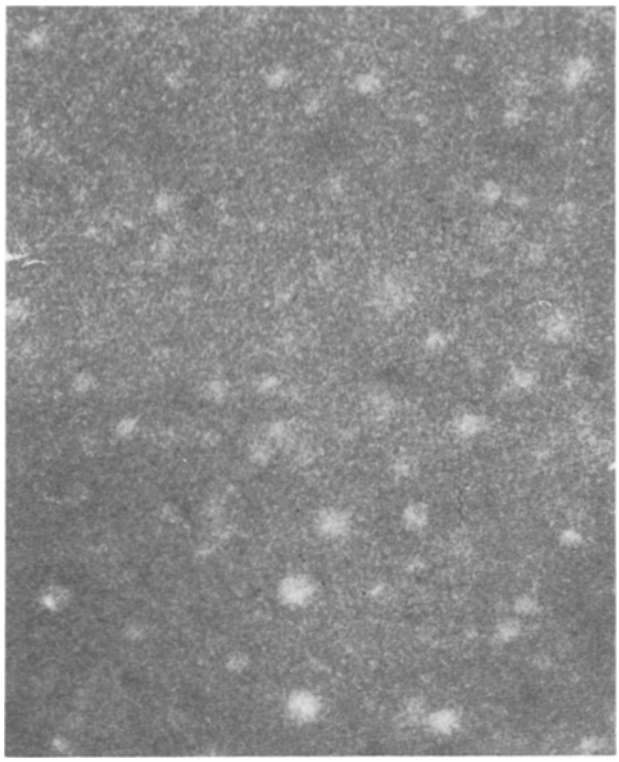


Figure 2 Scanning electron fractograph of clear as quenched glass 4 showing droplet-like microheterogeneities. (Magnification 1.12 × 10^4.)

3.2. Scanning electron microscopy

Secondary electron micrographs of as quenched glasses 1 and 4 (Pt/Rh and Al_2O_3 crucible melts, respectively) showed the presence of droplet-like microheterogeneities similar to that reported in [1, 6–10] (Fig. 2).

Scanning electron fractographs of samples 1 and 3 phase separated by heat treatment show strong crystallization in sample 1 (Fig. 3a) and phase separation only in sample 3 (Fig. 3b). Similar structural differences were reported previously [1, 2, 4, 5]. Sample 1 consists of hafnia–sodium–borate while sample 3 contains additional alumina. The role of Al_2O_3 additions which decreases the linear crystallization speed in the glass can be assumed [14] for the Na_2O–B_2O_3–HfO_2–Al_2O_3 melt. Comparison of the scanning electron fractographs of phase separated and then leached samples 1 and 3 in Fig. 4 confirms this observation. Sample 1 (Fig. 4a) shows crystallinity while sample 3 (Fig. 4b) has a glassy structure with droplet-like microheterogeneities present. Similar structural differences were reported previously [2, 4–6]. Heat treatment for densification of leached samples was carried out for a constant time of 30 min at temperatures of 1380, 1440 or 1500° C. The influence of this on the structure of the resulting materials is demonstrated in Fig. 5.

In Fig. 5a the scanning electron fractograph of sample 1 fired at 1440° C shows well developed crystals. At 1500° C, however, the morphology of crystals changed (Fig. 5b). For comparison, the firing of an Al_2O_3 containing sample 4 at 1500° C also caused marked crystallization in contrast to the heat treated and leached Al_2O_3 containing samples which were glassy. The structure of fired sample 4 is shown in Fig. 5c.

3.3. Wet chemical analysis

A wet chemical analysis of the leached samples 1 and 4 is compared to the original batch glass composition in Table II. The addition of Al_2O_3 in the leached sample 4 originates from Al_2O_3 crucible erosion. It can

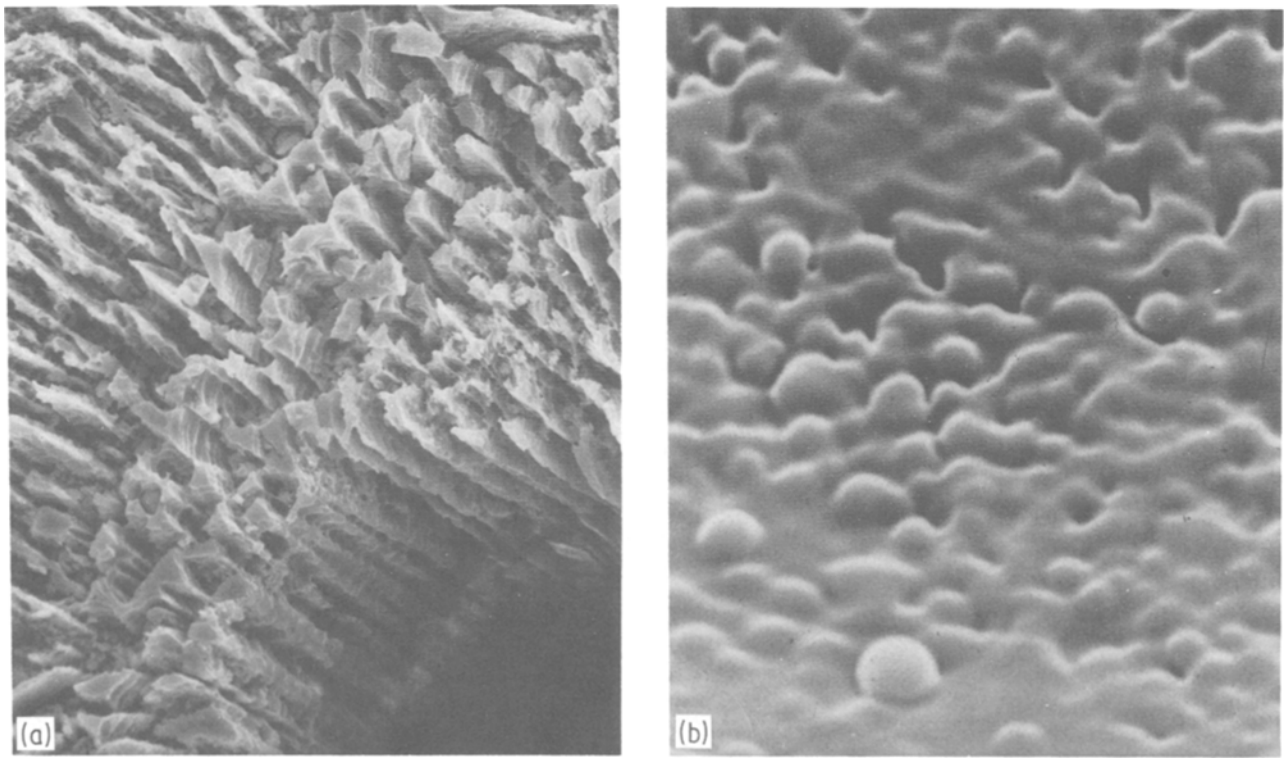


Figure 3 Scanning electron fractographs of heat treated glasses: (a) crystallized and etched sample 1 (Pt/Rh crucible melt) magnification 0.7 × 10^3, (b) phase separated sample 3 (Al_2O_3 crucible melt), with marked content of Al_2O_3, magnification 1.05 × 10^4.

TABLE II Chemical compositions before and after leaching in wt %

	Sample 1 calculated from batch	Sample 1 analysed after leaching 24 h	Sample 4 calculated from batch	Sample 4 analysed after leaching 24 h
Na_2O	14.93	–	14.93	2.76
B_2O_3	58.71	12.83	58.71	14.39
HfO_2	26.36	87.68	26.36	43.66
Al_2O_3	–	–	–	40.02
	100.00	100.51	100.00	100.83

be seen from Table II that Na_2O in sample 1 was totally leached out while the remaining amount of B_2O_3 in the porous skeleton indicates too short a leaching time of 24 h which was later extended to up to 72 h. A 24 h leaching time is evidently too short for sample 4. It should be emphasized that the content of 40 wt % Al_2O_3 was found in leached sample 4. This content is far higher than that to be expected in the melt. During leaching an enrichment of the "skeleton forming" oxides (HfO_2 and Al_2O_3) occurs. (See Table II for HfO_2 in sample 1). An analysis of Al_2O_3 content in the melt was however not made.

3.4. X-ray analysis

Powder X-ray diffraction studies were conducted on as-quenched, phase, separated, leached and then fired samples on a Rigaku Denki diffractometer (Rigaku Denki Ltd., Tokyo, Japan).

Various glassy and crystalline structures were observed. As-quenched samples 1 to 4 showed no significant crystalline peaks, only the characteristic pattern typical of a glassy state. After heat treatment and leaching however, samples 1 and 2 showed crystallization. The crystalline phase was monoclinic HfO_2. Samples 3 and 4 containing a significant amount of Al_2O_3 were glassy after heat treatment and leaching.

Strong crystallization was observed after firing. After firing at 1500° C samples 1 and 4 showed the obvious presence of monoclinic HfO_2. In the Al_2O_3 containing sample 4 an additional crystalline phase, $9Al_2O_3 \cdot 2B_2O_3$ [15] was detected.

3.5. Heat treatment for densification

Specimens from leached sample 1 were fired for 30 min at 1380, 1440 or 1500° C to study the densification behaviour. After firing the specimens were tested for remaining pore volume and after crushing to a grain size of 0.5 to 1 mm for densification within the powder granules (bulk density). The results are shown in Fig. 6.

4. Discussion

A series of sodium–borate hafnium oxide glasses showed phase separation, leachability and porosity similar to that achieved in the ternary sodium–borosilicate system. A higher solubility of HfO_2 in the Na_2O–B_2O_3 matrix has been observed than that previously reported for ZrO_2 [16].

The Na_2O–B_2O_3–HfO_2 starting compositions in

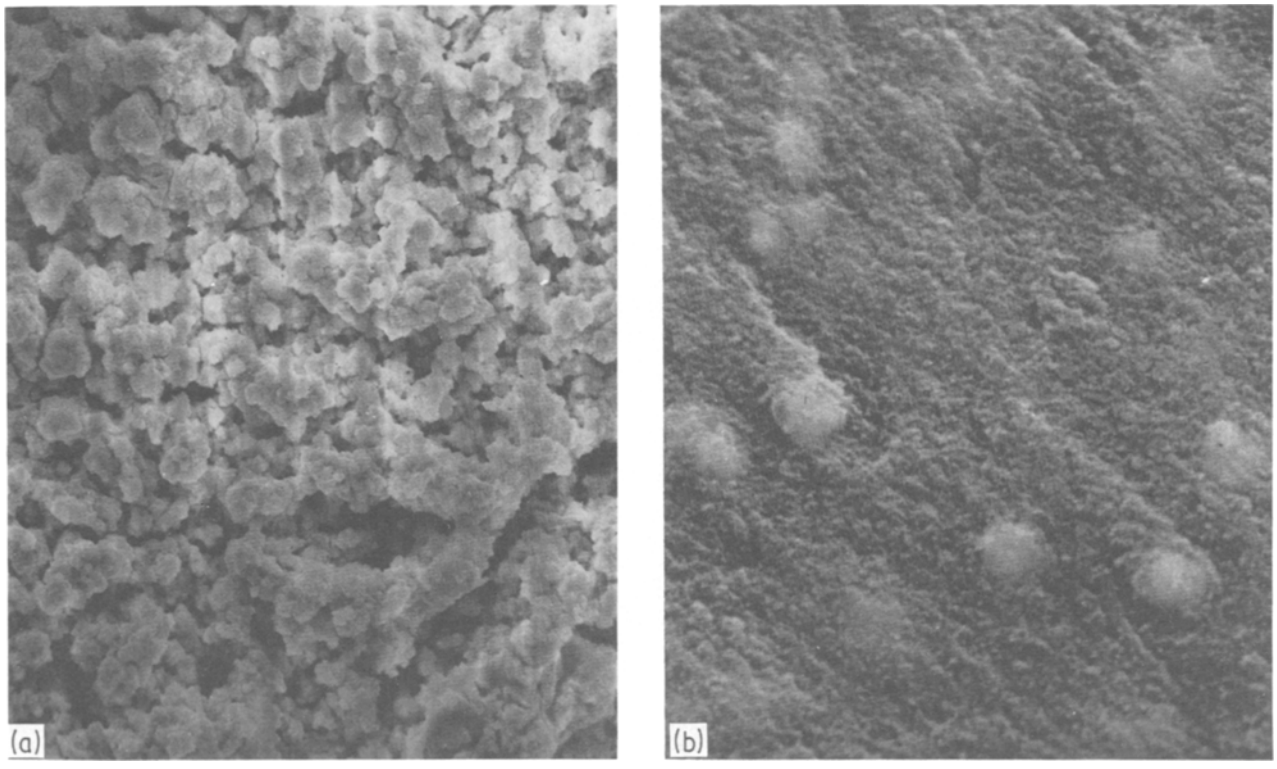
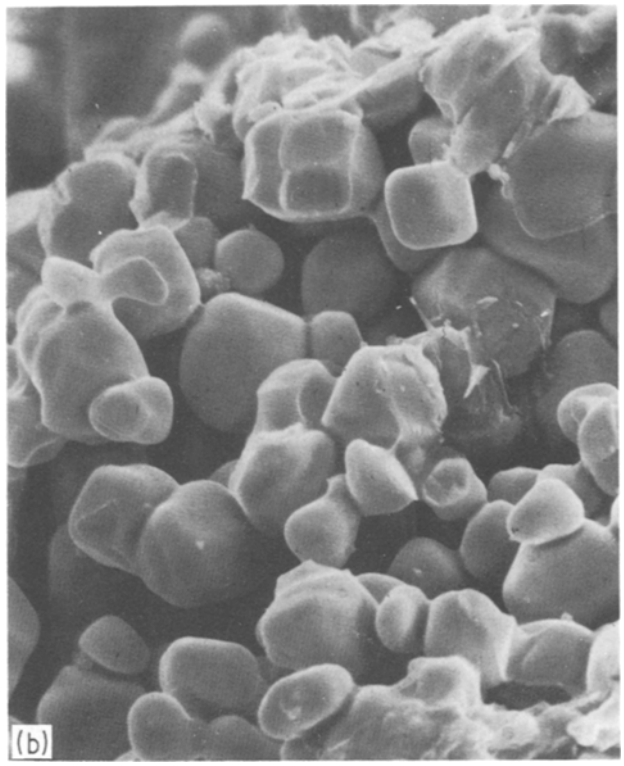


Figure 4 Scanning electron fractographs of phase separated and then leached samples: (a) leached sample 1 (no Al_2O_3 present) magnification 1.05×10^3, (b) leached sample 3 (marked Al_2O_3 content) magnification 5.6×10^3.



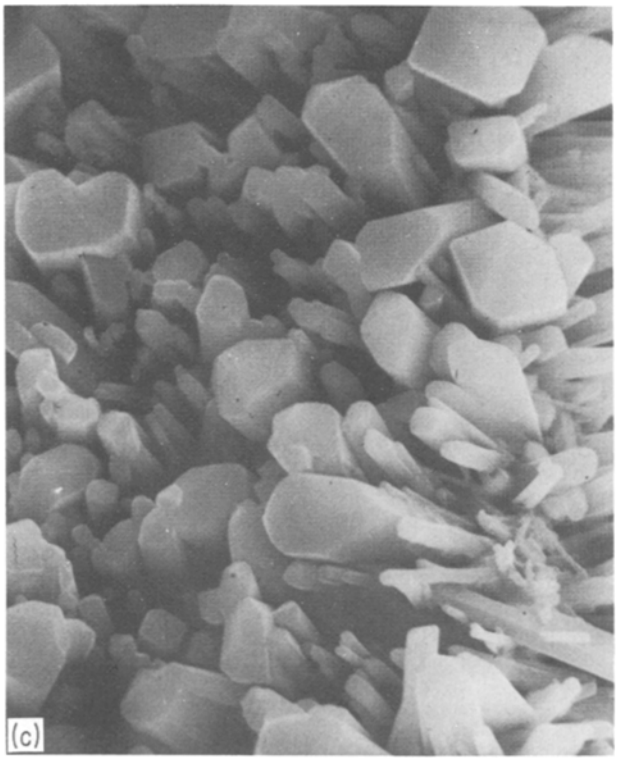


Figure 5 Scanning electron fractographs of phase separated and/or crystallized, leached and then fired samples: (a) HfO_2 rich sample 1 after firing at 1440° C for 30 min, magnification 2.1×10^3. (b) HfO_2 rich sample 1 after firing at 1500° C for 30 min, with changed crystal morphology, magnification 1.4×10^3. (c) HfO_2 rich Al_2O_3 containing sample 4 after firing at 1500° C for 30 min, magnification 2.1×10^3.

Fig. 1 indicate a narrow glass forming region for 5 to 20 wt % Na_2O content. Scanning electron microscopy studies revealed the presence of droplet-like micro-heterogeneities in clear glasses in which visually no cords, threads or striae were observed. In heat treated and leached samples melted in Pt/Rh crucibles crystalline monoclinic HfO_2 structures were found, whereas the melts containing additional Al_2O_3 were glassy in this state. After firing at 1500° C for 30 min both sets of samples showed the presence of monoclinic HfO_2. An additional phase $9Al_2O_3 \cdot 2B_2O_3$ reported by Uhlig [15] was detected for the alumina containing samples. The intended development of a HfO_2 rich skeleton having interconnected pores was achieved although a certain amount of B_2O_3 remained unleached. As in other reported materials [12] the presence of Al_2O_3 from crucible erosion induced the creation of materials with surface areas of interconnected pores far exceeding that found in HfO_2 skeletons containing no Al_2O_3.

Surface areas of up to $290\,m^2\,g^{-1}$ and mean pore radii between 1.2 and 15.2 nm are comparable with other systems [1–8, 10–13]. Because of the small amount of leached and/or fired material available in this study (approximately $0.5\,cm^3$ of each sample) the results of bulk density (within the powder granules) 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. 6 indicate a better heat resistance than that reported for porous SiO_2 glass.

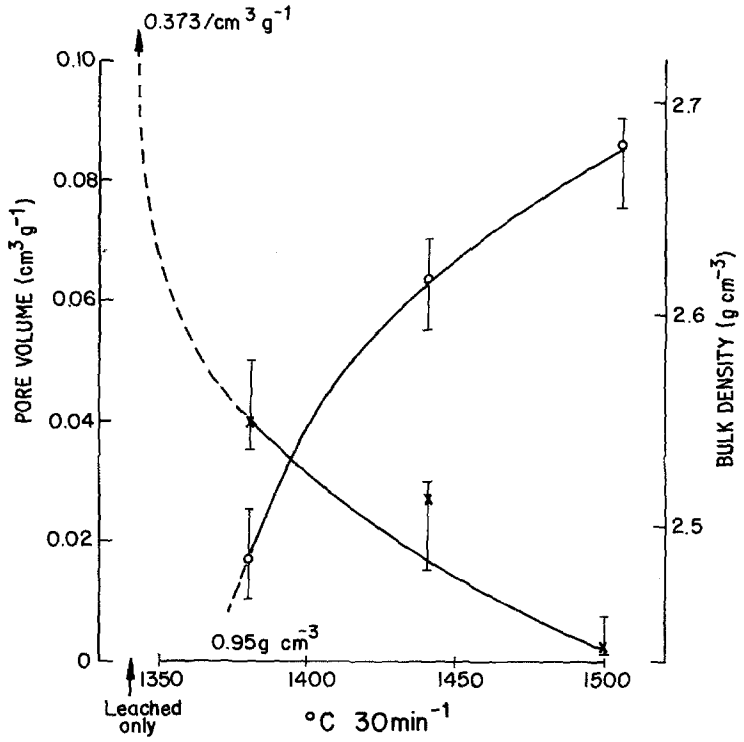


Figure 6 (x) Pore volume and (o) bulk density after firing steps for sample 1. (Previously heat treated and leached for 24 h. The results are qualitative.)

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