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A Ce–Hf oxide porous glass and glass–ceramic

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Substitution of the binary CeO_2–HfO_2 mixture for SiO_2 in the ternary Na_2O–SiO_2–B_2O_3 system resulted after melting in glassy and/or crystalline materials, depending on subsequent heat treatments. At least one of the phases present was water soluble. Quenching, heat treating, leaching and sintering altered the state of this ceramic. Crystalline forms found were cubic CeO_2, monoclinic $Ce(BO_2)_3$ and monoclinic HfO_2. Specific surface areas of the leached materials were from 120–233 $m^2\,g^{-1}$ with a calculated pore radii from 1.3–2.5 nm.

1. Introduction

A review of the literature (1938–1980) concerning porous silica glass produced by phase separation and leaching of Na_2O–SiO_2–B_2O_3 and Na_2O–SiO_2–P_2O_5 glasses has been given by Res *et al.* [1]. This 1982 paper also was the commencement of a comprehensive study intended to replace SiO_2 in the Na_2O–SiO_2–B_2O_3 glass by heat resistant and/or alkali resistant oxides. Into the Na_2O–B_2O_3 matrix either single oxides of Al, Ce, Ge, Hf, La, Nb, Nd, Sc, Ta, Th, Ti, Y and Zr, or their binary combinations were introduced. Portions of the melts were quenched or annealed. The annealed portion was phase separated by heat treatment and then leached, resulting in porous glassy or partially crystalline materials. These porous materials were then densified by sintering. Publications associated with this effort are listed by Richter *et al.* [2].

The purpose of the work presented here was to produce a binary CeO_2–HfO_2 rich, porous material. The single replacement of SiO_2 by either CeO_2 or HfO_2 in the Na_2O–SiO_2–B_2O_3 glass was reported by Res *et al.* [3, 4]. After the phase separating and leaching steps, porous materials resulted having specific surface areas between 25.5–119.3 $m^2\,g^{-1}$ for the CeO_2 single replacement and between 41.3–290 $m^2\,g^{-1}$ for the HfO_2 single replacement. Sintering temperatures of 1380–1500° C were higher than those for porous silica glass, e.g. 900–1200° C mentioned by Res *et al.* [5].

Replacement of SiO_2 by binary oxides, one of the binary being CeO_2, was reported by Res *et al.* [1] for a NaO_2–[CeO_2–Nb_2O_5]–B_2O_3 glass and by Res *et al.* [6] for a Na_2O–[CeO_2–TiO_2]–B_2O_3 glass. This study was extended by Bednarik *et al.* [7] who introduced into a Na_2O–B_2O_3 matrix a combination of CeO_2–Ta_2O_5 oxides. After phase separation and leaching porous materials resulted giving surface areas between 10–308 $m^2\,g^{-1}$. The presence of CeO_2 together with two to five other oxides selected from HfO_2, La_2O_3, ThO_2, Y_2O_3 and ZrO_2 introduced into a Na_2O–B_2O_3 matrix resulted, after phase separation and leaching, in porous glass-like materials as seen in [8, 9]. The structure produced remained glassy even after sintering at 1520° C for 30 min. The surface areas between 58–315 $m^2\,g^{-1}$ are comparable to those of porous silica and the alkali resistance of 5.12×10^{-3}–9.77×10^{-2} $mg\,dm^{-2}$ is superior to that of porous silica.

These properties along with the HfO_2 solubility of up to 35 mass % and the CeO_2 solubility of up to 40 mass % in the Na_2O–B_2O_3 matrix were the reasons for commencing the study of phase separation in the Na_2O–[CeO_2–HfO_2]–B_2O_3 glasses with the intention of developing heat resistant CeO_2–HfO_2 rich porous materials. This is supported by the high melting temperature of CeO_2 (~2600° C) and of HfO_2 (~2812° C).

2. Experimental procedure

2.1. Glass preparation

The glasses were prepared from the following laboratory grade chemicals: Na_2CO_3, H_3BO_3, CeO_2 and HfO_2. The six starting compositions are given in Table I. Batches of 50 g or 100 g were melted in Pt/Rh crucibles in an air atmosphere. The melting temperature was 1400° C for a duration of 4 h. A small portion of each melt was quenched and the remainder was cast in iron moulds lubricated with graphite. The cast samples were annealed from 600° C to room temperature overnight and then heat treated. The heat treatment consisted of additionally holding the annealed samples at 600° C for 2 h followed by cooling to room temperature overnight.

After the heat treatment step to produce phase separation and/or crystallization the water soluble phase was leached out in boiling distilled water for 72 h (96 h for sample No. 1). The samples were then rinsed in distilled water and dried at 120° C. The remaining porous skeleton was measured for void volume and surface area and also subjected to investigation by SEM, X-ray and wet chemical analysis. Different portions of leached sample No. 1 were sintered at different temperatures for 30 min in the 950–1400° C range. For each temperature a separate amount was used. These sintered samples were subjected to analysis by SEM and X-ray techniques and also tested for alkali resistance.

2.2. Analytical techniques

Pore size and surface areas were measured using a

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TABLE I Starting compositions and initial characterization for six glasses

From batch		CeO_2	HfO_2	B_2O_3	Na_2O	wpr† mpr‡	Void (Pore) volume ($ml\,g^{-1}$)	Bet ($m^2\,g^{-1}$)	Pore radii (nm)	Consistancy after leaching
No. 1*	Mass %	16.69	8.27	65.06	10.01	2/1	0.1408	216.18	1.3	Opaque, gray crumbled grains
	Mole %	7.87	3.18	75.84	13.11	2.5/1				
No. 2	Mass %	12.51	12.51	62.49	12.49	1/1	0.1126	151.16	1.5	Opaque, grayish brown crumbled grains
	Mole %	5.90	4.83	72.90	16.37	1.2/1				
No. 3	Mass %	8.34	16.65	60.01	15.00	1/2	0.1272	120.64	2.1	Lighter grayish brown crumbled grains
	Mole %	3.94	6.42	69.99	19.65	1/1.6				
No. 4	Mass %	20.01	9.99	60.00	10.00	2/1	0.2945	233.63	2.5	Sandy brown crumbled grain
	Mole %	9.80	4.00	72.61	13.59	2.5/1				
No. 5	Mass %	15.00	15.00	55.00	15.00	1/1	crumbled	207.63	-	Fine sandy slightly golden brown grain
	Mole %	7.32	5.99	66.36	20.33	1.2/1				
No. 6	Mass %	9.99	20.01	55.00	15.00	1/2	0.0964	140.99	1.4	(As No. 5) but richer colour coarser grains
	Mole %	4.90	8.02	66.66	20.42	1/1.6				

Cumulative melt weight 33.33 g.

*Batch No. 1: the only batch sintered and analysed further (see Table II).

†Weight % ratio of CeO_2/HfO_2.

‡Mole % ratio of CeO_2/HfO_2.

method relying on nitrogen absorption and desorption curves and on void volume determination [5]. SEM imaging was used to establish the qualitative degree of phase separation and the visual morphology of the porous materials. A wet chemical analysis indicated the compositional changes between the starting material and that of the material resulting after heat treatment and leaching. Alkali resistance was measured according to DIN 52 322 on a non-porous sample (the 1400° C sintered portion from batch No. 1) which had a surface area of $1.57\,cm^2$. Density of the sintered sample was determined by the Archimedes method with corrections for air bouyancy. The crystalline phases present and their transformation into glassy states as a function of sintering temperature was determined by powder X-ray diffraction (Rigaku D/Max III; 0.02°/step; 10 s/step; Si standard maximum error $\pm 0.025°$). The Joint Committee on Powder Diffraction Standards (JCPDS), was searched by the Johnson–Vand computer method and also by the usual visual method. Results are given in Table II.

TABLE II Crystalline analysis

Processing stage:	CeO_2 cubic No. 40593	$Ce(BO_2)_3$ monoclinic No. 230877	HfO_2 monoclinic No. 60318	unknown(s)
Quenched	No peaks: glassy			
Heat treated	X	0	0	0
Heat treated & leached	X	0	0	0
Sintered: 950° C	X	X	X	X
1050° C	0	0	X	0
1150° C	0	0	X	0
1250° C				
1350° C	No peaks: glassy			
1400° C				

X: Phase present.
0: Phase absent.

3. Results and discussion

The starting compositions of CeO_2: HfO_2 were 2 : 1, 1 : 1, 1 : 2 in mass ratio (2.5 : 1, 1.2 : 1, 1 : 1.6 in mole ratio) together with the variation of Na_2O–B_2O_3 additions are given in Table I. Also summarized in Table I are results of void (pore) volume and surface area measurements and pore radii calculations as well as the results of visual observation of the leached samples with respect to appearance and consistency. The quenched samples were all glassy. As the CeO_2 content increased, the quenched samples changed from light orange-brown to dark orange-brown. Sample No. 1 from Table I was selected for a larger melt and further processing and evaluation because of its relative high porosity compared to sample No. 4, but lesser content of the expensive HfO_2.

Detection of microphase segregation in glass by electron microscopy has been reported in some detail by Vogel [10]. SEM methods were used to observe the structures of the materials after different stages of

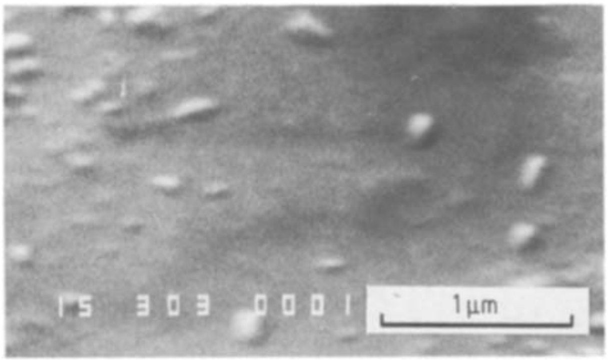

Figure 1 Scanning electron fractograph of the as quenched sample No. 1 showing droplet-like micro-heterogeneities.

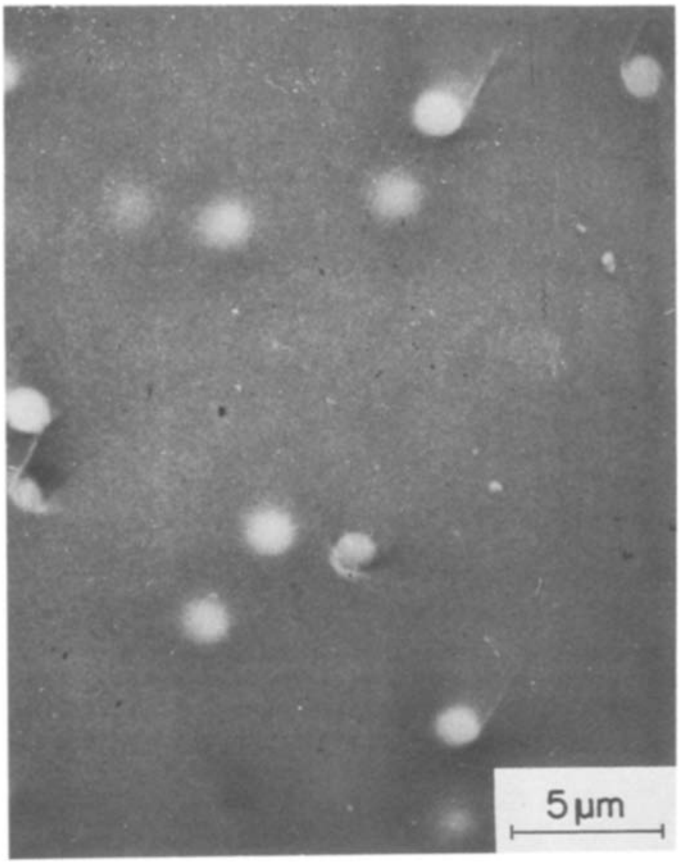

Figure 2 After a heat treatment the droplet-like micro-heterogeneities of sample No. 1 coarsened. For crystalline data see Table II.

treatment. The micrograph in Fig. 1 shows the presence of droplet-like micro-heterogeneities contained in the quenched portion of sample No. 1. A magnification of 30 000 was required to observe these droplets. Table II shows that these microphases are still in the glassy state. After a one stage heat treatment this microphase became more pronounced as the necessary magnification to see these droplets was only 3000 (Fig. 2). This was also confirmed by X-ray diffraction (XRD) (see Table II) which indicates the starting of crystallization. This heat treated sample was then leached and the micrograph in Fig. 3 shows its fractured surface. There can be seen a crystalline habit which was identified by powder X-ray analysis to be

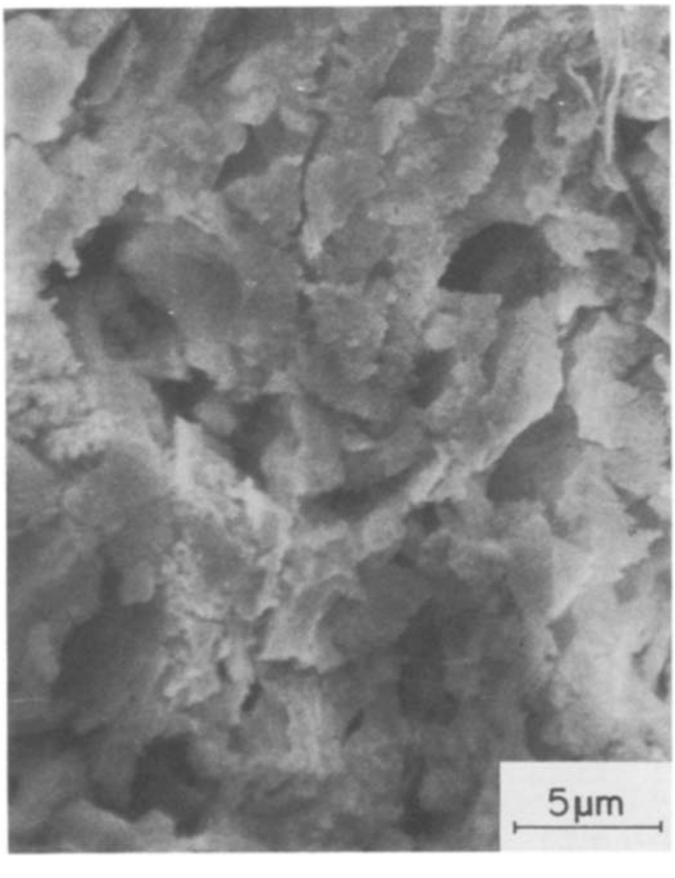

Figure 3 After leaching the crystalline nature of sample 1 seen in Fig. 2 becomes more pronounced.

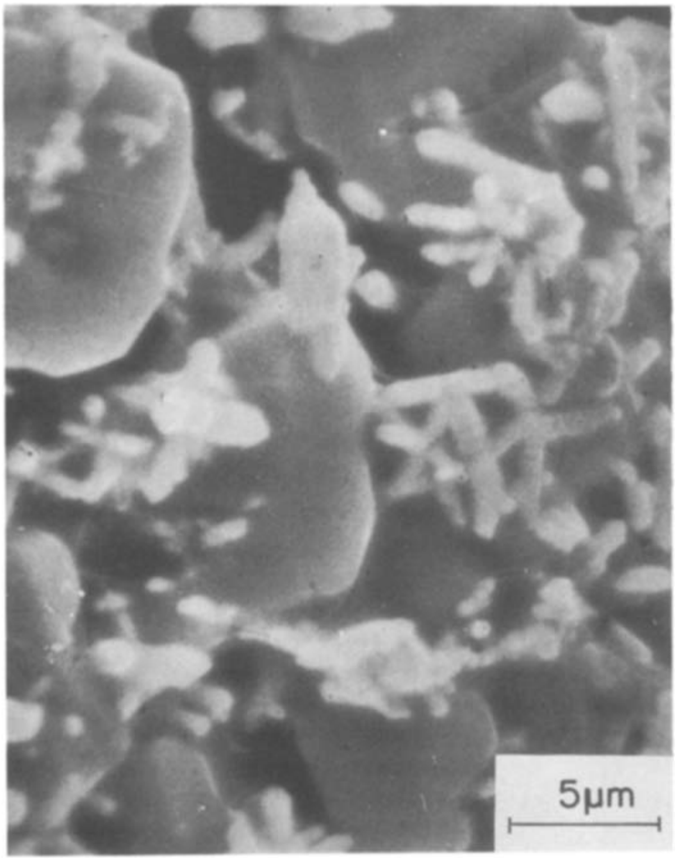

Figure 4 Scanning electron micrograph showing varied crystalline habits of sample No. 1 sintered at 950° C for 30 min.

cubic CeO_2 (JCPDF: 40593). This phase of the heat treated and leached sample No. 1 was more pronounced than that of its only heat treated counterpart. Leaching does not promote ordering of the present structure (phase) but removes only the soluble glassy Na_2O–B_2O_3 phase. Therefore the ratio of Na_2O–B_2O_3: CeO_2 in the heat treated phase changes in favour of CeO_2 after leaching. This resulted in a decreased X-ray absorption and an increased signal/noise ratio of the CeO_2 phase. At this treatment stage no crystalline form of HfO_2 was detected.

The next step was then to sinter a portion of the leached sample at 950° C for 30 min. (Other portions were sintered at higher temperatures also for 30 min). The 950° C sintering promoted strong crystallization as indicated in the micrograph in Fig. 4. The different habits of the particles are attributed to the different crystalline phases as the powder X-ray diffraction results in Table II indicate. The main crystalline phases present were cubic CeO_2, monoclinic $Ce(BO_2)_3$ and monoclinic HfO_2. Besides these there were two strong peaks and several minor peaks that were not accounted for. CeB_4 fit the strongest of these two peaks and it also fit other peaks but all significant peaks from the JCPDS on CeB_4 were not accounted for. The presence of the crystalline phase CeB_4 should be excluded with caution. The remaining peaks corresponded mostly with sodium–boron–oxygen compounds but not in a convincing manner. Since the JCPDS was searched both by the Johnson–Vand computer method and by the usual visual method with no definitive match, the remaining peaks belong to a crystalline phase not listed in the JCPDS and should be subjected to further studies.

At the sintering temperature of 1050° C the phases containing cerium present at the 950° C sintering were transformed to an amorphous state and all peaks mentioned above which were not accounted for disappeared. However, the monoclinic HfO_2 phase remained. At a sintering temperature of 1150° C the monoclinic HFO_2 still remained but with weaker and fewer peaks. Sintering for 30 min above 1150° C transformed all crystalline phases into a transparent glass as represented by the micrograph in Fig. 5. Here are visible cracks common to a glassy state similar to that reported in [9]. XRD results in Table II also indicate no detectable crystalline phases in samples sintered above 1150° C.

Specific gravity measurements showed an increase of density from 2.76 g ml^{-1} for a sample of No. 1 sintered at 1150° C for 30 min to a density of 3.68 g ml^{-1} for a sample of No. 1 sintered at 1400° C also for 30 min. Another sample from batch No. 1 sintered at 1400° C for 30 min had an alkaline resistance of 509 mg dm^{-2} which is in the class 3 (strongly soluble in an alkaline medium). Fig. 5 shows the glassy morphology of this sample indicating that the alkaline medium primarily affected the surface. Void (pore) volume together with bulk density values are shown graphically in Fig. 6 confirming a high densification state or no porosity above 1250° C. Comparing this

TABLE III Wet chemical analysis

Chemical Composition mass %	CeO_2	HfO_2	B_2O_3	Na_2O
Before heat treatment	16.69	8.26	65.05	10.01
After heat treatment	46.65	23.50	27.67	1.82

Figure 5 Scanning electron micrograph showing the glassy morphology of sample No. 1 sintered at 1400° C for 30 min.

with the identical sintering conditions in Fig. 6 of Hart *et al.* [11] it can be seen that Na_2O–[ZrO_2]–B_2O_3 has a higher heat resistance i.e. the asymptoic behaviour in pore volume occurs at higher temperatures.

In Table III the chemical composition in mass % of sample No. 1 as calculated from the batch is compared with its chemical composition after heat treatment and leaching. The CeO_2 and HfO_2 increased in mass % by almost a factor of 3 while B_2O_3 decreased by almost a half. The remaining presence of a small amount of Na_2O indicates that leaching for 96 h was either not complete and/or that Na_2O was chemically bonded into unidentified compounds as mentioned in the evaluation of the X-ray analysis.

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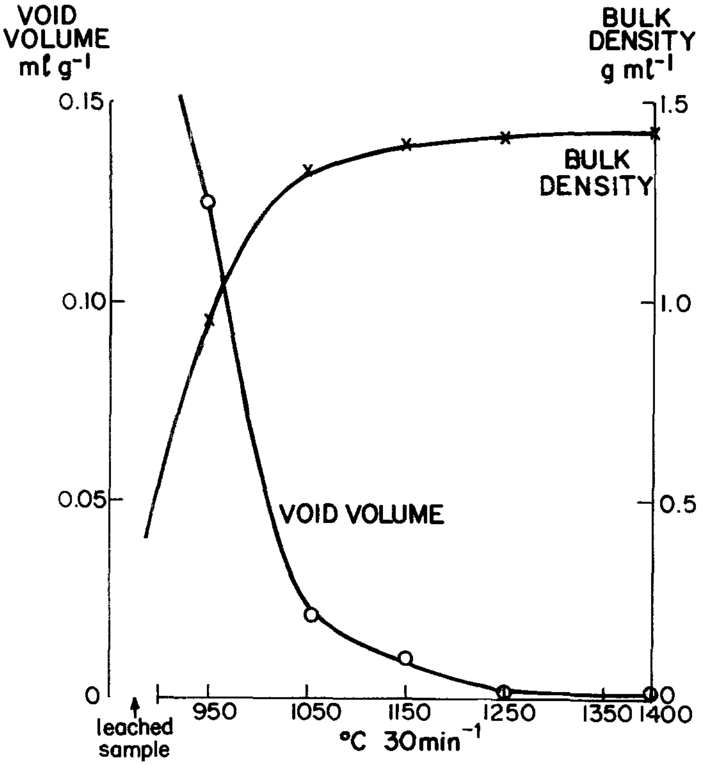

Figure 6 Pore volume and bulk density after sintering steps of 30 min on sample 1 heat treated and leached. (O) Pore (void) volume. (x) Bulk density.

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