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Transformation of Na_2O–CeO_2–B_2O_3 glass into a material with interconnected pores

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Substitution of SiO_2 with CeO_2 in the ternary sodium borosilicate system was found to produce phase-separable glasses. Heat treatment of these glasses resulted in separation into two different phases. The one phase enriched in sodium borate was then leached out leaving a CeO_2-rich framework. The structure of the leached material was crystalline (Pt/Rh crucible melt) which changed to a rather net-like appearance if Al_2O_3 resulting from erosion of alumina crucibles was added. B_2O_3 remained partially in the insoluble CeO_2-skeleton. X-ray diffraction analysis of leached material proved the presence of crystalline cubic CeO_2 and cerium borate (metaborate of the aragonite type) in Pt/Rh crucible melts, whereas cubic CeO_2, $2Al_2O_3 \cdot B_2O_3$ and traces of sodium borate were detected in Al_2O_3 containing melts. The specific surface areas of the leached materials ranged between 25 and $120\,m^2\,g^{-1}$ while the main radii of interconnected pores were calculated to be between 0.5 and 17 nm. A sintering temperature of about 1500° C was estimated from void volume and bulk density measurements.

1. Introduction

The development of porous silica glasses during the last 40 years has been reviewed by Res *et al.* [1]. Suitable heat treatment in sodium borosilicate glasses induces separation into two phases, one almost pure in SiO_2 and the other rich in Na_2O and B_2O_3. The sodium borate phase may be leached out leaving a porous SiO_2 skeleton. During the period of these developments different compositional changes have been reported. The most important were the replacement of Na_2O by K_2O, Li_2O or alkaline earth oxides, the substitution of B_2O_3 with P_2O_5 and the total or partial replacement of SiO_2 by GeO_2 and Al_2O_3 or $AlPO_4$. Minor components in the preparation of porous silica glasses were reported to be oxides of zirconium, tungsten, iron, cobalt, nickel, vanadium and molybdenum. Recent work investigated the introduction of intermediate or modifying oxides with good alkali and/or heat resistance into a NaO–Na_2O–B_2O_3 matrix with total replacement of SiO_2. Two or more oxides of the elements aluminium, cerium, hafnium, lanthanum, niobium, tantalum, thorium, titanium, yttrium and zirconium were introduced into a Na_2O–B_2O_3 matrix and melted. The resulting glasses were phase separated by a suitable heat treatment, leached and sintered. This led to the development of porous glass ceramics or glass-like materials with higher alkali and/or heat resistance [1–8]. The presence of Al_2O_3 in the melts, first introduced unintentionally as crucible contamination, was found to influence porosity and pore size; further experimental studies have resulted from observations of the presence of B_2O_3 in the porous skeleton of some of the new materials. Following on Vogel's [9] work on phase separation in binary B_2O_3 or SiO_2 systems an extensive programme has been initiated and the experimental work commenced, 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 containing hexagonal $ScBO_3$ and $2Al_2O_3 \cdot B_2O_3$, respectively, while Res *et al.* [12] reported on the development of a porous β-Ga_2O_3 structure.

The aim of the present work was to investigate sodium borate glasses containing CeO_2 as a third component. These glasses were expected to leave a cerium oxide rich porous skeleton after heat treatment and subsequent leaching. Selected batches were also melted in Al_2O_3 crucibles in order to study the influence of Al_2O_3 on these glasses.

2. Experimental details

2.1. Glass preparation

The glasses were prepared from chemically pure reagents H_3BO_3, Na_2CO_3 and CeO_2 (all from E. Merck A.G., Darmstadt, West Germany). Batches of 50 to 100 g were melted in Pt/Rh crucibles in air at a temperature of 1400° C. To investigate the effect of crucible erosion on the properties of the melt, one composition (sample 4 in Table I) was contained in a recrystallized Al_2O_3 crucible. The melting times were 3 to 4 h. Samples of the glasses were then cast in iron moulds, annealed and phase separated by heat treatment. The heat-treatment programmes applied to samples melted in Pt/Rh crucibles are included in Table I. The glasses melted in Al_2O_3 crucible were soaked for 20 h at 650° C, followed by a treatment of 8 h at 700° C. The phase-separated samples were leached in boiling distilled water for 24 to 72 h depending on the starting composition and the type of crucible used. Leached samples were then sintered at 1380, 1400 or 1500° C for 30 min.

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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 times (h)	Appearance of as-leached materials	Void volume (ml g^{-1})	BET surface area ($m^2 g^{-1}$)	Mean pore radius (nm)
	Na_2O	B_2O_3	CeO_2							
1	20.00	60.00	20.00	Pt/Rh	500 : 2* 550 : 2 600 : 2	7	Slightly greenish grey	0.1258	46.95	5.3
2	6.56	47.90	45.54	Pt/Rh	700 : 3	24	Slightly greenish grey	0.2659	57.8	9.2
3	10.50	54.50	35.00	Pt/Rh	550 : 3* 600 : 3	72	Slightly greenish grey	0.217	25.50	17.0
4	12.00	63.00	25.00	Al_2O_3	650 : 20* 700 : 8	72	Very slightly brownish and yellowish green	0.02989	119.3	0.5

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

2.2. Characterization of the glasses

The techniques used in the present work for the characterization of the glasses and glass-like materials produced include BET nitrogen adsorption and desorption [8], pore volume measurements [1], scanning electron microscopy [2], X-ray diffraction analysis [5], qualitative bulk density measurements [10] and sintering experiments [12]. Chemical analysis was performed by means of atomic absorption (AA), inductively coupled plasma (ICP) and X-ray fluorescence (XRF) techniques.

3. Results

The starting compositions of the glasses including the glass region and the region of "other formations" are shown in Fig. 1. The latter include opaque and crystallized samples as well as phase separation which occurred in the crucible during melting. Chemical and physical data of four selected samples are given in Table I. These include calculated composition, crucible type, heat-treatment programme and appearance of as-leached samples as well as pore and surface area characteristics. The composition of the melts calculated from batch in Fig. 1 covered a region of 5 to 20 wt % Na_2O, 40 to 90 wt % B_2O_3 and 5 to 50 wt % CeO_2. The general appearance of the samples denoted 1, 2, 3 and 4 prior to heat treatment, was orange to very dark orange in reflected light changing to slightly greyish appearance after heat treatment and/or leaching. X-ray fluorescence analyses showed that melts prepared in alumina crucibles contained additionally about 30% Al_2O_3.

Some of the as-quenched $Na_2O–B_2O_3–CeO_2$ glasses (Pt/Rh crucible melt) showed an approximately 0.2 mm thick crystallized surface layer while the rest of the samples were glassy. The general appearance of glasses containing additional Al_2O_3 was transparent. The microstructure of these glasses is shown in the

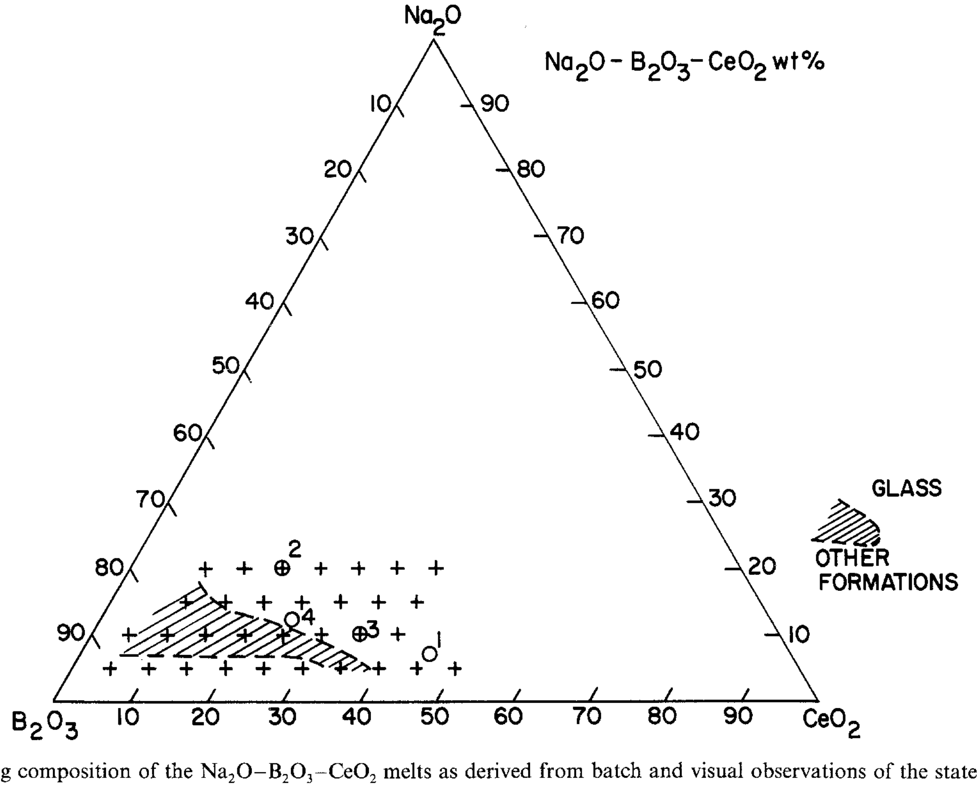

Figure 1 Starting composition of the $Na_2O–B_2O_3–CeO_2$ melts as derived from batch and visual observations of the state of the melt.

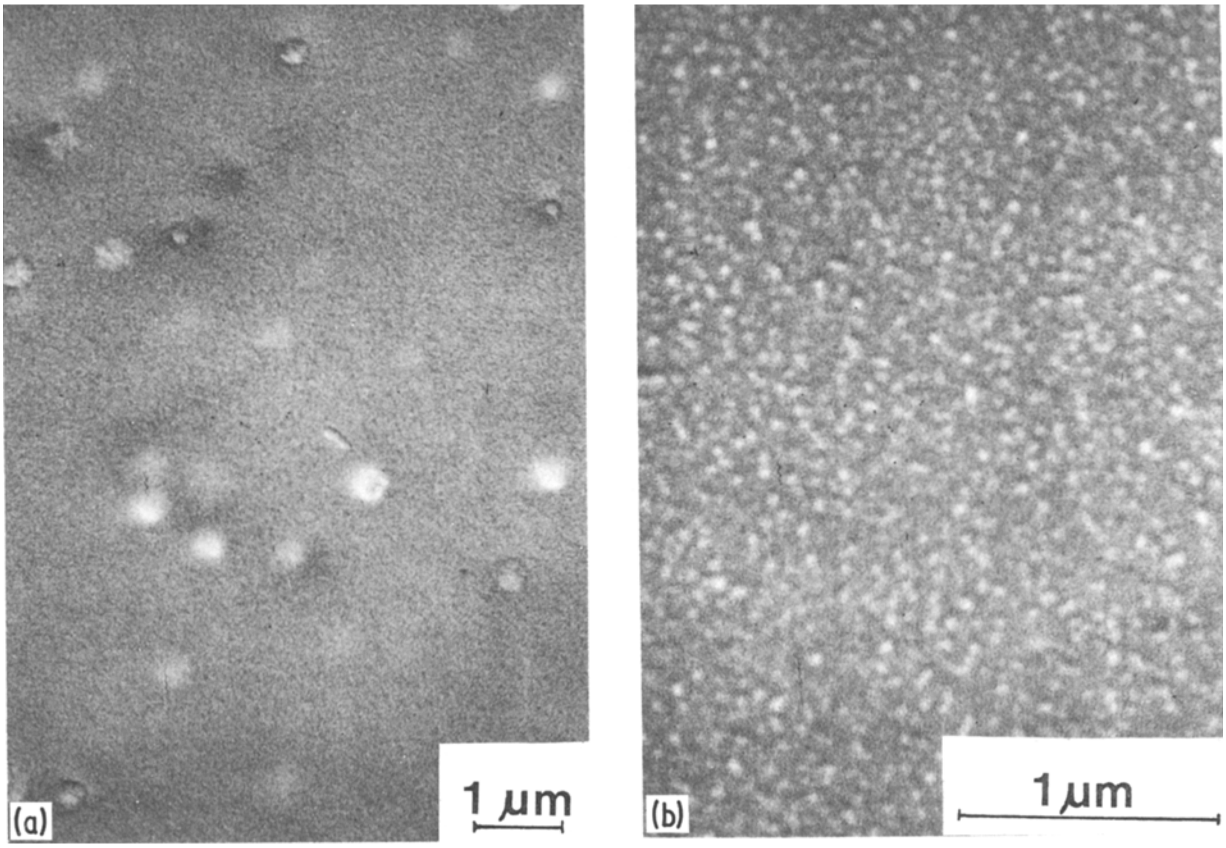

Figure 2 Droplet-like microheterogeneities present in as-quenched samples — scanning electron micrographs. (a) Pt/Rh crucible melt, sample 3; (b) Al_2O_3 crucible melt, sample 4.

secondary electron micrographs of polished cross-sections displayed in Fig. 2. Droplet-like microheterogeneities can be seen which are similar to that reported earlier [1, 6–8, 10]. The microheterogeneities present in glass 4 (Fig. 2b), which contained additional Al_2O_3 were much smaller but more abundant than those detected in glass 3 (Fig. 2a).

A multi-stage heat treatment was carried out on

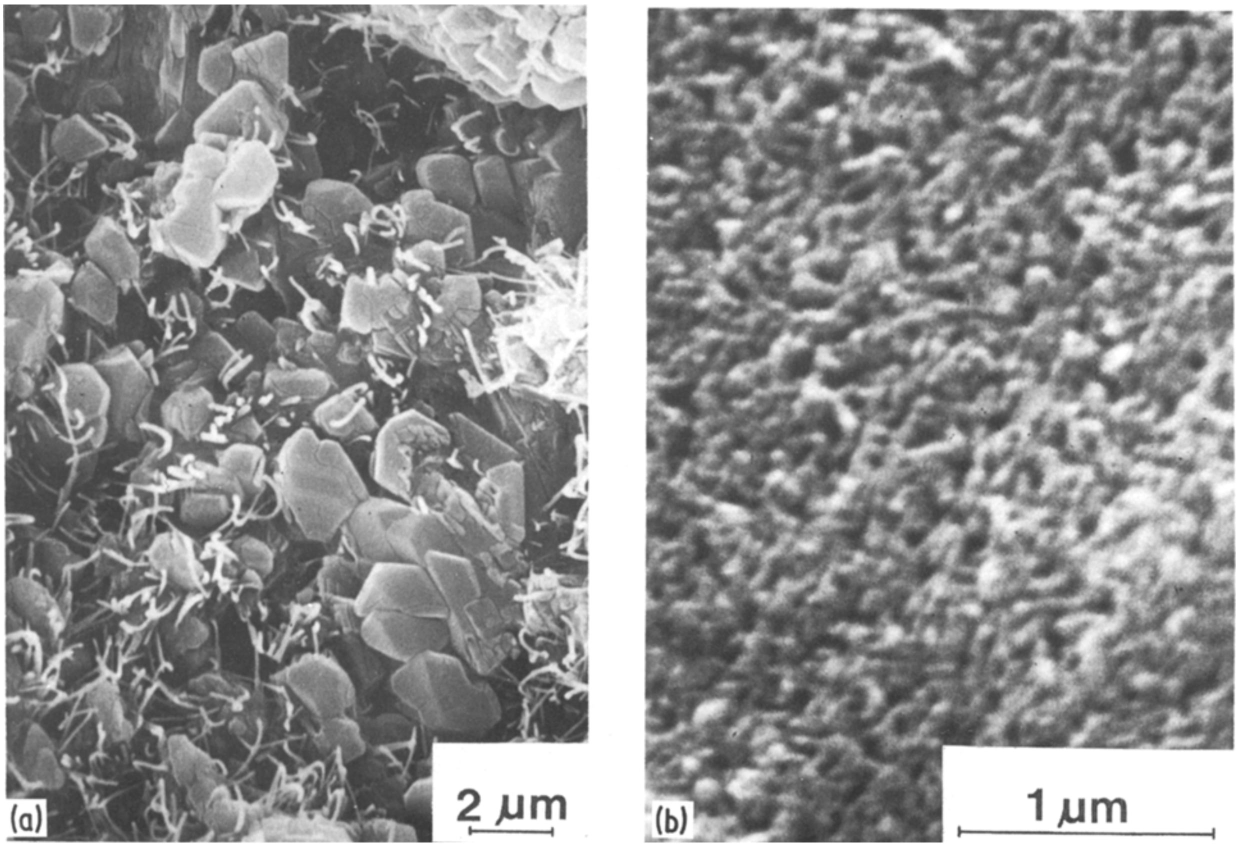

Figure 3 Habit modification of heat-treated (phase-separated) samples — scanning electron micrographs. (a) Pt/Rh crucible melt, sample 3; (b) Al_2O_3 crucible melt, sample 4.

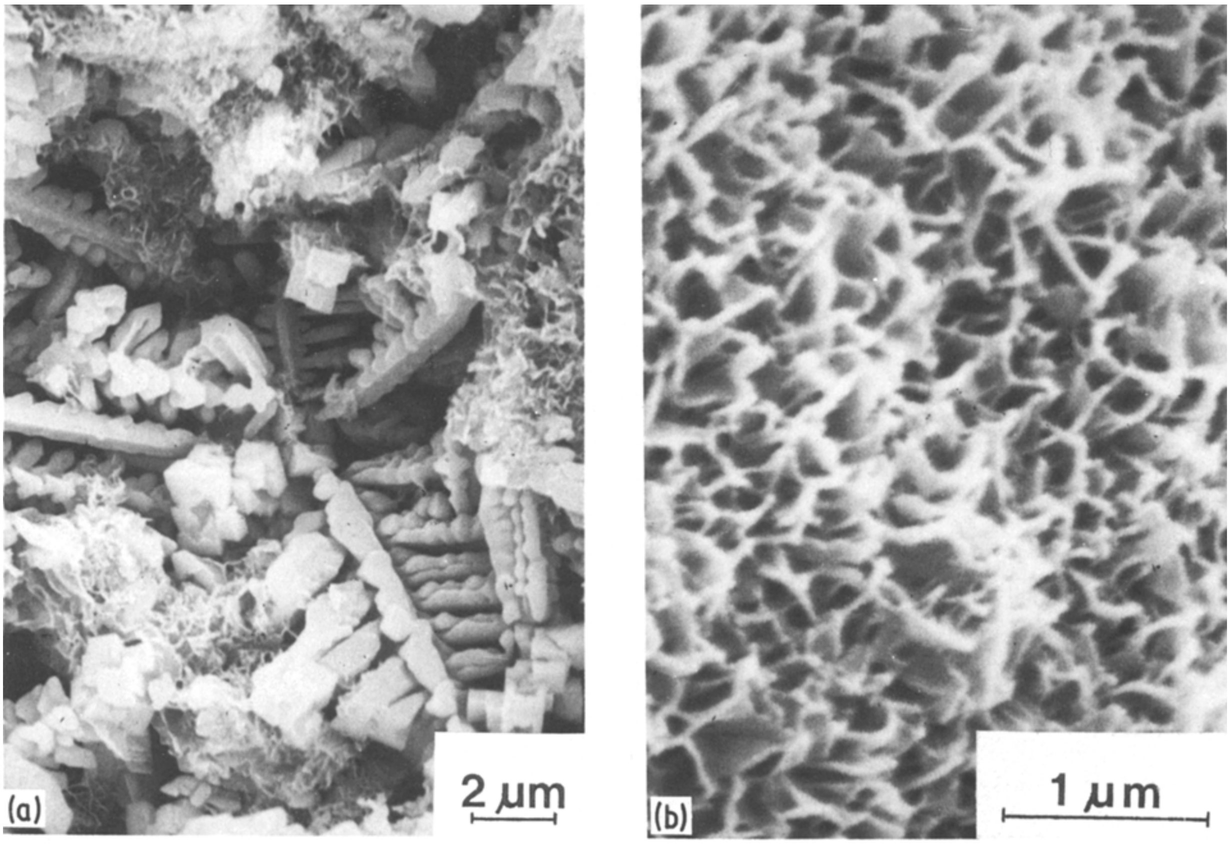

Figure 4 Appearance of heat-treated and then leached samples — scanning electron micrographs. (a) Pt/Rh crucible melt, sample 3; (b) Al_2O_3 crucible melt, sample 4.

these glasses and the resulting structures are shown in Fig. 3. The typical crystalline structure of the Pt/Rh crucible melts (sample 3) is evident from Fig. 3a. Fig. 3b shows the phase separation in an Al_2O_3 crucible melt (sample 4) which has a rather amorphous appearance and is similar to that earlier reported [7, 8].

The phase-separated samples 3 and 4 were leached in boiling distilled water and the resulting structures were then studied in an SEM. A clearly crystalline structure was observed for sample 3 as is seen in Fig. 4a whereas sample 4 showed a net-like morphology as illustrated in Fig. 4b. Similar effects of Al_2O_3 on the

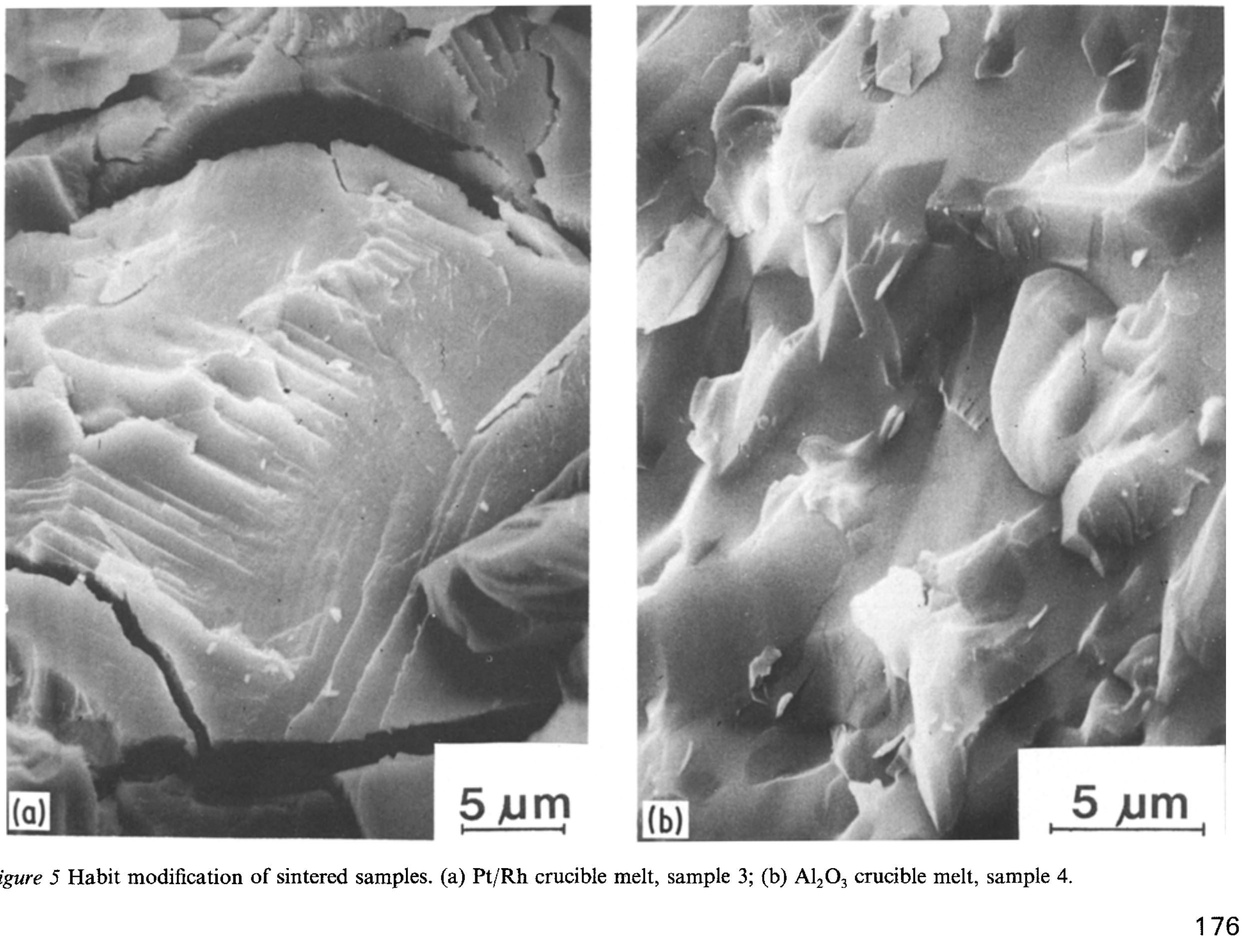

Figure 5 Habit modification of sintered samples. (a) Pt/Rh crucible melt, sample 3; (b) Al_2O_3 crucible melt, sample 4.

TABLE II Chemical composition of as-quenched and then leached sample from $Na_2O-B_2O_3-CeO_2$ glass

State of sample	Na_2O (wt %)	B_2O_3 (wt %)	Ce_2O_3 (wt %)
Sample no. 2 as-quenched (calculated from batch)	6.56	47.90	45.54
Sample no. 2 leached	—	31.7	69.1

microstructure (alumina crucible melts) have been observed previously [2–4]. Additions of Al_2O_3 to the glass composition decrease the linear crystallization speed [13]. The leached samples 3 and 4 were subsequently sintered at 1500° C for 30 min. The appearance of the sintered material shown in Fig. 5 does not show typical crystalline structures as were observed on other materials [1–3, 5, 10–12] but is closer to the habit-forming modification of sintered materials [7, 8].

A sample from a Pt/Rh crucible melt has been analysed by means of atomic absorption (AA) and inductively coupled plasma (ICP) spectroscopic techniques and the results are given in Table II. It can be seen from this table that Na_2O was totally leached out while a considerable amount of B_2O_3 remained in the porous skeleton.

Powder X-ray diffraction studies were conducted on as-quenched, annealed, phase separated, leached and sintered samples, to study the degree of crystallization in the various stages of sample preparation. The system employed was a Phillips PW 1010 diffractometer using nickel-filtered Cu$K\alpha$ radiation as primary source.

Samples in the as-quenched condition did not show any significant diffraction peaks, but simply the pattern which is characteristic for glasses. The annealed, heat-treated, leached and sintered materials, however, produced diffraction patterns containing significant peaks. The crystalline phases identified are given in Table III.

In the $Na_2O-B_2O_3-CeO_2$ glasses, the main crystalline phases identified in the annealed, heat-treated and leached conditions were cubic CeO_2, monoclinic $Ce(BO_2)_3$ and smaller amounts of $CeBO_3$ of the aragonite type, whereas only cubic CeO_2 could be identified in the sintered material. Somewhat different phases were identified in the $Na_2O-B_2O_3-CeO_2-Al_2O_3$ glass. In the annealed material a sodium borate ($Na_2O \cdot 4B_2O_3$) and an aluminium borate ($2Al_2O_3 \cdot B_2O_3$ plus $9Al_2O_3 \cdot 2B_2O_3$) phase were just detectable. In the heat-treated, leached and sintered materials, however, various crystalline phases were clearly identified: cubic CeO_2, sodium borate ($Na_2O \cdot 4B_2O_3$ plus $Na_2O \cdot 3B_2O_3$) and aluminium borate ($2Al_2O_3 \cdot B_2O_3$ plus $9Al_2O_3 \cdot 2B_2O_3$) in the annealed material; cubic CeO_2, sodium borate ($Na_2O \cdot 4B_2O_3$ plus $Na_2O \cdot 3B_2O_3$) and only one aluminium borate phase ($2Al_2O_3 \cdot B_2O_3$) in the leached material; and surprisingly only aluminium borate ($2Al_2O_3 \cdot B_2O_3$) in the sintered condition.

Specimens from leached sample no. 3 were fired for 30 min at 1380, 1440 or 1500° C for 30 min to study the sintering behaviour. After the sintering steps 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. 6.

4. Discussion

The $Na_2O-B_2O_3-CeO_2$ starting compositions for the region of 5 to 20 wt % Na_2O (see Fig. 1) indicate a relatively narrow glass forming region. A series of phase-separable glasses was prepared that showed leachability similar to that found in the ternary sodium-borosilicate system [1].

Scanning electron microscopy studies of the as-quenched sodium borate cerium oxide glasses, having a clear appearance, showed the presence of droplet-like microheterogeneities. These heterogeneities, which developed in both Pt/Rh and Al_2O_3 crucible melts, give evidence of the onset of phase separation during melting and quenching. The mechanism of this phase separation seemed to be significantly influenced by the presence of Al_2O_3. The microstructure in as-quenched glasses melted in Pt/Rh crucibles (samples 1, 2 and 3) consists basically of randomly distributed spherical particles (see Fig. 2a). This morphology is typical of nucleation and growth [14] leading to crystallization in the heat-treated glasses (see Fig. 3a).

The as-quenched glass containing in addition about 30 wt % Al_2O_3 shows second phase particles with a tendency for connectivity (see Fig. 2b) resulting in a morphology which may resemble that of the early stages of spinodal decomposition [14]. This possible explanation is supported by the structure observed in a heat-treated glass sample (see Fig. 3b). The morphology developed in the present material is similar to that observed in heat-treated $Na_2O-B_2O_3-GeO_2-$

TABLE III Crystalline phase identified in the investigated glasses and glass-ceramics

Structures of the material				
Glass type	Annealed	Heat treated	Leached	Sintered
$Na_2O-B_2O_3-CeO_2$ (Pt/Rh crucible melt)	Cubic CeO_2; orthorhombic $CeBO_3$ of aragonite type	Cubic CeO_2; Monoclinic $Ce(BO_2)_3$; aragonite type $CeBO_3$	Cubic CeO_2 $Ce(BO_2)_3$ $CeBO_3$	Cubic CeO_2
$Na_2O-B_2O_3-CeO_2-Al_2O_3$ (Al_2O_3 crucible melt)	$Na_2O \cdot 4B_2O_3$ $2Al_2O_3 \cdot B_2O_3$ plus $9Al_2O_3 \cdot 2B_2O_3$	Cubic CeO_2; $Na_2O \cdot 4B_2O_3$ plus $Na_2O \cdot 3B_2O_3$ $2Al_2O_3-B_2O_3$ plus $9Al_2O_3-2B_2O_3$	Cubic CeO_2 $Na_2O \cdot 4B_2O_3$ plus $Na_2O \cdot 3B_2O_3$ $2Al_2O_3-B_2O_3$	$2Al_2O_3 \cdot B_2O_3$

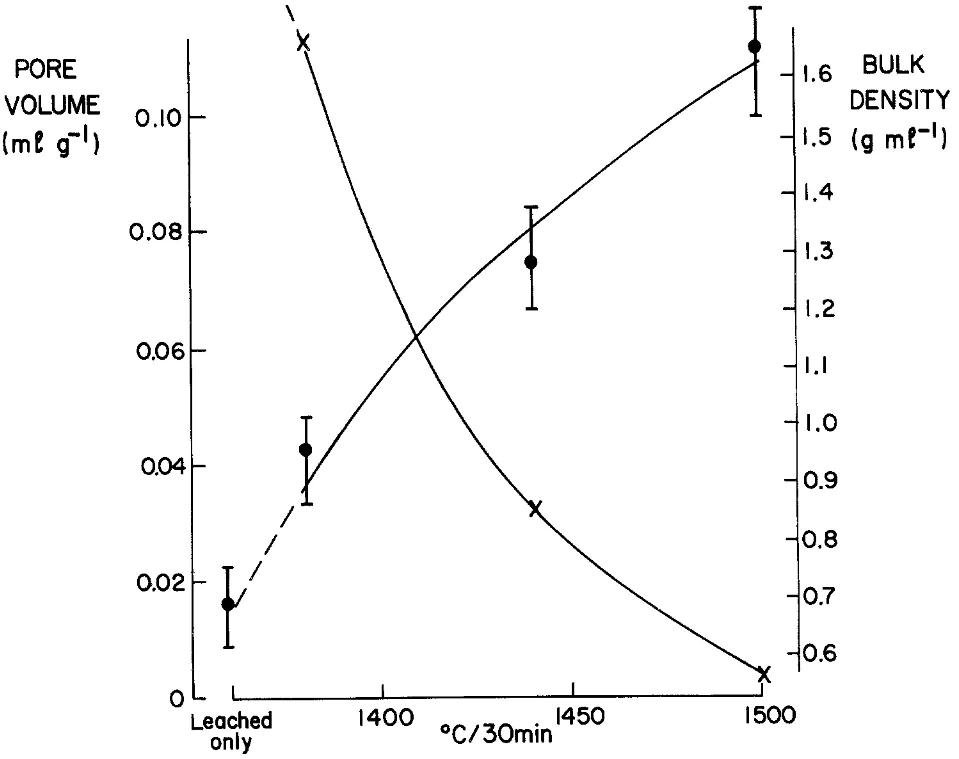

Figure 6 Pore volume (ml g^{-1}) and bulk density (g ml^{-1}) after sintering steps for sample 3 (previously heat treated and leached for 96 h). Bulk density is qualitative. ×, pore volume; ●, bulk density.

SiO_2 glasses [15] which has been explained in terms of spinodal decomposition. It must, however, be mentioned that the morphology of the microstructure above serves only as an indicator for the mechanism of phase separation and should not be taken as unambiguous proof [16].

The difference in the microstructural appearance imposed by the presence of Al_2O_3 is even more pronounced in leached samples of the heat-treated glasses (see Fig. 4). The leached Na_2O–B_2O_3–CeO_2 glasses developed a rather regular, crystalline structure (see Fig. 4a) in contrast to the Al_2O_3 containing sample which produced a net-like morphology (see Fig. 4b).

The morphology of sintered samples (see Fig. 5) was found to be similar for both types of glasses investigated and the structure observed was comparable to the habit-forming modification of sintered materials reported earlier [7, 8].

The X-ray diffraction studies gave sufficient evidence of the glassy state in the as-quenched glasses (see for instance Fig. 2), whereas the diffraction pattern recorded from the annealed samples showed very weak and broad peaks above the background level indicating the onset of crystallization (see Table III). Cubic CeO_2, which was used as basic raw material, and orthorhombic $CeBO_3$ of the aragonite type were detected in the Na_2O–B_2O_3–CeO_2 glass. The crystalline phase which could be identified in the Na_2O–B_2O_3–CeO_2–Al_2O_3 glass were $Na_2O \cdot 4B_2O_3$ and aluminium borate, probably consisting of $2Al_2O_3 \cdot B_2O_3$ plus $9Al_2O_3 \cdot 2B_2O_3$ as described by Scholze [17].

Significant diffraction peaks were produced from the heat-treated materials. The main crystalline phases in the Na_2O–B_2O_3–CeO_2 glasses were cubic CeO_2 and monoclinic $Ce(BO_2)_3$ as well as a smaller amount of $CeBO_3$ of the aragonite type. These results are in agreement with Weidelt [18] who described the formation of crystalline $CeBO_3$ of the aragonite type in cerium oxide–borate melts. The presence of the unreacted CeO_2 could be due to the non-stoichiometric conditions in the present Na_2O–B_2O–CeO_2 system as compared to the binary system CeO_2–B_2O_3 studied by Weidelt [18]. The addition of Al_2O_3 (Al_2O_3 crucible melt) resulted in the formation of two crystalline phases not found in the Na_2O–B_2O_3–CeO_2 glass, i.e. sodium borate and aluminium borate ($2Al_2O_3 \cdot B_2O_3$ plus $9Al_2O_3 \cdot 2B_2O_3$), which had already been detected in the annealed Na_2O–B_2O_3–CeO_2–Al_2O_3 glass. The sodium borate phase, although not unambiguously identified in the present diffraction pattern, seemed to consist of $Na_2O \cdot 4B_2O_3$ plus $Na_2O \cdot 3B_2O_3$ as described by Milman and Bouaziz [19] and Morey and Merwin [20].

The crystalline phases found in leached samples of the investigated glasses were very similar to those identified in the heat-treated materials. The main crystalline phases in the Pt/Rh crucible melts were CeO_2 and cerium metaborate and in the Al_2O_3 crucible melt cubic CeO_2, sodium borate ($Na_2O \cdot 4B_2O_3$ plus $Na_2O \cdot 3B_2O_3$) and a small amount of $2Al_2O_3 \cdot B_2O_3$ were found. It has further been found that, as compared to the heat-treated material, the content in sodium borate decreased considerably as a result of leaching. It should be noted that crystalline cerium borate could not be found in any of the treated Al_2O_3 crucible melts. The cerium borate perhaps remains either amorphous or glassy or alternatively B_2O_3 prefers the bonding to Na_2O so that CeO_2 remains unreacted in the presence of Al_2O_3.

The main crystalline phases after sintering were cubic CeO_2 and $2Al_2O_3 \cdot B_2O_3$ for the Pt/Rh and Al_2O_3 crucible melts, respectively. The crystalline cerium borate phase detected in the leached samples of Pt/Rh crucible melts seems to be transformed to a glassy phase during sintering. This may be a possible explanation considering the relatively low temperatures which are necessary for glass formation [18]. Only one crystalline phase, $2Al_2O_3 \cdot B_2O_3$, was detected in sintered samples of the Al_2O_3 crucible melt indicating that the other crystalline phases present in the leached material have undergone phase transformations during sintering at 1500° C.

A surface area of up to $119\,m^2\,g^{-1}$ and mean pore radii between 0.5 and 17 nm have been found in leached material and these results are comparable with other systems [1–8, 10–12]. Because of the small amount of sintered material available in this study (0.5 to 1 ml) the results of bulk density measurements could only be evaluated qualitatively. The results show the trend of densification of the porous material with decreasing pore volume and increasing bulk density correlating with increasing sintering temperatures after each of the sintering steps. This sintering behaviour indicates a better high temperature resistance in this system, than that reported for sintering of porous SiO_2 glass (present material 1500° C for 30 min compared to SiO_2 900 to 1200° C [7]).

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