Characterization and sintering of a porous glass-ceramic in the system Na_2O–B_2O_3–Ta_2O_5

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Substitution of SiO_2 in the ternary sodium borosilicate system with Ta_2O_5 was found to produce glasses, which after heat treatment separated into immiscible microphases, one of which was water soluble. The structure of the leached material after heat treatment was a well developed low temperature form of Ta_2O_5. After firing at temperatures between 1100 and 1550 °C X-ray diffraction analysis showed the presence of low and high temperature forms of Ta_2O_5 and of orthorhombic $Na_2Ta_5O_{21}$. The high solubility of up to 40 wt % Ta_2O_5 in the sodium–borate matrix resulting in clear glasses is of practical interest. The specific surface areas of the leached materials ranged between 5.54 and 35.57 $m^2 g^{-1}$ while in an additionally Al_2O_3 doped material the value of 307 $m^2 g^{-1}$ was measured. Mean pore radii of interconnected pores were calculated to be between 18.63 to 41.12 nm in the Ta_2O_5-rich materials while the additional Al_2O_3 doping decreased the value to 2.71 nm. A sintering temperature between 1500 and 1550 °C is estimated from void volume measurements after a series of firing steps at temperatures between 1100 and 1550 °C were undertaken.

1. Introduction

Observations of phase separation in binary borate and silicate melts containing, as a second compound, oxides of elements Al, Ga, Te, Y, La, Sn, Pb, Ti, Zr, Hf, Th, Nb, Ta, Mo and W were reported by Vogel [1]. Even additions of a third compound resulted in glasses in which, in most cases, microheterogeneities could be detected. A series of experimental studies have been carried out in this laboratory, where sodium–borate matrices containing one or more oxides of the above-mentioned elements were phase separated, leached and sintered. The intention was to study the possibility of leaching out soluble phases to measure the pore characteristics (pore volumina, specific surface areas and average pore radii) of the resulting porous materials and observe their sintering behaviour. References concerning these new porous materials are listed in Richter et al. [2]. In the previous investigation oxides of elements Al, Ce, Ga, Hf, La, Nb, Nd, Ta, Th, Ti, Sc, Si, Y and Zr were introduced into a sodium–borate matrix. The resulting glasses were phase separated by heat treatment and leached, while a portion of the leached materials was sintered. Specific surface areas and pore characteristics were comparable to that of porous silica based material, while in many cases higher heat and/or chemical resistance was observed.

The present work investigates sodium–borate glasses containing Ta_2O_5 as a third component. Ta_2O_5 is not unknown in the preparation of porous materials. White et al. [3] reported on La–Ta(Al)–oxide porous glass ceramics and Bednarik et al. [4] studied Ce–Ta–(Al) oxide porous glasses and their sintering. Additions of 10 to 18 wt % Ta_2O_5 into a complicated Na_2O–B_2O_3–Sb_2O_3–V_2O_5–Ta_2O_5–La_2O_3–TiO_2–

ZrO_2 system resulted in phase separable and leachable porous glasses as reported by Res et al. [5]. In a study of binary systems replacing SiO_2 in the phase separable and leachable Na_2O–B_2O_3–SiO_2 glasses Potgieter et al. [6] reported on porosity and heat resistance of an Al_2O_3–Ta_2O_5-rich material. Schmid et al. [7] continued the work on porous materials containing Ta_2O_5 and provided an in-depth structural study of Na_2O–B_2O_3–SiO_2–Ta_2O_5 glass. They applied scanning electron microscopy, transmission electron microscopy, and X-ray diffraction analysis. From the results they suggest a structural model for their glass to be intermediate between the continuous random network theory and the crystallite theory. The Ta_2O_5 containing glasses showed specific surface areas of interconnected pores 10 to 352 $m^2 g^{-1}$ and higher sintering temperatures than those of silica glass. Emphasis has here been given to a survey of the maximum Ta_2O_5 content in the sodium–borate matrix which could produce clear glass in the as-quenched state. A Ta_2O_5-rich porous skeleton was expected to result after heat treatment to achieve phase separation and/or crystallization and after subsequent leaching.

2. Experimental procedure
2.1. Glass preparation

The glasses were prepared from chemically pure reagents Ta_2O_5, H_3BO_3 and Na_2CO_3. Batches of 50 to 200 g were melted in Pt/Rh and, for control purposes, in Al_2O_3 crucibles. Melting temperatures between 1350 and 1400 °C for 3 to 4 h (in air) in an electrically heated furnace equipped with SiC elements

were used. A small portion of the melt was quenched on a cold steel plate while the majority of the glass mass was cast into graphite lubricated iron moulds and annealed. Phase separation was induced by heat treatment. The phase samples were leached for 1 to 72 h in boiling distilled water depending on sample composition and crucible type. Selected leached samples were fired at 1250 and 1550 °C in steps of 50 °C, each step for 5 min, while for structural studies a sintering was carried out for 24 h at 1100 °C.

2.2. Characterization of glasses

Methods used in the present work for material characterization include pore volume measurements [8], scanning electron microscopy [9], X-ray diffraction analysis [4], Brunauer, Emmett and Teller (BET)

nitrogen absorption and desorption [10] and sintering experiments [11]. Wet chemical analysis was performed on selected samples after leaching to show compositional changes between the melt and the leached sample.

3. Results
3.1. Characterization of resulting materials

The starting glass compositions calculated from a batch of as-quenched samples are shown in Fig. 1. The term "other formations" means opaque glasses and slightly or fully crystallized samples. Six samples were selected for evaluation of conditions leading to phase separation and porosity of the $Na_2O-B_2O_3-Ta_2O_5$ glasses. The results are given in Table I. The table includes starting compositions calculated from batch,
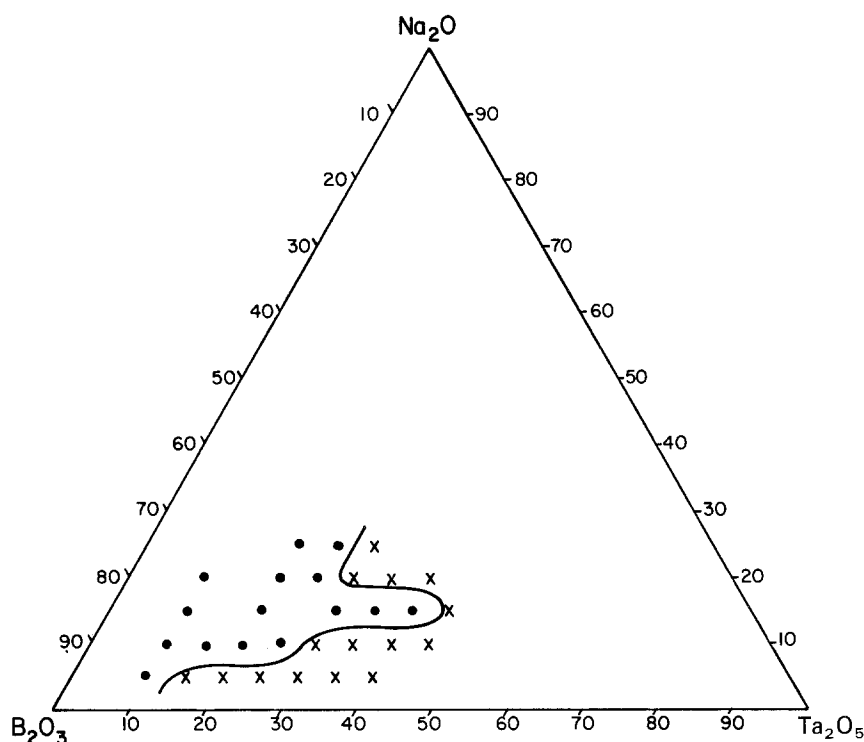

Figure 1 Starting compositions (wt %) and clear glass (●) region of as-quenched $Na_2O-B_2O_3-Ta_2O_5$ melts (× other formations).

TABLE I Treatment and characterization of leached samples

Sample	Chemical composition calculated from batch			Crucible type	Heat treatment °C/h	Leaching (h)	Appearance of sample		Void volume $(m^2 g^{-1})$	BET surface area $(m^3 g^{-1})$	Mean pore radii (nm)
	Na_2O (wt %)	B_2O_3 (wt %)	Ta_2O_5 (wt %)				as-quenched	leached			
1	12.92	52.56	34.52	Pt–Rh	600/3	2	clear glass	opaque white	0.3003	24.50	24.51
2	10.00	60.00	30.00	Al_2O_3	600/2 600/3 700/2	72	opaque white	opaque white	0.4166	307.00	2.71
3	10.00	55.00	35.00	Pt–Rh	600/3	1	glass with opaque veins	opaque white	0.3314	35.57	18.63
4	15.00	50.00	35.00	Pt–Rh	600/3	1	clear glass	opaque white powder	–	5.54	–
5	20.00	50.00	30.00	Pt–Rh	600/3	1	clear glass start of opacification	opaque powder	–	6.51	–
6	10.00	50.00	40.00	Pt–Rh	600/3	1	opaque white	opaque white	0.2825	13.74	41.12

crucible type, heat treatment and leaching procedures and the appearance of as-quenched and leached samples 1 to 6. The porosity after leaching is characterized by void volume, BET surface area measurements and by calculated mean pore radii.

The studied region of phase separable glass compositions was limited to 5 to 25 wt % Na_2O, 40 to 85 wt % B_2O_3 and to 10 to 45 wt % Ta_2O_5.

The general appearance of as-quenched samples 1 to 4 was clear glass while sample 5 was a clear glass showing the onset of surface opacification and sample 6 was opaque white. In two glasses very friable material resulted after leaching while the other samples crumbled.

3.2. Scanning electron microscopy

Secondary electron micrographs of as-quenched glass 1 showed, in Fig. 2, the presence of droplet-like microheterogeneities with a background of onset of phase separation similar to that reported by Vogel, White et al., Potgieter et al. and Res et al. [1, 3, 6, 8, 10]. After heat treatment coarsening of the separated phases occurred as shown in Fig. 3. The crystalline structure of heat treated and then leached sample 1 is shown in Fig. 4.

A 24 h 1100 °C sintering step of leached sample 1 was undertaken for structural studies according to Schmid et al. [7]. The micrograph of the resulting crystalline structure is shown in Fig. 5.

Heat treatments to study the densification of leached sample 1 were carried out for a constant time of 5 min at temperatures between 1250 and 1550 °C in steps of 50 °C. In Figs 6a to c the growth of crystals and densification can be seen.

3.3. Wet chemical analysis

A wet chemical analysis of sample 1 after 24 h leaching time is compared to the original batch glass composition in Table II. The remaining rather high amount of B_2O_3 in the porous skeleton indicates 24 h to be too short a leaching time. The presence of Na_2O in the skeleton can be ascribed to the formation of sodium-

tantalates found in sintered samples as mentioned in Section 3.4.

3.4. X-ray analysis

Powder X-ray diffraction studies were carried out on as-quenched, phase separated, leached and then fired samples on a Rigaku Denki Diffractometer.
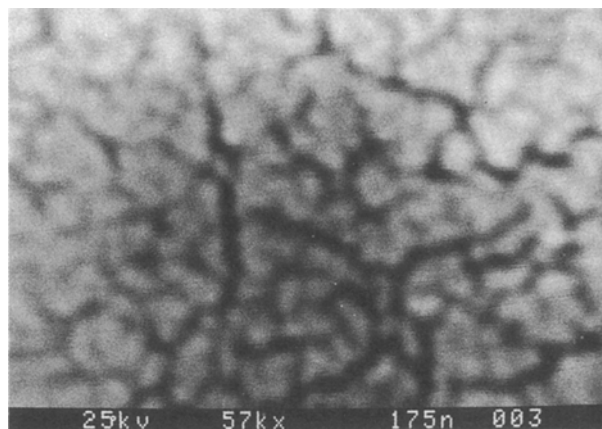

Figure 3 Scanning electron fractograph of annealed sample with coarsening of separated phases from Fig. 2 apparent.
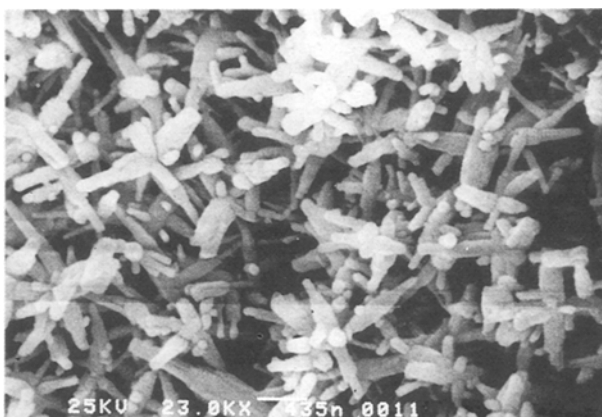

Figure 4 Scanning electron fractograph of heat treated and leached sample showing the porous crystalline skeleton.
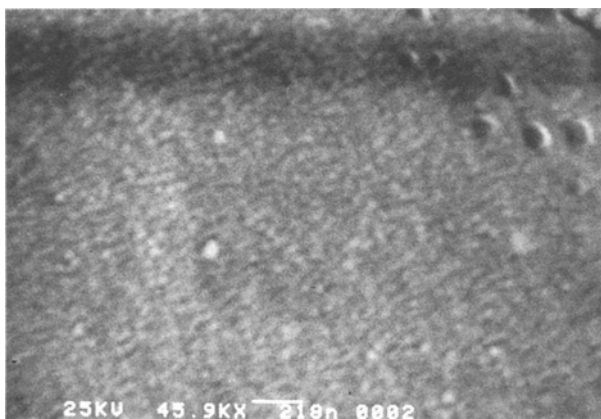

Figure 2 Scanning electron fractograph of clear quenched glass showing droplet-like microheterogeneities with a background of onset of phase separation.

Figure 5 Scanning electron fractograph of sample sintered at 1100 °C for 24 h showing a crystalline structure with no apparent densification.

TABLE II Chemical compositions of sample 1 before and after leaching

	Calculated from batch (wt %)	After leaching 24 h (wt %)
Ta_2O_5	34.52	87.3
B_2O_3	52.56	10.6
Na_2O	12.92	2.5

Sample 1 was selected for X-ray studies due to its visually glassy quenched state.

In the as-quenched state a typical glassy X-ray trace was obtained with only one small peak at 23.22° (2θ) (3.827 in d-spacing) probably indicating the start of crystallization (at least on the surface of the sample). After annealing (500 °C to room temperature in 4 h) the sample still showed a mainly glassy state. Small peaks were identified as consistent with a low temperature orthorhombic form of Ta_2O_5. This finding is in agreement with Roth et al. [12] who describe this form as stable up to 1360 °C. The presence of a second minor phase possible $Na_2Ta_5O_{21}$ can, however, not be excluded.

After heat treatment and after leaching of the heat treated sample 1 the glassy X-ray trace is transformed into a well developed spectrum of the low temperature form of orthorhombic Ta_2O_5.

The leached sample 1 was subjected to different temperature steps e.g. 1100 °C for 24 h, 1250, 1450 and 1550 °C for 5 min. All sintered samples showed a spectrum of well defined peaks, which indicates that an extensive crystallization had occurred. The resulting phase compositions are similar in all samples. The major phases are Ta_2O_5 and orthorhombic $Na_2Ta_5O_{21}$. After the first two steps (1100 and 1250 °C sintering temperatures) Ta_2O_5 is present in its orthorhombic low temperature form, which is in agreement with Roth et al. and Waring et al. [12, 13] as well as with Reisman et al. [14] and Terao's [15] findings. The temperature related polymorphism of Ta_2O_5 is well known and has been extensively studied. All authors agree on the transformation of Ta_2O_5's low temperature to high temperature form which occurs at temperatures above 1360 °C. Roth et al. [12] describe this change as sluggishly reversible. When quenched from temperatures above the equilibrium phase transition, the apparently tetragonal high temperature form transforms through a monoclinic polymorph into a third metastable polymorph, which appears to be triclinic at room temperature. The triclinic polymorph form was found in samples sintered at 1450 and 1550 °C for 5 min.

3.5. Heat treatment for densification
Specimens from leached sample 1 were fired for 5 min at 1250, 1300, 1350, 1400, 1450, 1500 and 1550 °C to study the densification behaviour. After firing, the samples were tested for remaining pore volume. The results are shown in Fig. 7.
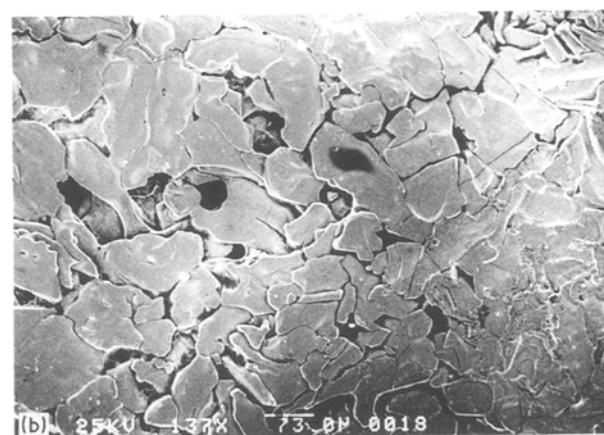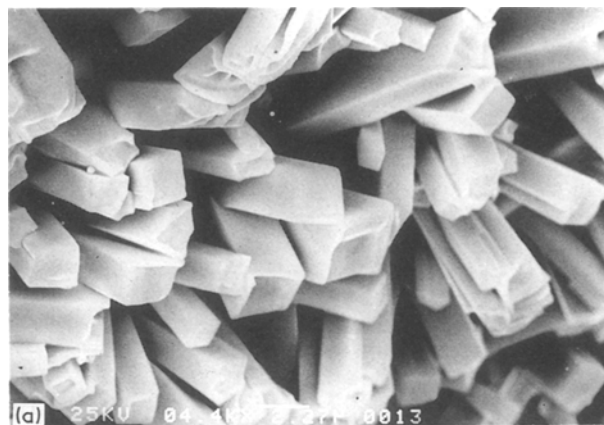

Figure 6 Scanning electron fractograph of sintered sample depicting densification steps (a) sintering at 1250 °C for 5 min, (b) sintering at 1350 °C for 5 min and (c) sintering at 1550 °C for 5 min.

3.6. Discussion
A series of sodium–borate tantalum oxide glasses showed phase separation, leachability and porosity similar to that achieved in other phase separable glasses listed in Richter et al. [2]. A wide glass forming region of up to 40 wt % Ta_2O_5 was observed in this system of phase separable glasses (see Fig. 1).

Scanning electron microscopy studies revealed the presence of droplet-like microheterogeneities in clear glasses in which visually no cords, threads or striae were observed. This is similar to previous observations e.g. Potgieter et al., Res et al. [6, 8]. In heat treated and leached samples crystalline tantalate structures were found. At temperatures between 1100
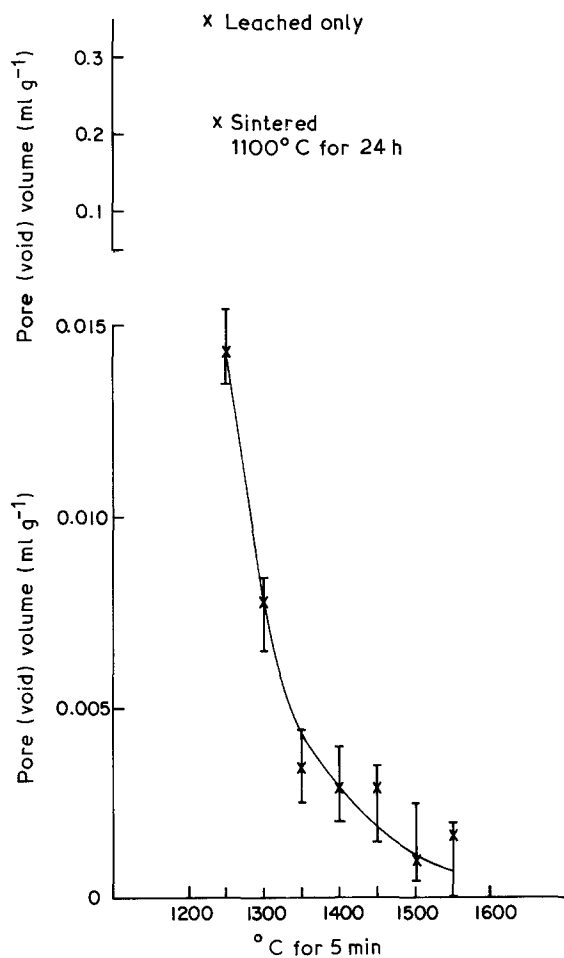
6545

X Leached only

X Sintered
1100°C for 24 h

Figure 7 Pore volume measurements after firing steps for sample 1 previously heat treated and leached for 72 h.

and 1550 °C, Ta_2O_5 and $Na_2Ta_5O_{21}$ phases were observed. X-ray analysis revealed Ta_2O_5 to be present in orthorhombic tetragonal or triclinic form depending on the previous firing temperature, while $Na_2Ta_5O_{21}$ was present in orthorhombic form. The results are in agreement with Roth et al. [12], Waring et al. [13], Reisman et al. [14] and Terao [15]. The intended development of a Ta_2O_5 rich skeleton having interconnected pores was achieved, although a certain amount of B_2O_3 remained unleached. Some Na_2O remains in the porous skeleton after leaching as part of the undissolved $Na_2Ta_5O_{21}$.

Surface areas of between 5 and 35 $m^2\,g^{-1}$ and mean pore radii of 18 to 41 nm were increased by an undissolved amount of Al_2O_3 to 307 $m^2\,g^{-1}$ and decreased to 2.7 nm, respectively. Densification, evaluated by void volume measurements, indicates a better heat resistance than that reported for porous SiO_2 glass, Richter et al. [2].

References

1. W. VOGEL, *J. Non-Cryst. Solids* **25** (1977) 172.
2. P. W. RICHTER, M. A. RES, H. SCHÖNBERGER, J. T. THIRWALL, *SA Tydskr. Natuurwet. & Tegnologie* **5** (1986) 32.
3. R. W. WHITE, M. A. RES and J. BEDNARIK, *J. Mater. Sci.* **18** (1983) 1021.
4. J. F. BEDNARIK, M. A. RES and R. W. WHITE, *Glass Technol.* **24** (1983) 122.
5. M. A. RES, F. BLUM, J. BEDNARIK and H. D. H. SCHÖNBERGER, *ibid.* **27** (1986) 164.
6. E. POTGIETER, M. A. RES, I. SIGALAS, H. SCHÖNBERGER and J. BEDNARIK, *J. Mater. Sci.* **22** (1987) 752.
7. H. K. SCHMID, M. A. RES, F. BLUM and H. D. H. SCHÖNBERGER, *Glastechnische Berichte*, March or April, 1988.
8. M. A. RES, S. T. FOURIE, R. W. WHITE and J. BEDNARIK, *J. Amer. Ceram. Soc.* **65** (1982) 184.
9. M. A. RES, F. BLUM, J. BEDNARIK and R. W. WHITE, *Glastechnische Berichte* **55** (1982) 50.
10. R. W. WHITE, M. A. RES and J. BEDNARIK, *J. Mater. Sci.* **19** (1984) 1109.
11. M. A. RES, J. BEDNARIK, J. T. FOURIE and J. L. ALBAIN, *J. Amer. Ceram. Soc.* **67** (1984) C-264.
12. R. S. ROTH, J. L. WARING and W. S. BROWER, *Journal Res. NBS* **74A** (1970) 477.
13. J. L. WARING and R. S. ROTH, *ibid.* **72A** (1968) 175.
14. A. REISMAN, F. HOLTZBERG, M. BERKENBLIT and B. BERRY, *J. Amer. Chem. Soc.* **78** (1956) 4514.
15. N. TERAO, *Jpn J. Phys.* **6** (1967) 21.