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# A lanthanum–tantalum (Al) oxide porous glass ceramic

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The substitution of the end-member oxides in the ternary glass forming sodium borosilicate system was studied. The replacement of $SiO_2$ with combinations of $La_2O_3$ and $Ta_2O_5$ was found to produce glasses which, after heat treatment decomposed to form a leachable sodium borate phase and an insoluble ceramic phase. The mode of phase decomposition is sensitive to impurities: the importance of crucible selection, e.g. $Al_2O_3$ or Pt/Rh is demonstrated by resulting differences in pore size, surface area, chemical resistance and structure of the insoluble phase for a series of $La_2O_3$–$Ta_2O_5$ and $La_2O_3$–$Ta_2O_5$–$Al_2O_3$ glass ceramic. These new materials have a specific surface area of up to 145 $m^2\,g^{-1}$ and average pore radii ranging between 0.7 and 28.6 nm and show a varying degree of chemical resistance.

## 1. Introduction

Certain compositions of the glass-forming region in the ternary sodium borosilicate system undergo a glass-in-glass decomposition. This proceeds in such a way that an essentially sodium borate glass can be leached out leaving an insoluble porous $SiO_2$ glass.

The possible substitution of the end-member oxides in the system by other oxides which are expected to exhibit similar behaviour has been discussed by Res *et al.* [1].

Previous work [2–4] has shown that $Na_2O$ can be replaced by $K_2O$ and $Li_2O$ as well as by the alkali earth oxides. This end-member has also successfully been replaced by ZnO and PbO. The possible replacement by $Rb_2O$ and $Cs_2O$ is still an open question.

The only known success in the replacement of $B_2O_3$ was reported by Rabinovich *et al.* [5, 6] where a new phase-separable and leachable sodium phospho-silicate system resulting in porous high silica glass is described.

The successful replacement of $SiO_2$ by $Al_2O_3$ (up to 4% mass) by $AlPO_4$ (up to 35% mass) and by $GeO_2$ (totally) was intended primarily to produce improved porous glasses. The substitution of $SiO_2$ could only be extended experimentally by replacing the $SiO_2$ by network formers. In this category oxides of aluminium, titanium, zirconium, niobium, tantalum and possibly hafnium, or as reported in [7] combinations of oxides with some glass-forming ability, might for the present purpose be considered as potential substitute network formers.

According to [8] a wide spectrum of binary borate and silicate melts containing gallium, hafnium, lanthanum, molybdenum, niobium, tantalum, titanium, thallium, tungsten, yttrium and zirconium tend to segregate either by means of spinodal decomposition or at least to exhibit a marked trend towards microphase separation [8].

The present work has concentrated on sodium borosilicate glasses containing $La_2O_3$–$Ta_2O_5$, a system which after heat treatment and leaching is expected to leave a $La_2O_3$–$Ta_2O_5$-rich skeleton. The spatial distribution of the liquid phases after separation in the glasses is of interest. Leachability of the Na-rich phase would be favoured if the interconnected structures are formed as a result of metastable immiscibilities; porous materials with such interconnected structures are of technological importance.

The choice of $3La_2O_3 \cdot 7Ta_2O_5$ as a replacement for $SiO_2$ is based on the findings of Shishido

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*et al.* [7] who observed glass forming in La–Ta systems for rapidly quenched materials. A glassy state for this system has been observed in the mol ratio range of between 1 : 1 to 1 : 7 ($La_2O_3$ : $Ta_2O_5$).

## 2. Experimental details

### 2.1. Glass preparation

The glasses were prepared from chemically pure grade reagents: $H_3BO_3$ and $Na_2CO_3$ from Merck and $Ta_2O_5$ and $La_2O_3$ from BDH. 50 g batches of glasses were melted in Pt/Rh or $Al_2O_3$ crucibles, examples of the void volume BET [9], and pore radii of the glasses are illustrated in Table I.

The melts were made under atmospheric conditions in an electrically heated furnace having SiC elements. Melting temperatures ranged between 1350 and 1400° C and melting times were less than 4 h. The glasses were cast in preheated iron molds, annealed and heat treated. Three different heat treatments, depending on the glass compositions, were applied to the samples from the melts made in the $Al_2O_3$ crucibles and two different heat treatments were carried out on the samples from melts made in the Pt/Rh crucibles.

The samples were cut into slices 3 mm thick and subjected to staged heat treatments, which allowed controllable phase separation.

After the phase separation resulting from these heat treatments, the sodium borate-rich phase was leached out in boiling distilled water, leaching times being 72 h and 24 h for the $Al_2O_3$ and Pt/Rh crucible melts, respectively. After leaching, the samples were rinsed in distilled water and dried at 100° C.

### 2.2. Evaluation of the samples

### *2.2.1. Void volume determinations*

About 1 g of dried sample was weighed and then soaked in distilled water for half an hour at room temperature and pressure, after which it was daubed with a damp tissue and then placed in the relative humidity chamber of a void volume apparatus where it was subjected to the influence of a steady flow of dry air (rate about $6 \, l \, min^{-1}$) under ambient conditions of temperature and pressure. The relative humidity of the air exhausted from this chamber, determined electronically, was plotted against time by means of a suitable recorder. When the critical moisture content point was determined, the sample was removed from the apparatus and reweighed, the difference in weights indicating the residual water retained in the pores of the sample from which weight the void volume was calculated.

Samples showing a void volume of less than $0.01 \, ml \, g^{-1}$ were reserved for later investigations.

### *2.2.2. Surface area measurements*

Another 1 g of dried sample was subjected to $N_2$ absorption determination on a BET gas adsorption balance [9] and the surface area of the sample thus evaluated. For comparative purposes it was assumed that the pores were cylindrical in form and so from these two evaluations the average pore radius was calculated. Pore size distribution evaluations were not carried out as part of this work.

### *2.2.3. Chemical resistance tests*

The materials were tested for chemical resistance, largely in accordance with DIN specification methods [10, 11]. The apparatus used for the determinations was, however, not in all cases as specified. Since the results were required only for comparative purposes between samples, use of conventional laboratory apparatus was considered justifiable.

### *2.2.4. Analytical tests*

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) was made after all the major experimental stages, namely of melted, heat-treated, leached and sintered samples.

A powder X-ray diffraction technique was used to identify the crystalline phases present. For this purpose the lattice parameters and space group data given in the ASTM powder data file were used for comparison purposes.

## 3. Results

The glasses were all opaque and white throughout the range of compositions shown with the $Na_2O$ and $B_2O_3$ ratio in the region of the boron anomaly line for the sodium borosilicate system. By analogy with this system, this is the region in which porous glasses may be expected.

The effect of crucible choice and the resultant impurities on pore size is shown in Table I, which presents a cross-section of the results obtained on selected samples from the work done. Starting composition, chemical resistance, crucible used for the melt, heat treatments, leaching times, void volumes, surface areas (assuming cylindrical shaped pores) and average pore radius are given.

The calculated starting composition (mol %) of

TABLE I Experimental details of selected samples

| Sample number | Composition* (Wt%/Mol%) | | | | Alkali resistance (mg dm$^{-2}$) | $H_2O$ resistance | | Crucible | Heat treatment temperature (° C)/ Time (h) | Leach time† (h) | Void volume (ml g$^{-1}$) | Surface area (m$^2$ g$^{-1}$) | Radius (nm) | Appearance |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $B_2O_3$ | $Na_2O_3$ | $Ta_2O_5$ | $La_2O_5$ | | ml g$^{-1}$ (DIN 12) | mg g$^{-1}$ $Na_2O$ (DIN 13) | | | | | | | |
| 78 | 38.1/65 | 10.44/20 | 39.16/10.52 | 12.3/4.48 | Not | 156.6 | 45.5 | Pt | 650/2<br>700/2<br>750/2 | 24 | 0.196 | 34.47 | 16.0 | White glassy opaque |
| 79 | 30.86/60.05 | 9.14/19.98 | 45.6/13.98 | 14.4/5.99 | 2 158 | 20 | 6.2 | Pt | 650/2<br>700/2<br>740/2 | 24 | 0.013 | 20.98 | 1.24 | White glassy opaque |
| 81 | 33.3/65.06 | 6.8/14.92 | 45.5/14.00 | 14.4/6.02 | 3 411 | Not done | | Pt | 650/2<br>700/2<br>740/2 | 24 | 0.140 | 28.74 | 9.74 | White glassy opaque |
| 77 | 30.86/60.05 | 9.14/19.98 | 45.6/13.98 | 14.4/5.99 | 3 503 | 57 | 17.7 | Al | 650/2<br>700/2<br>740/2 | 72 | 0.021 | 69.4 | 0.61 | Soft chalky – white opaque |
| 129 | 33.3/65.06 | 6.8/14.92 | 45.5/14.00 | 14.4/6.02 | Not | Not done | | Al | 650/2<br>700/2<br>740/2 | 72 | 0.041 | 117.4 | 0.69 | White glassy opaque |
| 130 | 33.3/65.06 | 6.8/14.92 | 45.5/14.00 | 14.4/6.02 | Sample falls apart | | | Al | 650/2<br>700/2<br>790/2 | 72 | 0.063 | 99.3 | 1.26 | Weak white glassy opaque |
| 140 | 25.12/55.03 | 8.11/19.96 | 50.75/17.51 | 16.02/7.50 | 2 018 | Not | | Pt | 650/2<br>700/2<br>750/2 | 24 | 0.146 | 15.37 | 19.0 | White glassy opaque |
| 189 | 31.73/69.47 | 2.03/5.72 | 50.32/17.36 | 15.92/7.45 | Sample falls apart | | | Al | 650/2<br>700/2<br>750/2 | 72 | 0.041 | 96.5 | 0.85 | Weak white opaque |
| 190 | 30.86/60.05 | 9.14/19.98 | 45.6/13.98 | 14.4/5.99 | Not | 17.6 | 5.5 | Al | 650/2<br>700/2<br>740/2 | 72 | 0.085 | 144.57 | 1.18 | Soft white opaque |

*Glass composition calculated from batch in wt%/mol%.

†Leaching times established experimentally.

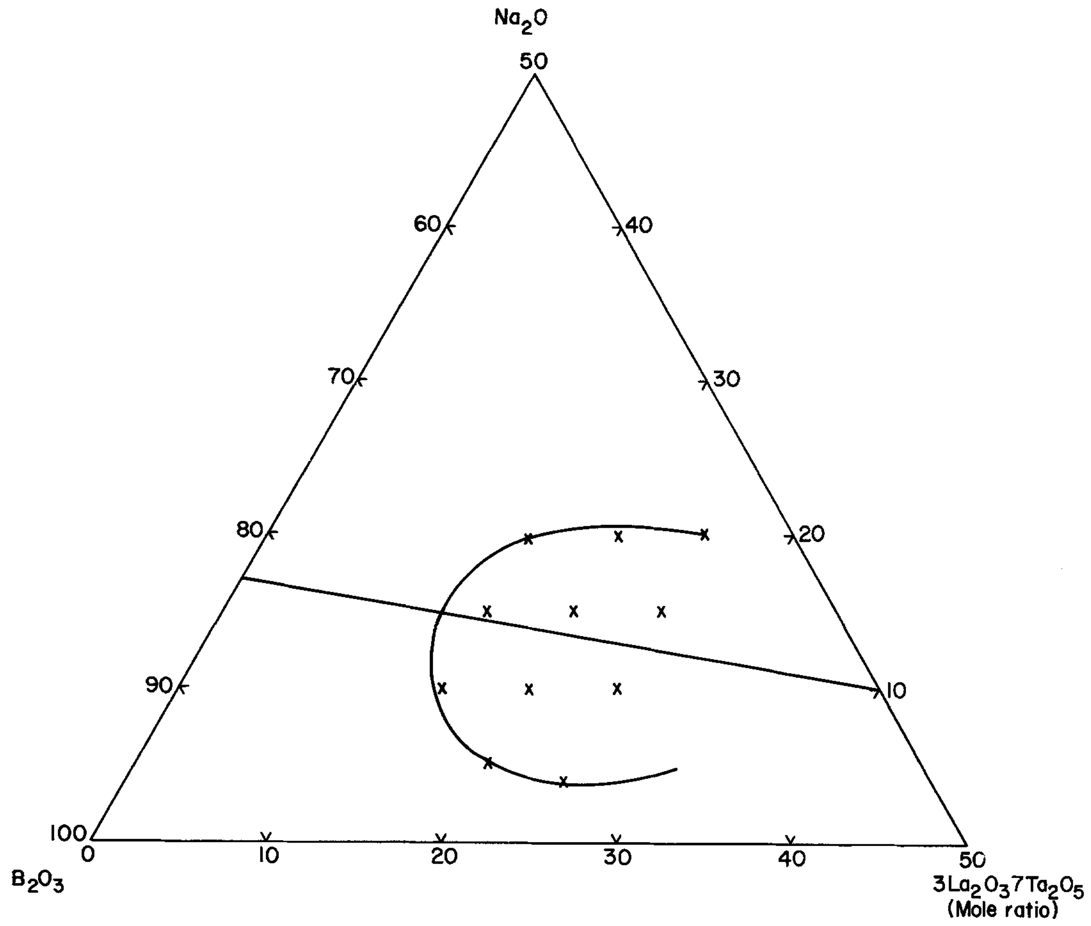

*Figure 1* Phase diagram showing region occupied by samples prepared for the work.

the phase separable $Na_2O$–$B_2O_3$–$La_2O_3$–$Ta_2O_5$ glasses, and their relationship to the boron anomaly line for the sodium borosilicate system, is illustrated in Fig. 1 showing the region of the phase diagram studied in this work.

The detection of microphase segregation in glass using electron microscope techniques has been discussed in some detail by Vogel [8]. Figs. 2 and 3 show the EDX analysis of sintered samples from the melts made in $Al_2O_3$ or Pt/Rh crucibles. The presence of an aluminium line is clearly shown in those samples made from $Al_2O_3$ crucible melts.

A scanning electron micrograph of sample 81 at 2000 times magnification is seen in Fig. 4. This sample was prepared in a Pt/Rh crucible, heat treated, and leached as shown in Table I. Fig. 5 shows a similarly magnified SEM picture of sample 129 which had the same composition as sample 81, but was melted in an $Al_2O_3$ crucible, then heat treated and leached. The effect of the crucible-sourced impurity on the pore size is clearly illustrated. X-ray analysis was made on leached samples. This showed that the major component was tetragonal $La_2O_3 \times 3Ta_2O_5$ in the form of a perovskite type of compound $A_{0.33}BO_3$ (where A are rare earths and B is niobium or tantalum).

This finding is in agreement with the works of Shishido *et al.* [7] and of Afonskii and Neiman [12] who studied the La–Ta system with similar 3 : 7 mol ratios. According to Rooksby *et al.* [13] rare earth oxides except $Sc_2O_3$ form perovskite-like compounds.

Apart from the $La_2O_3 \times 3Ta_2O_5$ phase a minor phase, lanthanum orthotantalate ($La_2O_3 \times Ta_2O_5$), was observed. This is in agreement with the findings of Shishido *et al.* [7] and Afonskii and Neiman [12]. The *d* spacing of this material does not agree with the ASTM powder data file. There is, however, close agreement with the values determined by Krylov, Pinaeva-Strelina [14] for this type of monoclinic compound.

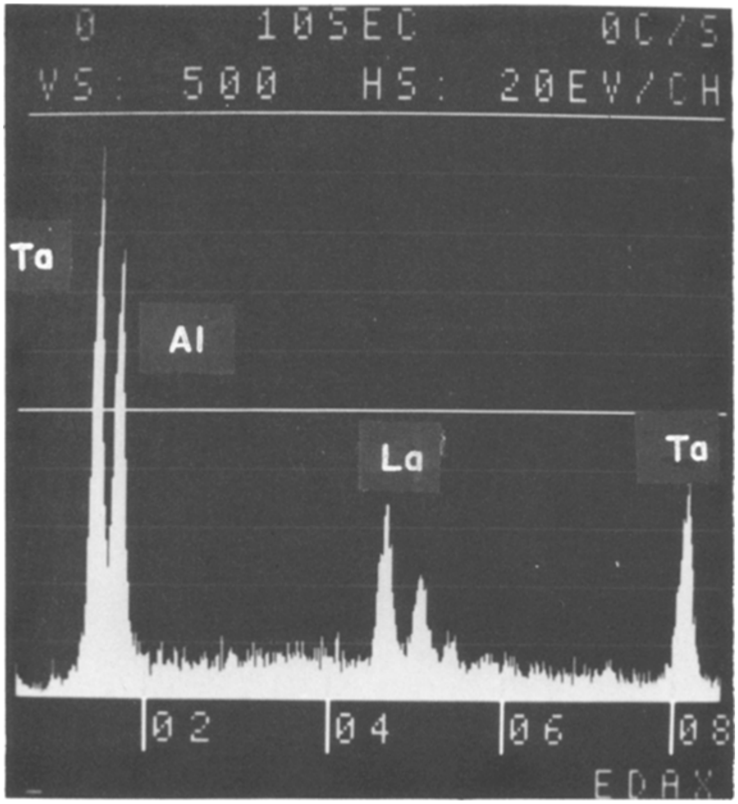

*Figure 2* EDX of sample melted in $Al_2O_3$ crucible.

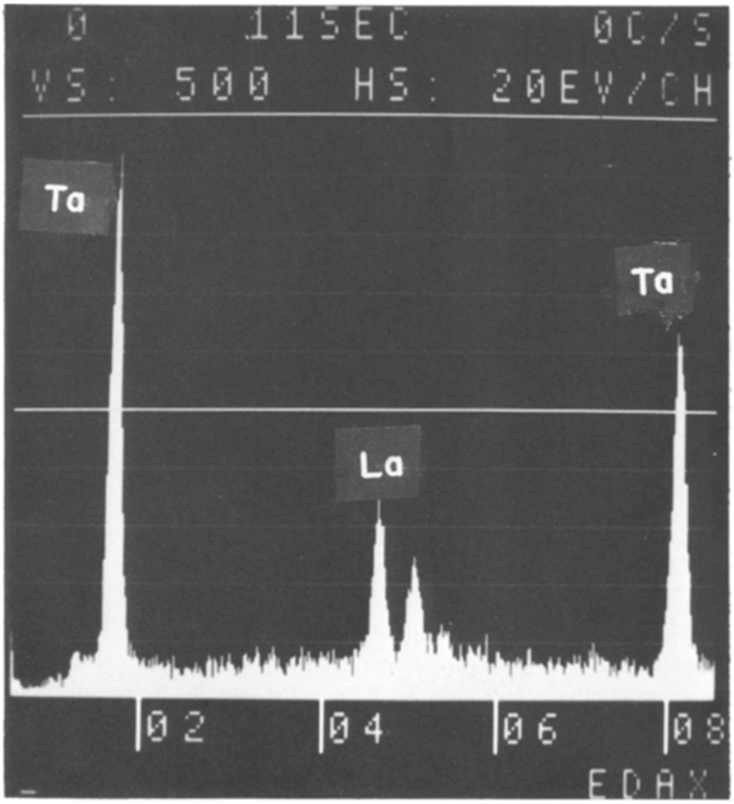

*Figure 3* EDX of sample melted in Pt/Rh crucible.

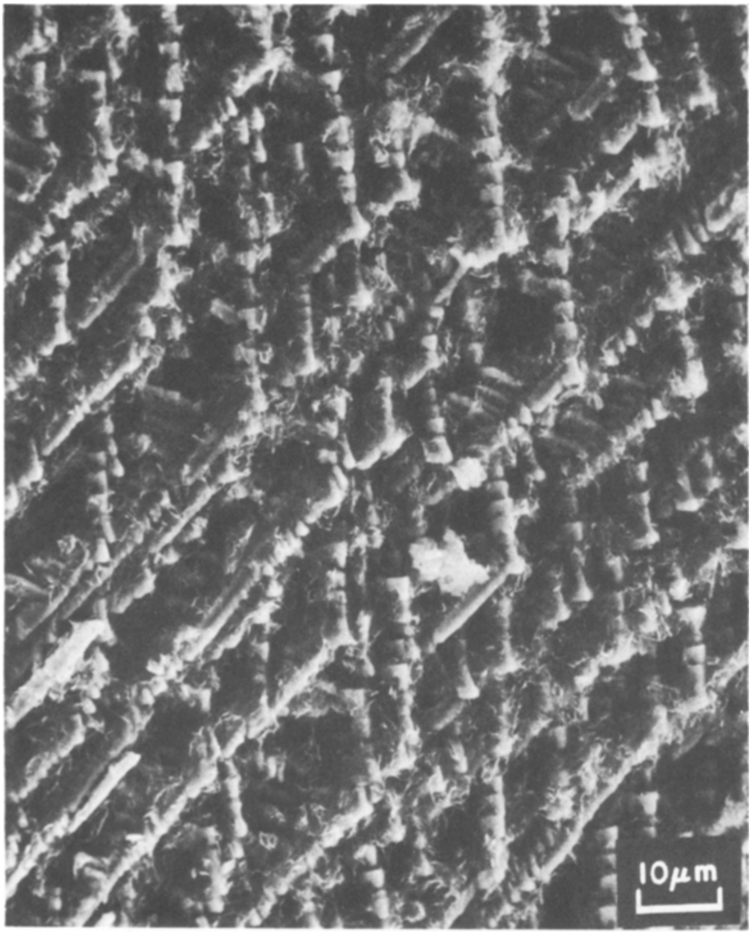

*Figure 4* SEM of sample melted in Pt/Rh crucible (leached).

The sample from the $Al_2O_3$ crucible melt only showed La–Ta compounds of the perovskite type as a major phase and an orthotantalate as a minor phase. No Al-containing crystalline phase was determined despite EDX-SEM analysis showing the presence of 40% mass $Al_2O_3$ through the whole sample. This was taken to indicate that the alumina is only present in the amorphous or glass-bonding component.

## 4. Discussion

A series of Na–La–Ta–B oxide glasses showed phase separation, leachability and porosity after heat treatment, similar to that achieved in a ternary sodium borosilicate system. The porous glass ceramic containing $Al_2O_3$, as a result of contamination from the crucible in which the melts were made, showed poor crystallinity, whilst those melts made in a Pt/Rh crucible showed well-developed crystals with consequent effect on the pore size and surface area of the samples.

No glasses containing $Al_2O_3$ as a raw material were prepared nor were any quantitative analyses undertaken for this work.

The results indicate that at the glass-melting temperatures (1350 to 1400° C) the interaction of $La_2O_3$ and $Ta_2O_5$ leads to the formation of tantalates in the leached material. In the system investigated microphase separation occurs after heat treatment and the phase-separated glasses can be leached, resulting in porous glass-ceramics with surface areas of up to $145\,m^2\,g^{-1}$ and pore radii ranging from 0.7 to 28.5 nm.

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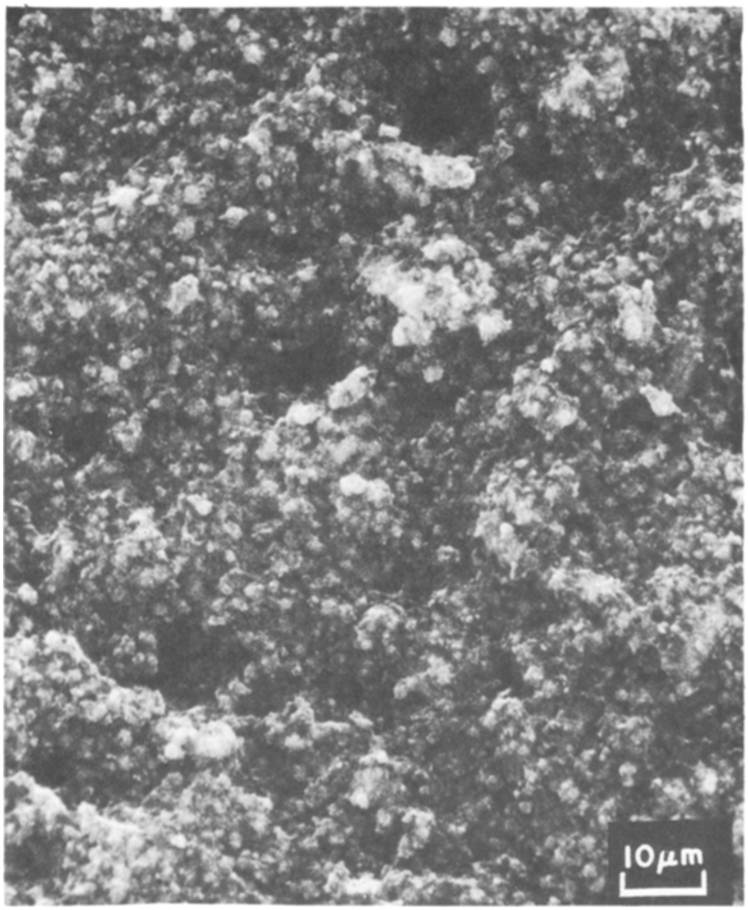

*Figure 5* SEM of sample melted in $Al_2O_3$ crucible (leached).

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