JOURNAL OF MATERIALS SCIENCE 29 (1994) 2531–2535

Microstructural evolution of sol–gel-derived phosphosilicate gel with heat treatment

Y. S. KIM*, R. E. TRESSLER
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

The microstructure of phosphosilicate gel prepared by a sol–gel process was investigated as a function of the heat-treatment temperature. Crystalline phases, $Si_3(PO_4)_4$ and SiP_2O_7, were identified in the heat-treated phosphosilicate gel containing 56 mol% P_2O_5. It was found from the Fourier transform infrared spectra that phosphorus enters into the copolymer structure at ~ 600 °C. The specific surface area of the gel increased with the heat-treatment temperature. An increase of the density of open pores with the heat-treatment temperature was observed in the secondary electron micrographs.

1. Introduction

The so-called sol–gel process is one of the most promising methods for the manufacture of glasses, pure fine powders and ceramics. The prime technological importance of the sol–gel process is that it opens up a possibility of preparing homogeneous glasses and glass ceramics at lower temperatures, which are hard to prepare by melting of oxide mixtures [1–6]. It was suggested by Roy [2] that a gel may be converted to a glass below the normal melting temperature of that composition because of the excess free energy of a gel compared to a glass of the same composition. The sol–gel process is known to be particularly suitable for coating deposition and fibre fabrication.

The theoretical considerations, processing techniques and applications related to sol–gel-derived ceramics have been reviewed by many authors [3–6]. Glass preparation via the gel route can be described by three stages: (1) gelation, (2) drying, and (3) gel-to-glass or gel-to-ceramic conversion. During gelation, the overall medium becomes viscous and is then solidified by a coherent network of particles. In forming gels, the most widely used and most extensively investigated starting materials are the acids and metal alkoxides. Polymeric oxide gels are made almost exclusively from metal alkoxides. With additions of water, the metal alkoxides readily hydrolyse; and with appropriate control of hydrolysis and condensation reactions, polymerized oxide networks can be formed.

Most of the research on two-component phosphosilicate glasses has been made on films produced on substrates from the gas or liquid phase by heating [7–9]. A few investigators have studied phosphosilicate glasses prepared by the sol–gel method. Thomas [10] has provided in his patent a method for producing phosphosilicate glasses. Silicon alkoxide was reacted with phosphoric acid to produce a homogeneous gel. By this method, a granular oxide product consisting of about 8–26 wt % P_2O_5 and about 92–74 wt % SiO_2 could be produced.

Jabra *et al.* [11] studied the gels of the SiO_2–P_2O_5 system prepared by the sol–gel method. Silica was introduced as a hydrosol (LUDOX AS) which is stabilized by the presence of NH_4^+ ions. The P_2O_5 was introduced as an aqueous solution of phosphoric acid or ammonium phosphate $(NH_4)_2HPO_4$. The two solutions were brought to pH5 and mixed under constant stirring at room temperature. Increasing the pH to 6 brought about gel formation in approximately 1 h. Gels containing 5–20 mol % P_2O_5 were obtained in this way. The conversion of gels into glasses was obtained by hot-pressing techniques using graphite dies. By this method they could produce transparent glasses containing 5–15 mol % P_2O_5.

The object of this work was the study of the microstructural change of a phosphosilicate gel with heat-treatment temperature. The sol–gel method of making phosphosilicate glass was chosen as a low-temperature route because melt forming of these high P_2O_5 content glasses would be difficult owing to the high volatility of phosphorus oxide at high temperatures.

2. Experimental procedure

2.1. Preparation of gels

In this work, the phosphosilicate gel containing 56 mol % P_2O_5 was prepared by a sol–gel process. Tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$) and phosphoric acid (H_3PO_4) were used as raw materials. The general procedure for the preparation of phosphosilicate gels containing 56 mol % P_2O_5 is described below.

Because the number hydroxyl groups in phosphoric acid is sufficient to completely hydrolyse TEOS, no water was added in the sol–gel process. To slow down

---

* *Present address*: Department of Mineral Resources and Energy Engineering, Chon-Nam National University, Kwangju 500-757, Korea.

0022–2461 © *1994 Chapman & Hall*

the gelation process, TEOS and phosphoric acid were diluted with ethanol before they were mixed. The gelation time varied depending on the volume ratios of ethanol to TEOS and ethanol to phosphoric acid. In Table I the gelation time is presented with the volume ratios of ethanol to TEOS and ethanol to phosphoric acid. It shows that the gelation time increased as the volume ratio of ethanol to total volume increased. After drying at ~ 45 °C in the oven, each gel powder was heat treated at 500 °C for 4 h in flowing oxygen. X-ray diffraction analyses were carried out on the heat-treated gel powders. The X-ray diffraction patterns of these gels are shown in Fig. 1. The peaks for $Si_3(PO_4)_4$ and the tetragonal polymorph of SiP_2O_7 appear in all three diffraction patterns. However, the intensities of the crystalline peaks from Gel III, which was prepared with the largest amount of ethanol, were much smaller than those shown in the other patterns. Thus Gel III was chosen to be used for further experiments.

TABLE I Gellation time for gels prepared with three different volume ratios of ethanol to TEOS and ethanol to phosphoric acid.

	$R1^a$	$R2^b$	Gellation time
Gel I	1	0	~ 20 s
Gel II	1	1	~ 10 min
Gel III	3	3	2–3 h

[a] $R1$ = vol (EtOH)/vol (TEOS).

[b] $R2$ = vol (EtOH)/vol (H_3PO_4).

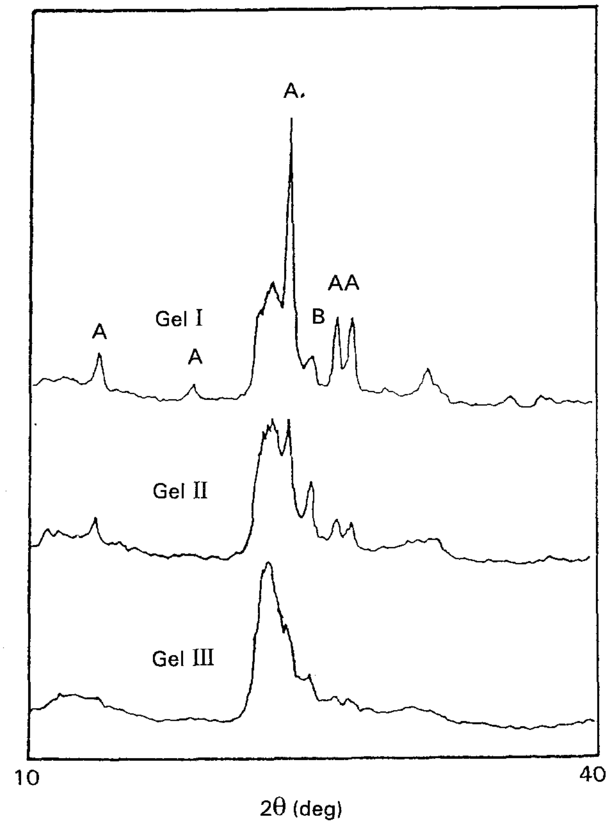

Figure 1 X-ray diffraction of the 56% phosphosilicate gel heat treated at 500 °C for 4 h in flowing oxygen. A, SiP_2O_7; B, $Si_3(PO_4)_4$.

All the gels after drying at ~ 45 °C were hand-ground with a mortar and pestle. To study the microstructural evolution of the 56 mol % phosphosilicate gel with heat treatment, gel powders were heated to various temperatures at a heating rate of 1 °C min^{-1} in flowing oxygen and cooled in the air.

2.2. Measurements of properties

Identification of crystalline phases in the powder samples was performed using an automated X-ray diffractometer. A CuK_α source was used for all analyses. The patterns were generally run at 1° 2θ min^{-1}.

Infrared study of the gel powder was performed using a DIGILAB FTS-60 infrared spectrometer. The gel powder and KBr powder were dried in an oven at 110 °C for one day. To prepare samples, 1 mg sample powder was mixed with 300 mg KBr powder and pressed into a pellet at 150 MPa. The absorbance spectra were collected in the mid-infrared region of 450–4000 cm^{-1} by 100 scans with a resolution of 2 cm^{-1}.

The specific surface area of powders was determined by flowing a gas mixture of nitrogen and helium through the sample – nitrogen as adsorbate and helium as inert non-adsorbable carrier gas. In this study, a three-point BET method was used with 20%, 25%, and 30% nitrogen gas mixtures. The process of adsorption and desorption is monitored by measuring the change in the thermal conductivity of the gas mixture. Prior to the measurement, the powder was outgassed at 150 °C for 2 h in flowing nitrogen. The instrument was calibrated by injecting a volume of nitrogen which would match the desorption peak.

The gel powder was examined by scanning electron microscopy (SEM). For the powder samples, the powder was dispersed in methanol. A drop of the solution was placed on an aluminium sample holder and allowed to dry. All the samples were gold coated to prevent the specimen from charging.

3. Results and discussion

3.1. Crystallization

The phosphosilicate gel powder was examined by X-ray diffraction analysis (XRD) after heat treatment at 500 °C for 4 h in an oxygen ambient. In the gel containing 56 mol % P_2O_5, crystalline phases of $Si_3(PO_4)_4$ and SiP_2O_7 were detected by XRD. These results are in good agreement with the work of other investigators [12, 13] where they established the existence of the compounds $Si_3(PO_4)_4$ and SiP_2O_7.

The sequence of the crystallization was studied with 56 mol % gel powders which were heated to various temperatures at a heating rate of 1 °C min^{-1} in oxygen and cooled in air. The X-ray diffraction patterns of the gel powders are presented in Fig. 2. The gel dried at 50 °C was X-ray amorphous. When the gel was heated to 300 °C, crystalline phases of $Si_3(PO_4)_4$ and SiP_2O_7 appeared. But the intensity of the strongest peak of $Si_3(PO_4)_4$ was higher than that of SiP_2O_7 at 300 °C. As the temperature increased, the intensities of the peaks of the SiP_2O_7 crystalline phase increased at

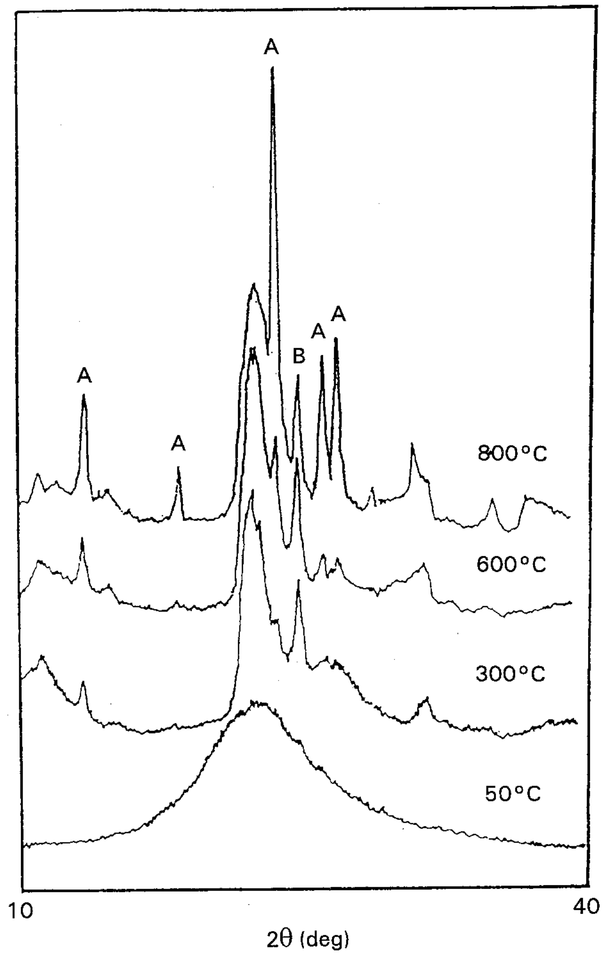

Figure 2 X-ray diffraction of the 56% phosphosilicate gel heat treated to various temperatures. A, SiP_2O_7; B, $Si_3(PO_4)_4$.

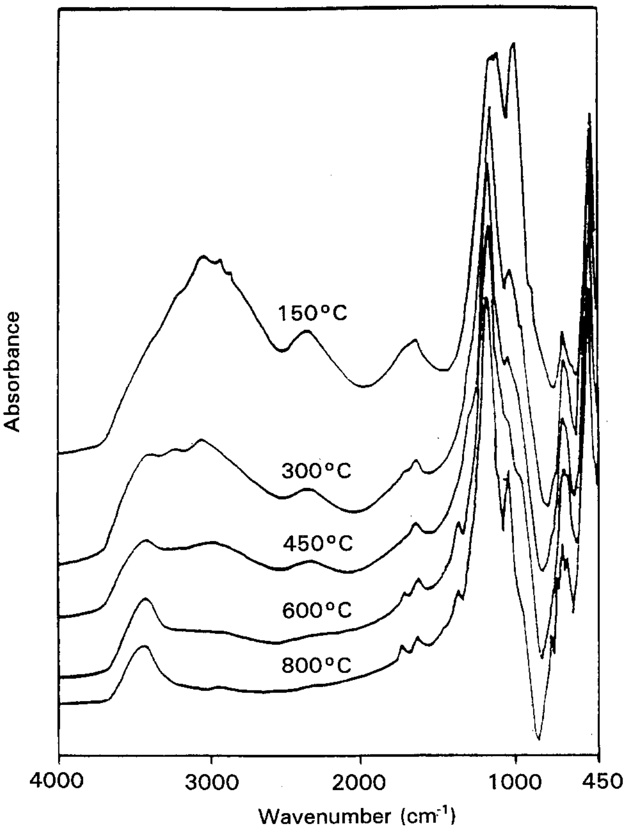

Figure 3 IR absorbance spectra of the 56% phosphosilicate gel heat treated to various temperatures.

the expense of the glass phase, while those of the $Si_3(PO_4)_4$ crystalline phase remained nearly constant.

3.2. Fourier transform infrared (FTIR)

IR spectroscopy was employed to study the molecular structural changes of the gel powders as the heat-treatment temperature increased. The IR spectra of 56 mol % gel powders heated to various temperatures are presented in Fig. 3. The broad band in the region of 3000 cm^{-1}, which is significant at low temperatures, is thought to be due to the water present in the gel. But at high temperatures, these bands may not account for the water in the gel. They may be due to the water absorbed in the KBr pellets which are very hygroscopic.

IR spectra of the phosphosilicate phases have been studied by many authors [14–17]. Based on these studies, the peak assignment may be made for the phosphosilicate gel powders. The strong peak at ~ 1160 cm^{-1} evident in all spectra in Fig. 3 is assigned to a combination of P–O stretching vibration of the P–O–P and P–O–Si linkages. The peak at ~ 500 cm^{-1} is assigned to O–P–O bending vibrations, while that at ~ 1030 cm^{-1}, which began to appear at 300 °C, can be assigned to Si–O stretching vibrations of the Si–O–P linkage. The peak at ~ 680 cm^{-1} can be assigned to O–P–O bending vibrations, while the peak in the region of 990 cm^{-1} at 150 °C may be due to the presence of an OH group as a silanol. This peak disappeared as the heat-treatment temperatures increased. The peak at 1360 cm^{-1}, which appeared after heat treatment at 600 °C, is assigned to P=O stretching vibrations. The broad band at ~ 2350 cm^{-1}, which disappeared at 600 °C, is assigned to P–OH stretching vibrations. The peak at 1630 cm^{-1} is generally assigned to the bending vibrations of water and that at 1720 cm^{-1}, which appeared at high temperatures, may be due to the CO_2 gas trapped in the pores inside the gel.

Given the above information, it may be concluded that the large decrease in the intensity of the broad band in the region of 3000 cm^{-1} and the peak at 1630 cm^{-1} with increasing heat-treatment temperature is due to the loss of H_2O from the gel. As the temperature increased to 600 °C, the band at ~ 2350 cm^{-1} disappeared and the peak at 1360 cm^{-1} appeared, which indicates that the phosphorus entered into the copolymer structure at ~ 600 °C. The split of the broad band at ~ 680 cm^{-1} into several peaks at high temperatures is thought to be due to the crystallization of the gel powders. The crystalline $Si_3(PO_4)_4$ and SiP_2O_7 phases have been detected by XRD analysis in the gel powders heated to 300 °C and above, as was discussed in the previous section.

3.3. Specific surface area

To study the microstructural development of the gel with temperature, the specific surface area of the gel powder heated to various temperatures was measured by BET surface area analysis. The gel powders dried at ~ 45 °C were hand-ground with a mortar and pestle and sieved to − 200 mesh. These powders were heated to various temperatures at a heating rate of $1\,^{\circ}\mathrm{C\,min^{-1}}$ in oxygen and cooled in the air. The specific surface areas of 56 mol % gel powders heated to various temperatures in oxygen are presented as a function of temperature in Fig. 4. Unlike other silicate gels which generally have high surface areas, the surface areas of these gel powders were very low at low temperatures. At 150 °C, the surface area of the gel powder was less than $1\,\mathrm{m^2\,g^{-1}}$. As the temperature increased, the surface area increased. At temperatures above 600 °C the surface area was about $4\,\mathrm{m^2\,g^{-1}}$.

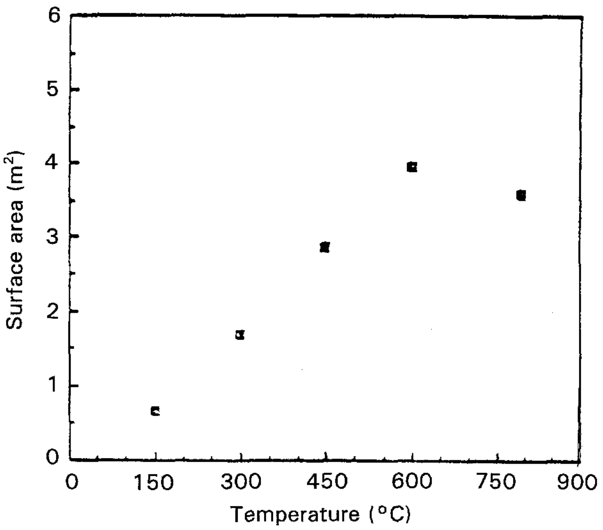

Figure 4 Variation in specific surface area of the 56% phosphosilicate gel powder with heat-treatment temperature.

Suzuki *et al.* [18] have investigated the gels of the system Al_2O_3–P_2O_5–SiO_2 with P_2O_5 concentrations ranging from 7.5–30 mol %, and reported that the specific surface area of the gel with higher P_2O_5 concentration was much lower than that of the gel with lower P_2O_5 concentration, even at low temperatures. Gels with higher P_2O_5 concentration seem to become more dense during the drying process. It is suspected that at low temperatures some phosphoric acid remained unreacted or partially reacted filling the pores of the gel. This effect is believed to contribute to the low specific surface area and to lead to the phase separation. Phase separation in phosphate gels or glasses has been reported by many authors [14, 18–20]. As the temperature increased, the water and organic residues were eliminated giving rise to formation of pores in the gel. The phosphoric acid remaining unreacted in the gel at low temperatures could be

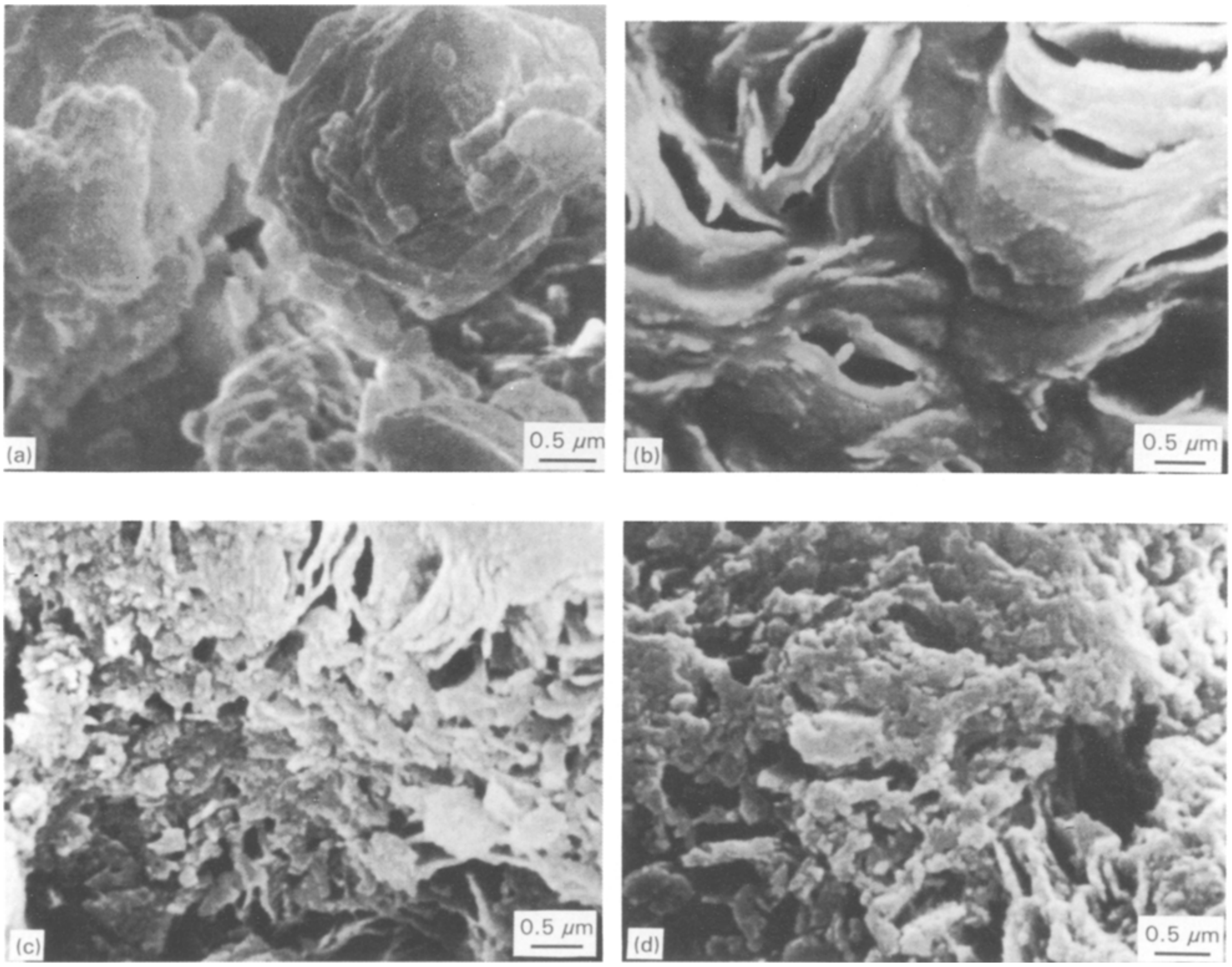

Figure 5 Secondary electron micrographs of the 56% phosphosilicate gel powder heat treated to various temperatures: (a) 150 °C, (b) 300 °C, (c) 600 °C and (d) 800 °C.

incorporated into the structure as the temperature increased [16].

3.4. Change of microstructure with temperature

The microstructures of the gels were examined by scanning electron microscopy (SEM). The secondary electron micrographs of the gel powders heated to each temperature are presented in Fig. 5. The surface of the gel powder heated to 150 °C was smooth and no large pores were detected in the gel. As the heat-treatment temperature was increased, the gel densified. At 300 °C some large pores began to appear. After heating at 600 and 800 °C the density of open pores was much greater than that observed for the gels heated at lower temperatures. These observations of the microstructures of the gel powder are in good agreement with the results of the BET surface area measurement where the specific surface area appeared to increase with increasing heat-treatment temperature.

4. Conclusion

The phosphosilicate gel containing 56 mol % P_2O_5 was prepared by a sol–gel process and the change of the gel microstructure with heat-treatment temperature was studied.

Crystalline phases, $Si_3(PO_4)_4$ and SiP_2O_7, were identified in the heat-treated phosphosilicate gel containing 56 mol % P_2O_5. When the heat-treatment temperature was low (~ 300 °C), $Si_3(PO_4)_4$ was the main crystalline phase in the gel. As the temperature was increased to 800 °C, SiP_2O_7 crystalline phase grew rapidly and became the dominant crystalline phase. From FTIR spectra of the phosphosilicate gel, it was shown that phosphorus entered into the copolymer structure at ~ 600 °C.

Unlike other silicate gels, the specific surface area of the dried phosphosilicate gel was small and increased with increasing heat-treatment temperatures. The increase of the surface area was found to be due to the increase of the density of open pores with the heat-treatment temperatures as shown in the secondary electron micrographs.

Acknowledgement

This work was supported by the Carborundum Company.

References

1. M. YAMANE and T. KOJIMA, *J. Non-Cryst. Solids* **44** (1981) 181.
2. R. ROY, *J. Am. Ceram. Soc.* **52** (1970) 344.
3. S. SAKKA, in "Treatise on Materials Science and Technology", Vol. 22, edited by M. Tomozawa and R. H. Doremus (Academic Press, 1982) p. 129.
4. B. J. J. ZELINSKI and D. R. UHLMANN, *J. Phys. Chem. Solids* **45** (1984) 1069.
5. S. P. MUKHERJEE, *J. Non-Cryst. Solids* **42** (1980) 477.
6. H. DISLICH, *ibid.* **57** (1983) 371.
7. L. H. KAPLAN and M. E. LOWE, *J. Electrochem. Soc.* **118** (1971) 1649.
8. J. WONG, *J. Non-Cryst. Solids* **20** (1976) 83.
9. R. A. BOWLING and G.B. LARRABEE, *J. Electrochem. Soc.* **132** (1985) 141.
10. I. M. THOMAS, US Pat. 3767434 (1973).
11. R. JABRA, J. PHALIPPOU and J. ZARZYCKI, *J. Non-Cryst. Solids* **42** (1980) 489.
12. A. BOULLE and R. JARY, *Compt. Rend.* **237** (1953) 328.
13. W. R. JACOBY, PhD thesis, Rutgers University (1956).
14. G. R. LEVIAND and G. PEYRONEL, *Z. Kristallogr.* **92** (1935) 190.
15. I. N. CHAKRABORTY and R. A. CONDRATE, *Phys. Chem. Glasses* **26** (1985) 68.
16. V. M. KEDYARKIN, T. I. FIRSOVA, N. N. VYSHINSKII, V. A. ALFEROV, G. T. VLASENKO, and S. A. KRIVELEVICH, *Izvest. Akad. Nauk SSSR Neorg. Mater.* **18** (1982) 1904.
17. V. A. KOLESOVA and A. E. MALSHIKOV, *Fizi. Khim. Stekla* **10** (1984) 641.
18. H. SUZUKI, H. SAITO and T. HAYASHI, *J. Mater. Sci.* **19** (1984) 396.
19. A. ROZAJ-BRVAR and R. F. DAVIS, *J. Mater. Sci.* **18** (1983) 2108.
20. C. NELSON and D. R. TALLANT, *Phys. Chem. Glasses* **25** (1984) 31.

Received 28 July 1992
and accepted 31 August 1993