

# A new polymeric route to silicon carbide and silicon nitride using elementary silicon as starting material

M. DECKWERTH, C. RÜSSEL

*Otto-Schott-Institut, Universität Jena, Fraunhoferstr. 6 D/07743 Jena, Germany*

Elementary silicon activated with copper was heated up in tetraethylene pentamine to 300 °C. After drying in vacuum, an amorphous solid was obtained. Calcining this solid under argon at temperatures of up to 1200 °C led to amorphous products, while at higher temperatures silicon carbide was obtained. Calcining in ammonia at temperatures of up to 1000 °C also led to amorphous products. At calcination temperatures of 1200 and 1400 °C crystalline silicon nitride and silicon nitride fibres respectively were obtained. The dependence of the fibre growth on the ammonia flow rate, as well as the occurrence of spherical iron-enriched particles terminating these fibres gave evidence for a vapour–liquid–solid mechanism being responsible for the fibre growth.

## 1. Introduction

In the past few years, a great deal of interest has been focussed on non-oxide ceramics, mainly on silicon carbide and nitride, due to their potential use as high temperature, high strength materials. Until recently, the industrial production of the raw materials had predominantly been based on two different high temperature processes: carbothermal reduction [1, 2] and direct synthesis from the elements using elementary silicon and carbon or nitrogen [3]. Both silicon carbide and nitride possess strong covalent bonds and hence sintering is difficult due to their low self-diffusion coefficients. Therefore, in the last few years, numerous routes have been developed in order to synthesize powders possessing better sinterability than those produced using high temperature routes. Besides routes via the gas phase, such as the reaction of silicon tetrachloride with gaseous ammonia, various routes via tractable polymers have been described in the literature (e.g. [4–6]). The most commonly used techniques for the formation of silicon carbide and nitride use alkylchlorosilanes as starting materials. These silanes are industrially produced from elementary silicon and alkylchlorides using the Rochow synthesis route [7]. During these reactions, various gaseous and monomeric products are formed which can be separated by distillation. For the production of the silicon nitride polymers [8,9] these alkylchlorosilanes are reacted with ammonia or an organic amine. The reduction of alkylchlorosilanes with alkali metals leads to the formation of polysilanes which can be used for production of silicon carbide [10, 11]. In many cases, further reaction steps are required in order to increase the degree of polycondensation or to achieve cross-linking [12–14].

By contrast to the routes described above, this paper introduces a method which uses elementary

silicon and produces tractable polymers in a one-step reaction.

## 2. Experimental procedure

Metallurgical silicon (Alfa Products) was milled in a ball mill until a mean grain size of around 30 µm was reached and then was etched with fluoric acid (20%) for 10 min. After drying, the silicon powder was dispersed in hexane and mixed with copper(I)chloride (CuCl:Si = 1:10), dried again and subsequently heated up to 350 °C for 4 h in argon. The residual powder was added to tetraethylenepentamin ( $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ) and heated under argon and refluxed up to 300 °C for 24 h. After cooling, the suspension obtained was filtrated under pressure ( $5 \times 10^5$  Pa) using a Teflon membrane (pore size 0.45 µm). The solution obtained was dried by slowly heating up ( $3 \text{ K min}^{-1}$ ) to 450 °C. At first a highly viscous solid was obtained which, during the drying procedure, transformed to a solid. Calcining this solid was carried out in a gas tight silica tube under argon or ammonia using a heating rate of  $5 \text{ K min}^{-1}$ , soaking time of 1 h and a maximum temperature of 1300 °C. Calcining at higher temperatures (up to 1500 °C) was carried out in a carbon tube furnace.

The products and intermediates were characterized using X-ray diffraction (XRD; Siemens D500), Fourier transform infrared spectroscopy (FTIR; Mattson Polarix), electron paramagnetic resonance (EPR; Bruker Spectraspin ER 414), thermal gravimetric analysis (TGA; Netzsch STA 409) and scanning electron microscopy (SEM; Cambridge Instruments S250 MK3). The silicon, oxygen and carbon contents were determined using X-ray fluorescence (RFA; Spectra-trace 5000 Tracor X-Ray), high temperature ex-

traction (Leco TC-136) and a carbon analyser (Leco CS-125), respectively.

### 3. Results

Fig. 1 shows XRD-patterns of the initial silicon powder (line a), the silicon powder, activated with CuCl after heat treatment (line b), and the activated Si/Cu-powder after reacting with tetraethylenepentamine for 24 h. In line a, peaks were solely attributable to elementary silicon as can be seen, lines b and c showed lines due to  $\text{Cu}_3\text{Si}$  and metallic copper. The intensity of the  $\text{Cu}_3\text{Si}$ -lines, however, were higher in line b than in c.

Fig. 2, lines a-c, show FTIR-spectra of tetraethylenepentamine, the precursor solution and the dried precursor respectively. In line a, N-H stretching vibrations can be seen at  $3291 [\nu_s(\text{N-H})]$  and  $3358 \text{ cm}^{-1} [\nu_{as}(\text{N-H})]$ . The lines at  $2818$  and  $2930 \text{ cm}^{-1}$  were due to  $\nu(\text{CH}_3)$  vibrations. The broad peak at  $1594 \text{ cm}^{-1}$  was attributable to the  $\delta(\text{NH}_2)$  vibrations, while the peak  $1459 \text{ cm}^{-1}$  was due to the  $\delta_s(\text{CH}_2)$  vibrations. At ca.  $1305 \text{ cm}^{-1}$ , the deformation vibration  $\delta(\text{CH}_2)$  (wagging and twisting) can be seen. The peak at  $1127 \text{ cm}^{-1}$ , and probably that at  $1011 \text{ cm}^{-1}$  was due to  $\nu(\text{C-N})$ , while those in the range of  $778\text{--}913 \text{ cm}^{-1}$  were attributable to  $\delta'(\text{CH}_2)$  (twisting and wagging). Line b, presenting the precursor solution showed a fairly similar spectrum, the most pronounced differences being the appearances of a shoulder at ca.  $1650$  and of a peak at  $950 \text{ cm}^{-1}$ , which might be interpreted as  $\delta(\text{N-H})$  and  $\nu(\text{Si-N})$  [or  $\nu(\text{Si-C})$ ], respectively. During drying, however, the spectrum changed notably, a new line appeared at  $443 \text{ cm}^{-1}$

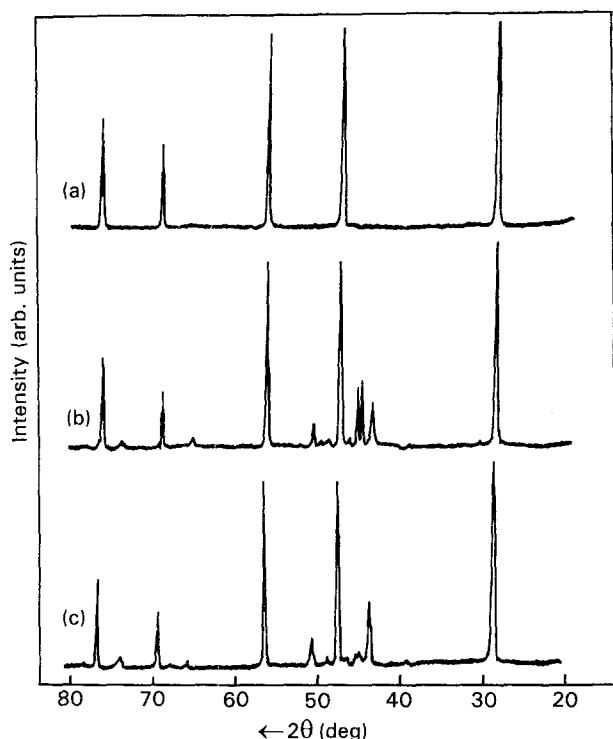


Figure 1 XRD-patterns of (a) elementary silicon; (b) silicon activated with CuCl and heat treated at  $350^\circ\text{C}$ ; (c) activated silicon powder after the reaction with tetraethylenepentamine.

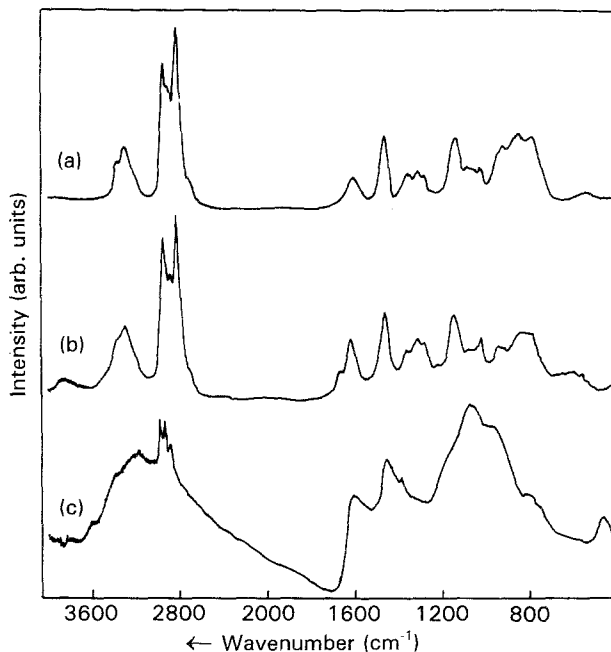


Figure 2 FTIR-spectra of (a) tetraethylenepentamine; (b) precursor solution; (c) the dried precursor.

and a broad peak in the range of  $940\text{--}1250 \text{ cm}^{-1}$ . The latter was attributed to Si-C or/and Si-N vibrations. In the  $\nu(\text{C-H})$  range  $2800\text{--}2960 \text{ cm}^{-1}$ , a new peak between those at  $2818$  and  $2930 \text{ cm}^{-1}$  was observed, possibly due to the formation of  $\text{CH}_3$  groups. EPR spectra showed a strong paramagnetic signal at a  $g$ -value of 2.0023.

Fig. 3 shows the TGA-profile of the dried precursor (heating rate  $5 \text{ K min}^{-1}$ ). A weight loss was not observed up to a temperature of  $400^\circ\text{C}$ . The weight then decreased up to a temperature of  $900^\circ\text{C}$  and subsequently remained constant. The ceramic yield was 24.5%. The analytically determined silicon content of the dried precursor was 17 wt%.

Fig. 4 shows XRD-patterns of the dried precursor (line a) and of products calcined at various temperatures in the range of  $1000\text{--}1400^\circ\text{C}$  under ammonia. While the dried precursor and products calcined at temperatures up to  $1000^\circ\text{C}$  were amorphous, the XRD-patterns of powders calcined at  $1200^\circ\text{C}$  showed extremely broadened lines, attributed to  $\alpha\text{-Si}_3\text{N}_4$  (ASTM card 9-250). At a calcination temperature of  $1250^\circ\text{C}$  these peaks were notably sharper. Increasing the temperature further led to line narrowing. At a temperature of  $1350^\circ\text{C}$ , additional lines attributed to  $\beta\text{-Si}_3\text{N}_4$  were observed. The intensities of these peaks were higher at a sample calcined at  $1400^\circ\text{C}$ . Products calcined at temperatures of up to  $1200^\circ\text{C}$  showed a strong paramagnetic signal ( $g$ -value 2.0023), at higher temperatures the paramagnetism disappeared.

Fig. 5 shows an SEM-micrograph of the product calcined at  $1400^\circ\text{C}$  in ammonia. Comparably coarse particles possessing grain sizes in the range of  $5\text{--}50 \mu\text{m}$  could be seen. Besides this, fine fibres possessing a length in the range of  $20\text{--}200 \mu\text{m}$  and a diameter of  $30\text{--}100 \text{ nm}$  were observed. Fig. 6 shows an SEM-micrograph of a product calcined at the same temperature ( $1400^\circ\text{C}$ ); by contrast to the conditions used for

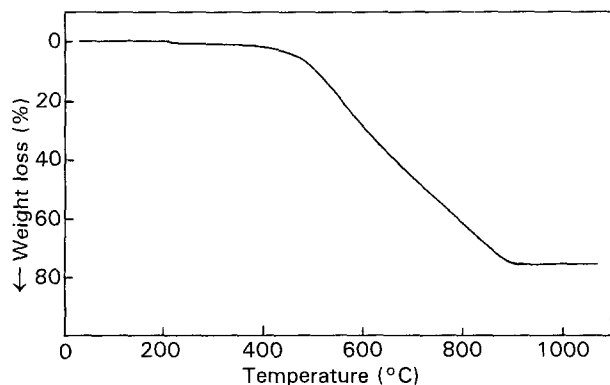


Figure 3 TGA-profile of the dried precursor.

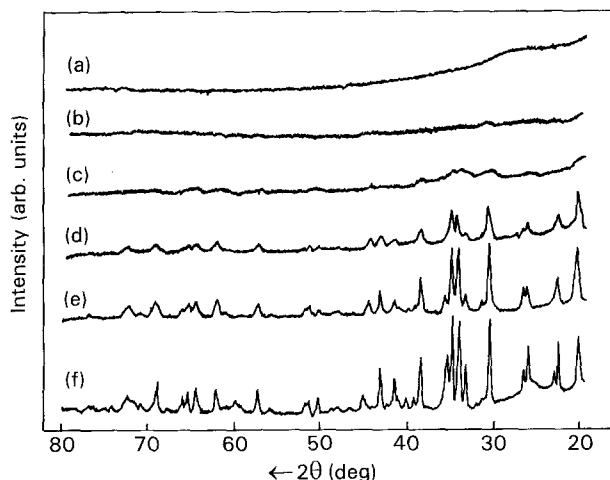


Figure 4 XRD-patterns of (a) dried precursor and products calcined under ammonia; (b) 1000 °C; (c) 1200 °C; (d) 1250 °C (e) 1350 °C; (f) 1400 °C.

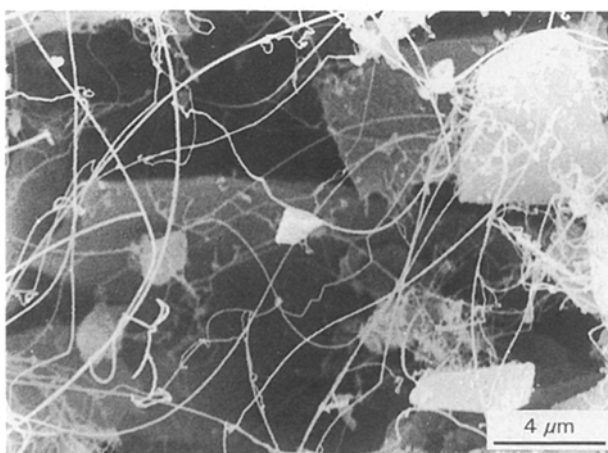


Figure 5 SEM-micrograph of a product calcined under ammonia at 1400 °C (flow rate: 50 ml min<sup>-1</sup>).

the product in Fig. 5, a higher flow rate of the calcination gas was used. Here, only very few particles possessing diameters in the range of 2–20 μm could be seen. The main products, however, were fibres, most of them with a length of several hundreds of micrometres. The diameters were in the range of 100 nm to 3 μm. In contrast to Fig. 5, the fibres can be seen to have possessed a very linear shape. The diameters of

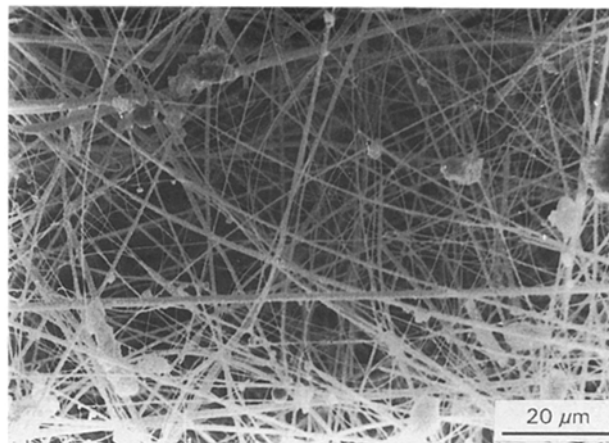


Figure 6 SEM-micrograph of a product calcined under ammonia at 1400 °C (flow rate: 120 ml min<sup>-1</sup>).

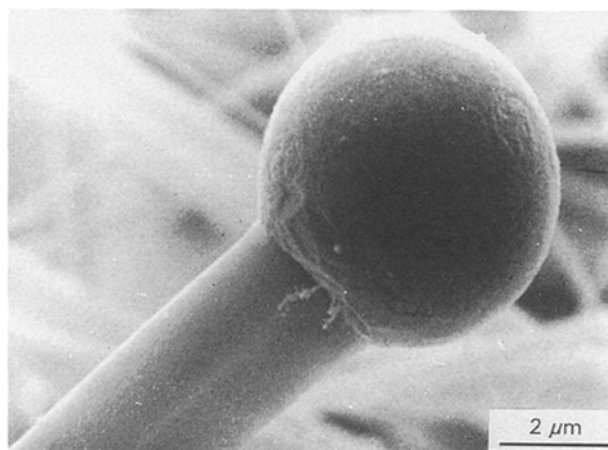


Figure 7 SEM-micrograph of a product calcined under ammonia at 1400 °C (flow rate: 120 ml min<sup>-1</sup>) (higher magnification).

the fibres shown in Figs 5 and 6 were approximately constant over their entire length. In Fig. 7, at a higher magnification, it can be seen that the surface of the fibres was very smooth. The fibres were terminated by spherical particles possessing diameters which were approximately twice those of the fibres. EDX-analysis of the spheres showed a notably higher iron concentration than in the fibres. Fig. 8 shows XRD-patterns of products calcined under argon at temperatures in the range of 1000–1500 °C. At temperatures up to 1200 °C amorphous products were obtained. Calcination at a temperature of 1300 °C led to a product showing extremely broadened lines attributable to β-SiC (ASTM card 29-1131). At higher calcination temperatures, peak narrowing occurred and the XRD-patterns showed lines predominantly due to β-SiC, minor quantities of α-SiC (ASTM card 29-1127), however, coexisted. Calcining at temperatures of 1400 and 1500 °C led to oxygen contents of 2.5 and 0.8 wt %, respectively.

#### 4. Discussion

Elementary silicon did not react with tetraethylpentamine. Mixing of metallurgical silicon with cop-

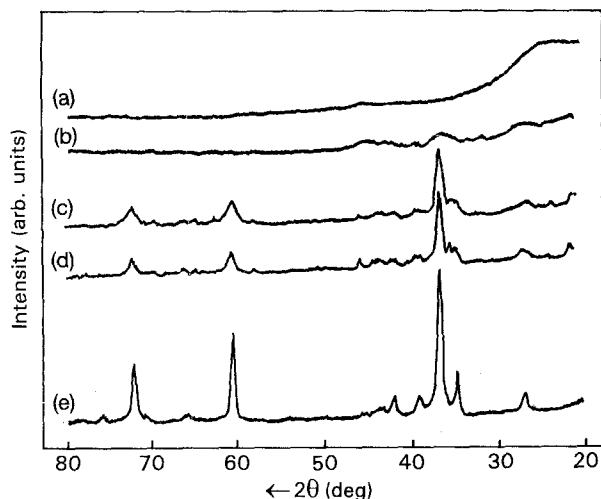


Figure 8 XRD-patterns of products calcined under argon. (a) 1000 °C; (b) 1300 °C; (c) 1400 °C; (d) 1450 °C; (e) 1500 °C.

per (I) chloride led to the formation of  $\text{Cu}_3\text{Si}$  and small quantities of metallic copper. This alloying procedure led to reactive silicon components, which were at least partly, dissolved in tetraethylenepentamine at 300 °C. Rochow synthesis routes with amine compounds in the gas are reported in the literature to be possible only if dimethylamine is used [the product in this case is Tris(dimethylamino)silane] [15]. If other organic amines are used for a gas phase reaction, passivating (and supposedly polycondensed) layers are formed. Performing a Rochow-like synthesis in the liquid phase, as opposed to the gas phase, required the use of an organic amine possessing a high boiling point and hence a high molecular weight. Tetraethylenepentamine has a boiling point of 340 °C and furthermore shows a high nitrogen content (N:C ratio = 5:8). It should be mentioned that tetraethylenepentamine is a large-scale low-cost industrial product, among other purposes it is used as a fertilizer. During the reaction with elementary silicon, large quantities of radicals are formed as proved by EPR-spectroscopy. The  $g$ -value of 2.0023 provided evidence for the occurrence of carbon radical [16]. The occurrence of a passivating layer was not observed and hence the reaction products were assumed to be dissolved in tetraethylenepentamine. By contrast, during a gas phase reaction, products of high molecular weight, such as oligo-polymers cannot be removed from the surface of elementary silicon and hence act as passivating layers.

The FTIR-spectrum of the precursor solution was only slightly different from that of tetraethylenepentamine, whereas the dried precursor showed a completely different spectrum. The broad peak due to Si-N- and/or Si-C- bonds as well as the occurrence of an additional C-H-vibration and the lack of the characteristic lines attributed to tetraethylenepentamine, proved that the formation of the precursor could not be described by a simple reaction of an N-H-acidic compound with a metal forming metal-nitrogen bonds and gaseous hydrogen. The paramagnetism of the precursor also provided strong evidence for a radicalic and more complex reaction mechanism. The agreement of the ceramic yield of

24.5 wt % measured by thermogravimetric analysis and calculated from the silicon content of the dried precursor (as SiC 24 wt %) proved that volatile silicon compounds were not formed during calcination. By comparison to the calcination behaviour reported in the literature from polysilazanes [17, 18], this could be considered as strong evidence for a highly polymeric and cross-linked precursor. Other evidence for a high degree of polycondensation (or polymerization) were the occurrence of the broad FTIR-peak at  $950\text{ cm}^{-1}$  and the X-ray amorphism.

Calcination of the dried precursor at a temperature of 1400 °C in argon led to the formation of  $\beta$ -SiC possessing an oxygen content of ca. 2.5 wt %. Calcining at 1500 °C led to a notable decrease in the oxygen content to ca. 0.8 wt %, supposedly due to the evaporation of SiO. Simultaneously, the  $\beta$ -SiC was partly transformed to  $\alpha$ -SiC. The analytical carbon content of 30 wt% was in good agreement with that of stoichiometric silicon carbide.

At temperature above 950 °C the weight remained constant, crystallization, however, required much higher temperatures. The extremely broadened XRD-lines observed after calcining in ammonia at 1200 °C were attributed to  $\alpha$ - $\text{Si}_3\text{N}_4$  possessing a mean crystallite size of ca. 8 nm, as calculated using the Scherrer equation. Higher calcination temperatures led to peak narrowing due to crystal growth, and, with further increasing temperatures to a transformation of  $\alpha$ - $\text{Si}_3\text{N}_4$  to  $\beta$ - $\text{Si}_3\text{N}_4$ . Calcination at 1400 °C caused the formation of  $\beta$ - $\text{Si}_3\text{N}_4$ -fibres. The shape of these fibres, as well as the occurrence of spherical particles terminating the fibres, were fairly similar to those observed during SiC-whisker growth in a gas phase reaction. It should be noted that also in SiC-whisker growth, an enrichment of iron in the spheres was observed. Usually, whisker growth requires the coexistence of a solid, liquid and vapour phase (vapour-liquid-solid mechanism). Therefore, Fig. 7 shows strong evidence that the growth of the  $\text{Si}_3\text{N}_4$  fibres during calcining the polymeric precursor, depended on the same mechanism. Then, the iron enriched spheres should form the liquid phase at temperatures as high as 1400 °C. Further evidence for the participation of the gas phase was the influence of the ammonia flow rate illustrated in Figs 5 and 6. This could be interpreted assuming a higher flow rate facilitating the transport of silicon compounds in the gas phase and hence accelerating the whisker growth. It should be noted that whisker growth could not be observed at temperatures below 1400 °C.

## Acknowledgement

This work was funded by the Deutsche Forschungsgemeinschaft (DFG).

## References

1. A. SZWEDA, A. HENDRY and K. H. JACK, *Proc. Brit. Ceram. Soc.* **31** (1981) 107.
2. G. C. WEI, C. R. KENNEDY and L. A. HARRIS, *Amer. Ceram. Soc. Bull.* **63** (1984) 1054.

3. J. S. HAGGERTY, A. LIGHTFOOT, J. E. RITTER, S. V. NAIR and P. GENNARI, *Ceram. Eng. Sci. Proc.* **9** (1988) 1073.
4. D. SEYFERTH, G. H. WISEMAN, J. M. SCHWARK and Y.-F. YU, *Amer. Chem. Soc.* **71** (1988) 143.
5. R. W. RICE, *Amer. Chem. Soc.* **62** (1983) 889.
6. B. E. WALKER, R. W. RICE, P. F. BECHER, B. A. BENDER and W. S. COBLENZ, *Amer. Ceram. Soc. Bull.* **62** (1983) 916.
7. E. G. ROCHOW, *J. Amer. Chem. Soc.* **67** (1945) 963.
8. S. YAJIMA, J. HAYASHI and M. OMORI, *Chem. Lett.* (1975) 931.
9. T. ISHIKAWA, M. SHIBUYA and T. YAMAMURA, *J. Mater. Sci.* **25** (1990) 2809.
10. D. SEYFERTH, G. H. WISEMAN and C. PRUD'HOMME, *J. Amer. Ceram. Soc. Commun.* **66** (1983) C-13
11. Y. D. BLUM, K. B. SCHWARTZU and R. M. LAIN, *J. Mater. Sci.* **24** (1989) 1707.
12. D. SEYFERTH and G. H. WISEMAN, *J. Amer. Ceram. Soc.* **67** (1984) C-132
13. R. M. LAINEET, Y. D. BLUM, A. CHOW, R. HAMLIN, K. B. SCKWARTZ and D. J. ROWECLIFFE, *Polymer Preprints* **28** (1987) 393.
14. C. L. SCHILLING, J. P. WESSON and T. C. WILLIAMS, *Amer. Ceram. Soc. Bull.* **62** (1983) 921.
15. B. KANNER, in "Silicon chemistry", edited by E. R. Corey, (John Wiley & Sons, New York, 1988) p. 123.
16. G. D. SORARU, *J. Mater. Sci.* **25** (1990) 3886.
17. C. L. SCHILLING, J. P. WESSEL and T. C. WILLIAMS, *J. Polym. Sci. Polym. Symp.* **70** (1983) 121.
18. D. SEYFERTH and G. H. WISEMAN, *J. Amer. Ceram. Soc.* **67** (1984) C-132.

*Received 23 June 1993  
and accepted 28 February 1994*