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Near-stoichiometric silicon carbide from a poly(methylsilylene)/tetra-allylsilane mixture

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This paper describes the use of a bi-component mixture of poly(methylsilylene), PMS, and tetra-allylsilane, TAS, in variable composition, as a pyrolytic precursor to SiC. The ceramic products were characterized by elemental analysis, ^{29}Si MAS NMR, actual density measurements, XRD and TEM. The PMS/TAS mixture produces, in an appropriate ratio, near-stoichiometric SiC with an apparent composition of 99% SiC and 1% C, after pyrolysis up to 1000 °C under inert atmosphere, in a reasonable yield. © *1999 Kluwer Academic Publishers*

1. Introduction

The use of polymers as precursors to silicon carbide, SiC, has received continuous attention, since Yajima *et al*. [1] developed a poly(carbosilane) suitable for conversion into SiC-based fibers. Due to the polymeric nature of these ceramic precursors, this process can be extended to production of ceramic composites [2], monoliths [3], powders [4], and coatings [5].

A great variety of preceramic organosilicon polymers have been developed in the last two decades with significant improvements in the synthetic route, purity and mainly in the ceramic yield of the final product. However, these materials usually showed an excess of carbon in their compositions [6]. The pyrolysis of poly(silaethylene), PSE [7], and poly(methylsilylene), PMS [8], both with 1 : 1 Si : C ratio, was studied in order to achieve a stoichiometric product. Nevertheless, the former requires an expensive method of preparation, whereas PMS obtained from relatively low cost reagents produces SiC with an excess of Si.

Knowledge of the structural evolution by which the polymer is converted to ceramics is important for making changes in the structure of the precursor, in order to improve its performance. Our previous studies have demonstrated that a mixture involving PMS and tetra-allylsilane, TAS, can be a good candidate to a SiC precursor system [9]. In this report, the pyrolysis of several different compositions of PMS/TAS mixtures was investigated in order to produce near-stoichiometric SiC.

2. Experimental procedure

2.1. General comments

All manipulations involving the organosilicon compounds before their ceramization were carried out under argon atmosphere, in oven-dried glassware and in some cases, inside a glove-bag filled with argon. Solvents were purified and dried using standard techniques. CH_3HSiCl_2, $(CH_3)_3SiCl$ and $SiCl_4$ were freshly distilled in presence of CaH_2 prior to their use. $CH_2{=}CHCH_2Br$ was distilled under argon before use. Magnesium turnings were washed with benzene, followed by acetone, and dried at 100 °C for 3 h immediately before their use.

2.2. PMS synthesis

Poly(methylsilylene) was prepared according to the conventional Wurtz reaction between CH_3HSiCl_2 and Na in toluene. At the final stage of the reaction, $(CH_3)_3SiCl$ was added into the reactional solution as the blocking-chain agent. More details about the PMS synthesis can be found in our previously reported procedure [10]. Found composition (from ^{1}H NMR data): $Me_3Si\text{-}[(CH_3HSi)_{0.7}(CH_3Si)_{0.3}]_n\text{-}SiMe_3$, $n \sim 23$, $M_n = 1000$, in a 50% yield. FTIR (neat, cm^{-1} (assignment) [11, 12]): 2956, 2893 (νCH, CH_3), 2104 (νSiH), 1408, 1247 (δCH, $SiCH_3$), 1038 (νSiOSi), 931 (γSiH_2), 866 (ρCH_3), 774, 685 (νSiC). ^{29}Si NMR (ppm, assignment [8a, 10, 13]): -68.0 ($SiCH_3$), -63.0 ($HSiCH_3$), and minor peaks at -34.9, 7.5 and 20.4 from $-Si(CH_3)H_2$, $-Si(CH_3)_3$ and $-Si(H)(Cl)CH_3$ end groups, respectively. ^{1}H NMR (ppm, assignment [13]): ($HSiC\boldsymbol{H}_3$), 3.93, 4.10 (SiH), 5.14 (SiH_2 and $Si(\boldsymbol{H})(Cl)CH_3$ end groups), 5.55 (SiOH traces).

2.3. TAS synthesis

Tetra-allylsilane was prepared by a reaction between $CH_2{=}CHCH_2MgBr$ and $SiCl_4$, according to the procedure described by O'Brien *et al*. [14]. Its synthesis was confirmed by FTIR and ^{1}H NMR spectra [15].

2.4. PMS/TAS mixture

PMS was dissolved in TAS, under inert atmosphere, and stored in a Schlenk-type reservoir until use. The ratios

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TABLE I Composition of the PMS/TAS mixtures

Code	PMS/TAS molar ratio	SiH/C=C bonds molar ratio
P_1	1/0.5	8/1
P_2	1/1.3	3/1
P_3	1/2.2	1.8/1
P_4	1/2.8	1.4/1
P_5	1/3.6	1.1/1

and respective codes for the several prepared mixtures are displayed in Table 1.

2.5. Ceramic conversion

The samples were pyrolyzed in alumina crucibles in a EDG tube furnace, model EDGCON 5P, equipped with a temperature controller, under an atmosphere of flowing argon (50 ml/min). The final temperature (1100 °C) was reached with a heating rate of 10 °C/min. Typically, each sample was held at this temperature for 3 h. The ceramic material derived from P_1 composition (see Table I) was fired at 1500 °C for 2 h, under ambient atmosphere, in a EDG F-1700 furnace.

2.6. Characterization

Elemental analyses were performed in a Perkin Elmer 2400 Elemental Analyzer using the procedure suggested by [16]. The accuracy was checked with reference samples and the deviation was around 3%. The products were analyzed by Fourier transform infrared spectroscopy (FTIR) as neat samples or as the conventional KBr pellets on a Perkin Elmer 1600 spectrometer. Solid state ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) (59.6 MHz) spectra were run with samples spinning at ~5 kHz on a Bruker AC300P instrument, using a pulse width of 3.5 μs and a pulse delay of 1 s. TMS (tetramethylsilane) referenced the chemical shift. For thermogravimetric analyses, a DuPont 1090B thermogravimetric analyzer, on line with a DuPont 951 thermal analyzer, was used at a heating rate of 10 °C/min, under argon flux. Differential scanning calorimetry (DSC) measurements were done in a TA Instruments DSC 2910 calorimeter on line with a TA Instruments 2100 thermal analyzer. The curves were obtained without previous thermal treatment of the samples, in a temperature range of 20 to 300 °C, under argon flux (50 ml/min). Samples were put in closed aluminum reservoirs, and were heated at a 10 °C/min rate. X-ray diffraction patterns (XRD) were recorded on a Schimadzu diffractometer, model XD3A, using CuKα radiation. The grain size values were calculated from the FWHH (full width of half height) of the peak centered at 35.6°, through the use of Scherrer's equation [17]. For transmission electron microscopy observations (TEM), the samples were ground to a very fine powder, then dispersed in isopropanol and transferred onto a 100 mesh copper grid (parlodium coated) using an eye dropper. These examinations were performed on a Zeiss CEM 902 microscope using 80 eV electrons. Actual density measurements were obtained from a 1305 picnometer Micromeritics by the method of gas dislocation. The samples were dried at 120 °C for 1 h and purged with He at least 10 times before measuring. Finally, the number-average molecular weight, M_n, of PMS was determined by vapor pressure osmometry (VPO) on a Knauer instrument using toluene solutions thermostatically controlled at 45 °C.

3. Results and discussion

PMS was obtained as a very air-sensitive viscous liquid. If exposed to air for a few minutes, the pyrophoric character of the SiH bonds could set materials like paper or wool on fire [18]. Some of the SiH bonds were consumed by the metallic sodium during the Wurtz coupling; therefore, the resultant polymer is actually a polysilylene-polysilyne copolymer: $Me_3Si\text{-}[(CH_3HSi)_{0.7}(CH_3Si)_{0.3}]_n\text{-}SiMe_3$. Despite having a 1 : 1 Si : C ratio, its pyrolysis up to 1100 °C under argon leads to a silicon-rich ceramic material (62% SiC, 38% Si) in a poor yield (~20%). Several authors have reported similar results [8, 19]. This somewhat disappointing performance is mainly attributed to the volatilization of CH_4, H_2, cyclic organosilanes, and oligomers during pyrolysis [6, 20]. To overcome this problem, PMS was crosslinked by addition of TAS through a hydrosilylation reaction [21]. The cure step of this system occurs during the pyrolysis in the absence of catalyst (to avoid metal contamination) at around 200 °C [9]. TAS was chosen as the tetra-functional reactant because its boiling point (215 °C) is high enough to allow hydrosilylation to take place before its evaporation. Its inferior analogue, tetravinylsilane, has low boiling point (131 °C) and therefore is unsuitable for these purposes. TAS has a 1 : 12 Si : C ratio, and can also serve to diminish the excess of Si in the final products.

PMS/TAS mixtures were prepared in several compositions (Table I). The ratio of C=C to SiH bonds gets progressively higher from P_1 to P_5 composition. Fig. 1 shows the DSC curves of these mixtures. As expected,

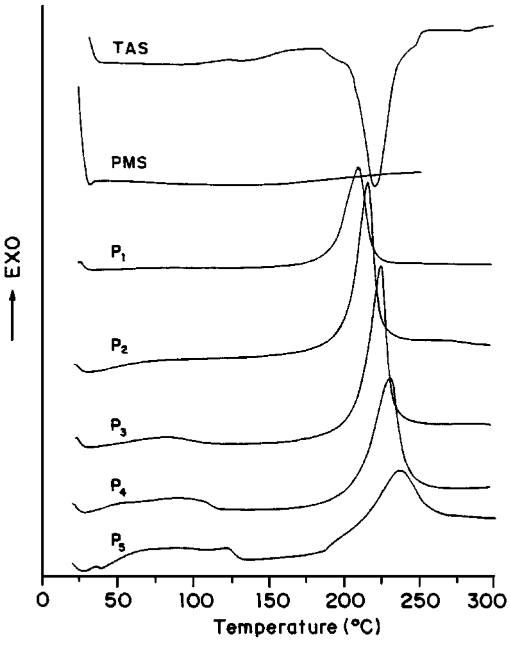

Figure 1 DSC curves of the PMS/TAS mixtures and pure PMS and TAS.

TABLE II Temperature of hydrosilylation, T_{hyd}; its associated enthalpy, ΔH_{hyd}; and the enthalpy normalized in relation to the C=C bonds molar content, $N\Delta H_{hyd}$

Precursor mixture	$T_{hyd,}$ (°C)	$\Delta H_{hyd,}$ (J/g)	$N\Delta H_{hyd,}$ (J/g)
P_1	209	276	1970
P_2	216	471	1625
P_3	224	448	1051
P_4	230	406	864
P_5	237	381	712

each curve has an exothermal peak assigned to the hydrosilylation process, which becomes broader as the PMS/TAS ratio decreases from P_1 to P_5 compositions.

Table II shows the data obtained from the DSC experiments. The hydrosilylation temperature, T_{hyd}, was taken as the temperature at the peak maximum. A shift of its value upward from P_1 to P_5 compositions can be observed, i.e., T_{hyd} increases as the relative SiH content in the PMS/TAS mixtures decreases. This behavior suggests that SiH bonds drive the hydrosilylation reaction in these experimental conditions.

ΔH is invariant for a given reaction if the molar quantity of the limiting reagent is kept constant and there are no changes in the reaction yield [22]. In this particular system, TAS is always the limiting reagent in the hydrosilylation reaction. Therefore, ΔH_{hyd} values once normalized in relation to the molar amount of TAS (coded $N\Delta H_{hyd}$) can be a probe for reaction yield changes. Table II shows that the $N\Delta H_{hyd}$ magnitude decreases as the SiH/C=C molar ratio decreases, confirming the role of SiH bonds as the active species in these thermally induced reactions.

Even though rheological measurements have not been run, we observed visually a gradual increase of the viscosity of the PMS/TAS mixture, which passed from liquid to solid state, as the hydrosilylation reaction took place. These viscosity changes are potentially useful for spinning fibers or casting films. Furthermore, instead of oxidizing the poly(carbosilane) fiber to achieve dimensional stability as described by Yajima *et al.* [1], the PMS/TAS mixture could be heated under an inert atmosphere for a few minutes, avoiding the introduction of oxygen in the final SiC fiber, which would weaken its mechanical properties [6].

Table III shows data related to the ceramic products obtained after the pyrolysis of the precursor mixtures. An increase in the ceramic yield in relation to pure PMS is observed in all studied compositions. The ceramic composition is, as expected, a function of the starting PMS/TAS ratios, and the P_1-derived ceramics was obtained as a quasi-stoichiometric material, in a reasonable yield and high purity. These results were reproduced in three consecutive pyrolyses, with a deviation of 3%.

When the pyrolysis was carried out with a holding plateau of 10 min at the respective T_{hyd} of each composition, there was an increase in all ceramic yields, probably due to an improvement on the curing process.

One can notice a certain relationship between the composition of the ceramics and its actual density value (i.e. free of the contribution of pores). The quasi-stoichiometric product shows exactly the expected density for β-SiC, whereas the Si-rich or C-rich materials display lower values, since both Si and C are less dense than SiC [23].

Reflections centered at 35.6° (111), 60.2° (220), and 71.8° (311) (2θ) in the XRD patterns confirmed the presence of β-SiC crystallites [24]. ^{29}Si MAS NMR investigations, however, also showed a minor presence of α-SiC indicated by shoulders on the main peak ($\delta = -15.3$ ppm) at -19.8 and -23.5 ppm [25] (Fig. 2). The occurrence of α-phase at low temperatures is not usual, but has already been reported [8a].

The average grain size of the β-SiC crystallites shows a slight tendency to decrease as the excess of carbon in its composition increases. This behavior can be attributed to the effect of grain growth control of carbon when dispersed in SiC matrix [26]. Actually, a little excess of carbon is not totally undesirable, since grain growth during a thermal treatment could crack an eventual SiC-made device [6].

P_1 derived material was submitted to a firing at 1500 °C for 2 h under ambient atmosphere. As a result, the average grain size jumped from 40 Å to 60 Å, and a coating of silica was formed on the SiC surface. The appearance of a reflection at 21.9° (2θ) in the XRD pattern and a band at 621 cm^{-1} in the FTIR spectrum confirmed this silica layer crystallized as α-cristobalite [24, 27], (Figs 3 and 4).

Quantitative ^{29}Si MAS NMR showed that the extension of the oxidation was 10% in weight (SiC versus SiO_2). Further heating for another 4 h, at the same temperature, did not change this value, but a shoulder at -58.7 ppm ($CSiO_3$ species) [28] appeared in the ^{29}Si MAS NMR spectrum.

Finally, Fig. 5 shows by TEM micrographs that SiC was obtained as nanocrystallites, which are homogeneously distributed in the ceramic matrix, with no evidence of pores.

TABLE III Ceramic yield (with and without an isotherm at T_{hyd}); composition; actual density; and estimated grain size of the prepared ceramic materials

Sample	Ceramic yield (TGA, std run), (%)	Ceramic yield (TGA, with an isotherm at T_{hyd}), (%)	Apparent ceramic composition, (%)	Actual density, (g/cm^3)	Average grain size, (Å)
PMS	20	—	60 SiC; 38 Si	2.95	40
P_1	57	64	99 SiC; 1 C	3.21	40
P_2	58	63	87 SiC; 13 C	3.16	34
P_3	47	57	86 SiC; 14 C	2.61	32
P_4	53	59	83 SiC; 17 C	2.54	29
P_5	50	57	80 SiC; 20 C	2.30	27

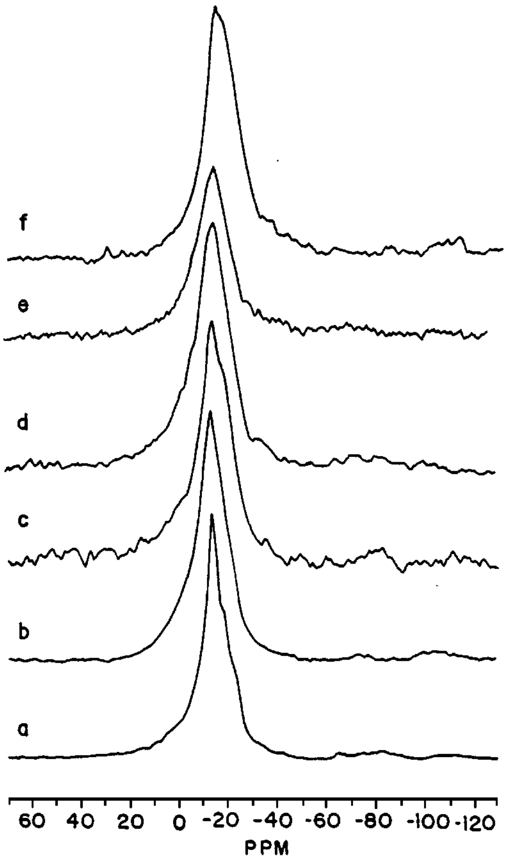

Figure 2 ^{29}Si MAS NMR spectra of SiC prepared from (a) PMS; (b) P_1; (c) P_2; (d) P_3; (e) P_4; (f) P_5.

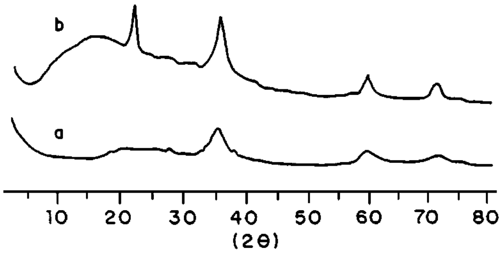

Figure 3 XRD patterns of SiC derived from P_1 composition (a) before and (b) after a heating treatment at 1500 °C, for 2 h, under ambient atmosphere.

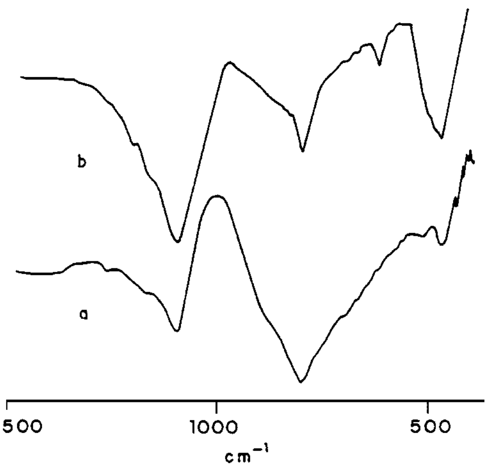

Figure 4 FTIR spectra (KBr pellets) of SiC derived from P_1 composition (a) before and (b) after a heating treatment at 1500 °C, for 2 h, under ambient atmosphere.

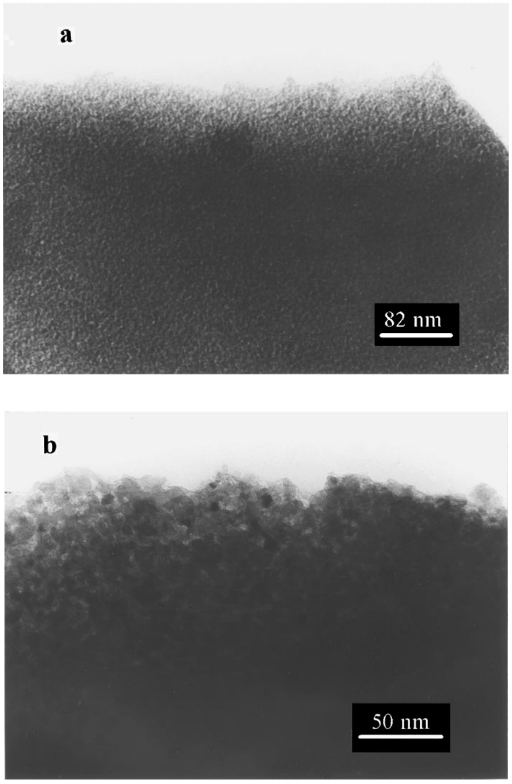

Figure 5 TEM micrographs of SiC derived from P_1 composition (a) before and (b) after a heating treatment at 1500 °C, for 2 h, under ambient atmosphere.

4. Summary and conclusions

The reported investigations show that the PMS/TAS mixture is suitable as a SiC precursor. By varying the starting PMS/TAS ratio it is possible to control the composition of the ceramic material. In this manner, a near stoichiometric product could be obtained. An increase of the viscosity of the precursor slurry during the ceramization process was observed. This property is potentially useful in the molding steps.

The ceramic products presented SiC nanocrystallites homogeneously distributed, with no evidence of voids or pores. The average grain size of the β-SiC crystallites showed a decrease as the excess of carbon in its composition increased.

Annealing at 1500 °C of the P_1-derived ceramic, in air, created a cristobalite layer that protected it against further oxidation. However, some grain growth did take place.

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References

1. (a) S. YAJIMA, J. HAYASHI and M. OMORI, *Chem. Lett.* (1975) 931; (b) S. YAJIMA, M. OMORI, J. HAYASHI, K. OKAMURA, T. MATSUZAWA and C.-F. LIAW, *Chem. Lett.* (1976) 551; (c) S. YAJIMA, T. SHISHIDO and H. KAYANO, *Nature* **264** (1976) 237.

2. (a) C. MROZ, *Ceram. Bull.* **72** (1992) 89; (b) D. SEYFERTH and P. CZUBAROW, *Chem. Mater.* **6** (1994) 10; (c) D. BARIL, S. P. TREMBLEY and M. FISET, *J. Mater. Sci.* **28** (1993), 5486; (d) C. K. NARULA, J. E. ALLISON, D. R. BAUER and H. S. GANDHI, *Chem. Mater*. **8** (1996) 984.
3. B. E. WALKER, R. W. RICE, P. F. BECHER, B. A. BENDER and W. S. COBLENZ, *Ceram. Bull.* **62** (1983) 916.
4. K. E. GONSALVES, P. R. STRUTT, T. D. XIAO and P. G. KLEMENS, *J. Mater. Sci.* **27** (1992) 3231.
5. (a) M. R. MUCALO, N. B. MILESTONE, I. C. WICKRIDGE and M. V. SWAIN, *J. Mater. Sci.* **29** (1994) 4487; (b) M. R. MUCALO and N. B. MILESTONE, *J. Mater. Sci.* **29** (1994) 5934.
6. R. M. LAINE and F. BABONNEAU, *Chem. Mater.* **5** (1993) 230.
7. H.-J. WU and L. V. INTERRANTE, *Macromolecules* **25** (1992) 1840.
8. (a) Z.-F. ZHANG, F. BABONNEAU, R. M. LAINE, Y. MU, J. F. HARROD and J. A. RAHN, *J. Am. Ceram. Soc.* **74** (1991) 670; (b) D. SEYFERTH, T. G. WOOD, H. J. TRACY and J. L. ROBISON, *J. Am. Ceram. Soc.* **75** (1992) 1300; (c) D. SEYFERTH, M. TASI, H.-G. WOO, P. CZUBAROW, H. J. TRACY, J. L. ROBISON and G. KOPPETSCH, *Abstr. of papers of the Am. Chem. Soc.* **20**5 (1993) 127.
9. M. F. GOZZI and I. V. P. YOSHIDA, *Eur. Polym. J.* **33** (1997) 1301.
10. M. F. GOZZI and I. V. P. YOSHIDA, *Macromolecules* **28** (1995) 7235.
11. M. SCARLETE, S. BRIENNE, I. S. BUTTLER and J.-F. HARROD, *Chem. Mater.* **6** (1994) 977.
12. J. BULLOT and M. P. SCHIMIDT, *Phys. Stat. Sol. B.* **143** (1987) 345.
13. (a) H. MARSMANN, in “NMR Basic Principles and Progress” (Springer-Verlag, Berlin, Hildenberg and New York, 1981); (b) J. SCRAML and J. M. BELLAMA, in “Determination of Organic Structures by Physical Methods” (Academic Press, New York, 1976); (c) R. K. HARRIS and B. J. KIMBER, *J. Magn. Reson.* **17** (1975) 174.
14. S. O’BRIEN, M. FISHWICK, B. McDERMOTT, M. G. H. WALLBRIDGE and G. A. WRIGHT, *Inorganic Synthesis* **13** (1971) 73.
15. (a) G. DAVIDSON, P. G. HARRISON and E. M. RILEY, *Spectrochim. Acta, Part A* **29** (1973) 1265; (b) L. DELMULLE and G. P. VAN DER KELEN, *J. Mol. Struct.* **66** (1980) 315.
16. P. P. BORDA and P. LEGZIDINS, *Anal. Chem.* **52** (1980) 1777.
17. B. D. CALLITY, in “Elements of X-ray Diffraction” (Addison-Wesley, Reading, MA, 1978).
18. J. Y. COREY, in “The Chemistry of Organosilicon Compounds,” eds. S. Patai and Rappoport, (John Wiley & Sons, Chichester, 1989).
19. (a) T.-A. KOBAYASHI, T. SAKAKURA, T. HAYASHI, M. YUMURA and M. TANAKA, *Chem. Lett.* (1992) 1157; (b) E. HENGGE and M. WINBERG, *J. Organomet. Chem.* **433** (1992) 21.
20. R. J. P. CORRIU, D. LECLERQ, P. H. MUTIN, J.-M. PLANEIX and A. VIOUX, *Organometallics* **12** (1993) 454.
21. J. L. SPEIER, *Adv. Organomet. Chem.* **17** (1979) 407.
22. I. N. LEVINE, in “Physical Chemistry” (McGraw-Hill Book Company, New York, 1983).
23. Gmelin Handbook of Inorganic Chemistry, Suppl vol **B2** (1984) and vol **B3** (1986) (Springer-Verlag, Berlin).
24. Powder Diffraction File Search Manual, Joint Committee on Powder Diffraction Standards (Swarthmore, 1973).
25. J. S. HARTMANN, M. F. RICHARDSON, B. L. SHERIFF and B. G. WINSBORROW, *J. Am. Chem. Soc.* **109** (1987) 6059.
26. R. HAMMINGER, *J. Am. Ceram. Soc.* **72** (1989) 1741.
27. (a) J. ETCHEPARE, M. MERIAN and M. KAPLAN, *J. Chem. Phys.* **68** (1978) 1531; (b) D. TAFFOLO and J. N. LECKINTON, *Am. Ind. Hyg. Anoc. J.* **42** (1981) 579.
28. Z.-F. ZHANG and C. G. PANTANO, *J. Am. Ceram. Soc.* **73** (1990) 958.

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