JOURNAL OF MATERIALS SCIENCE 30 (1995) 2686–2693

# Synthesis of silicon carbide through the sol–gel process from different precursors

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Silicon carbide (SiC) was synthesised from silicon alkoxides and various carbon sources. Tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and a mixture of TEOS and MTES were hydrolysed in the presence of phenolic resin, ethylcellulose, polyacrylonitrile (PAN) and starch to incorporate the gel into the carbon source in the silica network. The gel thus obtained was carbonized at 800 °C in an argon atmosphere to obtain the mixture of silica and carbon which when heated to 1550 °C in argon yielded silicon carbide. The characterization of the product by X-ray, FTIR and SEM showed it to be β SiC with different crystallite and grain sizes. The difference in the crystallite and grain sizes is attributed to the nature of the carbon source. The density of the SiC obtained by the sol–gel process was found to be lower than the values reported for SiC and this is ascribed to the porous nature of the products generally obtained by this process.

## 1. Introduction

Silicon carbide is an important non-oxide ceramic which has various industrial applications. The conventional method of preparation involves heating silica or colloidal silica with carbon at very high temperatures [1–5]. The recently developed sol–gel technique offers an easy route to synthesise silicon carbide by employing alkoxides and a suitable carbon source [2, 6–11]. Synthesis of silicon carbide through the sol–gel process without using an external carbon source has also been reported [6–10]. The present investigation employs the sol–gel process by preparing silica gel containing carbonaceous materials such as phenolic resin, ethylcellulose polyacrylonitrile (PAN) and starch by hydrolysis condensation of easily available tetraethoxysilane (TEOS), monomethyl triethoxysilane (MTES) and a mixture of TEOS and MTES in the presence of phenolic resin, ethylcellulose PAN and starch. The gel obtained when carbonized at 800 °C in argon and later heated to 1550 °C in argon yielded silicon carbide. The authors have also investigated the effect of heating the precursors at different temperatures and shown that the formation of crystalline silicon carbide takes place as low as 1350 °C.

## 2. Materials and methods

### 2.1. Preparation of gels

### *2.1.1. Preparation of gels with phenolic resin as carbon source*

60 g of phenolic resin was dissolved in 175 ml of acetone by constant stirring and 50 ml of TEOS (E'Merck 98%) was added followed by 30 ml of water and 15 ml of ethanol. The mixture was stirred well with a magnetic stirrer for about 5 h, and kept at 40 °C for gelling, ageing and drying. The same experiment was repeated with 30 g of phenolic resin dissolved in 60 ml of acetone and with a mixture containing 50 ml of MTES (Aldrich 98%), 25 ml of water and 48 ml of ethanol to incorporate the MTES gel into the phenolic resin. Preparation of the copolymer incorporated with phenolic resin was carried out using 80 g of phenolic resin, 120 ml of acetone, 50 ml of TEOS, 40 ml of MTES, 50 ml of ethanol and 25 ml of water.

### *2.1.2. Preparation of gel incorporated with ethylcellulose*

50 ml of TEOS, 25 ml of water, 150 ml of ethanol, 50 g of ethylcellulose and 50 ml of acetone were stirred for about 2 h. 25 ml of ammonium hydroxide (25%) was added to the solution and the stirring was continued for about 2 h. The sol was allowed to gel, age and dry at 40 °C. The same experiment was repeated with 50 ml of MTES, 25 ml of water, 175 ml of ethanol, 100 ml of acetone, 60 g of ethylcellulose and 25 ml of ammonium hydroxide.

### *2.1.3. Preparation of gel with PAN*

28 g of PAN was dissolved in 100 ml of dimethylformamide by heating. To this solution was added a well stirred mixture containing 50 ml of TEOS, 30 ml of water and 40 ml of ethanol. The solution was stirred well for about 3 h, breaking the lumps which are formed. The solution was left for gelling and ageing at 40 °C and dried at 60 °C.

### *2.1.4. Preparation of gel with starch*

50 ml of TEOS was mixed with a solution containing 50 g of starch, 100 ml of water and 100 ml of ethanol

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and stirred with a magnetic stirrer for about 5 h. The sol was kept at 40 °C for gelling, ageing and drying.

## 2.2. Carbothermic reduction of gels

The gels obtained above were pelleted (except the gel containing PAN), weighed and carbonized at 800 °C in a quartz tube furnace in an argon atmosphere and later heated at 1550 °C in an argon flow using a carbolite furnace fitted with a recrystallized alumina tube. The samples were kept at 1550 °C for about 2 h. A few samples were heated at 1300 and also at 1350 °C to study the optimum temperature conditions required for the synthesis of silicon carbide.

The products obtained were heated at 600 °C in air to remove excess carbon and then treated with dilute hydrofluoric acid to remove excess silica before testing resistance to acids, alkalies and also to heating at high temperatures.

## 2.3. Characterization

The products were analysed by Fourier infrared spectroscopy (KBr method) using a Nicolet instrument. The microstructures of the samples were determined by scanning electron microscopy (SEM) (Jeol, 35 CF using 25 kV accelerating voltage) and the X-ray patterns were obtained using a Siemens D-500 X-ray diffractometer.

The densities of the samples which were synthesized in the form of pellets were determined by Archimedes' principle using kerosine as the immersion liquid.

## 3. Results and discussion

The colour of the products ranged from light-green to greyish-black depending upon the amount of free carbon in the final product. The samples prepared with TEOS + phenolic resin, TEOS + PAN and TEOS + starch precursors were greyish-black since they contain a large excess of free carbon, and the samples prepared with MTES + phenolic resin and copolymer + phenolic resin were grey due to the presence of a small excess of free carbon. The samples prepared with ethylcellulose as the carbon source were light-green in colour due to the negligible amount of free carbon present in these samples.

The X-ray patterns of the samples are given in Figs 1–3. It is seen from the diffractograms that the

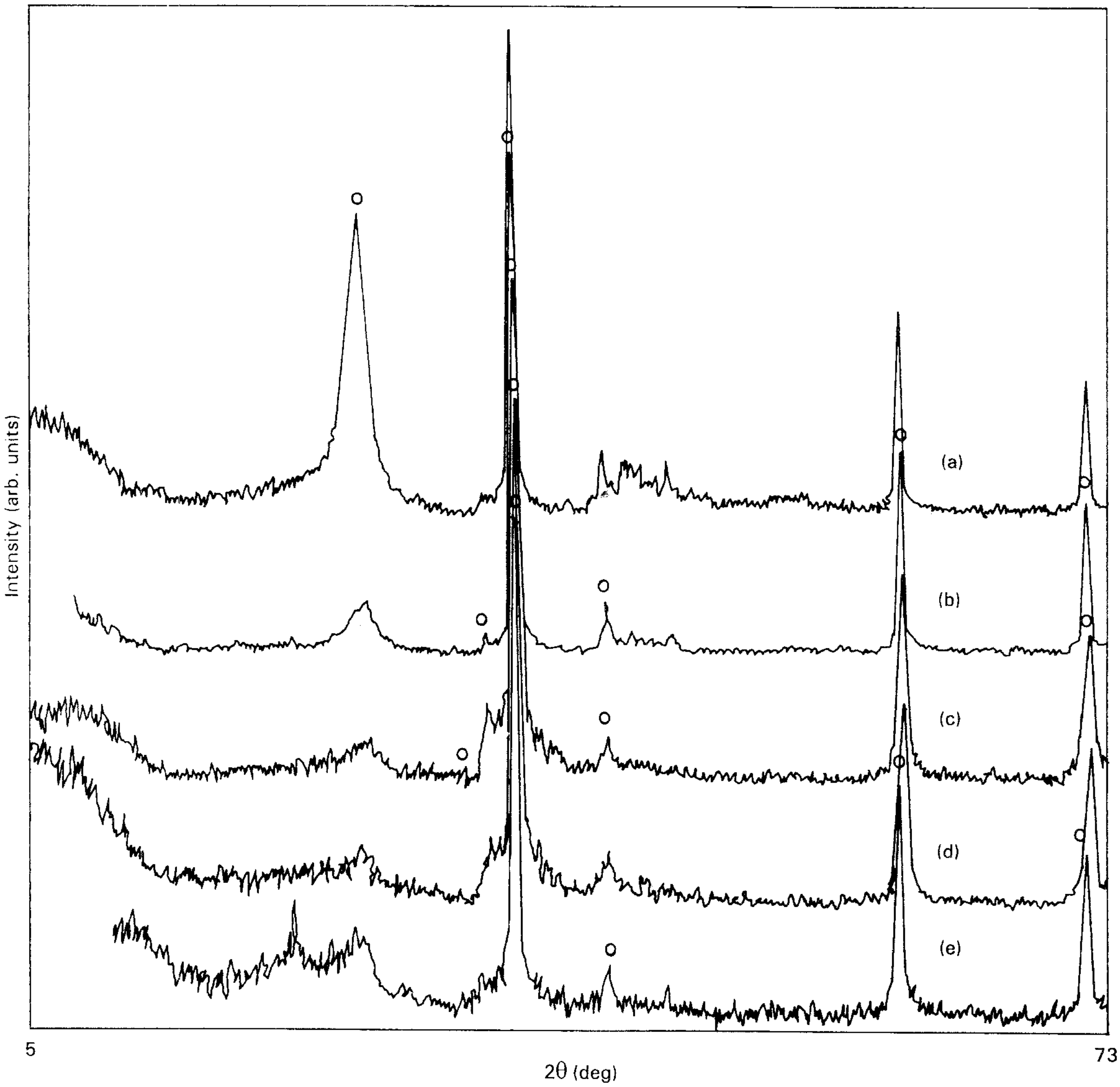


*Figure 1* X-ray diffraction patterns of SiC synthesized from (a) TEOS + phenolic resin, (b) MTES + phenolic resin, (c) copolymer + phenolic resin, (d) MTES + ethylcellulose, (e) TEOS + ethylcellulose.

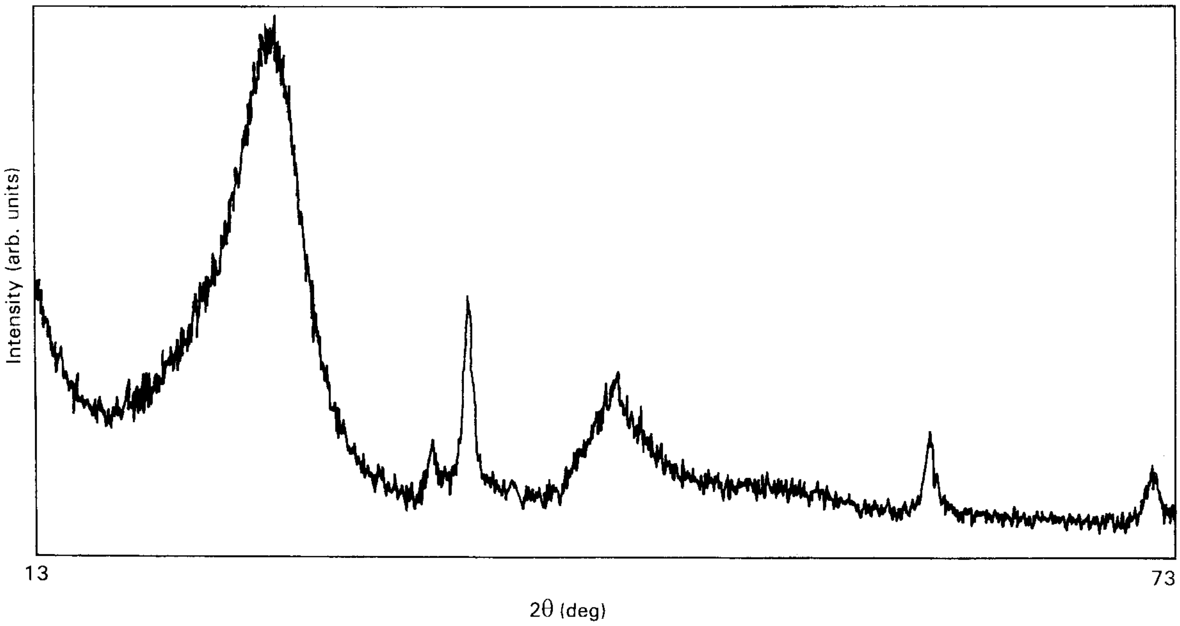


*Figure 2* X-ray diffraction pattern of SiC derived from TEOS + PAN.

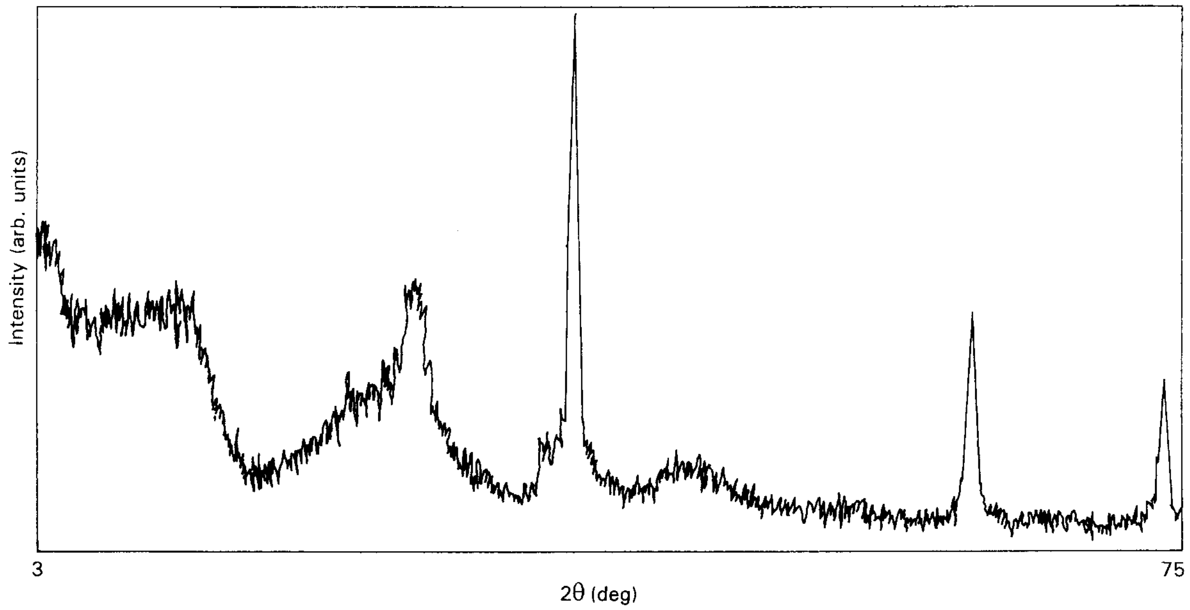


*Figure 3* X-ray diffraction pattern of SiC derived from TEOS + starch.

products obtained from all the precursors are β SiC. Samples obtained with TEOS + phenolic resin, TEOS + PAN and TEOS + starch give peaks due to carbon at $2\theta = 25.01$ in addition to the well defined β SiC. This is attributed to the higher mole ratio of $SiO_2$ : C in the precursors employed for their synthesis.

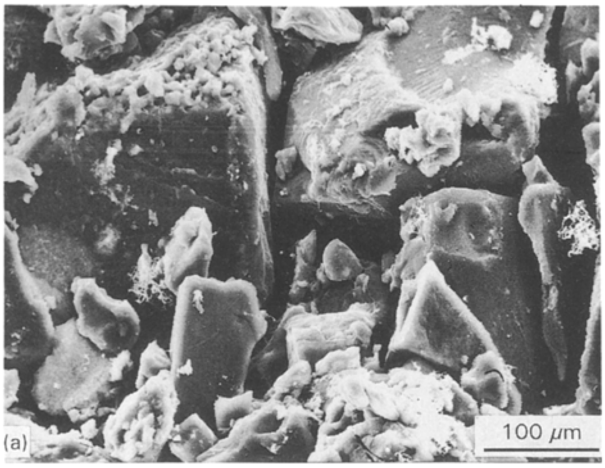
To study the difference in the X-ray patterns, crystallite sizes were calculated using Scherrer equation $L = K\lambda/B\cos\theta$ where $K$ is a constant (0.9), $\lambda$ is the X-ray wavelength, $B$ is the half width of the line and $\theta$ is the Bragg's angle. The values are listed in Table I. The crystallite size of SiC obtained with phenolic resin is higher compared with those procured with ethylcellulose, PAN and starch. This is in agreement with the patterns shown for the β SiC. This difference can only be attributed to the difference in the nature of carbon obtained from the various sources. The difference noticed with the same carbon source is probably due to Si–C of Si–$CH_3$ linkage present in MTES which is retained during carbonization and carbothermal reduction.

TABLE I SiC crystallite size

| SiC precursor | Crystallite size L(III) (nm) |
|---|---|
| TEOS + phenolic resin | 52.7 |
| Copolymer + phenolic resin | 52.7 |
| MTES + phenolic resin | 32.6 |
| MTES + ethylcellulose | 9 |
| TEOS + ethylcellulose | 23.3 |
| TEOS + starch | 21.3 |

The SEM photographs comprise Fig. 4. The grain size of the SiC in the samples prepared with phenolic resin and TEOS is larger than in those prepared with ethylcellulose, PAN and starch. The SiC prepared with the copolymer shows a mixture of small and large grains and this is attributed to the Si–C of Si–$CH_3$ in MTES which is unaffected during carbonization and carbothermal reduction. SiC obtained from MTES is probably smaller in size.

The IR spectra are given in Figs 5–7. The band at 800 $cm^{-1}$ is characteristic of the Si–C bond. The bond at 1100 $cm^{-1}$ is due to the traces of silica retained in the sample.



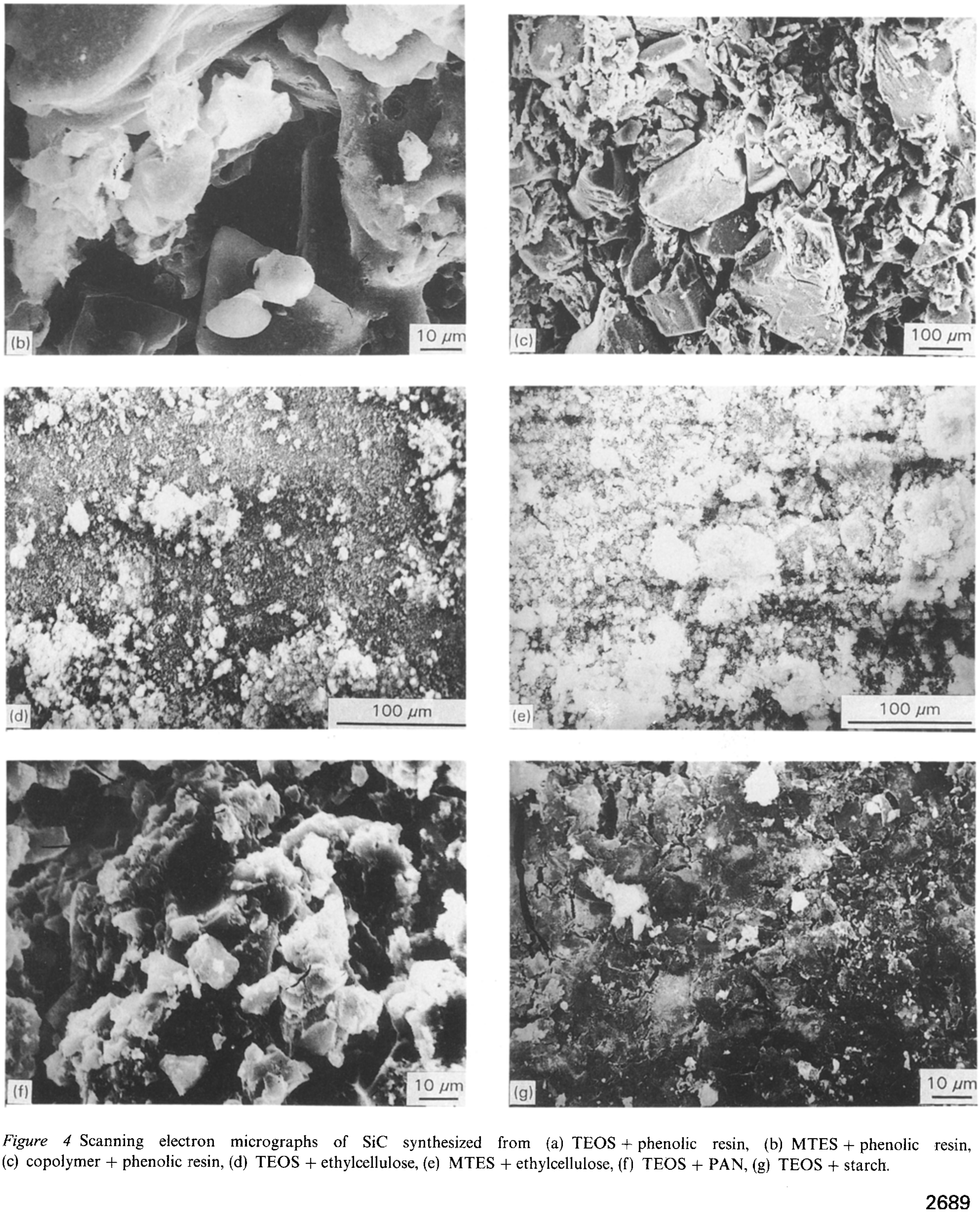


*Figure 4* Scanning electron micrographs of SiC synthesized from (a) TEOS + phenolic resin, (b) MTES + phenolic resin, (c) copolymer + phenolic resin, (d) TEOS + ethylcellulose, (e) MTES + ethylcellulose, (f) TEOS + PAN, (g) TEOS + starch.

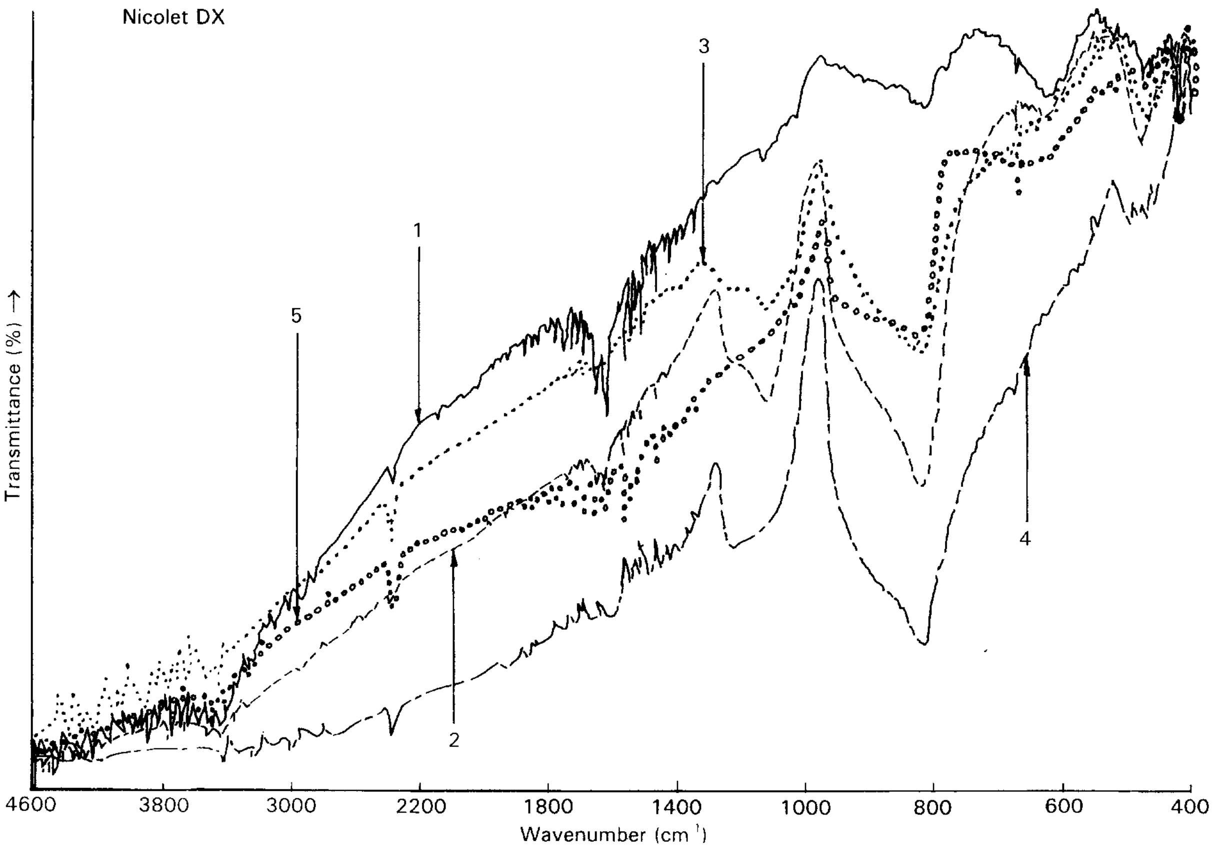


*Figure 5* FTIR spectra of SiC synthesized from (1) TEOS + PAN, (2) TEOS + ethylcellulose, (3) MTES + phenolic resin, (4) MTES + ethylcellulose, (5) copolymer + phenolic resin.

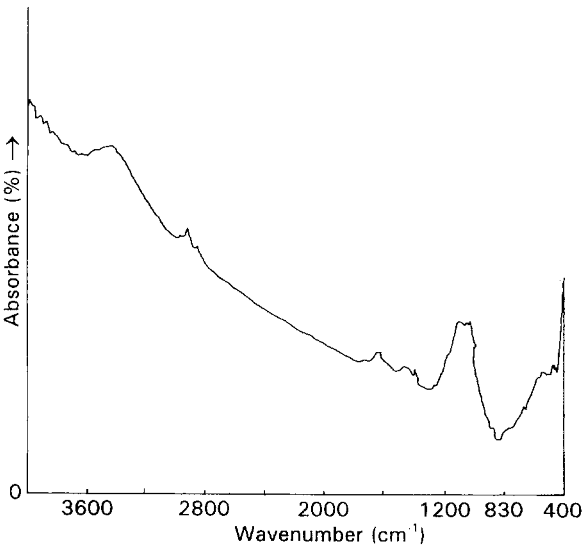


*Figure 6* FTIR spectra of SiC derived from TEOS + phenolic resin.

Close examination of IR absorption values reveal that the bands around 800–900 cm$^{-1}$ are split in a few samples and the splitting of the band is related to the crystallinity of the samples [5]. The splitting is clearly noticeable in the sample synthesized with TEOS + phenolic resin and also with the copolymer + phenolic resin, thereby showing that the SiC obtained from the above precursor is more crystalline when compared with that obtained with ethylcellulose, PAN, starch and MTES. This is in agreement with the X-ray studies which show a higher crystallite size value in the case of SiC prepared with TEOS + phenolic resin and copolymer + phenolic resin.

The weight loss observed during carbonization and carbothermal reduction of a few samples are given in Table II. It is evident from the values that weight loss during carbonization is mainly due to the removal of moisture, hydrogen, oxygen and nitrogen present in the carbon source, and these vary considerably depending on the carbon source. The weight loss noticed during carbothermal reduction is lower in the case of TEOS + phenolic resin and TEOS + starch and this is attributed to the higher molar ratio of $SiO_2$:C in these samples which is around 1:8 compared with 1:5 in the case of samples prepared with MTES, copolymer and ethylcellulose.

The densities of the samples are listed in Table III; they were determined without further densification at higher temperatures. The samples prepared by the sol–gel technique were highly porous in nature due to the evolution of gases during carbonization and carbothermal reduction of gel precursors and thus exhibit lower densities compared with the theoretical value for SiC. It should be noted that the gel precursors prepared in the present investigation with a silane:water molar ratio of 1:4–7 were more porous compared with those prepared with a silane:water ratio as high as 1:18 by Wei *et al.* [2]. These porous gels accommodate the carbon source in the silica network. These precursors when carbonized lost solvents, hydrogen, oxygen and nitrogen, resulting in the formation of porous product (silica and carbon) which

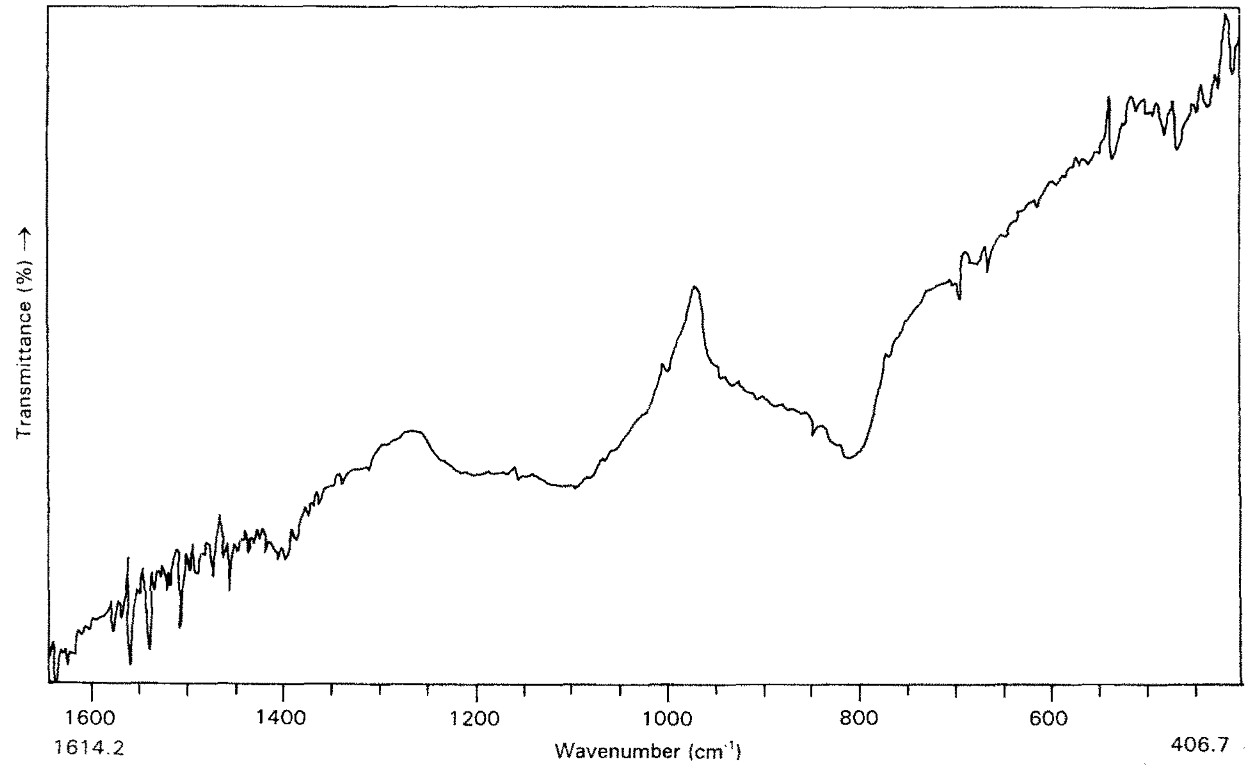


*Figure 7* FTIR spectra of SiC derived from TEOS + starch.

TABLE II Weight loss studies on cabonization and carbothermal reduction

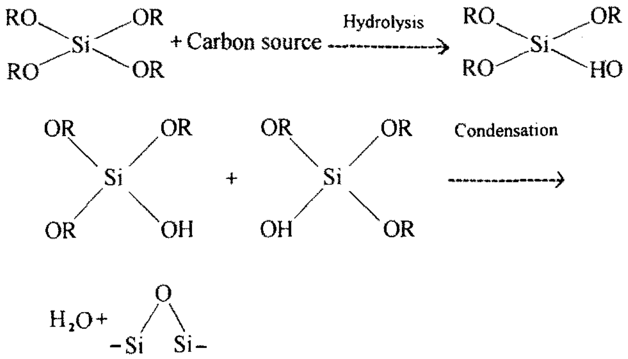
| SiC precursor | Weight loss at 50–800 °C (%) | Weight loss 800–1550 °C (%) |
|---|---|---|
| TEOS + phenolic resin | 43.3 | 28 |
| Copolymer + phenolic resin | 39.38 | 40.62 |
| MTES + ethylcellulose | 77.90 | 41.50 |
| TEOS + ethylcellulose | 72.60 | 43 |
| TEOS + starch | 73.70 | 28 |

TABLE III SiC density (present method)

| SiC precursor | Density (g cm$^{-3}$) |
|---|---|
| TEOS + phenolic resin | 1.64 |
| Copolymer + phenolic resin | 1.86 |
| MTES + phenolic resin | 1.60 |
| MTES + ethylcellulose | 1.76 |
| TEOS + PAN | 1.38 |
| TEOS + starch | 1.80 |

on carbothermal reduction yielded porous SiC with evolution of carbon monoxide.

The formation of SiC from the gels can be explained on the basis of carbothermal reduction of silica. The gels when carbonized at 800 °C yielded a black mass which is an intimate mixture of silica and carbon because on heating this mass in air at 800 °C silica was obtained. The silica in black mass when heated at 1550 °C undergoes carbothermal reduction by reacting with carbon in the same mass to yield SiC. The whole process can be explained as follows:



(Silica gel network incorporated with carbon sources)

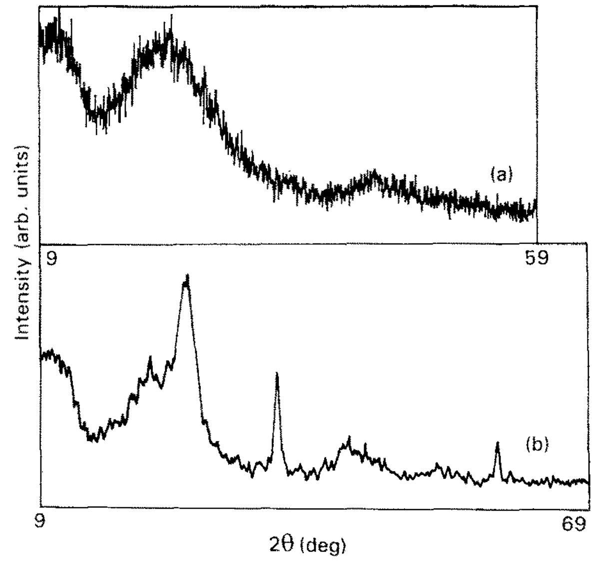


*Figure 8* X-ray diffraction patterns of (a) TEOS + phenolic resin gel heated to 800 °C in argon, (b) TEOS + phenolic resin gel heated to 1350 °C in argon.

Silica gel incorporated with carbon source

$$\xrightarrow[800^\circ\mathrm{C\ in\ Ar}]{\mathrm{heat}} \mathrm{SiO_2 + C}\ \text{(intimate mixture)}$$

Carbothermal reduction

$$\mathrm{SiO_2 + 3C \longrightarrow SiC + 2CO\uparrow}$$

$$\mathrm{SiO_2 + C \longrightarrow SiO\uparrow + CO\uparrow}$$

$$\mathrm{SiO + 2C \longrightarrow SiC + CO\uparrow}$$

The carbothermal reduction of $SiO_2$ and subsequent formation of SiC takes place only above 1300 °C. The X-ray patterns of the TEOS + phenolic resin heated at 800 and 1350 °C in Ar and of TEOS + PAN heated to 1300 °C are given in Figs 8 and 9. The patterns obtained at 800 and 1300 °C show peaks related to the $SiO_2$ and carbon only while the pattern obtained with gel heated up to 1350 °C show peaks attributable to the presence of β SiC which become

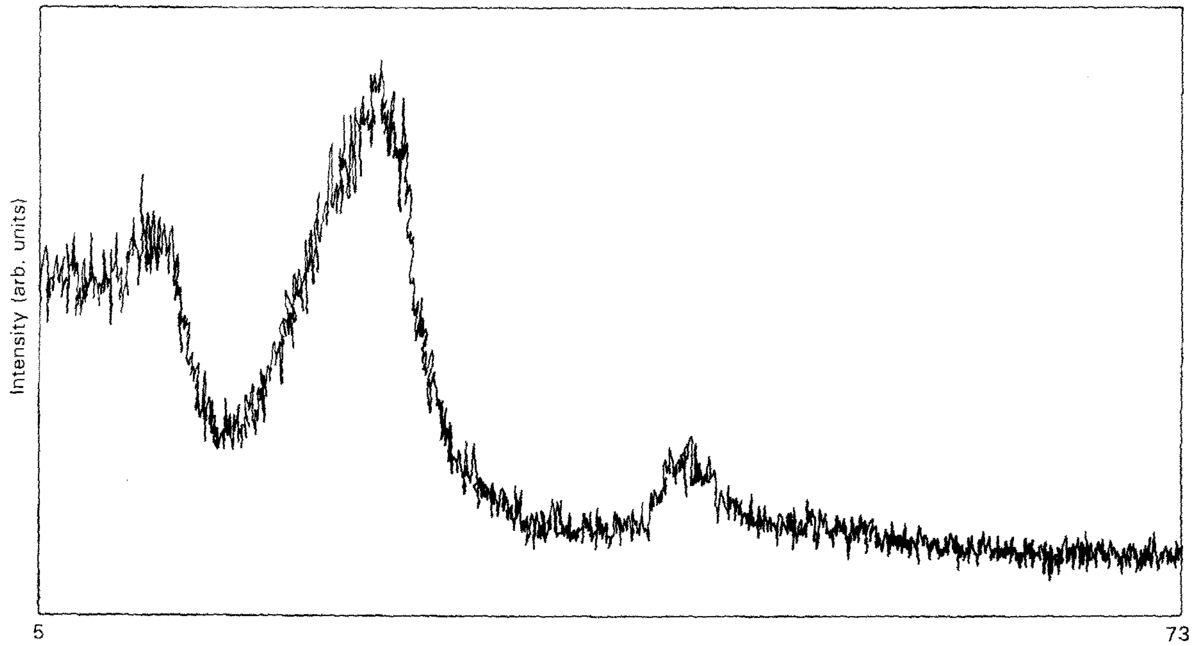


*Figure 9* X-ray diffraction pattern of TEOS + PAN gel heated to 1300 °C in argon.

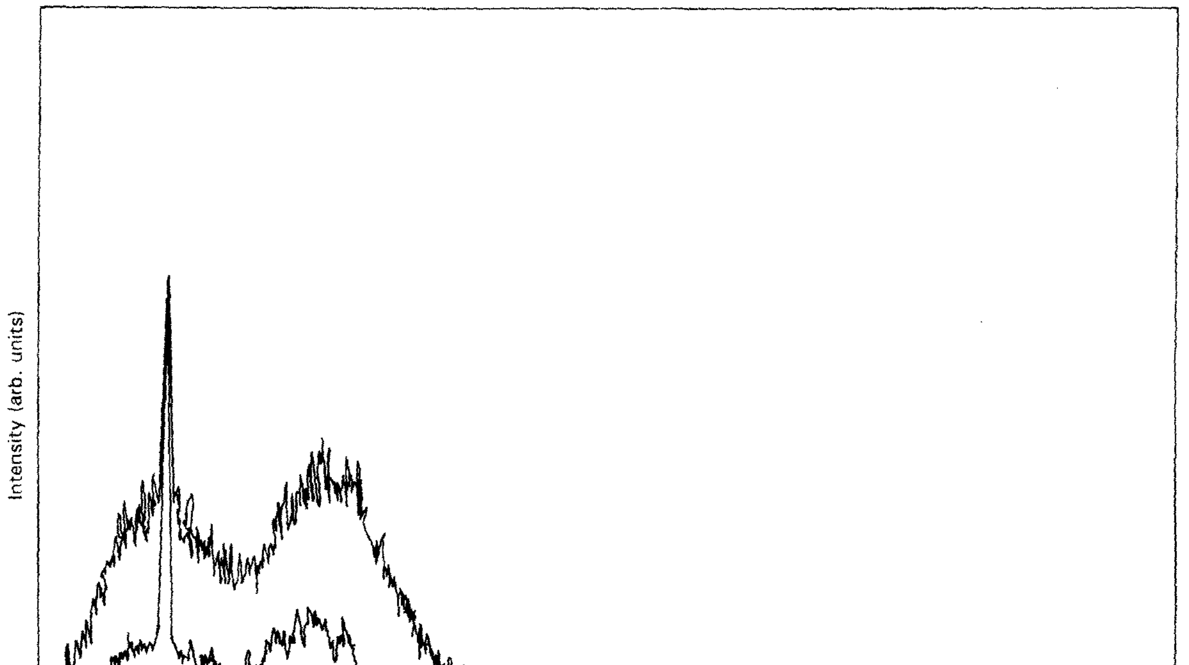


*Figure 10* X-ray diffraction patterns of (a) ethylcellulose, (b) TEOS + ethylcellulose gel.

well defined when the sample is heated to 1550 °C.

The incorporation of carbon source in the gel is also indicated by the X-ray powder patterns of the gel. It is well known that the silica gels are amorphous in nature. The presence of ethylcellulose has induced some orderliness in the patterns which are shown in Fig. 10.

## 4. Conclusion

SiC is synthesized by hydrolysis-condensation reactions of silicon alkoxides and their copolymers in the presence of phenolic resin, ethylcellulose, PAN and starch. The crystallite and the grain size of the samples differed depending on the carbon source. The present investigation shows that β SiC can be synthesized by the sol–gel technique at a relatively low temperature with easily available chemicals. SiC obtained is also found to be porous in nature.

## Acknowledgement

The authors are grateful to Dr E. S. R. Gopal, Director, NPL, India for encouragement throughout this investigation and also for his kind permission to publish the results.

## References

1. L. A. HARRIS, C. R. KENNEDY, G. C. WEI and F. P. JEFFERS, *J. Amer. Ceram. Soc.* **67** (1984) C-121.
2. G. C. WEI, C. R. KENNEDY and L. A. HARRIS, *Amer. Ceram. Soc. Bull.* **63** (1984) 1054.
3. K. V. KRISHNARAO, *J. Mater. Sci. Lett.* **12** (1993) 1268.
4. T. HASE and H. SUZUKI, *Yogyo Kyokaishi* **86** (1978) 541.
5. A. JULBE, A. LARBOT, C. GUIZARD, L. COT, J. CHARPIN and P. BERGEZ, *Mat. Res. Bull.* **25** (1990) 601.
6. F. HATAKEYAMA and S. K. KANZAKI, *J. Amer. Ceram. Soc.* **73** (1990) 2107.
7. D. A. WHITE, S.M. OLEFF, R. D. BOYER, P. A. BUNDINGER and J. R. FOX, *Adv. Ceram. Mat.* **2** (1987) 45.
8. K. C. CHEN, K. J. THORNE, A. CHEMSEDDINE, F. BABONNEAU and J. D. MACKENZIE, *Mat. Res. Symp. Proc.* **121** (1988) 571.
9. J. R. FOX, D. A. WHITE, S. M. OLEFF, R. D. BOYER and P. A. BUDINGER, *ibid.* **73** (1986) 395.
10. I. S. SEOG and C. H. KIM, *J. Mater. Sci.* **28** (1993) 3277.
11. H. TANAKA and Y. KURACHI, *Ceram. Int.* **14** (1988) 109.

*Received 11 November 1993*
*and accepted 27 May 1994*