

A solid state ^{29}Si and ^{13}C NMR study on the synthesis of thin silicon–oxycarbide glass sheets by a sol–gel route

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^{29}Si and ^{13}C MAS NMR spectroscopy, DTA–TG and elemental analysis were used to study the evolution of metastable oxycarbide phases starting from thin gel sheets derived from methyltriethoxysilane (MTEOS), tetraethoxysilane (TEOS) and a colloidal silica containing sol, up to 1450 °C under a nitrogen atmosphere. The stoichiometric formulae of the glasses obtained by the semi-quantitative analysis of ^{29}Si MAS NMR spectra were found to be in good agreement with those obtained by chemical analysis. It was found that the addition of colloidal silica sol delays the decomposition of methyl groups in MTEOS containing condensates. This delayed decomposition of the methyl groups was attributed to facilitate the strengthening of the matrix, thus leading to crack free sintering of sheets up to 400 °C in air and for $T > 900$ °C under nitrogen. A significant portion (>40%) of the total carbon present in the glasses was found to exist as free carbon. ^{13}C NMR showed that unsaturated C=C bonds exist in gels heat treated at 1000 °C, but they disappear in heat treated gels at 1200 and 1450 °C. Both ^{29}Si and ^{13}C NMR spectra indicate the formation of a *ca.* 15 atom% SiC phase in the glass sheets sintered at 1450 °C, which were found to be amorphous up to 1200 °C.

Introduction

Silicon oxycarbide glasses,¹ also called ‘black glasses’, are amorphous solids derived from the silica structure by replacing part of the bivalent oxygen atoms by tetravalent carbon atoms in a way that silicon is bonded simultaneously to oxygen and carbon atoms.² Thinking on the line of oxynitride^{3–5} glasses where trivalent nitrogen replaces oxygen, a replacement of bivalent oxygen by tetravalent carbon should lead to even a greater degree of cross-linking in the glass structure. Risbud and coworkers,^{6–9} for the first time, prepared glasses from the Mg–Al–Si–O–C system and showed that the density, elastic moduli, hardness and the fracture toughness increased with the amount of bonded carbon and the rate of increase was greater than observed for oxynitride glasses of similar composition. In addition, the incorporation of carbidic carbon in the glass structure enhances the glass stability by hindering crystallisation. The melting of silica based glass in the presence of silicon carbide was used in these attempts for the synthesis of oxycarbide glasses and the amount of carbon that could be incorporated into the glass was restricted to *ca.* 2.5 wt%.⁸ As an alternative, the sol–gel process allows the synthesis of metastable silicon oxycarbide phases in the form of fibers, monolithic pieces, coatings or powders at temperatures around 1000 °C.^{10,11} Further, it also allows the incorporation of up to 10 wt% of carbidic carbon in the glasses.¹²

The sol–gel approach to SiC_xO_y compositions^{12–17} is based upon the use of alkoxy- or chloro-silanes with non-hydrolysable alkyl groups bonded to the silicon atom. These Si–C bonds are retained during the pyrolysis process thus resulting in an oxycarbide phase. The distribution of $\text{SiC}_x\text{O}_{4-x}$ tetrahedra in the glass has been found to depend on the O/Si ratio of the precursors and on the temperature of pyrolysis. However, in most cases irrespective of the type of precursor chosen, the pyrolytic conversion of the starting gel into an oxycarbide glass leads to the formation of free carbon along with the oxycarbide phase, imparting a black colour to the glass. Several efforts

have been made in the past to synthesise an oxycarbide glass free of unbonded carbon.^{17–19} Although none of these efforts resulted in a ‘pure’ oxycarbide glass, Soraru reported an oxycarbide glass containing only 3 wt% of the total carbon as free carbon starting from a precursor containing triethoxysilane [$\text{HSi}(\text{OEt})_3$] and methyldiethoxysilane [$\text{MeHSi}(\text{OEt})_2$] in 2 : 1 ratio. No attempt has been made to correlate the thermal, mechanical and dielectric properties of oxycarbide glasses with the amount of free carbon present in it. It is therefore not clear at this stage, whether the effect of this free carbon on various properties of the resulting oxycarbide glass is detrimental or otherwise.

Silicon oxycarbide glasses have been reported to show a thermal expansion coefficient of *ca.* $3.14 \times 10^{-6} \text{ K}^{-1}$, a dielectric constant of *ca.* 4.4 in the frequency range from $10\text{--}10^7$ Hz,¹ a fracture strength in the range 150 ± 84 to 550 ± 230 MPa,²⁰ and a sintering temperature of *ca.* 1000 °C. These values suggest their suitability for applications such as micro-electronic packaging. However, no specific bulk forms such as monolithic plates, tubes or rods of oxycarbide glass have been developed so far, which could have any application potential. Polycarbosilane derived fibers (NicalonTM^{21,22} and TyrannoTM²³) consisting mainly of an SiC phase (C/Si 1.3–1.5) are the only products available.

A method for the synthesis of large area (up to 35×20 cm) gel sheets in the thickness range of *ca.* 40–1000 μm has been developed by us,^{24,25} using an ethanol diluted and base catalysed sol consisting of tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS) and colloidal silica (Nissan Chemicals, MA-ST, 30 wt% in methanol). These gel sheets, containing 0.10–0.35 mol of colloidal silica per mol of alkoxide, could be converted to crack free, dense, black glass sheets by heat treatment under nitrogen at different temperatures between 900 and 1450 °C.²⁶ The resulting glass sheets showed maximum fracture strengths (three point bending) for sintering temperatures of 1000 °C, where the values ranged between 230 ± 35 and 309 ± 44 MPa, depending upon the amount of colloidal silica. The corresponding values of Young’s modulus ranged between 101 ± 9 and 113 ± 5 GPa. Gel sheets containing no colloidal silica, on the other hand, showed cracking during

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sintering under the same conditions. It was found that an addition of 0.25 mol colloidal silica per mol alkoxide increases the density of the gel from 1.34 to 1.48 g cm⁻³, the specific surface area (SSA) from 0.55 to 4.48 m² g⁻¹ and the pore volume from 0.003 to 0.026 cm³ g⁻¹.^{24,25} It was proposed that the increased porosity facilitates the outgassing of organic residuals during sintering, resulting in crack free sintered sheets. It was a curiosity, however, to check whether it is this change in porosity which is responsible for the above behaviour during sintering, or if there is any further structural modification induced because of the incorporation of colloidal silica. The objective of the present study was to follow the structural evolution of oxycarbide phases during heat treatment of gel sheets up to 1450 °C by DTA–TG, solid state ²⁹Si and ¹³C MAS NMR and elemental analysis, in order to understand the above effects. Since the amount of colloidal silica had no significant effect on the mechanical properties of the glasses, glasses containing 0.25 mol of colloidal silica per mol alkoxide and those containing no colloidal silica only, have been studied in the present work. Synthesis of thin sheets of oxycarbide glass, use of base as catalyst and the incorporation of colloidal silica to generate porosity, facilitating the removal of organics during sintering, are aspects which have not been covered in the literature so far.

Experimental

For the synthesis of thin gel sheets, a mixture consisting of 0.9 mol MTEOS and 0.1 mol TEOS was diluted with 4.5 mol of ethanol and 0.25 mol colloidal silica sol (Nissan Chemicals, 30 wt% in methanol) was added to this mixture while stirring. 4 mol of water containing 5 × 10⁻³ mol of ammonia was used for the hydrolysis of the sol. This precursor mixture was reacted at 80 °C for 96 h in a flask, attached to an intensive reflux cooling set-up with a controllable reflux ratio arrangement, and placed in a silicone oil-bath. The reaction mixture was stirred continuously and a two-step process with 96% reflux (*i.e.*, 96% of the liquid evaporated is continuously collected back in the sol and the remainder discarded) for the first 48 h followed by 93% reflux for another 48 h was chosen for the synthesis of the sol. A viscous sol with a solid content of *ca.* 70% was obtained after this procedure. The sols obtained were cast in the form of thin sheets by the 'doctor's blade' method²⁷ in polystyrene substrates and dried between 45 and 60 °C for 15 h. Afterwards, dried gel sheets were separated from the substrates. The flowchart for the synthesis of gel sheets is shown in Fig. 1. The gel sheets were further dried for 4 h at 80 °C. For comparison, gel sheets were also prepared from a sol containing pure MTEOS or 90 mol% MTEOS–10 mol% TEOS (without

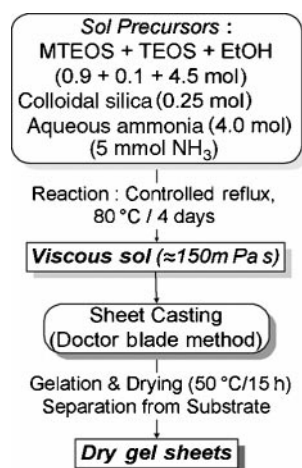


Fig. 1 Flow diagram showing the synthesis of thin methyl modified silica gel sheets.

colloidal silica) under similar conditions. Details of the synthesis of gel sheets have been reported elsewhere.

During heat treatment, sheets were placed between two alumina plates with spacers of appropriate thickness and heated to different temperatures up to 1450 ± 15 °C. Two types of heat treatment procedures were chosen. The first was done directly under a nitrogen atmosphere (designated as N type glasses) at a heating rate of 75 K h⁻¹. Alternatively, the gel sheets were first heat treated in air up to 400 °C at 75 K h⁻¹, held there for 0.5 h and then from 400 °C upward using a nitrogen atmosphere up to the final temperatures (designated A type glasses). In all cases the power was switched off after the completion of the heating schedule and the samples were cooled in the closed furnace.

Dried gel sheets were crushed and the powders obtained were analysed by DTA–TG under air and nitrogen atmospheres up to 1200 °C at a heating rate of 300 K h⁻¹. The silicon content of the gel powders was determined using HF dissolution followed by ICP analysis, whereas for analysis of silicon content of the glasses, the glass powder was fused with lithium metaborate at 1000 °C for 10 min, dissolved with HNO₃ and HCl and analysed by ICP. Oxygen contents of the gel and glass powders were determined using a LECO elemental analyser. The hydrogen content of the glasses was determined using a LECO C,H,N analyser, whereas the carbon content was determined by M/s LECO Instruments GmbH, Krefeld, Germany.

The powders obtained by crushing gel and glass sheets sintered at different temperatures were analysed by solid state MAS ²⁹Si and ¹³C NMR. For comparison, silica powder obtained after drying the colloidal silica sol at 80 °C for 96 h was also characterised by ²⁹Si NMR. ²⁹Si and ¹³C NMR measurements were performed using a Bruker MSL 200 instrument operating at a field of 4.7 T. Single pulse ²⁹Si{¹H} MAS experiments were performed with the following conditions: pulse width 3.3 μs (60°), repetition time 60 s, acquisition 100–10 000 scans, rotation frequency 3 kHz and Q₈M₈ (trimethylsilyl ester of cubic octameric silicate) as external standard. Reported percentage values are obtained directly from the NMR signal intensities. Because of the long relaxation time of Si atoms, the used repetition time is inadequate for an exact correlation of signal intensities with the amount of Si-building units. However, they are sufficient for a reliable comparison of relative changes within the structural units. ¹³C NMR: Cross polarisation experiments, contact time 3 ms, pulse width 3 μs, repetition time 5 s, number of scans 4000–10 000 scans, 3 kHz rotation frequency, adamantane as external standard.

The samples have been assigned the following nomenclature: the first three letters 'MTC' indicate that they are derived from MTEOS, TEOS and colloidal silica. The fourth and fifth symbols signify the colloidal silica content (*e.g.* '25' indicates 0.25 mol of colloidal silica per mol of alkoxides and '00' indicates colloidal silica free gels). Subsequent numbers indicate the temperature of heat treatment. The final symbols A and N have been alluded to earlier.

Results and discussion

Thin large area gel sheets, completely free of cracking and buckling, in the thickness range from 40 to 1000 μm and sizes up to 35 × 20 cm were obtained from the MTEOS–TEOS–colloidal silica system upon gelation and drying of the cast sol for *ca.* 15 h at 40–60 °C.^{24,25} The ²⁹Si NMR spectrum of a gel derived from MTEOS and dried at 80 °C is shown in Fig. 2(I). The spectrum shows all three types of Si atoms in condensed T units with chemical shifts δ of *ca.* -50 (T¹), -57 (T²) and -66 (T³). Additional broad signals at δ = 100 and -110 for Si atoms in branched Q³ and cross-linked Q⁴ units are detectable in the

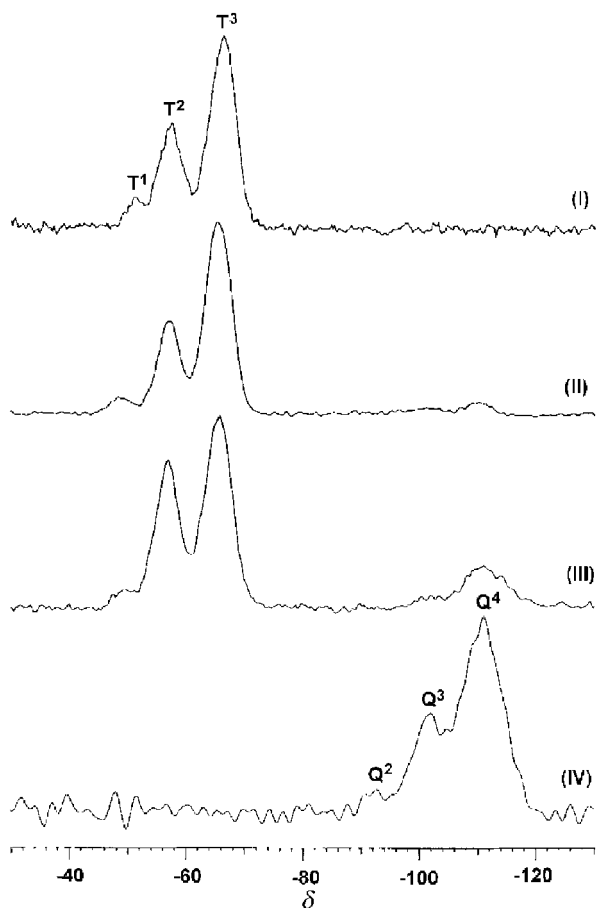


Fig. 2 Solid state ^{29}Si NMR spectra of the gels (dried at 80°C) derived from the sols with molar ratios: (I) MTEOS, (II) 90 mol% MTEOS–10 mol% TEOS, (III) 90 mol% MTEOS–10 mol% TEOS+0.25 mol colloidal SiO_2 per mol alkoxide, and that for (IV) colloidal SiO_2 (80°C , 4 d).

spectrum of the gel obtained from 90% MTEOS–10% TEOS [Fig. 2(II)]. As expected, the intensity of Q^3 and Q^4 signals was increased after the addition of the third component (0.25 mol of colloidal silica per mol of alkoxide), for the synthesis of the sol [Fig. 2(III)]. For comparison the spectrum of the silica powder obtained after drying the colloidal silica sol at 80°C for 4 days is shown in Fig. 2(IV). From spectrum IV a distribution of Q^2 (6%), Q^3 (26%) and Q^4 (68%) units in the silica powder can be evaluated. The calculation of the ratio of Q:T in a gel containing 0.25 mol of colloidal silica per mol of alkoxide from the signal intensities results a ratio of 0.25:1. This ratio is *ca.* 35% lower than the theoretical value of 0.39:1 for the starting composition. The difference can be explained by the high relaxation times of the Si atoms in Q units, so that under the used acquisition conditions a decreased intensity of the Q signal is observed. Furthermore, broad Q signals with low intensity and poor signal to noise ratio can contribute to this difference. Comparison of the signal intensities in the spectra shows that the individual ratios of T^1 , T^2 and T^3 units of MTEOS condensates do not change significantly as a result of the addition of TEOS or colloidal silica.

It is well known that in a gel dried at 80°C , besides CH_3 groups bonded to Si atoms in MTEOS there are still some solvent and organic terminal $-\text{OR}$ groups. Comparison of the C content (18 wt%) determined by elemental analysis in the colloidal silica free gel dried at 80°C (that also contains *ca.* 20 wt% adsorbed water) with the theoretically expected amount (15 wt%) confirms this assumption. If such a gel is heat treated directly in nitrogen, this organic component is expected to remain in the glass as free carbon trapped in the glass. It is unlikely that this carbon reacts with the silica to form

an oxycarbide phase *via* a the carbothermal reduction unless the temperature is higher than 1300°C .²⁸ Therefore, to monitor the effect of removing such organics on the bonded and free carbon content of the final glass, two types of glasses were prepared. Type A samples were obtained by first heating the gel in air up to 400°C , holding for 30 min and then using nitrogen for further heat treatment up to different temperatures. Type N samples were obtained by sintering the gels directly under nitrogen atmosphere up to the target temperatures. DTA–TG studies under synthetic air showed that the removal of $-\text{CH}_3$ groups begins around 400°C in such gels containing colloidal silica²⁴ and thus this temperature was chosen as the upper temperature for the heat treatment in air.

^{29}Si NMR spectra of the samples, containing 0 or 0.25 mol of colloidal silica per mol of alkoxide, heat treated at 400°C in air (type A) or nitrogen atmosphere (type N), are shown in Fig. 3. The distribution of Si atoms in T and Q units for the gels dried at 80°C and for those heat treated at 400°C in nitrogen and air are given in Table 1. For MTC00 gels, a significant fraction of methyl groups in T units appear to have pyrolysed after heat treatment at 400°C in air [Fig. 3(I)] leading to more Q units, but only small changes are detected in the Q:T ratio after heat treatment in a nitrogen atmosphere [Fig. 3(II)]. For gels containing colloidal silica heat treatment at 400°C in air [Fig. 3(III)] leads to an increase in the concentration of Si atoms in Q units at the expense of T units, however this change is relatively small as compared to that in the gel containing no colloidal silica. This ‘methyl group stabilisation’ effect of

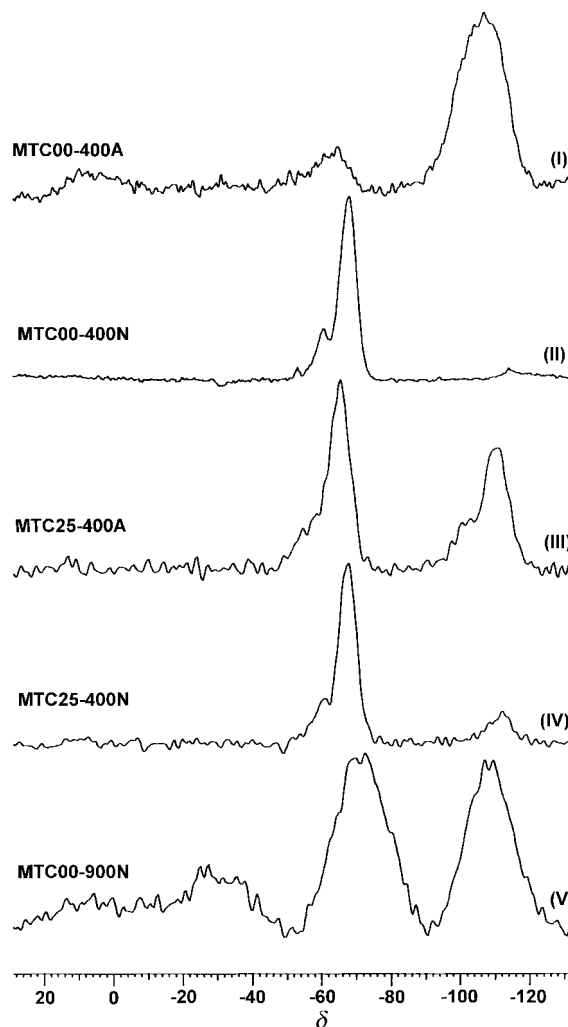


Fig. 3 Solid state ^{29}Si NMR spectra of MTEOS–TEOS derived gels with and without colloidal silica heat treated at 400°C in air (series A) and nitrogen (series N) atmospheres and for an MTC00 sample heat treated at 900°C under nitrogen.

Table 1 T/Q ratios of gels containing 0 and 0.25 mol of colloidal silica per mol alkoxide dried at 80 °C and for those heat treated at 400 °C in air and in nitrogen atmospheres

Sample	T ¹	T ²	T ³	Q ²	Q ³	Q ⁴	T/Q
MTC00-80	5	25	62	—	4	4	100/9
MTC00-400A	—	4	9	—	53	34	100/658
MTC00-400N	1	15	77	—	—	8	100/8
MTC25-80	4	30	46	1	2	17	100/25
MTC25-400A	5	11	41	—	9	35	100/79
MTC25-400N	3	11	66	3	4	13	100/25

colloidal silica is consistent with results reported previously,²⁴ that the DTA peak corresponding to the decomposition of methyl groups shifts towards a higher temperature by *ca.* 35 °C as a result of the incorporation of colloidal silica sol. The T/Q ratio for the MTC25 sample heat treated up to 400 °C in nitrogen [Fig. 3(IV)] was 100/25 confirming that during the heat treatment under nitrogen, the T/Q ratio remains constant as also observed for the MTC00 sample (Table 1).

From the ²⁹Si NMR spectra it follows that during the heat treatment of the starting gels at 400 °C, the less condensed units (T¹, T² and Q³) condense further thus resulting, as expected, in more completely condensed T³ and Q⁴ units and a higher degree of condensation. This trend of increasing condensation as a function of temperature was also found to continue in the samples heat treated at 600 °C.

A remarkable rearrangement was found to take place between 600 and 900 °C. The ²⁹Si NMR spectrum of the MTC00-900N sample as shown in Fig. 3(V) shows, in addition to the signals in the T and Q region, very broad signals in the range δ -30 to 0, which can be attributed to Si atoms in M (SiC₃O), D (SiC₂O₂) and SiC₄ units.¹⁶ However based on XRD and HR-TEM studies²⁶ (and also from information available from the literature), the presence of SiC₄ units in samples heat treated below 1200 °C can be ruled out. The appearance of these D and M units was also observed in both A and N type glass samples containing 0.25 mol of colloidal silica sol per mol of alkoxide heat treated at 900 °C (*i.e.*, MTC25-900A and MTC25-900N). ²⁹Si NMR spectra for MTC25A samples heat treated at different temperatures are shown in Fig. 4. Table 2 shows the percentage signal intensities of each SiC_xO_{4-x} site, determined using integration and deconvolution of the ²⁹Si NMR spectra for different samples. An increase in the amount of Q units and a decrease in the amount of M, D and T units is observed on heating the glasses to temperatures of >900 °C. Finally, after treatment at 1450 °C [Fig. 4(IV)], mainly Q⁴ and a new signal at δ *ca.* -10 to -15 is observed. According to the literature²⁹ this signal can be attributed to SiC.

The theoretical stoichiometry of an oxycarbide phase, assuming that the carbon atoms are present in the network of silica glass as bonded carbon and no Si-Si or C-O bonds are formed, is SiC_{x/2}O_{2-x}, *i.e.* each carbon atom replaces two oxygen atoms. Therefore, the amount of bonded carbon can be calculated using the relation $(C/Si)_{\text{glass}} = [2 - (O/Si)_{\text{glass}}]/2$ using the above assumptions. The stoichiometric formulae of the glasses estimated in this manner are given in Table 2. It can be seen that the stoichiometric formulae of the glasses do not change significantly between 1000 and 1200 °C. For glasses sintered at 1450 °C, a higher amount of carbon is present in the glass network and such glasses show nearly 15 atom% of the SiC phase as indicated by the ²⁹Si NMR signal at δ *ca.* -16. This increase in the amount of bonded carbon can be accounted for by the fact that at such an elevated temperature carbothermal reduction of SiO₂ by free carbon takes place resulting in the formation of SiC.²⁸ The formation of crystalline SiC was also confirmed using X-ray diffraction²⁵ and high resolution transmission electron microscopy studies.²⁶ The SiC phase was not detected in glasses sintered at 1000 or 1200 °C.

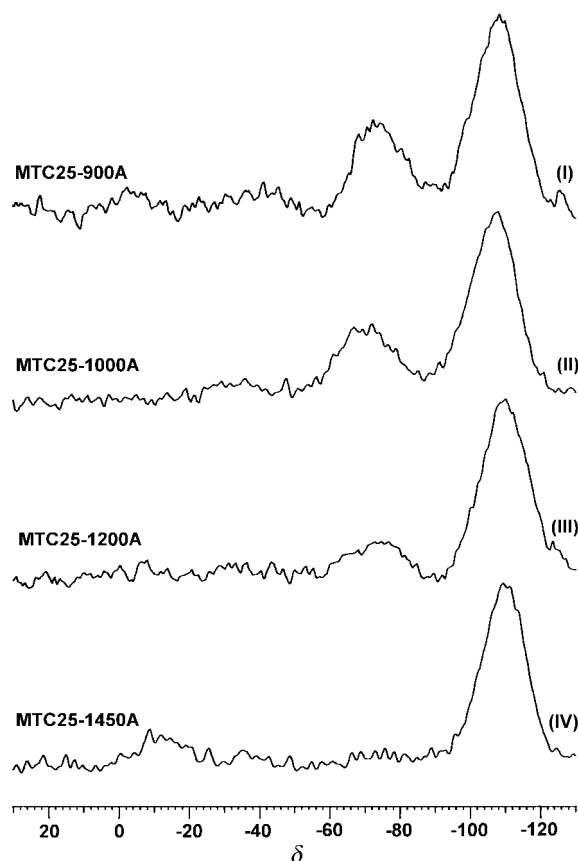


Fig. 4 Solid state ²⁹Si NMR spectra of type A glasses containing 0.25 mol colloidal silica per mol alkoxide, heat treated at (I) 900, (II) 1000, (III) 1200 and (IV) 1450 °C.

In order to calculate the fraction of carbon that is not bonded to silicon (*i.e.*, free carbon), the total amount of carbon present in the glasses needs to be known. To estimate the exact chemical composition of the glasses and the amount of free carbon, chemical analysis was performed on samples sintered at different temperatures. The results of the chemical analysis and the estimated amount of free carbon are given in Table 3. The amount of free carbon is expressed in terms of the weight percentage of the total carbon present in the glass and has been calculated using $C_{\text{free}} = 100(C_{\text{total}} - C_{\text{bonded}})/C_{\text{total}}$.¹² An uncertainty of *ca.* 1% is expected in the determination of each element by chemical analysis and the maximum error is expected for oxygen. As a consequence, the amount of oxygen determined by the difference method [*i.e.*, $O\% = 100 - (C + H + Si)\%$] (Table 3), was taken for calculation of the stoichiometric formulae of the glasses while experimentally determined values of the oxygen content are given in parentheses (Table 3). The presence of hydrogen has been neglected in the calculation of stoichiometric formulae of the glasses owing to its low (<0.9%) content (Table 3). The presence of such amounts of hydrogen for temperatures up to 1000 °C is consistent with literature data.²⁰

The above ²⁹Si NMR and chemical analysis results are

Table 2 Distribution of various $\text{SiC}_x\text{O}_{4-x}$ units (%) and stoichiometric formulae of glasses heat treated at different temperatures as determined by ^{29}Si NMR

Sample	SiO_4 (Q)	SiO_3C (T)	SiO_2C_2 (D)	SiOC_3 (M)	SiC_4	Stoich. formula
MTC25-900N	48	36	8	8	—	$\text{SiC}_{0.19}\text{O}_{1.62}$
MTC25-1000N	50	38	12	—	—	$\text{SiC}_{0.16}\text{O}_{1.69}$
MTC25-1200N	61	14	25	—	—	$\text{SiC}_{0.16}\text{O}_{1.68}$
MTC25-1450N	67	8	10	—	15	$\text{SiC}_{0.23}\text{O}_{1.55}$
MTC25-900A	56	27	10	7	—	$\text{SiC}_{0.17}\text{O}_{1.66}$
MTC25-1000A	69	25	6	—	—	$\text{SiC}_{0.09}\text{O}_{1.82}$
MTC25-1200A	70	24	6	—	—	$\text{SiC}_{0.09}\text{O}_{1.82}$
MTC25-1450A	75	6	4	—	15	$\text{SiC}_{0.19}\text{O}_{1.63}$
MTC00-900N	37	44	12	7	—	$\text{SiC}_{0.22}\text{O}_{1.56}$
MTC00-1200N	67	23	10	—	—	$\text{SiC}_{0.11}\text{O}_{1.78}$

Table 3 Proportion of individual elements (wt%), glass compositions, stoichiometric formulae and amount of free carbon (wt%) in glasses sintered at various temperatures as determined by chemical analysis

Sample	C	Si	H	O ^a	Glass comp.	Stoich. formula ^b	C _{free} ^c
MTC25-900N	9.7	45.6	0.9	43.8(41.0)	$\text{SiH}_{0.55}\text{C}_{0.50}\text{O}_{1.68}$	$\text{SiC}_{0.16}\text{O}_{1.68}$	65
MTC25-1000N	10.0	46.1	0.4	43.5(44.8)	$\text{SiH}_{0.24}\text{C}_{0.51}\text{O}_{1.65}$	$\text{SiC}_{0.18}\text{O}_{1.65}$	62
MTC25-1200N	9.9	46.3	—	43.8(43.4)	$\text{SiC}_{0.50}\text{O}_{1.66}$	$\text{SiC}_{0.17}\text{O}_{1.66}$	64
MTC25-1450N	9.6	49.0	—	41.4(42.1)	$\text{SiC}_{0.46}\text{O}_{1.48}$	$\text{SiC}_{0.26}\text{O}_{1.48}$	41
MTC25-900A	6.9	45.0	0.4	47.7(46.0)	$\text{SiH}_{0.25}\text{C}_{0.36}\text{O}_{1.86}$	$\text{SiC}_{0.07}\text{O}_{1.86}$	79
MTC25-1000A	8.4	44.8	0.3	46.5(45.0)	$\text{SiH}_{0.19}\text{C}_{0.44}\text{O}_{1.82}$	$\text{SiC}_{0.09}\text{O}_{1.82}$	78
MTC25-1200A	8.6	44.2	—	47.2(47.5)	$\text{SiC}_{0.45}\text{O}_{1.87}$	$\text{SiC}_{0.07}\text{O}_{1.87}$	83
MTC25-1450A	7.9	48.7	—	43.4(45.0)	$\text{SiC}_{0.38}\text{O}_{1.56}$	$\text{SiC}_{0.22}\text{O}_{1.56}$	40
MTC00-900N	11.8	43.7	0.7	43.8(41.8)	$\text{SiH}_{0.45}\text{C}_{0.63}\text{O}_{1.75}$	$\text{SiC}_{0.13}\text{O}_{1.75}$	77
MTC00-1200N	11.5	45.1	—	43.4(39.9)	$\text{SiC}_{0.59}\text{O}_{1.68}$	$\text{SiC}_{0.16}\text{O}_{1.68}$	71

^aValues represent the oxygen content determined by the difference method [*i.e.*, $\text{O}\% = 100 - (\text{C} + \text{H} + \text{Si})\%$] with experimentally determined values given in parentheses. ^bDetermined using the relation $\text{SiO}_n\text{C}_{2-n/2}$, where n is O/Si ratio determined from chemical analysis. ^cCalculated using $\text{C}_{\text{free}} = 100(\text{C}_{\text{total}} - \text{C}_{\text{bonded}})/\text{C}_{\text{total}}$.

summarised in Fig. 5, which shows the distribution of Si atoms in Q units and the content of C_{free} and C_{bonded} in A and N type glasses heat treated at different temperatures up to 1450 °C for the MTC25 series. It can be seen that the type N samples show the highest amount of bonded carbon and the lowest amount of free carbon, whereas type A samples show the reverse trend. It is also clear that in all the cases, except for the glasses heat treated at 1450 °C, a major fraction of the total carbon (*i.e.*, > 62 wt%) remains as free carbon dispersed in the glass. For glasses heat treated at 1450 °C, only *ca.* 40 wt% carbon exists as free carbon. This decrease in the amount of free carbon can mainly be attributed to the formation of SiC at this temperature through carbothermal reduction of SiO_2 .

The stoichiometric formulae derived from ^{29}Si NMR (Table 2) are in fairly good agreement with those derived from chemical analysis (Table 3). The differences are more marked for samples heat treated at 900 °C as compared to those

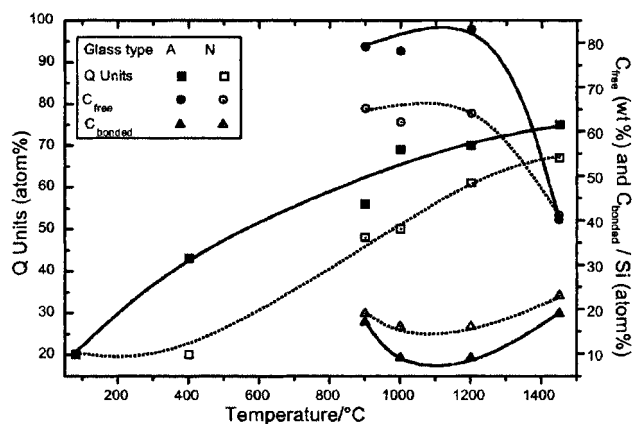


Fig. 5 Distribution of Si atoms in Q units as well as content of C_{free} and C_{bonded} in A and N type glasses from MTC25 series heat treated at different temperatures up to 1450 °C.

sintered at higher temperatures. The presence of volatile hydrocarbon species (≈ 0.9 wt% H) in samples heat treated up to 1000 °C may be responsible for this.

^{13}C NMR spectroscopy gives the information about the evolution of the local environment of the carbon sites during the pyrolysis process. Fig. 6 shows the ^{13}C NMR spectra for active coal and for type A glasses containing 0.25 mol of colloidal silica per mol of alkoxide, sintered at 900, 1200 and 1450 °C. ^{13}C NMR spectra for the samples MTC00-900N, MTC25-900N and MTC25-900A were found to be very similar. Therefore only the MTC25-A series was chosen for the study of carbon environment at higher temperatures. Since ^{13}C NMR spectra recorded using the CP technique are only sensitive to the areas of the samples with residual protons, the NMR results discussed below may not be representative of all types of carbon sites.

^{13}C NMR spectra for active coal and glasses sintered at 900 °C [Fig. 6(I) and (II)], both show broad signals in the region δ 122–144. This broad signal can be assigned to the presence of raw soot like sp^2 -hybridised carbon³⁰ and unsaturated carbon atoms.³¹ It has already been suggested that unsaturated bonds are present in intermediate carbon phases which may be possible precursors for graphitic carbon which is formed at higher temperatures.^{2,31} There are two further signals at δ *ca.* 70 and 110 in the ^{13}C NMR spectra of active coal, which are also observed in the ^{13}C NMR spectra of oxycarbide glasses sintered at 900 °C. These signals closely resemble the sharp signals at δ *ca.* 110 and 70 ppm observed by Maniwa *et al.*³² for rhombohedral and face centred cubic (fcc) carbon phases synthesised under high pressure conditions. Maniwa *et al.* assigned such signals to sp^3 -like carbon. The signals observed at δ *ca.* 180–200 and 50–60 arise from spinning side bands.

^{13}C NMR spectra of type A glasses sintered at 900 °C also show a broad signal at δ *ca.* 10. Signals in the range δ 0–30 in ^{13}C NMR spectra can be attributed to the carbon groups such as CH_3 and CH_2 .³¹ Therefore, the observed broad signal is

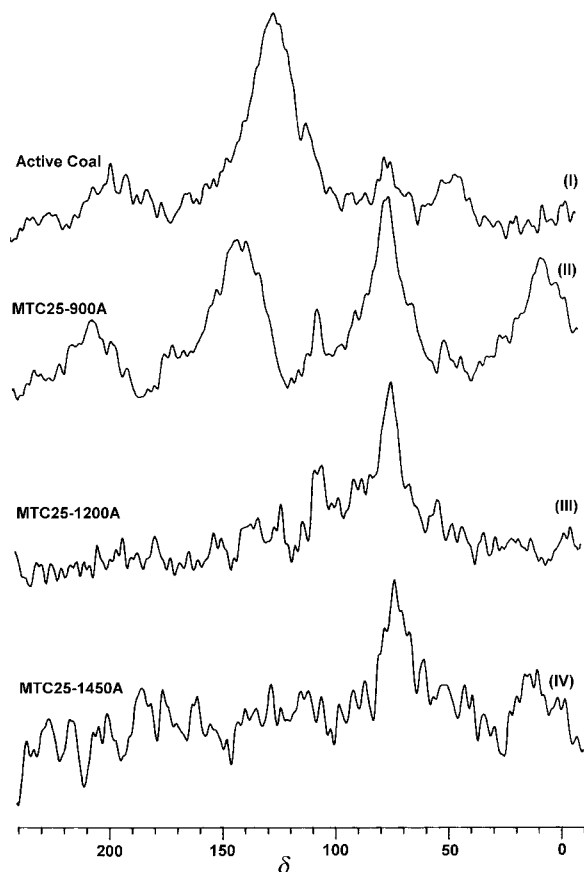


Fig. 6 Solid state ^{13}C NMR spectra of active coal (I) and type A glasses containing 0.25 mol colloidal silica per mol alkoxide heat treated at 900 (II), 1200 (III) and 1450 $^{\circ}\text{C}$ (IV).

attributed to aliphatic carbon with increased disorder in their local environment.

The ^{13}C NMR spectrum of the sample sintered at 1000 $^{\circ}\text{C}$ (not shown here) was very similar to that of the 900 $^{\circ}\text{C}$ sample. However, there was a remarkable change in the ^{13}C NMR spectrum for the glass heat treated at 1200 $^{\circ}\text{C}$. The intensity of the signal at δ ca. 10 is substantially reduced indicating the elimination of CH_n groups from the glasses. Further, the intensity of the signal at δ 144 is also decreased. As it has been shown above (chemical analysis and ^{29}Si NMR) that free carbon is present in the sample heat treated at 1450 $^{\circ}\text{C}$, the decrease in the intensity of the signal at δ 144 suggests the elimination of unsaturated carbon from the glasses heat treated at 1200 $^{\circ}\text{C}$. The signal at δ ca. 75, however, remains almost unchanged. Therefore, the sample heat treated at 1200 $^{\circ}\text{C}$ possibly consists of sp^3 -like carbon superimposed on the broad background signal representing raw soot like sp^2 -carbon.

The ^{13}C NMR spectrum for the sample sintered at 1450 $^{\circ}\text{C}$ shows only two broad and prominent signals at δ ca. 72 and 20. The signal at δ ca. 20 is attributed to the SiC phase³³ whereas that at δ 72 found to occur in all the above samples, indicates the presence of sp^3 -like carbon. The signal that indicates the presence of CH_n groups in the sample heat treated at 1000 $^{\circ}\text{C}$ in this region, vanishes for the 1200 $^{\circ}\text{C}$ sample and another signal in the same region indicating the presence of SiC replaces it for the sample sintered at 1450 $^{\circ}\text{C}$.

The simplest model for the silicon oxycarbide units in a glass

would be a random distribution of Si–O and Si–C bonds.^{2,17} In this model, the probability of finding a site $\text{SiO}_x\text{C}_{4-x}$ would depend only on the probabilities of Si–O and Si–C bonds, which can be expressed by,¹⁷

$$P(\text{SiO}_x\text{C}_{4-x}) = 4/x!(4-x)!(P_{\text{Si-O}})^x(P_{\text{Si-C}})^{4-x}$$

Applying the reasonable assumption that all the oxygen in oxycarbide glasses is bonded to Si in S–O–Si bridges and that Si is bonded to C and O atoms only (*i.e.*, there are no Si–Si or C=O bonds),¹⁷ then:

$$P_{\text{Si-O}} = (\text{O/Si})/2, P_{\text{Si-C}} = 1 - P_{\text{Si-O}}$$

For a glass derived from 90 mol% MTEOS–10 mol% TEOS, the O/Si ratio in the starting gel is 1.55, whereas for a gel derived from 90 mol% MTEOS–10 mol% TEOS and 0.25 mol of colloidal silica sol per mol of alkoxide, the O/Si ratio in the starting gel would be 1.64. The percentages of $\text{SiO}_x\text{C}_{4-x}$ sites as calculated from the above formulae for both these compositions are as given in Table 4.

On comparing these values with the experimentally measured distributions using ^{29}Si NMR spectra, as shown in Table 2, it can be seen that the theoretically calculated distribution of $\text{SiO}_x\text{C}_{4-x}$ sites matches fairly well with the ^{29}Si NMR results for the samples MTC25-900N and MTC00-900N. Thus, it can be inferred that a random distribution of oxycarbide units in these silicon oxycarbide glass sheets is attained around 900 $^{\circ}\text{C}$, which is also consistent with information available from the literature.^{2,17} At higher temperatures extensive diffusion takes place leading to the formation of stable SiO_2 and SiC phases and the distribution is no longer random. SiC, however, can also be formed by the carbothermal reduction of SiO_2 by carbon at temperatures above 1300 $^{\circ}\text{C}$.²⁸

Based on the above study, the observation that the sheets do not crack as a result of incorporation of colloidal silica appears to be the combined effect of an increase in the porosity,²⁴ a delay in the decomposition of methyl groups and the retention of a higher fraction of bonded carbon in the oxycarbide glass matrix. Further, since a random distribution of $\text{SiO}_x\text{C}_{4-x}$ units would be most effective in blocking crack propagation, thus leading to improved fracture strength, the maximum of the fracture strength at 1000 $^{\circ}\text{C}$ reported in our earlier study,²⁶ appears to be a compromise between the randomness of oxycarbide units and a sintering to a dense matrix.

Heating the samples first to 400 $^{\circ}\text{C}$ in air (*i.e.*, type A glasses) leads to glasses with the lowest amount of bonded carbon and the highest amount of free carbon (Tables 2 and 3). The effect of this is seen on the fracture strength of the glass sheets. The N type glass sheets sintered at 1000 $^{\circ}\text{C}$ showed fracture strength values ranging between 230 and 309 MPa depending upon the colloidal silica content,²⁴ whereas the values for A type glass sheets ranged between 108 and 150 MPa.²⁵ This suggests that a higher amount of bonded carbon and a lower amount of free carbon lead to higher fracture strength values. However, further study is needed to understand the effect of free carbon on the mechanical properties of the glass sheets. This would render valuable information about the practical usability of such thin oxycarbide glass sheets.

Conclusions

The present study shows that it is possible to synthesise crack free, thin sheets of silicon oxycarbide glass containing a

Table 4 Percentage of $\text{SiO}_x\text{C}_{4-x}$ sites for different O/Si ratios calculated based on a random distribution of Si–O and Si–C bonds

System	O/Si	SiO_4	SiO_3C	SiO_2C_2	SiOC_3	SiC_4
MTC25	1.64	45.21	39.70	13.70	1.92	0.15
MTC00	1.55	36.08	41.89	18.24	3.73	0.25

distribution of $\text{SiO}_x\text{C}_{4-x}$ sites depending upon the temperature and type of heat treatment. Incorporation of colloidal silica as a component of the sol, stabilises methyl groups against decomposition and leads to a higher amount of bonded carbon in the final glass, though it also increases the specific surface area and the pore volume of the gel sheets. The combined effect of this is a crack free sintering of the gel sheets to oxycarbide glass sheets. The amount of bonded and free carbon can be controlled depending upon the temperature and the type of heat treatment. In all cases, a substantial fraction of the total carbon (at least 40 wt%) present in the glasses was in the form of free carbon. A higher fraction of free carbon was found to deteriorate the fracture strength of the glass sheets.

Therefore, it can be stated that the incorporation of a nanoparticulate sol during the polymeric sol-gel transformation, provides a novel way to tailor the gel properties and shaping process, and therefore should be explored further in conjunction with other systems.

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