

Sol–gel processing of carbidic glasses[†]

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Abstract. Carbon incorporation into the silicate network results in the formation of rigid carbidic glasses with improved physical, mechanical and thermal properties. This generated great interest in the development of these heteroatom structured materials through different processing routes. In the present studies, sol–gel processing has been used to prepare silicon based glasses, especially oxycarbides through organic–inorganic hybrid gels by hydrolysis–condensation reactions in silicon alkoxides, 1,4-butanediol and furfuryl alcohol with an aim to introduce Si–C linkages in the precursors at sol level. The incorporation of these linkages has been studied using IR and NMR spectroscopy. These bonds, so introduced, are maintained throughout the processing, especially during pyrolysis to high temperatures. In FFA–TEOS system, copolymerization with optimized mol ratio of the two results in resinous mass. This precursor on pyrolysis to 1000°C results in Si–O–C type amorphous solid black mass. XRD studies on the materials heated to 1400°C exhibit presence of crystalline Si–C and cristobalites in amorphous Si–O–C mass. In organic–inorganic gel system, the pyrolysed mass exhibits phase stability up to much higher temperatures. The carbidic materials so produced have been found to exhibit good resistance against oxidation at 1000°C.

Keywords. Sol–gel; silicon oxycarbide; organically modified inorganic gels; hydrolysis; pyrolysis; silicon carbide; cristobalites.

1. Introduction

Thermal stability and mechanical properties of silica glasses can be enhanced by cationic and anionic substitutions. This generated interest in investigating techniques to substitute divalent oxygen atoms by tetravalent carbon atoms in silica structure, thus making carbidic glasses (Leohman 1983; Renlund *et al* 1991; Soraru 1994). Conventional glass making techniques by melt processing of the constituents does not always produce glasses with desired microstructures due to high temperatures required for melting which in turn causes oxidation of carbon and thus result in non-homogeneous structure. The preparation of glasses via solution routes is currently of great interest since this can lead to the fabrication of monoliths with desired constituents and homogeneity at molecular level. Over past one decade or so, work has been reported by various groups to develop carbon incorporated silica network, the silicon oxycarbide glasses or so called, black glass using sol–gel technique with modified silicates of the type $R'_n \text{Si}(\text{OR})_{4-n}$ as the starting material (Zhang and Pantano 1990; Mackenzie 1994; Babonneau *et al* 1994; Soraru *et al* 1995). The aim is to have silicon–carbon bond in the solution which may be carried on in the gel and sustain the high temperature pyrolysis. Present studies

have been performed using different sol–gel routes with unmodified silicates as source for silicon and using carbonaceous monomers and solvents as source for carbon. Following this route, the purpose is to introduce carbon containing organic groups in the molecular chain at the sol level during hydrolysis of TEOS and subsequent pyrolysis. The processing of gels and their pyrolysis at different temperatures to give carbidic glasses has been studied and reported here.

2. Experimental

Hybrid organic–inorganic gels were synthesized through two routes. In both the routes, the source of inorganic component was same, i.e. tetraethylorthosilicate (TEOS). The source of organic component was varied as furfuryl alcohol monomer and 1,4-butanediol. In route I, distilled furfuryl alcohol was added to hydrolyzed tetraethylorthosilicate under constant stirring. The ratio of TEOS to water and FFA was kept as 1 : 8 : 0.65. In route II, tetraethylorthosilicate (TEOS) and 1,4-butanediol (BD) were mixed in CCl_4 with molar ratios of TEOS : BD : CCl_4 :: 1 : 4 : 2. These ratios were optimized through a series of experiments to obtain gels of appropriate castable viscosity and desired Si, C and O ratio in the ultimate product. The sols were cast in plastic petridishes and kept for gellation at room temperature. This was followed by gradual drying at 180°C. This resulted in monolithic transparent material. Dried gel

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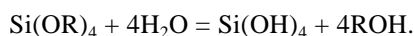
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samples made by both routes were pyrolysed at 3°C/min to 1000°C in presence of nitrogen. Some parts of the pyrolysed samples were further heated to 1400°C in nitrogen. The materials at gel stage as well as after heat treatment to different temperatures were characterized by Mettler Thermal Analysis system TA4000. The IR spectra were recorded using KBr pellet method on Hewlett Packard IR analyzer. X-ray diffraction studies were made on powdered samples using Rigaku X-ray diffractometer. NMR studies were made with JEOL FT NMR. The Raman spectra was recorded using Ar ion laser with Jobin Yvon/Atago Bussan T64000 triple spectrometer equipped with microscope optics.

3. Results and discussion

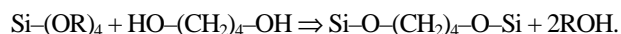
3.1 Studies on Si, C, O network gels

Tetraethylorthosilicate (TEOS) gets hydrolysed with water in presence of a catalyst according to the following reaction (Manocha *et al* 1997):



The ethoxy groups are replaced by hydroxyl groups. Further condensation reactions take place in Si(OH)_4 resulting in gelation and polymerization to silica network. Furfuryl alcohol monomer also gets polymerized in presence of hydroxyl groups. Following this scheme, furfuryl alcohol monomer was added to hydrolysed TEOS (before gelation) so that the two copolymerized in presence of hydroxyl groups. In case of TEOS/butanediol

system, the hydrolysis of TEOS takes place due to alcohol group in 1,4-butanediol as per following reaction (Amara 1994):



In this case, 1,4-butanediol effects both hydrolysis of TEOS and incorporation of carbon aromatic group in the molecular chain. The gelled samples were characterized by IR spectroscopy. Figure 1 shows IR spectra of dried gels made from the two systems. The spectra of gels show characteristic peaks at around 460 cm^{-1} and 800 cm^{-1} associated with Si-O-Si bond bending and symmetric bond stretching vibrations respectively. The band at 960 cm^{-1} is associated with stretching mode Si-OH and at 1220 cm^{-1} associated with LO mode of Si-O-Si asymmetric bond stretching vibration (Yoshino *et al* 1990). The intensities of these bands decrease during hydrolysis/condensation in presence of furfuryl alcohol. The spectra of FFA/TEOS gel system show peaks at 1300–1400 cm^{-1} due to alkyl bonding to silicon. Absence of a sharp peak around 1500 cm^{-1} assigned to furan rings suggests the reaction between Si-OH group of silica sol and -OH group of furfuryl alcohol during gelation and copolymerization. In TEOS/BD system, the intensities of the peak at 960 cm^{-1} and that of the band around 1170 cm^{-1} change with addition of butanediol. These decrease with increased butanediol content. This suggests that alcohol group of butanediol and ethoxy groups in TEOS are reacting. The hybrid gels show additional bands (n_{OH} at around 3400 cm^{-1} , n_{CH} at 2940–2880 cm^{-1} , d_{CH} at

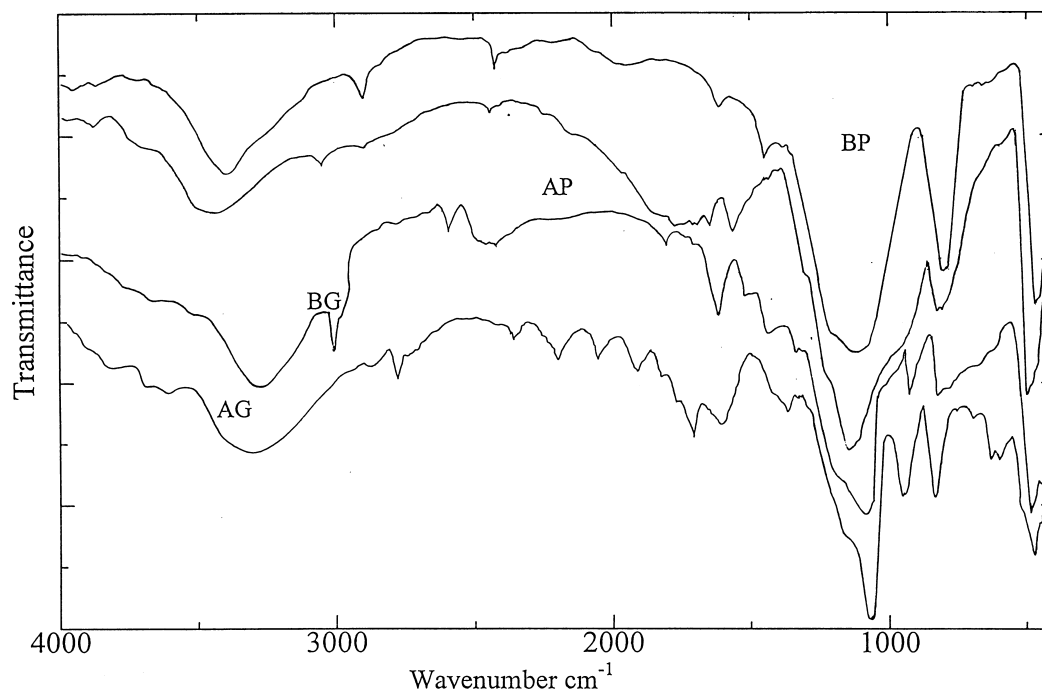


Figure 1. IR spectra of dried gels at 180°C and after pyrolysis to 1000°C (AG (TEOS/FFA gel), AP (TEOS/FFA pyrolysed), BG (TEOS/BD gel), and BP (TEOS/BD pyrolysed)).

1480–1440 cm^{-1} and d_{OH} around 1380 cm^{-1}) due to butanediol. The presence of two bands at 1080 and 840 cm^{-1} might be due to Si–O vibration in Si–O–C and Si–O–Si. The peak around 2300 cm^{-1} and low intensity peaks around 1260 cm^{-1} and 1360 cm^{-1} are due to CH_2 groups. These results show that TEOS is getting hydrolyzed by the –OH groups in butanediol with a result, the CH_2 groups are getting incorporated in the chain. The Si–C linkage is also evident from ^{29}Si NMR spectra of the gelled sample shown in figure 2. The shifts between –15 to –70 ppm are assigned to various Si, C, O linkages. These studies show that in both the routes, carbon containing components are introduced in the Si–O gel network.

3.2 Pyrolysis of gelled samples to Si–O–C glasses

The dried gel samples were transparent like tough plastics. The pyrolysis of the dried gels to 1000°C was studied by thermal techniques. Figure 3 shows TGA and DSC plots of the organic–inorganic hybrid gels. The dried gels exhibit an endothermic peak below 200°C and an exothermic peak above 400°C. Similarly, TGA plots show that the pyrolysis occurs mainly over two temperatures, low 200°C and a steady weight loss between 400 and 700°C, characteristic of condensation reactions and decomposition/rearrangement reactions in carbonaceous materials. The endothermic peak and weight loss below 200°C are associated with condensation reactions and evaporation of reaction products and residual water. The extent of these have been found to be lower than those for pure silica gels. The weight loss after 400°C is assigned to condensation of silanol groups and formation of inorganic network with removal of hydrogen containing compounds etc. Thermal cracking of hydrocarbon groups also results

in weight loss in this temperature range. The presence of exotherm in this temperature range suggests that a ring opening reaction (furan rings in FFA/TEOS systems) and thermal cracking of hydrocarbon CH_2 groups may also be taking place. This suggests that condensation of silanol groups and chain opening reactions are going on simultaneously. This may result in Si–C, Si–O–C type of bonding.

3.3 Characterization of pyrolysed (Si–O–C) materials

On pyrolysis to 1000°C, all samples resulted in fragmented, shining black, brittle, hard materials. The IR spectra of pyrolysed samples are shown in figure 1. On pyrolysis of the samples to 1000°C, the bands at 570 cm^{-1} , 960 cm^{-1} and 1630 cm^{-1} disappeared while those at 790 cm^{-1} and 470 cm^{-1} became more prominent suggesting presence of SiO_4 tetrahedron. Broadness of the peak at 800 cm^{-1} and of band at 1000–1250 cm^{-1} may presumably be due to simultaneous development of some overlapping peaks such as at 820 cm^{-1} due to Si–C linkages, at 1080 cm^{-1} due to Si–O–C, and at 1120 cm^{-1} due to Si–C etc. A small peak at 1360 cm^{-1} is observed in the pyrolysed samples. This may be due to carbonaceous materials as a result of cracking of hydrocarbon groups. In addition, the IR spectra of pyrolysed samples also show doublet at 830–850 cm^{-1} suggesting that some of the silicon atoms are bonded to carbon atoms (Renlund *et al* 1991). Thus the material appears to be a complex mixture containing Si–O, Si–C and C=C linkages.

This is further supported by NMR spectra of the pyrolyzed samples (figure 2). The shift between –15 ppm and –25 ppm is assigned to a mixture of SiC_4 and SiC_3O , while the one at –110 is assigned to cristobalite structure. Raman spectra (figure 4) of the pyrolysed samples confirms that free carbon present is of amorphous type, similar to the glassy carbons from polyfurfuryl alcohol. XRD spectra (figure 5) of the pyrolysed samples also show that the material is amorphous. The broad band around $2\theta = 22^\circ$ may be due to combined amorphous carbon and amorphous silica structures and hence of silicon oxycarbide family.

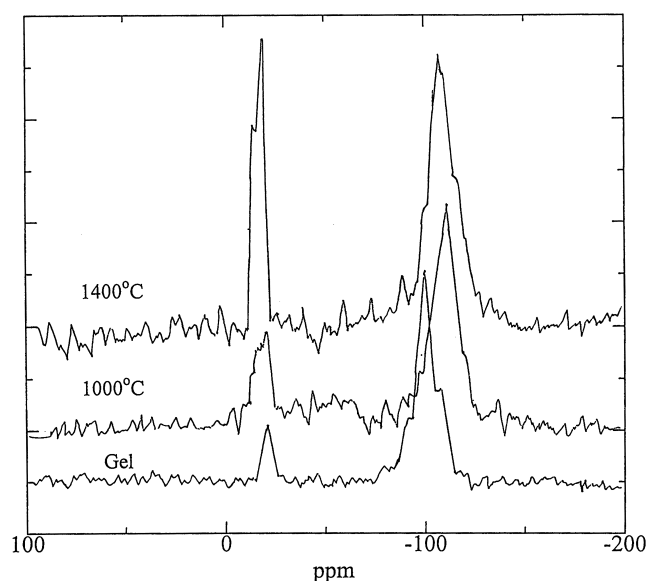


Figure 2. ^{29}Si NMR spectra of the gelled samples and samples heated to 1000°C and 1400°C.

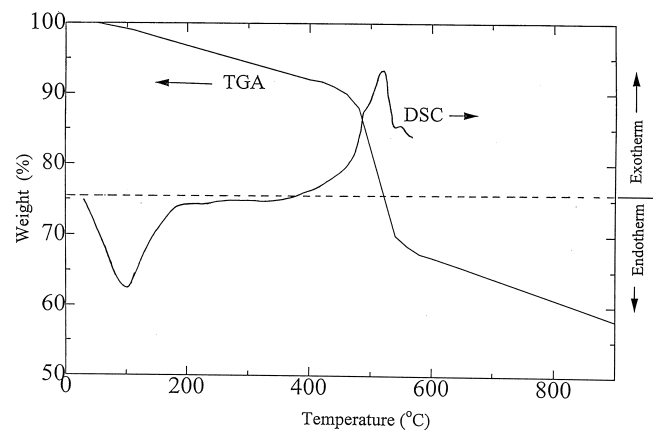


Figure 3. TGA and DSC plots in nitrogen for gel samples.

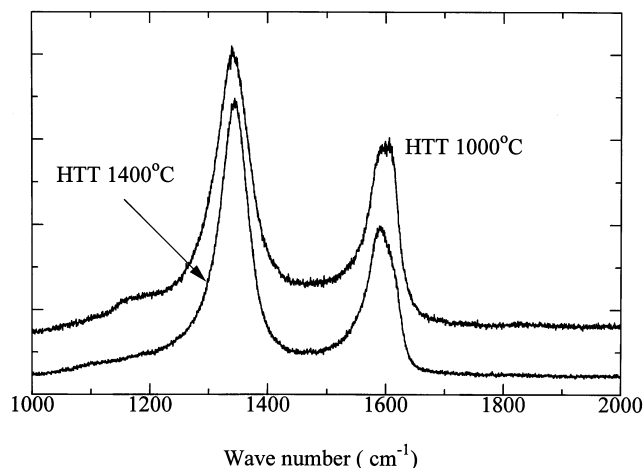


Figure 4. Raman spectra of the samples heat treated to 1000°C and 1400°C.

On further heating to 1400°C, the material initially in the powder form turned to black lump form. XRD of the samples heated at 1400°C show development of crystalline phases in amorphous black glass. The sample heated to 1400°C exhibits a band around $2\theta = 21^\circ$ ($d = 0.35\text{--}0.45\text{ nm}$) with a sharp peak at $2\theta = 21.7^\circ$ ($d = 0.408\text{ nm}$) due to cristobalite SiO_2 . The peak at $2\theta = 35.8^\circ$ ($d = 0.25\text{ nm}$) suggests development of small crystallites of silicon carbide. Peaks of lower intensities at $2\theta = 45.6^\circ$ and 48.3° with d values 0.198 nm and 0.188 nm respectively occurred presumably due to SiO_2 .

3.4 Oxidation studies on black glasses

One of the major considerations in developing silicon oxycarbide materials is to obtain a thermally stable material under oxidizing conditions. Therefore, black glasses obtained by heat treatment of above stated hybrid organic–inorganic gels were evaluated for resistance towards oxidation by heating the samples at 1000°C for 2 h under flowing oxygen. Weight loss was recorded after the experiment. Materials at 1000°C from the gels with BD/TEOS system exhibited negligible weight loss of 0.6%. On heat treatment to 1400°C, all the samples show almost same weight loss, higher than those heated at 1000°C. This carbon may be well encapsulated in the cristobalite phase.

4. Conclusion

The present studies were performed to develop silicon oxycarbide from organic–inorganic hybrid gels starting from unsubstituted silicate (TEOS) and carbon containing monomers. From the present studies it is concluded that sol–gel process gives a wider scope to add carbon con-

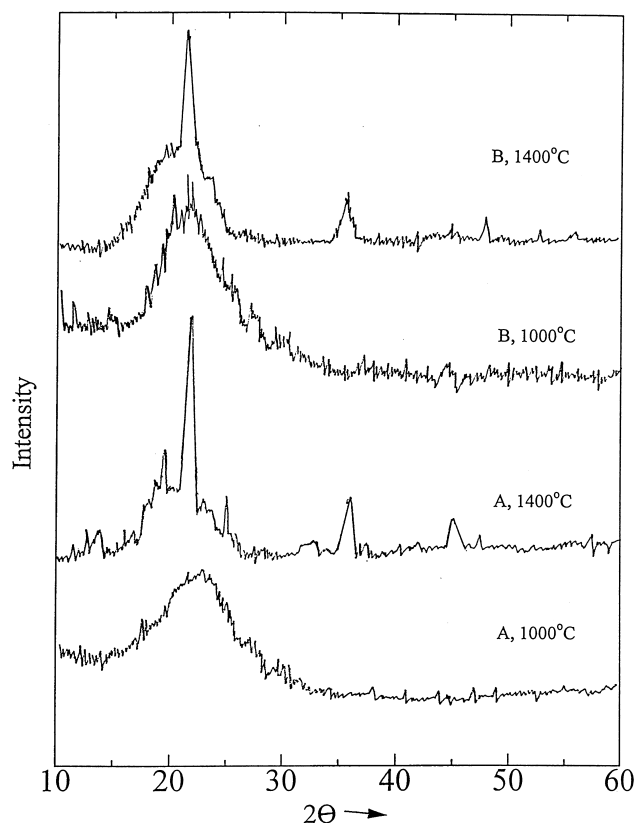


Figure 5. XRD patterns of silicon oxycarbide samples made with (A) TEOS/FFA and (B) TEOS/BD systems.

taining organic molecules in the silicate network structures at sol stage. TEOS gets hydrolysed by butanediol, which additionally, incorporates carbon containing groups in the so called organic–inorganic hybrid gels. These hybrid gels on pyrolysis, result in good oxidation resistance oxycarbide glasses. On heat treatment to a temperature around 1400°C, crystalline phase of SiC develops within the amorphous black glass. The onset temperature depends largely on the molecular nature and amount of additives.

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