

Effect of Additional Particulate Reinforcement on the Properties of Fibrous Ceramic Matrix Composites

Milan M. Vyas^a, L. M. Manocha^{a*}, S. Manocha^a and P. M. Raole^b

^aDepartment of Materials Science, Sardar Patel University, Vallabh Vidyanagar, Gujarat-388120, India

^bInstitute for Plasma Research, Bhat, Gandhinagar, Gujarat, India

Abstract

Composites, generally, consist of two phase i.e. matrix and reinforcement. Here in this work additional phase in terms of micro/nano particles was added in the fiber reinforced ceramic matrix composites and its effect on the final properties of composites was studied. Composites were prepared using sol derived from Tetraethoxysilane (TEOS) and Dimethyldiethoxysilane (DEDMS), and polycarbosilane (PCS) as matrix precursors and SiC fabric as reinforcement. To some composites another phase of solid, micro/nano powder precursor of SiC was added to decrease number of impregnation cycles. Latter composites resulted in higher density. Green composites were post-cured and pyrolyzed. Some of the composites were heated to 1500°C in argon atmosphere. Composites were characterized for density, microstructure and mechanical properties. It revealed that the resulting matrix was solid glass and addition of SiC powder facilitated the rapid densification. Composites prepared with SiC nanoparticles as well as SiC fabric as reinforcement exhibit higher flexural strength than those made without nanoparticles. The fracture behaviour is also seen to be of mixed mode failure type.

Introduction

Polymer impregnation and pyrolysis (PIP) and sol-gel process are two liquid phase processes that are used for synthesis of matrix for ceramic matrix composites. Sol-gel processing has been widely investigated, especially for the manufacture of glasses and ceramics based on oxide [1-4]. It has also been used to prepare non-oxide ceramics through incorporation of a carbonaceous precursor within the rigid oxide network [5]. Silicon alkoxide has been used with an outside carbon source to produce silicon carbide [6] or silicon oxy carbide [7]. Di or tri functional alkoxy silane in which carbon source is internal may be convenient precursors to prepare SiC [8]. Sol produced there from can be used to prepare ceramic matrix composite.

The PIP route results in ceramics with desired compositions, but the polymers required for PIP process are difficult to prepare and have very short shelf life. Also, polymer for PIP, generally PCS, needs to be stored under controlled inert conditions.

The other route for preparation of material for matrix is the solution route through sol-gel technique. It has advantages of providing ease of synthesis of polymer that is used for conversion into ceramic. It provides low temperature fabrication of ceramics with high purity of the final product depending on the purity of the organometallic compound used.

Also nanoparticles having special properties can add up to the properties of composites. Addition of micro/nano particles can improve the strength and toughness of ceramic matrix composites. An attempt was made to use the special properties of micro/nano reinforcement to modify the properties of ceramic matrix composites.

Experimental procedure

Raw materials

Tetraethoxysilane, Hexamethyldisiloxane, Dimethyldiethoxysilane (All Fluka, ~97%) were used as raw materials for sol-gel process. Ethanol (>99.5%) was distilled prior to use as solvent. Hydrochloric acid was used as catalyst for sol-gel process. Hydrofluoric acid (48%) was used to find free silica content.

*corresponding author. E-mail: manocha52@rediffmail.com

Preparation of matrix through sol-gel processing of Inorganic-organic compounds

Gels were prepared by hydrolysis-condensation (sol-gel) process of silicon containing inorganic-organic compounds. TEOS (Tetra ethyl ortho silicate) was selected as inorganic yielding compound and DEDMS (Diethyl dimethyl siloxane) was selected as organic (hydrocarbon containing silanes) compounds. Experiments were carried out for the system having molar ratio of TEOS/DEDMS/EtOH/H₂O=1/1/4/8. Ethanol was used as solvent. TEOS and DEDMS were added to ethanol and stirred for proper mixing. Calculated amount of acidic water was added dropwise to facilitate hydrolysis of organometallic compounds. After the addition of water, the mixture was stirred continuously till complete hydrolysis of the reactant. Sol was aged at room temperature. After stirring for required time, sol was casted into glass &/or teflon petridish. Petridish was covered with polyethylene sheet. Samples were allowed to dry at room temperature for several days. Dry gel was then post cured at 220-250°C. Post cured gel was heated to 1000°C in N₂ atmosphere.

Preparation of polycarbosilane particles

Polycarbosilane was cured in air and grinded in the planetary ball mill at the speed of 300 RPM for 12 hr. The speed ratio between the main dial and grinding station was 1:-3. Hi strength steel balls of density of approx. 7.8 gm/cc were used for the purpose. Combined effect of impact and shearing force led solid pieces to break into small particles.

Fabrication of composites

Composites were prepared by using SiC fabric as reinforcement and sol prepared from TEOS and DEDMS as matrix. Gel was applied on the SiC fabric. Plies were stacked over one another and pressed. Composites were then heated at 110 °C under pressure. Prepared green composites were post cured in air. Finally, composites were pyrolyzed at 1000 °C in presence of N₂ atmosphere. Composites were also prepared from the polycarbosilane. Cured PCS nanoparticles (precursor for SiC nanoparticles) were added as additional nano reinforcement. Green composites prepared from polycarbosilane were dried in air under pressure, postcured and finally pyrolyzed at 1000 °C in presence of N₂ atmosphere.

Pyrolyzed composites were then heated to 1500 °C in argon atmosphere. During the densification of composites by infiltrating sol or polycarbosilane, SiC nanoparticles were added to fill the pores of composites.

Characterization techniques

Thermogravimetric analysis of the dry gel and post cured gel was done on Mettler TG 50 analyzer at heating rate of 20 °C/min. FTIR analysis of dry gel, post cured gel and pyrolyzed mass was done using KBr pellet method with Shimadzu 8300 FTIR spectrometer. Gel was first crushed and mixed with KBr with 1:100 ratio. Mixture of KBr and gel was palletized and scanned for full range from 4000-400 cm⁻¹. Density of the dry gel, post cured gel and pyrolyzed gel was measured by archimedes principle with the help of Mettler AG 204 densitometer. Free carbon content was determined by heating the pyrolyzed gel to 650°C for 2 hr in air. Free silica content was determined by keeping the pyrolyzed gel into HF for 24 hr.

Results and Discussion

Density of various gels

Each stage of sol-gel process was characterized for density. Density at different stages is given in table 1. After pyrolysis, material turned black in color indicating conversion from polymer to ceramic. Density of gel also increased on pyrolysis.

Table 1.

Density of different gels

Material	Density (g/cc)
Dried gel	1.21
Post cured gel	1.3
Pyrolyzed gel	~ 2.0

Thermal behaviour of gel

TG scan of dry gel in air shows initial major weight loss in the range 50°C-100°C indicating presence of water at the surface in small amount. In the temperature range 200-300°C hydroxyl ions on the surface of the gel/glass pores undergo dehydroxylation via condensation of OH-OH leading to the formation of water. Therefore, weight loss was

observed in the temperature after 200 °C in TG graph due to removal of water. This is also confirmed by the decrease in the intensity of –OH peak of the post cured gel prepared from TEOS/DEDMS. With fast heating rate, water and solvent remained in the pores of gel evaporate instantaneously which may result in foaming, blotting and bubble formation. Dried gel shows rapid weight loss, approx. 9%, before 250 °C which was very less, approx. 1.5%, in case of post cured gel. Major weight loss in the temperature range of 400 – 600 °C was due to the combined effect of dehydroxylation and decomposition of gel network. Weight loss occurred in the temperature range 700 - 800 °C was due to dehydroxylation of Si-OH group.

FTIR analysis of gel

The dry gel, post cured gel and pyrolyzed gel were characterized for different functional groups. Dry gel possesses peak at 570 cm^{-1} corresponding to the unreacted ethoxy groups which show that some ethoxy group remained unreacted during hydrolysis-condensation process. Peak at 570 cm^{-1} was observed in case of dry gel, post cured gel. The intensity of peak corresponding to unreacted ethoxy group decreases as temperature increases and at 400 °C, it was very less intense indicating presence of very less amount of ethoxy group at that temperature. Peaks at 1627 cm^{-1} and 3430 cm^{-1} , corresponding to adsorbed water and silanol group respectively, were present in case of dry gel, post cured gel and gel heated at 400 °C. The intensity of peak at 1627 cm^{-1}

went on decreasing as temperature increased and after 250 °C very small amount of adsorbed water remain in the gel which is in agreement with the presence of very small peak at 1627 cm^{-1} . No peak was observed at 1627 cm^{-1} in pyrolyzed samples of different gel showing total removal of adsorbed water. Peak at 790 cm^{-1} and 450 cm^{-1} correspond to the symmetric stretching and bending of Si-O-Si bond. Peak in the region 1000-1200 cm^{-1} is due to the asymmetric stretching of Si-O-Si bond. Peak in the region 2800-3200 cm^{-1} is due to the stretching of C-H bond. Peak at 760 cm^{-1} corresponds to Si-C stretching and CH_3 rocking. Peak at 1255 cm^{-1} and 1411 cm^{-1} corresponds to CH_3 symmetric deformation and CH_3 asymmetric deformation of Si- CH_3 . It was observed that the intensity of both these peaks went on decreasing as temperature increases and it totally disappeared in pyrolyzed gel. Therefore, it was concluded that the Si- CH_3 bond breaks in the temperature range 250-1000 °C. Intensity of the peak related to C-H vibration went on decreasing with heating showing that C-H bond breaks and hydrogen was excluded from the gel network. At 1000 °C, peak at 800 cm^{-1} become prominent. So, during conversion from polymer to ceramic unreacted group, water and silanol get eliminated. Most of the Si- CH_3 and C-H bond got broken during the course of pyrolysis of the gel.

Estimation of free carbon and free silica content

Free carbon content of the pyrolyzed gel was found to be approx. 0.7%. Free silica content of the pyrolyzed gel was found to be approx. 83%.

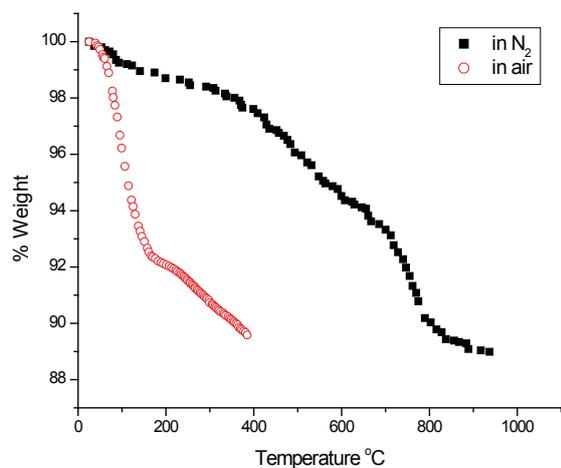


Fig. 1. TG scan of gel (TEOS/DEDMS=1) in air and in nitrogen atmosphere.

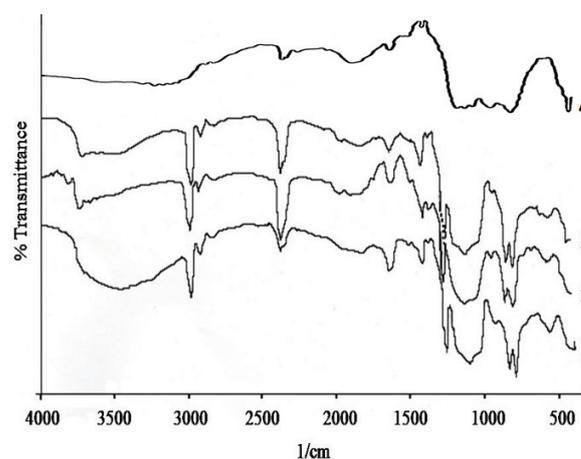


Fig. 2. FTIR spectrograph of gel prepared with DEDMS/TEOS=1: 1 – after drying at room temperature; 2 – after post curing; 3 – after heating to 400 °C in air; 4 – after pyrolysis.

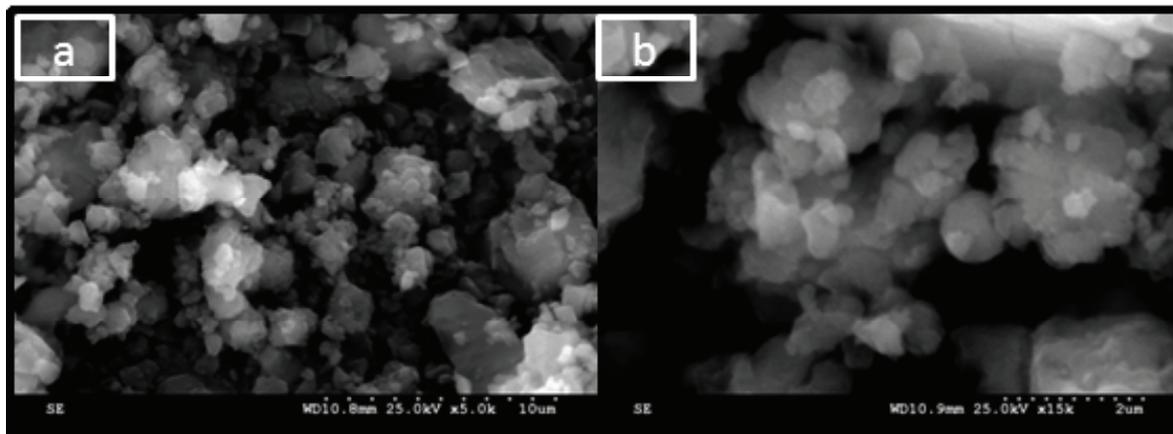


Fig. 3. SEM micrograph of polycarbosilane particles

Particle size of polycarbosilane

Particle size of polycarbosilane showed a wide range of distribution. Most of the particles were below the size of 10 μm . Maximum number of particles fall in the size range of 2 – 5 μm . It is clearly seen from the SEM micrograph that shape of particles is not of spherical. Due to grinding, the surface of particles is rough. Impact, in the planetary ball mill, caused the surface of the larger particles to peel off to form smaller particles.

Density of composites

Composites prepared from polycarbosilane showed increase in density on heating to 200 $^{\circ}\text{C}$. This

is due to the fact that oxygen is getting incorporated into the polycarbosilane to tightly bind the network. While the composites prepared from sol showed decrease in density due to removal of adsorbed water, unreacted ethoxy group and silanol compound. A variation in density of different composites prepared from polycarbosilane, on heating to 200 $^{\circ}\text{C}$, can be observed in fig. 4. This variation can be attributed to amount of oxygen being incorporated into the network. The ability of matrix, composed of polycarbosilane only, to incorporate oxygen is higher than that made up of adding polycarbosilane particles (either cured or pyrolyzed). Incorporation of oxygen into the network ultimately results in the increase in density. On heating to 1500 $^{\circ}\text{C}$, density of composites was found to increase due to formation

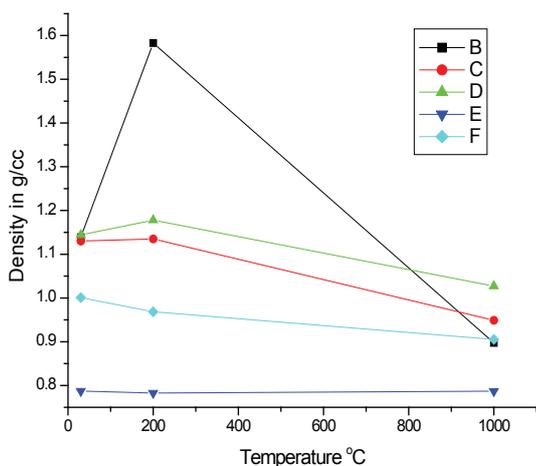


Fig. 4. Density of various composites: B – SiC/PCS composite; C – SiC/PCS+PCS as such particles composite; D – SiC/PCS+PCS pyrolyzed particles composite; E – SiC/Sol composite; F – SiC/Sol+SiC nanoparticles composite.

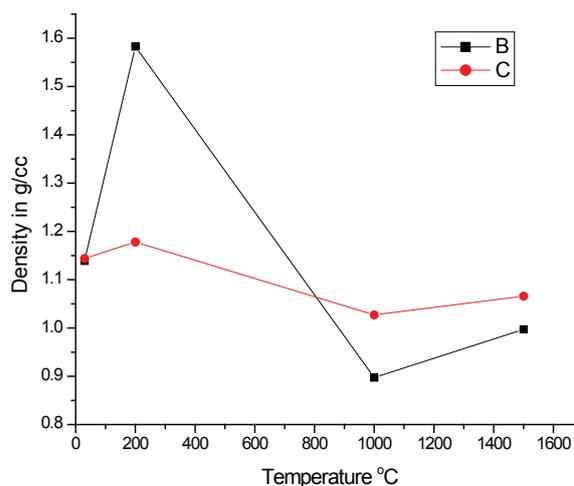


Fig. 5 Density of composites on heating to 1500 $^{\circ}\text{C}$: B – SiC/PCS composite; C – SiC/PCS+PCS pyrolyzed particles composite.

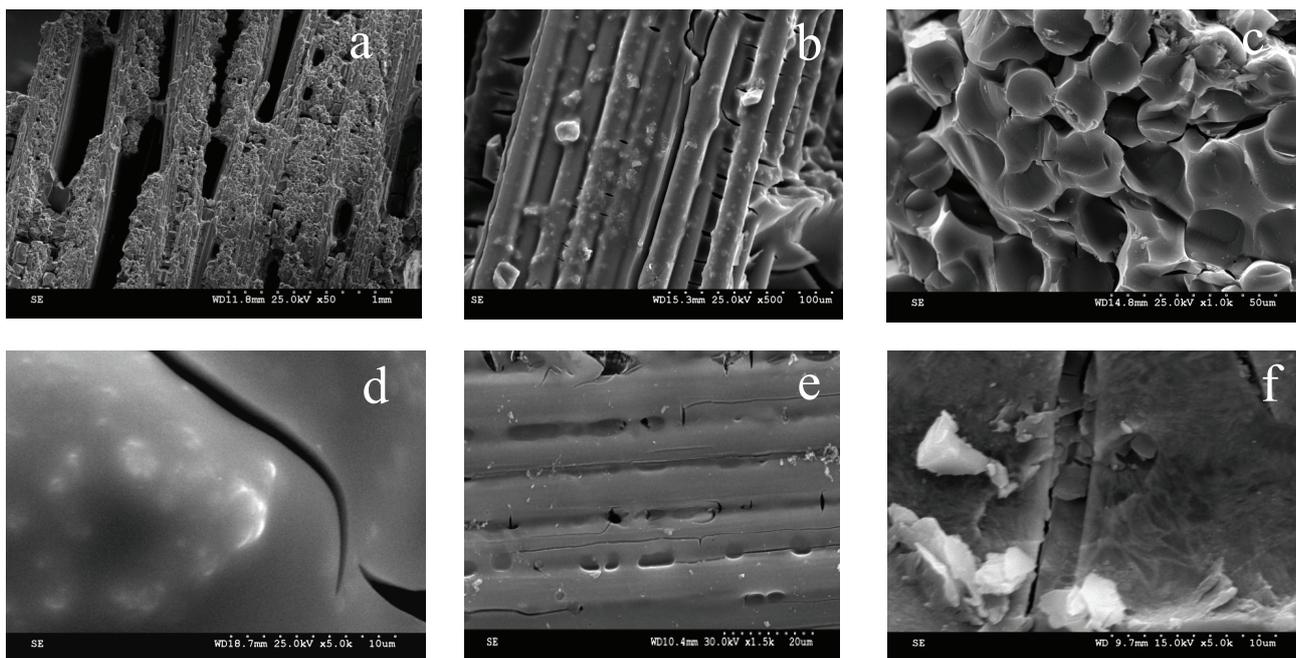


Fig. 6 SEM micrograph of composites: a – Cross section of composite showing presence of pores; b – Distribution of particles in the matrix; c – Matrix wets the fiber completely resulting into good fiber matrix bonding; d – Deflection of crack by particles; e – Composite after impregnation; f – Pores filled after impregnation.

of SiC which can also be seen from the XRD plot. Since the density of composites was less than the theoretical one, these composites were infiltrated to increase the density. Infiltration helps to fill the open pores of composites (fig. 6) resulting in an increase in the density.

SEM studies

Fig. 6 shows SEM micrograph of the composite. As seen from the figure, the matrix gets well infiltrated into the spaces between the fiber tows. Fiber/matrix is illustrated in Fig.6 which shows the SiC secondary particles distributed in the matrix.

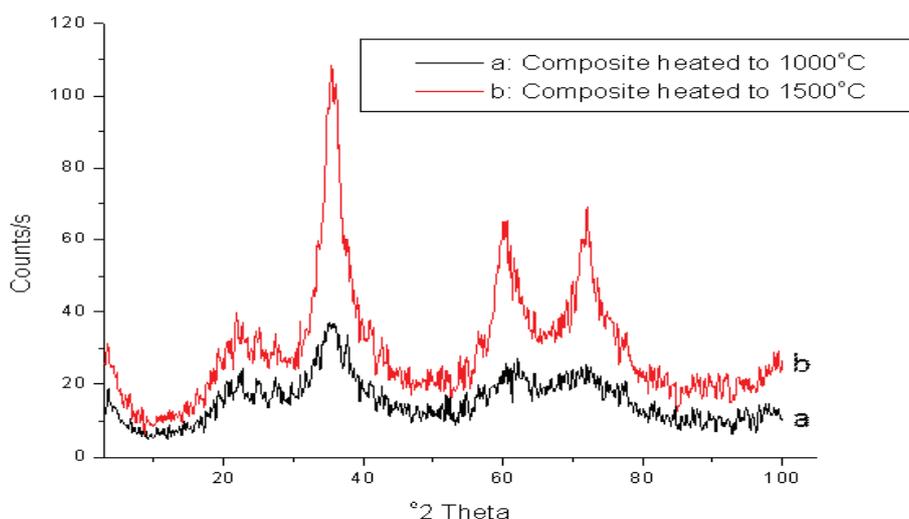


Fig. 7. XRD of Composites (a) HTT at 1000°C (b) HTT at 1500°C

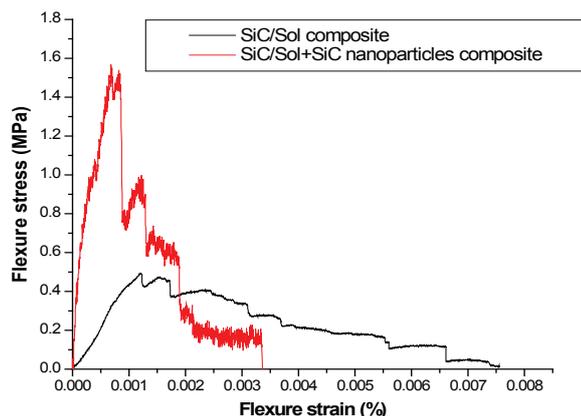


Fig. 8. Stress/strain curve of composites fabricated using sol.

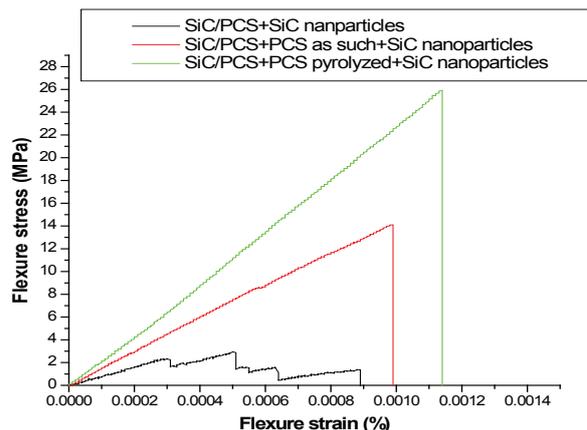


Fig. 9. Stress/strain curve of composites fabricated using polycarbosilane.

XRD analysis

Fig. 7 shows XRD analysis of the composite made with SiC and sol derived SiC. It shows amorphous nature of the matrix. However, on heat treatment to 1500°C, the amorphous matrix is found to have transformed into crystalline phase (Fig. 8).

Mechanical properties of composites

Figs. 8 and 9 show stress/strain curves of the composites. It shows that the strength of the composites get improved on addition of SiC nanoparticles behaving in a typical type I failure mode.

Conclusions

Hybrid organic-inorganic sol can be used as a matrix for ceramic matrix composite. Composites thus prepared, have low density and high porosity. So, infiltration cycle is needed to increase the density of composite. On adding the micro particular phase, these composites exhibit increase in strength. Also, addition of micro particles helps to trap or deflect crack.

Acknowledgement

Milan M. Vyas wishes to thank Institute for Plasma Research, Gandhinagar for providing JRF under the project NFP/MAT/04.

References

1. L.C. Klein, International Society for Optical Engineering-proceeding, 1991, vol. 1590.
2. D. Chakravorty, Sol-gel technique for materials synthesis, 1992, p. 170.
3. Jan J. Van Beek, D. Seykens and J. Ben, H. Jansen, J. Non. Cry. Sol. 146:111 (1992).
4. S. Chakrabarti, P. Pramanik, J. Mat. Sci. Let. 9:1135 (1990).
5. K.J. Wynne, R.W. Rice, Ann. Rev. Mater. Sci. 14:297 (1984).
6. D.A. White et.al., Adv. Ceram. Mat. 2:45 (1987).
7. L.M. Manocha, E. Yasuda, Y. Tanabe, S. Manocha, D. Vashistha, Bull. Mater. Sci. 23:1 (2000).
8. K.C. Chen, K.J. Thorne, A. Chemseddine, F. Babonneau, J.D. Mackenzie, Mat. Res. Soc. Symposium proceeding, Reno, Nevada, Vol. 121, 1988, p. 571.

Received 28 June 2010.