© Applied Science Innovations Pvt. Ltd., India *Carbon – Sci. Tech. 10/4(2018)67-75*

Carbon – Science and Technology

ISSN 0974 – 0546

http://www.applied-science-innovations.com

RESEARCH ARTICLE *Received: 15/07/2018, Accepted: 17/01/2019*

Synthesis of ultra-high temperature silicon oxycarbide (SiOC) glass by an organic-inorganic hybrid route

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Abstract: Silicon oxycarbide is a new generation amorphous glassy ceramic possessing unique electrical, mechanical, optical properties and ultra-high temperature stability upto 2730°C. It has numerous engineering applications in additive manufacturing, lithium-ion batteries, brake disks for sports car, ultra-fast and high voltage LEDs, MOSFETs, thyristors for high power switching, astronomical telescope, nuclear power reactor etc. In this work, SiOC was prepared by sol-gel technique using organic-inorganic hybrids as precursors. Tetraethoxysilane (TEOS) and Polydimethylsiloxane (PDMS) were used as silica and carbon sources respectively. SiOC sols were formed through hydrolysis of TEOS and PDMS. The used chemicals in this process involved isopropanol, distilled water and hydrochloric acid, which is used here as solvent, hydrolytic agent and catalyst respectively, at different refluxing condition, alkoxide to water ratios, pH levels etc. The sols thus formed were allowed to gel over a varying period (upto maximum of 10 days). After drying the gels for 24 hours, the same was pyrolysed at 1100°C under inert nitrogen atmosphere to yield SiOC. Phase formation was carried out by X-Ray Diffraction (XRD) technique, X-ray Photoelectron Spectroscopy (XPS) analysis and Raman Spectroscopic analysis. XRD data showed formation of a broad peak at $2\theta\sim22$ degrees indicating formation of amorphous SiOC and absence of any crystalline peaks indicating no SiC or Si was formed during pyrolysis. XPS data shows the presence of Si, O and C peaks in the range 100-200 eV, 530 eV and 285 eV, respectively, confirming formation of SiOC. It was revealed that within the random network of Si-O tetrahedra, islands of only C-C bonds were responsible for coloring the SiOC glass black. The estimation of mechanical properties revealed that the hardness value and Young's modulus, of the synthesized SiOC ceramic sample, was determined to be 11.67 GPa and 75.79 respectively which indicating the better mechanical properties than other reported SiOC systems.

Keywords: Photocatalysis, TiO_2, water purification, water pollution, grand challenges.

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1 Introduction: Among many other polymer derived high-performance glassy ceramic material, Silicon oxycarbide (SiOC) is receiving an immense attraction because of some of its novel properties and a wide range of potential applications. The incomplete exchange of oxygen by carbon throughout the silica network is responsible for various morphologies of SiOC glass ceramic material and increases the thermal, chemical and mechanical parameters of SiOC ceramic. These render them suitable for novel and emerging applications like electrodes for supercapacitors, anodes for Li-ion batteries, electromagnetic absorbing material, solar energy applications and so on [1-4]. Apart from the electrical and thermal properties, mechanical properties also have great relevance in many applications in aerospace and automotive structures [5-7].

In order to obtain crack or pore free highly dense SiOC ceramic, several approaches for synthesis and processing have been adopted. In one process, transition metal based reactive nanofillers, metal oxide/nitride, etc. are incorporated in the SiOC matrix [8-11]. In another process, silica containing polymers like polysiloxane [12], polycarbosilanes [13], silylcarbodiimides [14] etc. are employed which undergo thermal oxidation, hot pressing and pyrolyzing at high temperatures [15-17]. Completely intense SiOC ceramic system can also be obtained by photo reactive cross connecting followed a consequent high temperature heat treatment in controlled atmosphere of polysiloxane materials [18]. Chemical vapour deposition (CVD), RF magnetron sputtering and ion implantation techniques also have yielded crack free, highly dense SiOC ceramics [19-20]. All these are complex, multistep processes and adversely influence the cost of the SiOC material.

In comparison, sol-gel is a facile synthesis technique that can be employed to develop a colossal diversity in a composite material, its microstructures, physical and chemical properties contingent upon the chosen of polymeric composition or polysiloxane materials, different heat treatment conditions in different atmosphere, and possible stabilizer used [21-24]. Using organic-inorganic hybrid precursor materials and sol-gel route of synthesis, SiOC materials are obtained by pyrolysis of precursor gels followed by pressureless sintering. Often these processing leads to formation of porous SiOC of low mechanical strength and low density [3-11,15-18]. However, judicious selection of the mixture ratio of the SiOC raw precursors, crosslinking and carbonization conditions can produce fully dense SiOC ceramics having high structural and mechanical strength [12-14, 25].

In this work, a new generation of SiOC ceramic material has been synthesized by sol-gel process by tuning previously designed preceramic polymerization process and pyrolysis conditions without applying any pressure using TEOS/PDMS as raw materials. The synthesized SiOC materials were characterized by means of FTIR, XRD, RS, XPS and FESEM. The fully dense, crack free SiOC material have been found as high structural and mechanical strength and confirmed by nanoindentation.

1. Experimental

1. 1. Instrument Used: The existing elemental bond in the sintered SiOC ceramic sample was explored by Fourier Transform Infrared spectroscopic (FTIR) analysis by utilising Varian 4100 FTIR Excalibur Series equipment. The spectra were gathered in the transmittance mode in a range of 2000 – 400 cm^{-1} using KBr pellet. The wave number step size was 2 cm^{-1} and an average of 50 scans were used as the resulting spectra to analyse the synthesized sample. The XRD measurement was performed by X'pert pro MPD (PANalytical, Netherlands) diffractometer utilising X'Celerator functioning at 40 kV using Cu K_α radiation. The feature wavelength involved in Cu K_α radiation was 1.54 Å. A step size of 0.1° was used to carry out the XRD data. The Raman spectra were obtained using Renishaw inVia Quontor Raman spectrometer (United Kingdom). The excitation wavelength was 514 nm subsequent to an Ar^+ laser. A wavenumber range of 200 - 3200 cm^{-1} was examined. The morphology of the SiOC sample was investigated by FESEM (Supra VP35, Carl Zeiss, Germany). The representative elemental compound of the synthesized SiOC sample was acquired by the energy dispersive X-ray analysis (EDAX) linked to the FESEM. The surface analysis was carried out by ultra high vacuum (10^{-6} < Pa) phi 5000 versaprobe ll X-ray photoelectron spectroscopy (XPS) from 0 to 1000 eV. The spectrum was carried out at 50 W, utilising monochromatic Al source with 200 μm beam diameter with the angle of 45°. The nanomechanical characterization was carried out by Hysitron TI Premier nanoindenter, Bruker, Singapore.

1.2. Chemicals used: In order to synthesize SiOC precursor, Tetra ethyl orthosilicate (TEOS), reagent grade 98 %, Hydrochloric acid (HCl) 37 % and Iso propyl alcohol (i- PrOH), 99.7 % were purchased from Sigma Aldrich. Hydroxy terminated Polydimethyl siloxane [(PDMS) (C_2H_6OSi) n] M.W. 4200, was purchased from Alfa Aesar.

1.3. Synthesis and Development: In a typical sol-gel synthesis route [25], Tetraethylortosilicate (TEOS), polydimethylsiloxane (PDMS) were used as the source of silica and carbon respectively. The Isopropyl alcohol (i-PrOH), distilled water (H_2O) and hydrochloric acid (HCl) was used as solvent, hydrolytic agent and catalyst respectively. The applied weight proportion of TEOS/PDMS was 70/30 and the ratio of molar concentration of TEOS/H_2O/HCl was 1.5/4/0.3. The volume of the solvent used for synthesis was 100 ml. Two batches of compositions were developed- one containing the measured volume quantity of PDMS, TEOS, and 50 % of i-PrOH and the another solution containing the left quantity of i-PrOH and the entire quantity of HCl and HCl. At first both these batches were prepared separately in a magnetic stirrer and blended for 2 hours to homogenise the solutions properly. Then both the solutions slowly merged and blended in a thermo stabilized container at 80 °C under refluxing condition and vigorous stirring. After 30 minutes the solution was collected and left for aging for approximately 10 days. The gel was dried at 80 °C for 24 hours. The dried samples were then pyrolysed at N_2 atmosphere at 1550 °C with heating rate of 3 °C /min and 2 hours dwelling time in every 300 °C interval. A process flow of the synthesis procedure is given in Figure (1).

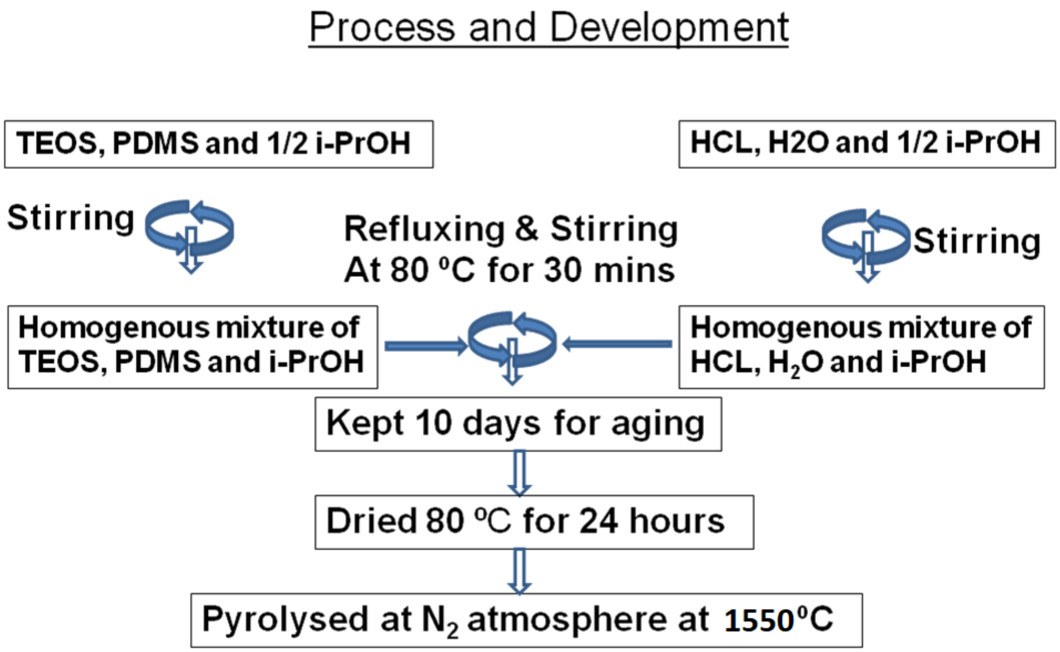


Figure (1). Flow chart for pressureless, high temperature synthesis of SiOC amorphous glass ceramic.

2. Results and discussion

2.1. Fourier Transform Infrared spectroscopy (FTIR): Figure (2) demonstrates FTIR spectra of the SiOC sample derived from TEOS/PDMS inorganic-organic crossbreed mixture, pyrolyzed at 1550 °C for 2 hours, in the selected range of 400–2000 cm^{-1}. The FTIR spectrum of the sample showed the characteristics transmittance bands at 470, 797, 1098 and 1630 cm^{-1}. The transmittance band at 470 cm^{-1} is associated with the O-Si-O bending frequency and transmittance at 797 cm^{-1} indicates the asymmetric nature of stretching band of Si-C bond. Based on the PDMS conformation, this band varies from 800-815cm^{-1}. If the polymer is linear the band appears at 800 cm^{-1} and if it is cyclic a band at 815 cm^{-1} may be obtained. In our work, the PDMS is linear in nature so we obtained the band at 797.41 cm^{-1}. According to literature, the band appearing in the range 1080-1180 cm^{-1} is associated with the Si-O-Si symmetric stretching band. Here the transmittance band appearing at 1098.19 cm^{-1} ensures the construction of Si-O-Si units **[25, 26]**.

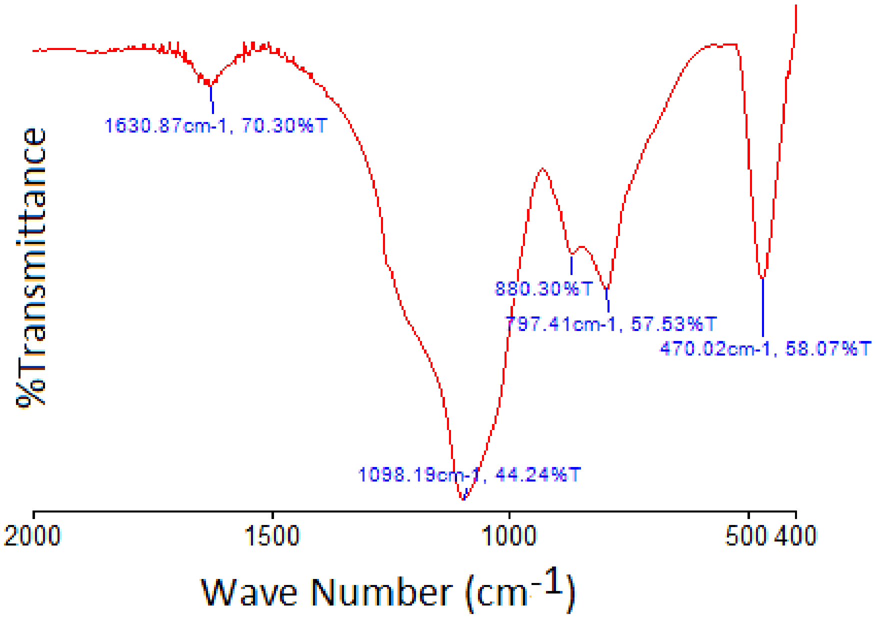


Figure (2). FTIR spectra of amorphous SiOC glass ceramic.

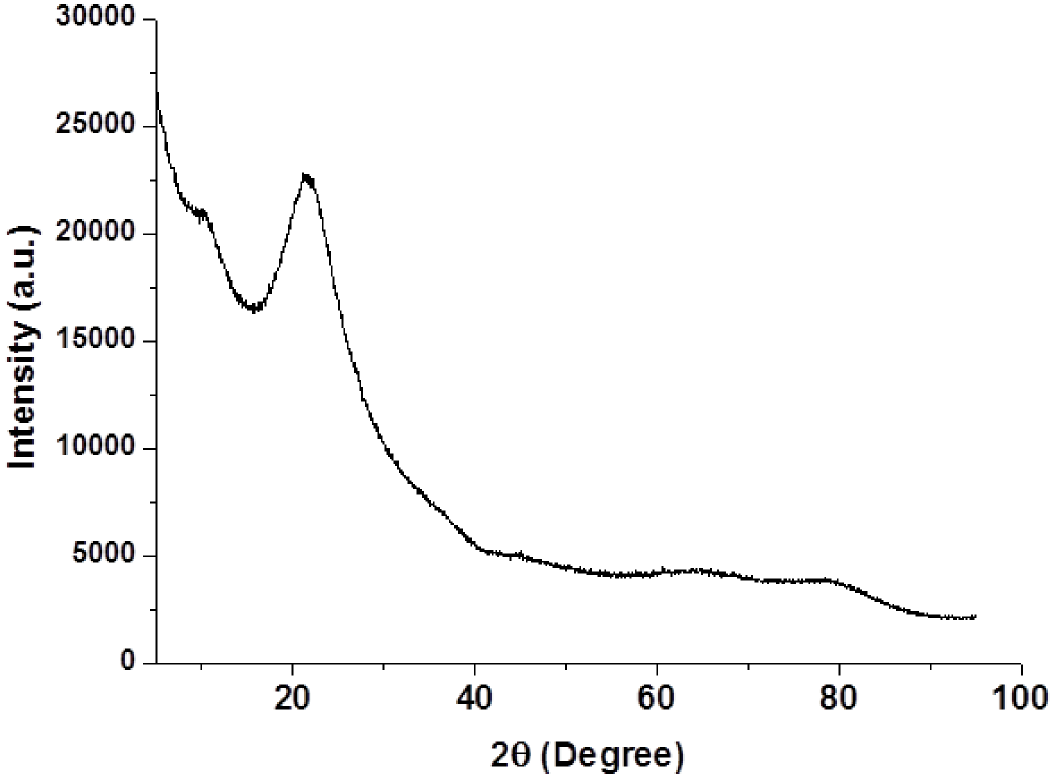


Figure (3). XRD pattern recorded for amorphous SiOC glass ceramic.

2. 2. XRD analysis: From the obtained XRD result [shown in Figure (6)], a broad peak is observed at 2Ѳ ≈ 22° indicating the SiOC ceramic developed at 1550ºC exhibits a broad peak related to the non-crystalline network. From the literature it was found that the pyrolysis at 1550ºC accelerates the initial crystallization behaviour of β-SiC, which is not found in our synthesized material. This may be due to the fact that silicon carbide crystallite size evolution is small enough to be masked by the same intensity of amorphous phase of the SiOC. Several authors **[23-25]** have recommended the possibility that the carbon like graphite network lessens the ability to growth of silicon oxycarbide network in the matrix and be a hindrance for the phase formation of SiO_4 and SiC_4 units results in consequent amorphous network in the matrix. So, it may be concluded from the above study that, the synthesized SiOC material derived from TEOS/PDMS inorganic-organic hybrid demonstrates decent thermal constancy under inert atmosphere at 1550ºC at least 2 hours **[3-11, 15-18]**.

2. 3. Raman Spectra: The Raman spectroscopy data of the sample is recorded with a 514 nm laser in the spectral region from 1200-1700 cm^{-1}, shown in Figure (4). Two peaks appeared at 1353 cm^{-1}, 1584 cm^{-1} and 1620 cm^{-1}. The bands 1353 cm^{-1} and 1584 cm^{-1} are associated with D, G and G' bands respectively. The appeared D band is correlated to the graphite like carbon phase i.e free carbon phase. The G band corresponds to the graphite single crystals and is associated with C-C vibrational modes allocated to doubly degenerate E_{2g}; whereas the D band is perpetually assigned for disordered phase of carbon network and has been stands for A_{1g} mode.

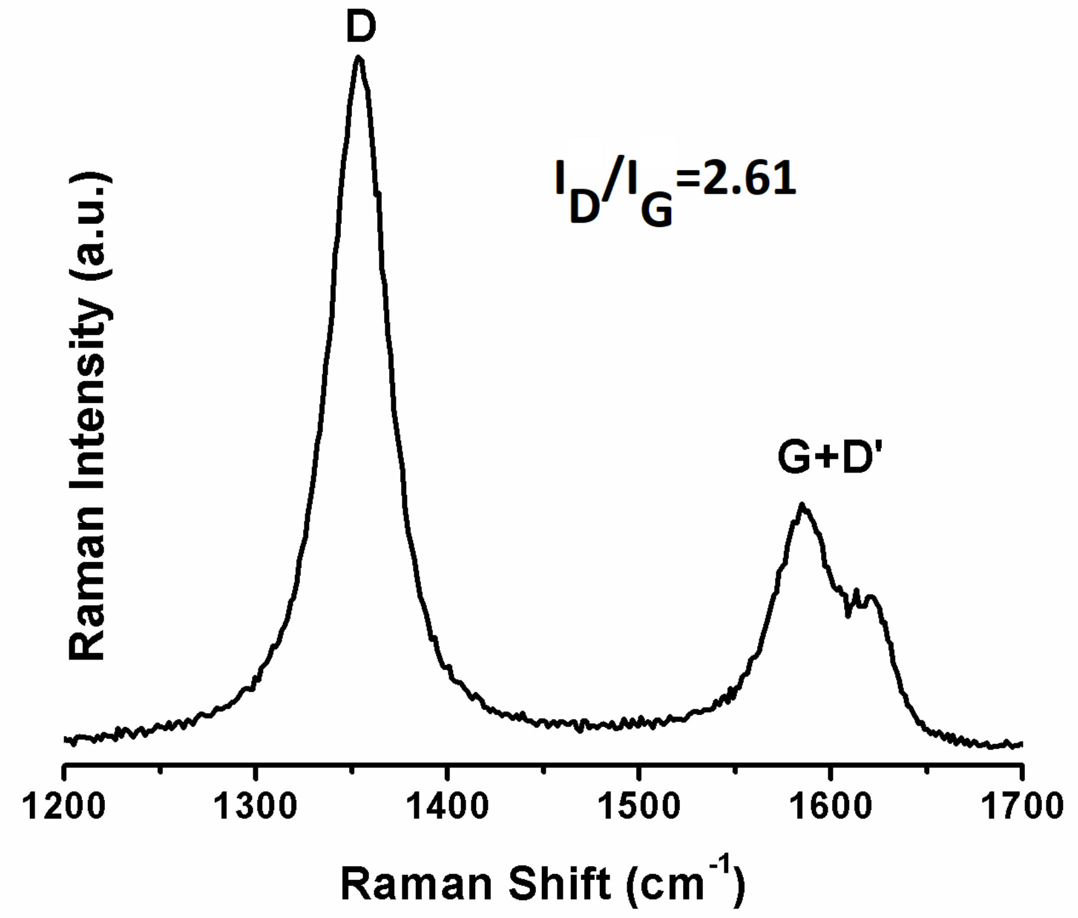


Figure (4). Raman spectra of amorphous SiOC glass ceramic.

From this spectra the in-plane crystal size of graphite is determined by using the following equation –

$$L_a = 4.4 \times \left(\frac{I_D}{I_G}\right)^{-1}$$

Where I_D is the intensity of the corresponding D band and I_G is that of the G band. In our case I_D/ I_G ratio is 2.61 and the L_a is 1.6 which almost matches with the literature data **[13-16, 27]**. Thus, from the above spectral indications we can prove the existence of carbon nanocrystals throughout SiOC matrix.

2. 4. XPS analysis: XPS scan reveals the existence of C, Si and O as the only constituents of the pyrolyzed sample, indicating formation of SiOC throughout the bulk of the sample. From the above spectra [Figure (5)] it has also found that there are two 2p and 2s peaks for Si between the ranges of 100 -200 eV. The oxygen 1s and the carbon peak have been observed at the binding energy of 530 eV and ~285 eV respectively. From the above spectra, it is confirmed that our synthesized SiOC material also consist of SiO_2, SiC, and free carbon. The binding energy value esteem for Si 2p is 104.11 eV, and the outcome attributed to the existence of siloxy groups **[28]**.

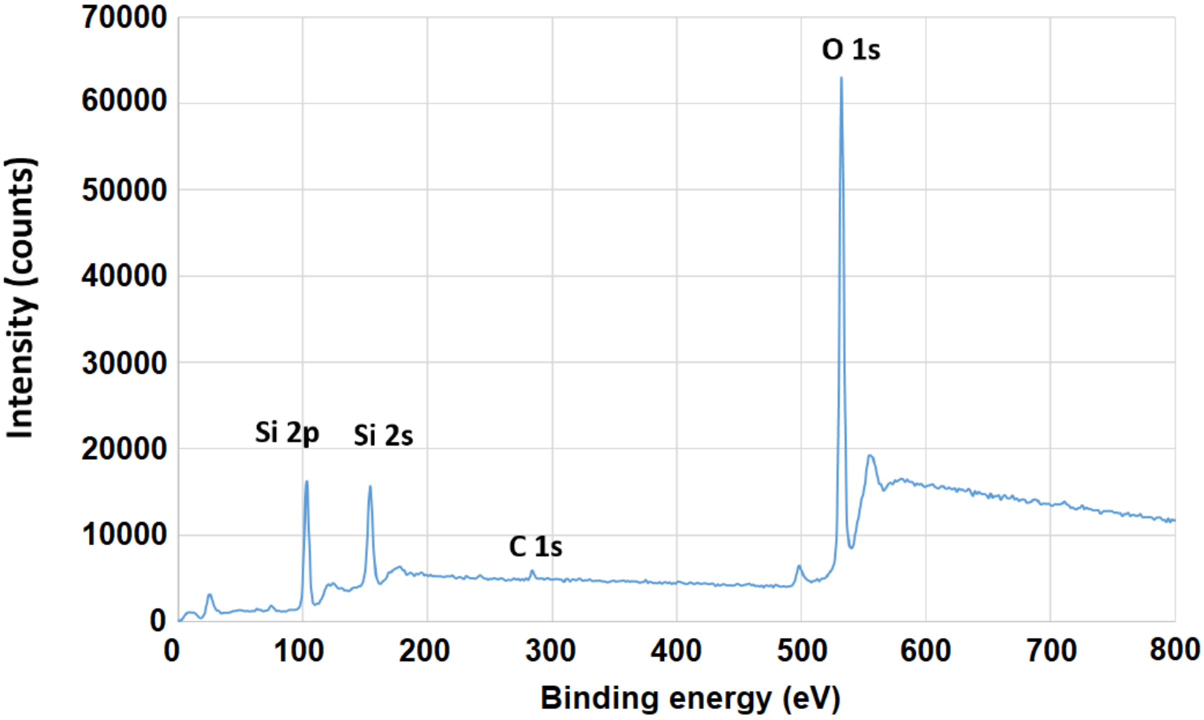
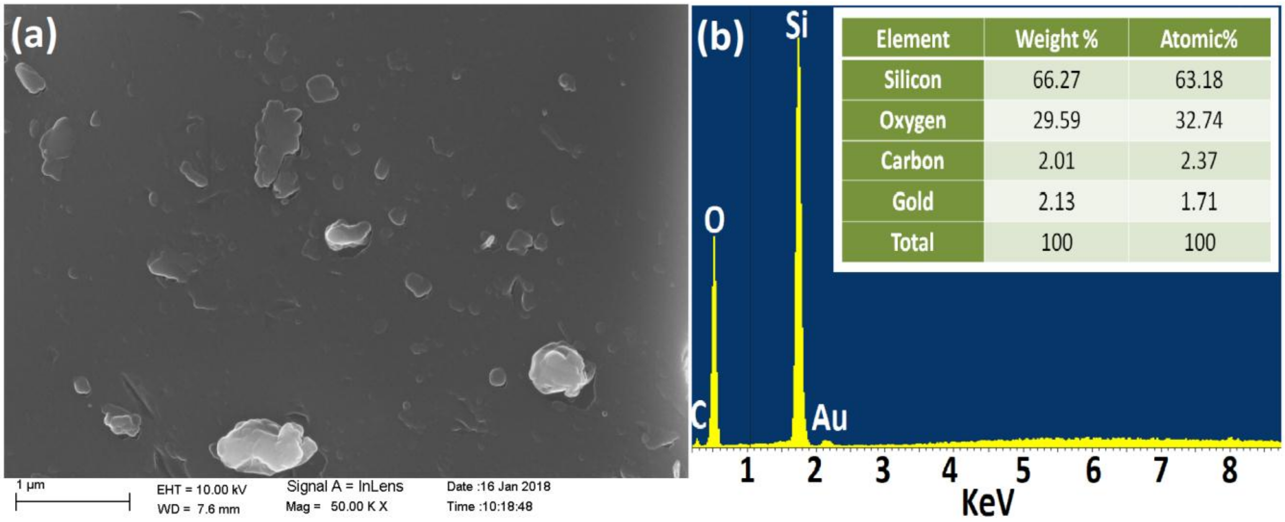


Figure (5). X-ray photoelectron spectroscopic analysis of amorphous SiOC glass ceramic.

2. 5. FESEM analysis: Surface morphology and microstructure of our synthesized SiOC material has been characterized by FESEM and shown in Figure (6a). From the surface image it has been clearly seen that the material contains glassy amorphous matrix, almost completely intense in nature and shows a pretty flat surface. From the image it is additionally observed that our synthesized SiOC ceramic is crack free. Figure (6b) shows the energy dispersive x-ray spectrum of our sintered sample. The EDX images confirm the existence of Si, C and O. Elements obtained from EDX study with their normality as well as weight percentages are shown in table inserted in inset of figure (6) (b). The presence of all expected elements confirmed formation of SiOC.



Element	Weight %	Atomic%
Silicon	66.27	63.18
Oxygen	29.59	32.74
Carbon	2.01	2.37
Gold	2.13	1.71
Total	100	100

Figure (6). Phase, structure and morphological analysis by Field emission scaning electron microscopy (FESEM) (a) and elemental analysis by Energy dispersive spectroscopy (EDX) of amorphous SiOC glass ceramic (b).

2. 6. Mechanical properties: The Nanoindentation load-displacement curve is shown in Figure (7). The elastic modulus and hardness values were estimated by means of the loading-unloading curvature. The nanoindentation investigation revealed the hardness value of the synthesized SiOC ceramic sample, sintered at 1550 °C as 11.67 GPa which indicates the improved hardness parameters than the SiOC ceramic material synthesized by others **[29-31]**. The Young's modulus value has been found to be 75.79 GPa, which is also in general agreement with the range of values for Young's modulus of SiOC ceramic (50–90 GPa) reported by others **[29-31]**.

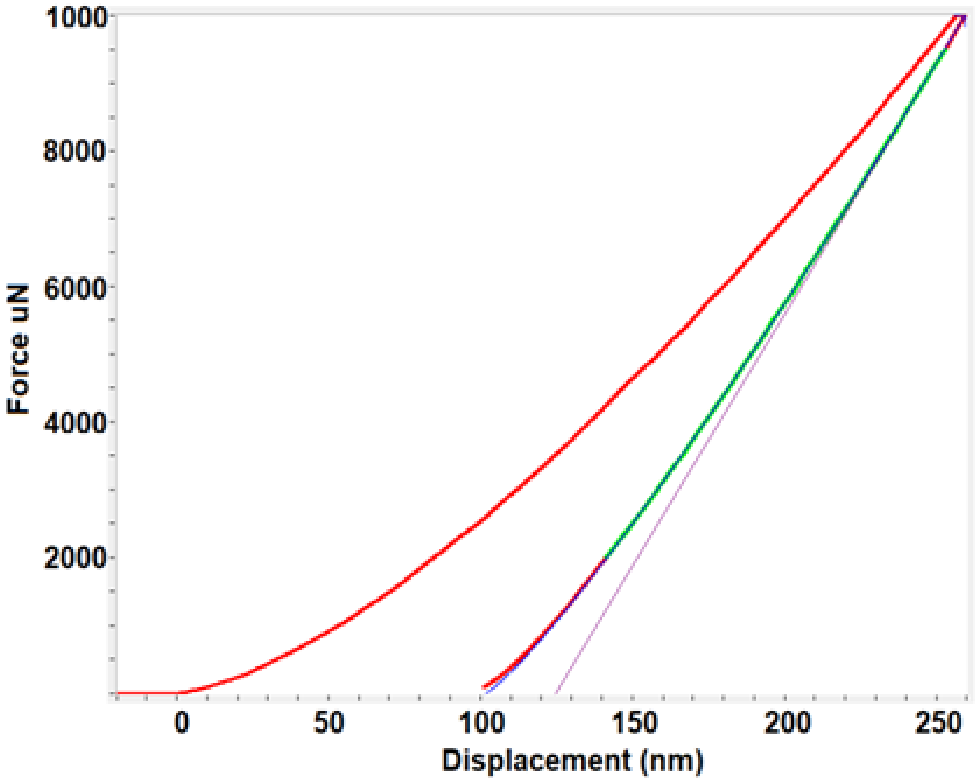


Figure (7). Mechanical properties of amorphous SiOC glass ceramic analysed by Nanoindentation load-displacement curves.

From the microstructural investigation [Figure 6 (a)], it can be seen that the absence of any significant crack and/or pores leads to the construction of fully dense SiOC glassy network. The depth of nano indentation is found to be 98.43 nm. Table 1 shows the values of different mechanical properties of our synthesized SiOC ceramic material.

Table (1). Different mechanical parameters of amorphous SiOC ceramic at load 10000μN.

Load 10000μN	
Reduced Young's modulus (Er)	75.793
Hardness (GPa)	11.67
Depth (nm)	98.43

3. Conclusions: In this study silicon oxycarbide ceramic has been developed by pyrolysing organic-inorganic (TEOS: PDMS = 70:30) hybrids at 1550 ºC for 2 hours under N_2 atmosphere. The volume loss in the overall process is found to be around 87 %. All the characteristics bands like Si-C, O-Si-O and Si-O-Si, found from FTIR spectra confirms the formation of SiOC ceramic. XRD pattern indicates amorphous glassy network is present with no other additional crystalline phase. Raman spectra confirm, random distribution of the carbon phase and two dimensional graphite sheets are present. XPS spectroscopy reveals the existence of C, O and Si as only constituents of the ceramic sample. Therefore, from the overall characterstic phase investigation it can be proposed that, the SiOC ceramic consisted of four phases: 1) The amorphous SiOC phase, 2) a silica matrix, 3) nanodomains of free carbon and 4) Silicon carbide. The presence of silicon carbide phase is indirectly inferred from XPS spectra as the XRD data could not reveal the same possibly due to the fact that silicon carbide crystallite size is small enough to be masked by the same intensity of amorphous phase of the SiOC. The major phases displayed an incipient crystalline growth, possibly due to the formation of nano domains of free carbon which decreases the formation of SiOC network and inhibits the matrix phase partition into SiO_4 and SiC_4 and their subsequently crystalline growth. FESEM microstructure and loading-unloading curve confirms the absence of any crack which promotes the development of completely dense matrix and good mechanical properties of pressureless SiOC ceramic synthesized at high temperature. From the above experimental analysis it can be concluded that synthesized SiOC ceramic can be used as a promising candidate for protective coating for thermal insulation in wide variety of technologically important component used in high temperature application.

4. Acknowledgements: The authors are thankful to Department of Science & Technology; New Delhi & Council of Scientific & Industrial Research for the financial support. The assistance and encouragement of Dr. K. Muraleedharan, Director, CSIR-CGCRI and the staff of Non-Oxide Ceramic & Composite Division, CSIR-CGCRI is gratefully acknowledged.

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