

Study of the pyrolysis process of an hybrid $\text{CH}_3\text{SiO}_{1.5}$ gel into a SiCO glass

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Received 3 April 2007; received in revised form 21 June 2007; accepted 2 July 2007

Available online 7 July 2007

Abstract

Silicon oxycarbide samples were prepared by polymer pyrolysis using a methyltriethoxysilane-derived precursor. Transparent crack-free gel samples were obtained from the alkoxide by the sol–gel process. The dried gel samples were pyrolysed at different temperatures in the range between 400 and 1500 °C in Ar atmosphere. The chemical and microstructural evolution during pyrolysis were followed by FT-IR absorption, Raman scattering and photoluminescence (PL).

The FT-IR spectra show the change in Si–O–Si asymmetric stretching, C–H_x, Si–CH₃ stretching vibrational bands. The peak position and shape of these bands were found stable up to 600 °C. Above this temperature, a remarkable change in shape and peak position of Si–O–Si related vibration, reduction in C–H_x and Si–CH₃ stretching absorption bands have been observed. Degradation of Si–CH₃ and the simultaneous formation of Si–CH₂–Si via Si–CH₂–CH₂–Si is explicitly observed, experimentally. Annealing the sample at 800 °C starts to show the clear presence of D and G bands, related to the free carbon precipitation and its segregation with the temperature. The broad PL spectra centered at around 670 nm for the samples pyrolysed at 1500 °C shows an important information regarding the presence of crystalline SiC.

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Keywords: Polymer pyrolysis; Silicon oxycarbide; FT-IR and Raman spectroscopy; Photoluminescence

1. Introduction

Silicon oxycarbide glasses, SiCO, are amorphous solids whose structure is derived from that of silica glass in which part of divalent oxygen atoms are replaced by tetra-coordinated carbon atoms. Accordingly, the resulting formula is: $\text{SiC}_x\text{O}_{2-2x}$. They have been extensively studied owing to their low density, high mechanical strength, low dielectric constant and high thermal shock resistance compared with those of the parent SiO_2 glass [1–4]. These distinct characteristics can be utilized for following applications: catalytic purposes [5], solid electrodes for fuel cells (thermal stability in the range between 600 and 1000 °C), for the storage

of hydrogen (SiCO annealed at moderate temperature) because of its property to contain remarkable quantity of surface carbon [6]. The pyrolysis residue of polysiloxane comes out with the formation SiCO ceramics can be used to synthesize silicon carbide on heating it at higher temperature (≥ 1400 °C) [7].

These SiCO glasses can be synthesized via sol–gel process using alkyl-substituted alkoxy-silanes $\text{R}'_x\text{Si}(\text{OR})_{4-x}$ with different R' groups. The gel-derived precursors are then pyrolysed at high temperature under inert gas atmosphere to get the desired SiCO glass. The pyrolysis product can be expressed as

$$\text{SiC}_x\text{O}_{2-2x} + y\text{C}_{\text{free}} \quad (1)$$

where $\text{SiC}_x\text{O}_{2-2x}$ describes the composition of the amorphous oxycarbide network and $y\text{C}_{\text{free}}$, the amount of excess carbon, typically present as a secondary free carbon phase. The amount of C bonded to Si, x value in Eq. (1), and of C_{free} , y value in Eq. (1), are related to the nature of the alkoxide precursor [8].

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The structural evolution occurring during the pyrolysis process of gel-derived precursors was investigated by different groups [9–11] by using FT-IR absorption spectroscopy, X-ray photoelectron spectroscopy (XPS), thermo-gravimetric analysis (TGA) coupled with mass spectrometer and ^{29}Si and ^{13}C magic angle spinning nuclear magnetic resonance (MAS-NMR) and Raman Spectroscopy. Recently, Chomel et al. [12] reported the structural characterization of a MTES-derived SiCO sample using vibrational spectroscopy methods describing, in details, regarding the evolution of SiCO material by FT-IR technique but author bypassed the Raman findings just quoting the crystallization and organization of free carbon with a rise in temperature without any further information about these free carbons quantitatively for this system. In spite of extensive research activity in the past, a detailed analysis on SiCO material using the observations from various techniques and the co-relation of these results are carried out systematically to understand its characteristic behavior in the broad range of temperature. In addition, it is found many confusions over the assignment of different vibrational bands; Si–O–Si asymmetric stretching and bending, Si–CH_x, and Si–C modes. In this work, it has been given attention to clarify it. Very little is known on Raman aspects for this kind of sample with thermal treatments. The change in compositional and structural picture due to pyrolysis process modifies the optical property (photoluminescence measurements) which will be discussed here first time in our knowledge opens new aspects in the study of SiCO system.

In the present work, a systematic characterization of SiCO sample prepared by sol–gel technique and thereafter thermally treated at different temperatures using a multi-technique approach based on TGA, FT-IR absorption, Raman scattering and photoluminescence analysis is reported. The chemical composition, the nature of different chemical bonds and their structural evolution, the reduction of free radicals, the occurrence of C-domain starting from 800 °C, and the formation of β -SiC crystalline phase at 1500 °C have been investigated.

2. Experimental

2.1. Sample preparation

MTES (ABCR, 98%) was hydrolyzed with acidic water (pH 1 by HCl) using an hydrolysis ratios $\text{H}_2\text{O}/\text{MTES} = 2.5$. Water addition was performed under vigorous stirring at 40 °C. After 20 min the solution was allowed to cool down at room temperature and then 1 ml of ammonia solution (30 wt%) per 10 ml of MTES was added to promote condensation. The solution was then transferred into test tube for gelation. Monolithic, cylindrical gel samples obtained in this way, were slowly dried in the oven up to a maximum temperature of 120 °C.

From these samples, thin gel disks, 0.3–0.6 mm thick, were subsequently obtained by sectioning the original monolithic gels. Pyrolysis was performed in an alumina tubular furnace under flowing Ar (100 ml/min) at temperatures (T_p) in the range 300–1500 °C with heating rate of 5 °C/min and dwell times at the maximum temperature of 1 h.

2.2. Characterization techniques

FT-IR measurements were carried out in transmission mode at room temperature in the spectral range between 4000 and 400 cm^{-1} using a JASCO spectrometer (mod. FT-IR–660 plus) equipped with a ceramic source, a KBr beam splitter and a triglycine-sulphate (TGS) detector. The measurements were performed under vacuum conditions. The KBr pellet method was employed for performing the IR measurement for all the samples with a resolution of 4 cm^{-1} . The number of scans for each spectrum being automatically chosen and averaged in order to ensure an optimal signal-to-noise ratio.

Micro-probe Raman spectra were excited at room temperature by the 488.0 nm line of an Ar⁺ ion laser in backscattering geometry through 100 \times objective of an Olympus microscope (model BHS-M-L2). The inelastically scattered radiation from the sample was filtered by a double-monochromator (Jobin-Yvon, model Ramanor HG2-S), equipped with holographic gratings (2000 grooves mm^{-1}). The output signal was detected by a thermo-electrically cooled (–35 °C) photo-multiplier tube (PMT) detector (RCA, model: C31034-02) operated in photon-counting mode. Raman spectra were recorded in the spectral range extending from 900 to 1800 cm^{-1} , where the scattering from carbon inclusions, if present, as a segregated phase within the amorphous silicon oxide matrix, was expected to occur.

PL measurements were carried out by using an Ar⁺ laser (488 nm emission line) with about 80 mW over a circular area of about 1 mm in diameter and a visible spectrometer with a CCD detector. PL spectra have been corrected for the spectral response of the optical set-up. For every measurements, the number of scanning is fixed for 1000, therefore, to show in real time acquisition the counts are divided by 1000 from each spectrum.

3. Results and discussions

3.1. TGA measurements

The TGA curve (not shown here) recorded on the precursor gel was consistent with the literature data [11,13,14]. The main decomposition step was centered between 650 and 900 °C and the total weight loss at 1000 °C was ca. 17%. Between 1000 and 1400 °C a small weight loss of less than 2% was observed and it can be assigned to the evolution of residual hydrogen present in the SiCO structures as CH or CH₂ groups. Indeed, the presence of H in the SiCO materials up to very high temperatures, 1400 °C, has been proposed after a systematic structural characterization of the high temperature behavior of nearly stoichiometric silicon oxycarbide glasses [15].

3.2. FT-IR absorption spectroscopy

The absorbance spectra of the as-prepared (AsPrep) gel and some representative pyrolyzed samples are shown in Fig. 1. The absorbance spectrum of the gel sample shows different features: peaks at around 450, 1035 and 1135 cm^{-1} related to the Si–O–Si related vibrations [16], peaks at 1275 and 1410 cm^{-1}

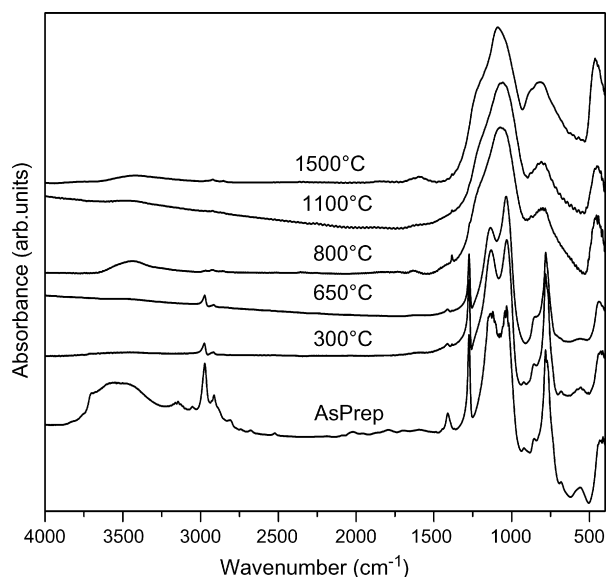


Fig. 1. Typical FT-IR spectra recorded in the spectral range of 4000–400 cm^{-1} from samples pyrolysed at different temperatures.

attributed to the methyl group vibrations [17,18], peaks around 2900 cm^{-1} assigned to the C-H_x stretching vibrations [19,20] and a broad band in the range between 3200 and 3800 cm^{-1} related to the O-H vibration of silanol groups and of adsorbed water [20,21]. In addition, one peak centered at 780 cm^{-1} with shoulder at 830 cm^{-1} is also present in the range of 650 – 850 cm^{-1} . This is a complex region [21] where different vibrational bands; Si-O-Si bending [16], Si-CH_3 rocking [22], combination of Si-C stretching and SiC-CH_3 rocking modes [23] fall. However, as it will become clear from the evolution of FT-IR spectra with the pyrolysis temperature reported later on, we can assign this peak to the rocking vibration of the Si-CH_3 group.

The evolution of the FT-IR spectra with the pyrolysis temperature will be discussed, considering the modifications occurring to the individual peaks (or group of peaks).

3.2.1. FT-IR spectra in the range between 1500 and 700 cm^{-1}

The evolution with the pyrolysis temperature of three peaks assigned to asymmetric (1410 cm^{-1}) and symmetric (1275 cm^{-1}) deformation of CH_3 group in Si-CH_3 configuration and the band in the complex region around 780 cm^{-1} is parallel (Fig. 2). Hence, we can associate this peak at 780 cm^{-1} to Si-CH_3 rocking vibration. At $800\text{ }^\circ\text{C}$, this band (780 cm^{-1}) disappears. The sharp peak at 780 cm^{-1} has left behind a broad band centered at around 800 cm^{-1} which can be assigned to Si-C stretching vibration. In the temperature range 700 – $900\text{ }^\circ\text{C}$, simultaneously to the disappearance of the band at 1275 cm^{-1} two new peaks appear: one at around 1385 cm^{-1} which is attributed to the CH_2 symmetric deformation vibration in $\text{Si-CH}_2\text{-CH}_2\text{-Si}$ structural unit [12] and the second one at around 1365 cm^{-1} which is assigned to the formation of $\text{Si-CH}_2\text{-Si}$ bridges [24].

It is well known that the organic-to-inorganic transformation of siloxane networks proceed via a radical reaction involving the cleavage of Si-C and C-H bonds with the consumption of

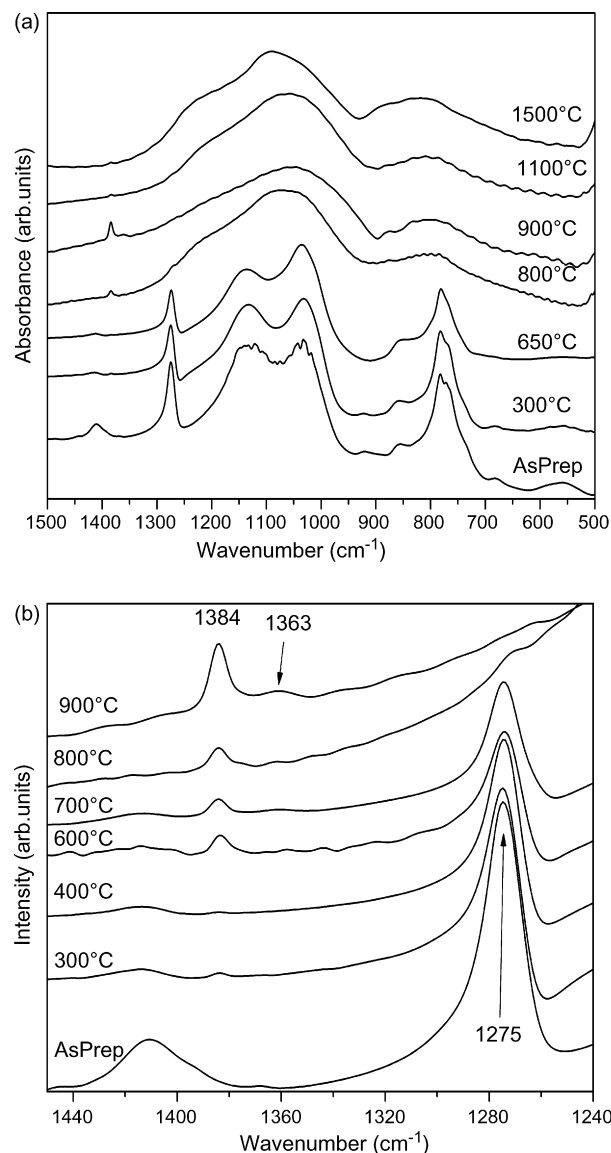
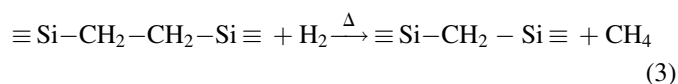
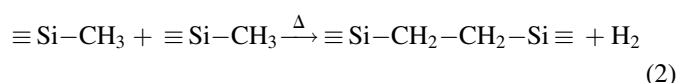


Fig. 2. (a) FT-IR spectra in the range between 1500 and 500 cm^{-1} showing structural evolution vs. pyrolysis temperature, (b) FT-IR spectra showing the vibrational band attributed to Si-CH_3 , $\text{Si-CH}_2\text{-Si}$ and $\text{Si-CH}_2\text{-CH}_2\text{-Si}$.

Si-CH_3 groups, the formation of gaseous species (CH_4 and H_2) and the final insertion of carbon atoms into the silica-based network. The observation in the FT-IR spectra regarding presence of new peaks at 1365 and 1385 cm^{-1} helps in understanding how carbon atoms can be inserted in the network with the formation of SiCO composite material. The following reactions, which have been extensively proposed in the literature, seem to apply to the present case [10,25]:



In order to quantify the contribution of CH_3 and CH_2 related bands and to follow their evolution with the temperature, we

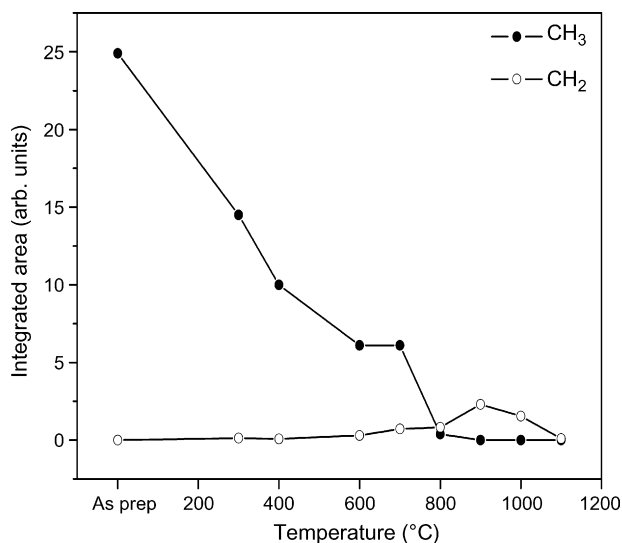


Fig. 3. Integrated area of CH₃ and CH₂ vibrational bands.

have fitted the absorption spectrum in the range between 1200 and 1400 cm^{-1} with mixed distribution functions {Gaussian/(Lorentzian + Gaussian)} using the curve-fitting analysis software program provide with the FT-IR instrument. The evolution of CH₃ and CH₂ vibrational band area with respect to the pyrolysis temperature is shown in Fig. 3. Here, it is important to note that the pyrolysis of sample causes: (a) the formation of –CH₂ group at the expense of –CH₃ group and (b) the dissociation of –CH₂ group. If the rate of former process is higher than the intensity of –CH₃ bands will decrease and the intensity of –CH₂ group will increase. On the other hand, if, the later process is faster, then, both –CH₃ and –CH₂ groups will decrease with temperature. In our case, Fig. 3 shows that the integrated intensity of –CH₃ related band is decreasing continuously and the integrated intensity of –CH₂ is slightly increasing up to $T=800^\circ\text{C}$. Above 900°C , the integrated intensity of –CH₂ group decreases, indicating that –CH₂ groups are going off from the glass. Both bands are no more observable after 1100°C .

3.2.2. FT-IR peaks in the range of 1135–1035 cm^{-1} (Si–O–Si vibration)

Typically in fused silica glass the Si–O–Si vibration gives rise to a single peak centered at 1078 cm^{-1} [17]. On the other hand, the Si–O–Si asymmetric stretching vibration bands centered at around 1035 and 1135 cm^{-1} found in our AsPrep sample (see Fig. 2) are typical peaks of polysilsesquioxanes. In particular, the absorption at 1135 cm^{-1} is assigned to Si–O–Si vibration having a bond angle higher than 144° such as those present in cage structures while the peak at 1035 cm^{-1} is due to Si–O–Si linkages in a network structure having a smaller bond angle [21,22,26].

By increasing the pyrolysis temperature, the intensity ratio of 1035 and 1135 cm^{-1} bands increases, as shown in Fig. 4a, suggesting that the siloxane structure evolves towards a more cross-linked one. This evolution seems complete at 800°C when the cage-related band at 1135 cm^{-1} is no more visible and a single band is left at around 1060 cm^{-1} (see Fig. 4b)

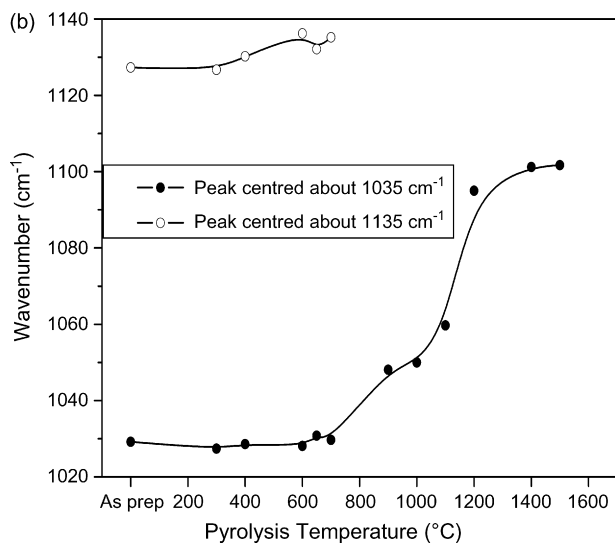
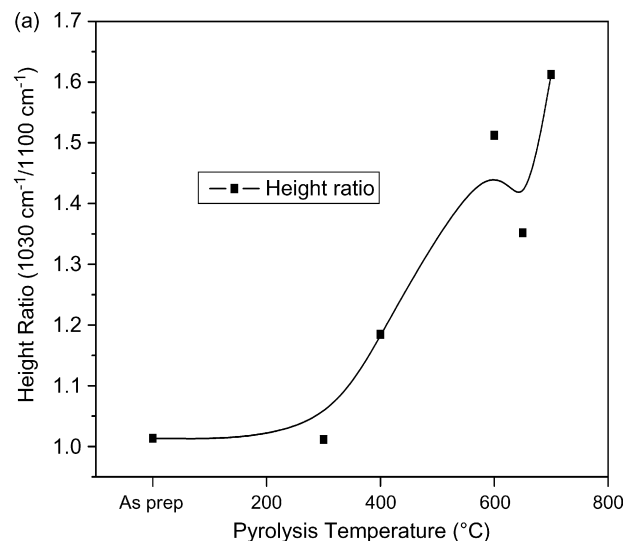


Fig. 4. Evolution with the pyrolysis temperature of the (a) intensities ratio of the $1030\text{ cm}^{-1}/1100\text{ cm}^{-1}$ peaks and (b) peak positions of Si–O–Si asymmetric stretching vibrational modes.

confirming the complete consumption of the initial polymeric precursor and the formation of inorganic SiCO network. By further increasing the pyrolysis temperature up to 1200°C , the absorption of the Si–O–Si band, which at 1000°C is found at 1060 cm^{-1} , shifts towards its final position around 1100 cm^{-1} . This value is higher than the usual one found for SiO₂ glass (around 1060 cm^{-1}) and can be assigned to the presence of Si atoms sharing bonds with C and O atoms in the silicon oxycarbide network.

3.2.3. FT-IR peaks related to C–H_x (3100 – 2750 cm^{-1}) and O–H (3600 – 3200 cm^{-1}) vibrations

The absorption peaks in the range between 3100 and 2750 cm^{-1} for AsPrep and pyrolysed polysilsesquioxane samples are attributed to the C–H_x stretching vibrations. For AsPrep sample, three major peaks centered at 2973 , 2910 with a shoulder at 2875 cm^{-1} are observed. They are attributed to the different C–H_x vibrations with sp^3 hybridization; CH₃

asymmetric, CH₂ symmetric, and CH₃ symmetric stretching vibration, respectively [27]. The occurrence of CH₂ symmetric stretching vibration can be assigned to the presence of non-hydrolysed ethoxy moieties (–OCH₂CH₃). On thermal treatment at 300 °C, it was found that the intensity of these bands at around 2975 cm⁻¹ reduces up to 25% of the intensity of these bands for AsPrep sample. This sharp reduction could be due to the evaporation of residual ethoxy groups as it is well known that the ethoxy groups of silica gels are removed in the early stages of the heat treatment due to the completion of condensation reactions. On further pyrolysis, these bands related to the C–H_x vibrations reduce sharply but they are still visible up to very high temperature (1500 °C). Interestingly, the broad peak in the range 3600–3200 cm⁻¹ assigned to O–H bonds present either as silanol groups or as adsorbed water, is rarely visible at 300 °C. This latter observation confirms that at 300 °C the hybrid gel is a well-condensed network at which terminal OH or OEt moieties are no more present. However, on further pyrolysis at 700 °C, the uptake of water in the sample was found, resulting in an enhancement in the intensity of broad band in the range of 3600–3200 cm⁻¹. This process is also observed by many groups in the past on SiOC samples [20,28].

3.3. Raman scattering spectroscopy

Raman spectroscopy is the most suitable non-destructive tool to characterize the various form of crystalline and disordered graphitic carbon. Raman spectra for the hybrid gel at various pyrolysis temperatures are reported in Fig. 5. Up to 700 °C Raman spectra do not show any structural information about the material apart from a strong photoluminescence background. The luminescence, generally observed in these materials, comes from the presence of free radical species generated during the pyrolytic conversion from the starting hybrid gel into the SiCO glass [8,29]. This luminescence background is maximum in the temperature

range 700–1000 °C and then starts decreasing. It becomes relatively weak for the sample pyrolysed at 1500 °C.

Starting from 800 °C, two main distinct broad bands are observed at around 1605 and 1355 cm⁻¹ which are well-known features of disordered graphite form of carbon (D and G bands, respectively).

The G band is due to the E_{2g} symmetry in-plane bond stretching of sp² carbon while the D band is related to the breathing mode of K phonon of A_{1g} symmetry [30,31]. The D band is inactive in single crystal graphite by selection rule for Raman spectroscopy and only becomes active in the presence of disorder arising from the crystal boundaries of polycrystalline graphite (pc-graphite). Indeed, the crystal momentum conservation is lost in this case, giving the contribution to Raman scattering around the brillouin zone. In order to determine the spectral parameters such as peak position, bandwidth and the integrated intensity of different bands, a spectral deconvolution was performed by a fitting procedure using Lorentzian distribution functions. The fitted spectra, shown in the inset of Fig. 5, illustrate three contribution centered at around 1610, 1500 and 1350 cm⁻¹ for the samples annealed at temperature up to 1200 °C. The bands at around 1610 and 1350 cm⁻¹ are related to the D and G bands of pc-graphite and the band centered at around 1500 cm⁻¹ reflects the presence of interstitial disorder site within the sample [32]. At 1400 and 1500 °C, the spectra can be fitted by using two lorentzian distribution functions at around 1600 and at around 1360 cm⁻¹ in the range between 1620 and 1330 cm⁻¹ without any other band around 1540 cm⁻¹. An additional band is observed at around 1250 cm⁻¹ for samples pyrolysed at 1400 and 1500 °C. Fukushima et al. [29] also observed the similar band and suggested that this band is due to the amorphous SiO₂, attached to the non-bridging or partially ionized oxygen atoms. The peak position, bandwidth and integrated area of D and G bands, and their ratio (*I_D/I_G*) are reported in Table 1. The increase

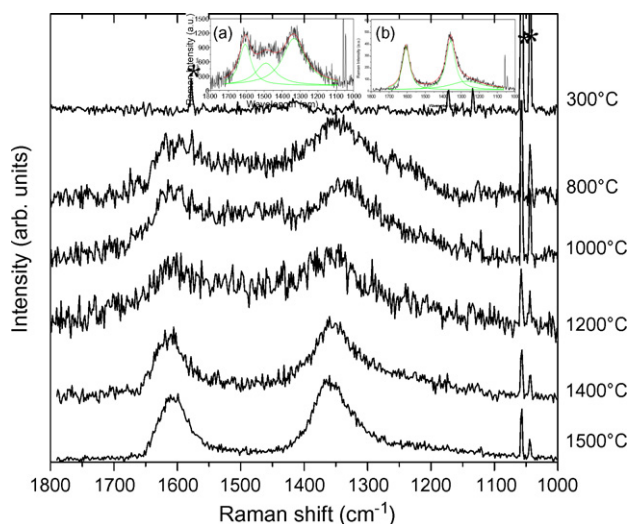


Fig. 5. Raman spectra for SiCO sample vs. pyrolysis temperature in the range between 1800 and 1000 cm⁻¹. The curve-fitting spectra for the sample treated at: (a) 1000 °C and (b) 1500 °C, are shown in the inset. Sharp peaks marked by “*” are contribution from plasma lines of 488 nm argon laser.

Table 1

The band characteristics (peak position, width and (*I_D/I_G*) ratio) of Raman bands

Temperature (°C)	Band (cm ⁻¹)	Width (cm ⁻¹)	Ratio (<i>I_D/I_G</i>)	Size (Å, C _χ = 35.1)
800	1342	170	2.89	12.1
	1509	106.3		
	1603	85.8		
1000	1333	153.6	2.21	16
	1490	138.8		
	1607	78.9		
1200	1359	145.9	2.20	16
	1514	93.5		
	1608	87.0		
1400	1247	115.2	1.69	20.8
	1352	75.4		
	1610	55.9		
1500	1269	219	1.42	24.7
	1359	60.7		
	1606	48.0		

The C-domain size is calculated using Tunistra and Koenig relation [35] modified by Matthews et al. [36].

in the intensity of G band and decrease of its bandwidth with the pyrolysis temperature reflects the increase of structural ordering in the carbonaceous material.

The peak position of the G band for our samples was always found higher than the typical value found in polycrystalline graphite, 1580 cm^{-1} , which suggests mixed peak of G and D' bands [33]. The peak at around 1610 cm^{-1} is defined as D' band and it is attributed to the tiny graphene layers with the edge carbon atoms, accompanying oxygen and/or radical species because the edge parts may cause the partially localized π -electrons to shift towards higher frequency. The decrease in bandwidth was observed for both D and G bands with thermal treatment. The narrowing in bandwidth is related to the removal of bond angle disorder and an increase in crystallinity within the sample [34]. From Table 1, it can be noticed that the line width of G band for all the samples is always narrower than the other bands which further confirms the presence of crystalline nano-domains of carbon.

As it is well known that highly oriented crystalline graphite gives only G band centered at about 1580 cm^{-1} and the emergence of D band in addition signifies the increase in disorder sites and hence an increase in amorphous structure within the sample. Keeping this in mind, the analysis of D or G band intensity shows that the amorphous contribution within the sample diminishes with the pyrolysis temperature.

The in-plane crystalline size of graphite domains, L_a , was calculated by using the relation:

$$L_a = C \left(\frac{I_D}{I_G} \right)^{-1} \quad (4)$$

where 'C' is the scaling coefficient derived by Tunistra et al. [35]. As discussed by Matthews et al. [36], the value of scaling coefficient 'C' varies with the laser wavelength, hence the crystallite size was calculated by using the coefficient value for 488.0 nm laser wavelength. The graphite domain size is also reported in Table 1. It shows that the size of graphite domains

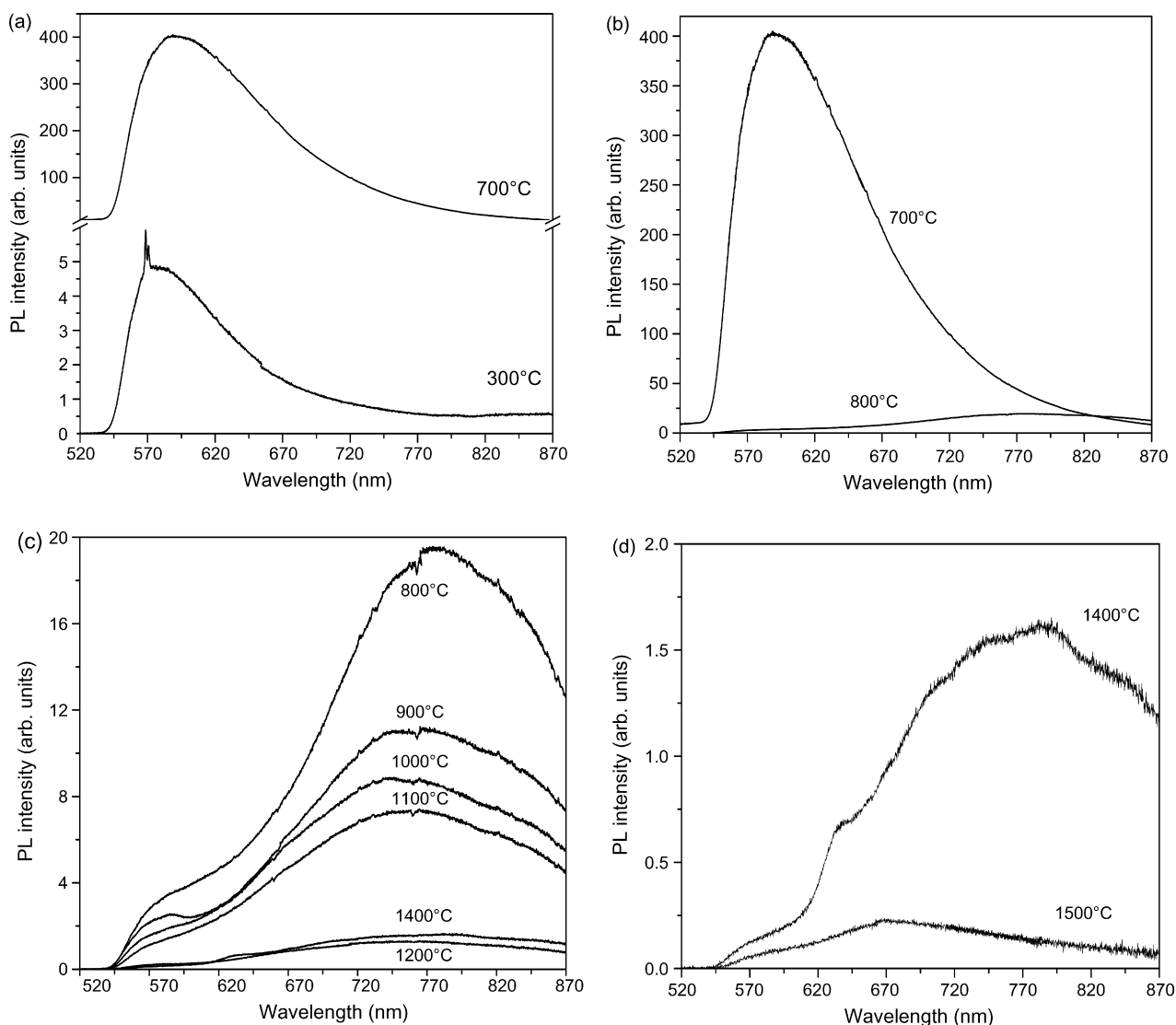


Fig. 6. Photoluminescence spectra for: (a) temperature 300 and 700 °C, (b) temperature 700 and 800 °C, (c) temperature in the range between 800 and 1400 °C, and (d) temperature 1400 and 1500 °C.

increases with the increase of temperature by agglomeration of precipitated carbon clusters dispersed in the matrix.

In addition, even the Si–C bonds were observed in similar SiCO glasses pyrolyzed at high temperatures by many researchers in the past [37] using NMR and X-ray diffraction techniques, the lack of Si–C bands in Raman spectra is due to both, the relatively high Raman efficiency of C–C bonds, about 10 times that of SiC [38], and to the formation of relatively small grains of SiC [39].

3.4. Photoluminescence measurement

Photoluminescence spectra show strong dependence on peak shape and position versus annealing temperature. Particularly, samples annealed at temperature up to 700 °C (Fig. 6a) show a maximum of the luminescent peak towards 600 nm, compatible with the glass defects band within the sample [40,41]. At 800 °C, the luminescence peak shifts strongly with its maxima reaching in the range of 750–800 nm, shown in Fig. 6b. Above 800 and up to 1400 °C, the PL peaks remains at the same position, the bandwidth increases and their intensity decreases with the pyrolysis temperature (Fig. 6c). This band centered at 750–800 nm can be assigned to carbon cluster present in the samples, as revealed by the Raman study. Indeed, the only other crystalline phase which could be present in these oxycarbide glasses, i.e. β -SiC, starts to appear for pyrolysis temperature above 1400 °C [42,43].

Accordingly, the peak shape changes drastically and peak position shifts towards the blue at 1500 °C due to the carbothermal reduction process which becomes more evidence above 1400 °C [12] (Fig. 6d), placing its maxima at 670 nm (spectra of the sample annealed at 1400 °C has a quite evident shoulder placed around 640 nm and probably from this it starts the modification in the glass structure responsible for the blue shift at higher temperatures). At this temperature, SiC starts to crystallize [39] and therefore we may assign this blue PL peak to the nanocrystalline β -SiC.

4. Conclusions

The main findings of the various spectroscopic techniques as a function of the annealing temperature for SiCO composite material can be summarized as following:

- FT-IR spectroscopy for AsPrep sample shows the clear presence of different vibrational bands; Si–CH₃ rocking, different Si–O–Si asymmetric stretching, CH₃ deformation of Si–CH₃, different C–H_x stretching vibration in addition to SiO–H and HO–H stretching vibrational bands [18,39]. The annealing of the gel causes the following changes;
 - the decomposition of C–H_x, Si–CH₃ and Si–CH₂–Si bonds because of the dehydrogenation and demethanation resulting the conversion of gel into inorganic glass [12];
 - the proposed transformation of Si–CH₂–Si from Si–CH₃ molecular bonds passing through the stage of Si–CH₂–CH₂–Si [10] is clearly shown through our deep FT-IR spectral analysis;

- the increase in the peak height ratio of Si–O–Si asymmetric stretching ratio (I_{1030}/I_{1100}) represents the cross-linked structure of SiCO system and the convergence of two Si–O–Si stretching vibration bands into a single band centered at around 1060 cm⁻¹, confirming the complete consumption of the initial polymeric precursor and the formation of inorganic SiCO network;
- the decrease in SiO–H and HO–H vibration bands up to 600 °C. Surprisingly, on further increase of temperature at 700 °C shows an increase in HO–H vibrational band because of adsorption of water [28];
- the sharp decrease in the intensity of C–H_x stretching vibration modes (around 75% loss in the C–H_x band) just at 300 °C which we suggest that it could be due to the evaporation of residual ethoxy groups. It decreases on further increase in temperature but, noticeably, it always present even at 1500 °C.
- The Raman findings on thermal treatment illustrates:
 - no Raman band is observed up to 700 °C except strong luminescence background which could be because of the presence of free radical within the sample;
 - the increase in the intensity and decrease in the width of G band due to the structural ordering in the carbonaceous material;
 - the evolution of sp²-hybridized phase of C-domain calculated by using Tunistra et al. [35] modified by Matthew et al. [36] reveals the increase in domain size due to segregation of nearby free carbon domains.
- The photoluminescence measurements demonstrate:
 - intense luminescence intensity peak centered at 590 nm was observed for sample treated at 700 °C, shows the clear co-relation with the Raman measurements [8];
 - with the decrease in free radicals and modification towards cross-linked polymer micro-structure within the sample, there is strong decrease in the PL intensity at 800 °C. The PL peak centered at 775 nm is assigned to the carbon clusters present within the sample;
 - the PL intensity decreases with the pyrolysis temperature up to 1400 °C keeping the PL peak centered at around 775 nm. The PL spectral profile changes drastically on thermal treatment at 1500 °C which could be related to formation of crystalline SiC.

The FT-IR, Raman and PL findings show the similar micro-structural evolution with the pyrolysis process. In conclusion, we propose that SiOC material shows three different evolution stage: (1) from AsPrep to 700 °C, where major cross-linking processes and reduction of free radical occur, (2) 800–1400 °C, where formation and aggregation of carbon clusters, and (3) 1500 °C, at which SiC crystalline phase occurs due to the carbothermal reduction process.

Acknowledgements

The authors are grateful to Dr. ssa Raquel De La Pena for helpful suggestions and stimulating discussions. The financial support of project COFIN 2006 is also acknowledged.

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