Gel to Glass Transformation of Methyltriethoxysilane: A Silicon Oxycarbide Glass Precursor Investigated Using Vibrational Spectroscopy

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Gel to glass transformation of methyltriethoxysilane was investigated using infrared and Raman spectroscopies. The vibrational frequencies of the Si−O network are found to be a sensitive probe of the gel to glass transformation, which is measured to be at ca. 950 °C for this system, under the experimental conditions used for the synthesis. Vibrational data are also compatible with an earlier suggestion of the presence of polyhedral silsesquioxanes type structures embedded in a 3-D network. Further evidence is presented for the formation of Si−CH_2−Si and Si−C_2H_4−Si units during the pyrolysis process.

Introduction

Silicon oxycarbide glasses are a new class of amorphous solid materials derived from the structure of silica glass in which part of the divalent oxygen atoms have been replaced with tetravalent carbon atoms.[1] These glasses can be produced by the pyrolysis of organosiloxane polymers in an inert atmosphere.[1,2] The precursors can be synthesized via the sol−gel route starting from alkoxysilanes, R'_x−$Si(OR)_{4-x}$, where R′ is usually a methyl group.[2−6]However, other organic groups containing more C atoms such as ethyl, propyl, phenyl, vinyl, or allyl[7−9] may also be used. In the case of silicon alkoxides with longer alkane chains, carbon is lost during the pyrolysis by β-elimination,[10] and thus the final C content is similar to that obtained with the methoxy analogues. In contrast, with phenyl or unsaturated side chains, the residual C content of the final glass is much higher and leads to the formation of a significant amount of free carbon. Methyl-substituted silica gels thus appear as the most suitable precursors for silicon oxycarbide glasses.

There are several reports in the literature of the use of monomethyltriethoxysilane, $CH_3Si(OC_2H_5)_3$ (MTES), the material under investigation in the present study. It has been used as one of the starting alkoxides in the sol−gel technology for making inorganic−organic composites such as ORMOSIL (*or*ganically *mo*dified *sil*icates),[11,12] and elastic CH_3-containing SiO_2 coating films.[13] Recently, monoliths of sol−gel-derived MTES xerogels have been used for embedding fluorescent dye molecules as materials for applications in the field of optical sensing.[14]

Carbon/SiO_2 glass composites have also been prepared by heating MTES-derived gels in an inert atmosphere.[15−17] These composites contained fine carbon particles up to 25−30 wt % and the included carbon has been characterized by X-ray diffraction,[15] Raman spectroscopy,[15] and electron microscopy.[15,16]

MTES-derived gel fibers have been converted to nitrogen-containing SiO_2 glass fibers by heating in an NH_3 atmosphere.[18] Their structures have been studied by infrared and X-ray fluorescence spectroscopies. The same authors have studied the thermal evolution of the gel, by employing IR spectroscopy and thermal analysis to examine their structures when heated in air, N_2, and/or NH_3.[19] X-ray and Neutron diffraction analysis of SiO_2 gels prepared from MTES have also been reported.[20,21] More recently, Trimmel et al.[22] have

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Table 1. IR and Raman Wavenumbers/cm^{-1} and Assignments of MTES Samples Fired at Low Temperatures[a]

120 °C		400 °C		600 °C		800 °C		1000 °C	
Raman	IR	Raman	IR	Raman	IR	Raman	IR	IR	assignmen t
	414(m)		**431(m)**		**444(m)**		**445(m)**	**445(m)**	**δ(SiOSi)**
468(w)		474(w)		475(w)					ring breathing vibration
	553(w)		552(w)		550(w)				δ^{sym}(OSiO)
682(w)	682(w)	685(w)	681(w)	685(vw)	690(w)				ν(Si−C)
744(w,b)	769(s)	745(vw,b)	769(s)	760(w,b)	769(s)				$\rho(CH_3)$
800(w)	**780(s)**	**798(vw)**	**780(s)**	**792(vw)**	**781(s)**		**793(m)**	**795(m)**	**ν^{sym}(SiOSi)**
855(vw)	**854(w)**		**859(m)**		**857(m)**				**δ^{asym}(OSi H)**
							875(w)		δ(SiH) from $HSi(CH_3)$ O_2
							883(w)		δ(SiH) from $HSiO_3$
	1033(vs)		**1027(vs)**		**1034(s)**		**1044(s)**	**1055(s)**	**ν^{asym}(SiO Si)**
1095(w)	1125(vs)	1092(w)	1132(vs)	1095(w)	1133(s)				ν^{asym}(SiO C)
1273(w)	1273(s)		1274(s)		1273(m)		1275(vw)		$\delta^{sym}(CH_3)$
							1350(w)		**δ(CH_2 from $SiCH_2Si$**
							1385(vw)	**1385(vw)**	**δ(CH_2 from $SiCH_2CH_2Si$**
1413(w)	1411(w)	1414(w)	1414(w)	1413(w)					$\delta^{asym}(CH_3)$
						1632(w)	1631(w)		$\delta(H_2O)$
							2199(vw)		**ν(SiH) in $HSi(CH_3)O_2$**
							2250(w)		**ν(SiH) in $HSiO_3$**
2808 (w)		2811(w))		2811(w)					overtone
2913(vs)	2913(w)	2913(s)	2916(w)	2912(s)	2912(vw)		2919(vw)		$\nu^{sym}(CH_3)$
2974(s)	2974(w)	2973(m)	2975(w)	2974(s)	2973(vw)		2971(vw)		$\nu^{asym}(CH_3)$
							2850(vw)	2850(vw)	ν(C−H) from CH_2
							2919(vw)	2920(vw)	ν(C−H) from CH_2
	3450(w)						3450 (m)	3439(w)	ν(O−H)

[a] The peak intensities are given in parentheses as (s) for strong, (m) for medium, (w) for weak, (vw) for very weak, and (b) for broad. The vibrations referred to in the text are indicated in bold.

used thermogravimetric analysis coupled with mass spectrometry (TG-MS) in an inert atmosphere and ^{29}Si and ^{13}C magic angle spinning nuclear magnetic resonance (MAS-NMR) to study the gel to glass transformation of MTES when used as a starting material.

The aim of the present study is to explore infrared and Raman spectroscopies to extend the understanding of the chemistry involved in the thermal conversion, of a siloxane gel, containing reactive Si−CH_3 groups, into a glass.

Experimental Procedures

Sample Preparation. Methyltriethoxysilane (MTES) was used as-received from Fluka (Riedel-de-Haën, Germany). The ethanol employed was obtained from Rectapur (96 vol %) Merck Eurolab Division Prolabo (Templemars, France) and dried over molecular sieves before use. To a stirred solution of MTES in ethanol (EtOH: MTES = 2) a stoichiometric amount of water at pH = 1 (aqueous HCl; −OEt:H_2O = 1) was added and the mixture refluxed for 2 h. After the mixture cooled to ambient temperature, concentrated NH_4OH was added (0.5 mL per 10 mL of precursor) and the resultant mixture poured into plastic tubes. These tubes were allowed to stand at ambient temperature for 7 days. The resultant gels were dried in an oven by raising the temperature every 2 days by 20 °C up to a maximum temperature of 120 °C.

Thermal treatment of the gel was carried out under flowing helium using a heating rate of 10 °C/min. Approximately 4 g of a sample with a particle size between 100 and 350 μm was employed. The furnace setup used consisted of a vertically mounted Al_2O_3 tube fitted with a programmable temperature controller and a control flowmeter. At the chosen temperature (120, 400, 600, 800, 1000, 1200, 1400, 1500 °C) an isothermal hold of 1 h was employed.

Characterization. Infrared spectra were recorded on powdered samples with the conventional CsI pellet technique,[23] using a Nicolet Impact 410 spectrometer. Dispersive Raman spectra, 4000−250 cm^{-1}, were recorded using a Jobin-Yvon 500M spectrophotometer equipped with a liquid nitrogen cooled CCD detector. The laser excitation used was ca. 35 mW at the sample from a Spectra-Physics Ar$^+$ laser at 514.5 nm. The spectral resolution was better than 4 cm^{-1}. The FT-Raman spectrometer used was a Bruker IFS66 FT-IR incorporating a FRA106 Raman module. This instrument features a Diode laser, delivering approximately 350 mW at 1064 nm at the conventional sampling position, and a liquid nitrogen cooled germanium detector.

All the samples pyrolyzed, at the rate of 10 °C/min, between 120 and 800 °C (referred to as "low-temperature samples"), were found to be better analyzed using FT-Raman spectroscopy with the 1064 nm excitation. Samples produced from 800 to 1500 °C (referred to as "high-temperature samples"), showed strong near-IR emission when excited with the 1064 nm radiation. FT-Raman spectroscopy was thus an unsuitable technique for the analysis of these samples. Dispersive Raman spectroscopy with a visible excitation at 514.5 nm radiation was thus used for the high-temperature samples. in the following text each sample will be referred to by the temperature at which it was fired during its preparation.

Results and Discussion

Infrared and Raman spectroscopic transition wavenumbers and assignments for all of the samples are given in Tables 1 and 2. These assignments are based on literature work by a number of groups.[24−29] Kamiya et al.[19] and Chi[30] have suggested the presence of polyhedral oligosilsesquioxanes

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Table 2. IR and Raman Wavenumbers/cm^{-1} and Assignments of MTES Samples Fired at High Temperatures[a]

1200 °C		1400 °C		1500 °C		
Raman	IR	Raman	IR	Raman	IR	assignments
	459(s)		**467(s)**		**464(s)**	**δ(SiOSi)**
	794(m)		**803(m)**		**813(m)**	**ν^{sym}(SiOSi)**
			889(m)		880(m)	ν(SiC)
	1089(vs)		**1089(vs)**		**1090(vs)**	**ν^{asym}(SiOSi)**
1355(m)		1349(s)		1353(vs)		Carbon D band
1603(m)		1617(s)		1605(s)		Carbon G band
1613(w)		1611(w)		1610(w)		$\delta(H_2O)$
	2920, 2953(vw)		2851, 2922(vw)		2850,2923(vw)	ν(C−H)
	3439(m)		3459(m)		3460(m)	ν(O−H)

[a] The vibrations referred to in the text are indicated in bold.

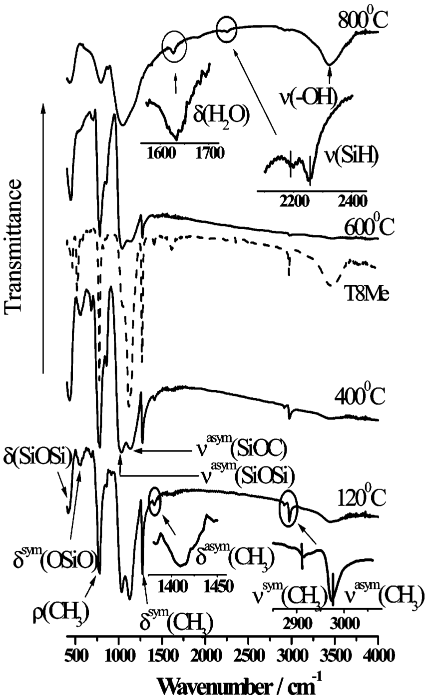

Figure 1. IR spectra of MTES samples fired at temperatures from 120 to 800 °C. The spectrum of pure nonpyrolyzed octamethylsilsesquioxane (T8Me) is shown for comparison (broken line).

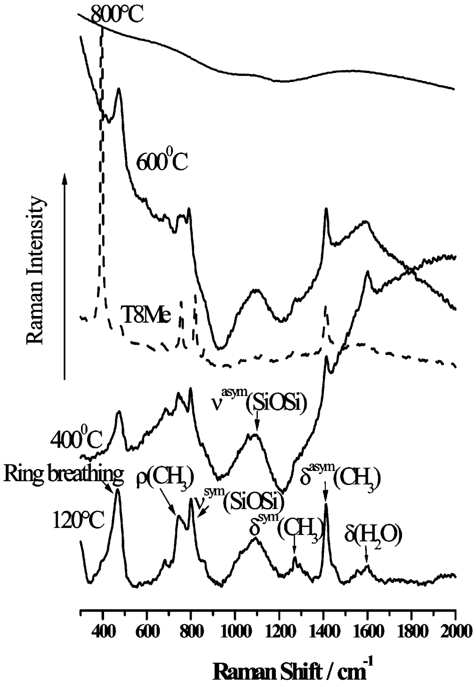

Figure 2. Raman spectra of MTES samples fired at temperatures from 120 to 800 °C. The spectrum of pure nonpyrolyzed octamethylsilsesquioxane (T8Me) is shown for comparison (broken line).

within a "ladder"-type structure for the MTES gel. In a recent paper we reported a detailed study of the IR spectrum of octahydridosilsesquioxane with a view to investigating the latter hypothesis using vibrational spectroscopy.[29] However, a different and probably a better model for such a comparison would be an octaalkylsilsesquioxane. This has the same Si_8O_{12} cube core but with an alkyl group attached to each of the Si atoms.[31] We have therefore obtained a sample of pure octamethylsilsesquioxane, and its IR and Raman spectra are used for the present investigation. Synthesis and characterization of these materials are already reported by Zhang et al.[31] IR spectra of the samples of MTES pyrolyzed between 120 and 800 °C with a comparison to spectra of pure nonpyrolyzed octamethylsilsesquioxane are shown in Figure 1.

The IR spectrum of octamethylsilsesquioxane clearly fits very well within that of the gel spectra, particularly with the lower temperature samples where one would expect methyl groups to still be present. However, the band at ca. 860 cm^{-1} of the gel spectra is not present in the octamethylsilsesquioxane model spectrum.

This band corresponds to a prominent band in the IR spectrum of octahydrosilsesquioxane.[29] The intensity of the latter band in the gel spectrum reaches a maximum at a temperature of ca. 400 °C, Figure 1. This may therefore be interpreted as an indication of the presence of a small concentration of the octahydridosilsesquioxane type of unit within the gel structure. The Si−H stretches of the octahydridosilsesquioxane units may be overlapped by the two bands at 2199 and 2250 cm^{-1} assigned in the literature to two different sites, $H-Si(CH_3)O_2$ and $H-SiO_3$.[32,33] Further evidence for the presence of polyhedral oligosilsesquioxanes structural features is to be found in a comparison of the Raman spectra, as shown in Figure 2. Again the Raman features of octamethylsilsesquioxane are well represented in

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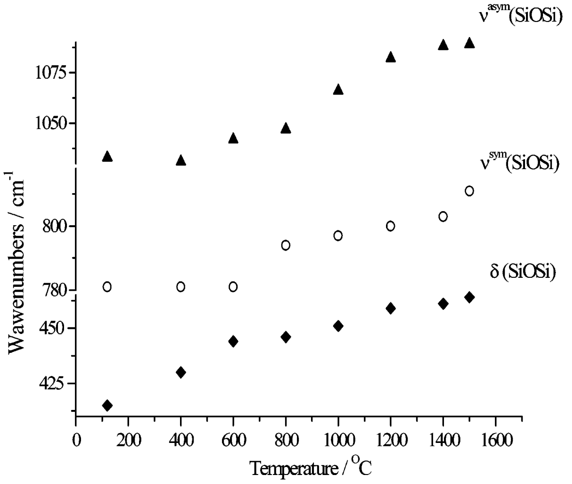

Figure 3. Evolution of the ν^{sym}(SiOSi), ν^{asym}(SiOSi), and δ(SiOSi) vibrational frequencies as a function of the firing temperature.

the spectra of the gels, Figure 2, apart from the band at ca. 400 cm^{-1} of the octamethylsilsesquioxane. The latter band shows a significant shift to higher wavenumber, to ca. 470 cm^{-1}, and broadening in going to the gel state. This vibration is assignable to the Si−O−Si symmetric stretching of the cluster, a cluster-breathing mode, symmetrical analogue of the IR active ν_{28} in octahydridosilsesquioxane.[29] Such a cluster-breathing mode will be volume changing, and as such is expected to be most sensitive to the attachment of the silsesquioxane structural moiety to a 3-D network, during the gel formation. Note that these pseudo-cubes in the gel will be attached with links different from those found in the model compound. This therefore explains the shift to higher wavenumber, and the broadening as a result of the heterogeneity of the sites in the gel.

The spectrum of pure nonpyrolyzed octamethylsilsesquioxane (T8Me) is shown for comparison (broken line).

Monitoring the vibrations assigned to the Si−O bonds of the network, during the sol−gel transformation, is of particular interest. There are essentially the symmetric and asymmetric stretching modes of the Si−O−Si units and its deformation. All these modes show an increase in wavenumber in going from the gel to the glass state as illustrated in Figure 3.

The most sensitive mode for this transformation is the ν^{asym}(Si−O−Si) mode with a shift of ca. 70 cm^{-1}. ν^{sym}(Si−O−Si) shifts by ca. 30 cm^{-1} and δ(Si−O−Si) by only ca. 16 cm^{-1}. The reasons for this upward shift in wavenumber of these modes may have two origins. The first one is a strengthening of the network which comes from an increase of the degree of cross-linking due to the reaction of the “pendent” CH_3 groups. The second origin would be a manifestation of lattice compression due to densification. These systematic frequency shifts to higher wavenumber are uniquely confined to these three vibrations in the spectra and appear to provide a sensitive probe of the gel to glass transition. It is possible to fit a sigmoidal curve to this variation, thus giving a gel to glass transition temperature of ca. 950 °C, Figure 4. ν^{asym}(Si−O−Si) was chosen for this as it is the most sensitive probe with the largest wavenumber shift. Note that this transition temperature will be dependent on the experimental conditions of the pyrolysis.

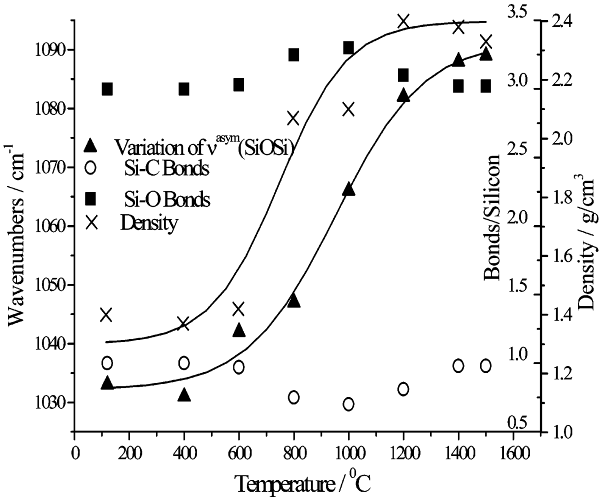

Figure 4. A comparison of the temperature evolution of ν^{asym}(SiOSi) (shown as filled triangles) vibrational frequency with the amounts of Si−C (shown as open circles) and Si−O (shown as filled squares) bonds per Si atom, estimated from the ^{29}Si MAS NMR spectra,[22] and the macroscopic density of the sample (shown as crosses). The two lines are fits to density variation (top) and frequency variation (bottom).

Figure 4 also compares the wavenumber variation of the most sensitive mode ν^{asym}(Si−O−Si) with the NMR data showing the estimated changes in the number of Si−C and Si−O bonds.[22] The increase in wavenumber starts just below the temperature where NMR evidence suggests the beginning of the redistribution reactions involving the exchange of Si−CH_3 with Si−O−Si bonds. These reactions are characterized by the formation of new units such as D and Q units according to the following reaction

$$2CH_3SiO_{1.5} \rightarrow SiO_2 \text{ (Q unit)} + (CH_3)_2SiO \text{ (D unit)}$$

Further heating (T > 600 °C) the gel built of D and Q units leads to the formation of M units $(CH_3)_3SiO_{0.5}$ according to the following reaction.

$$(CH_3)_2SiO \text{ (D unit)} + CH_3SiO_{1.5} \text{ (T unit)} \rightarrow SiO_2 \text{ (Q unit)} + (CH_3)_3SiO_{0.5} \text{ (M unit)}$$

The labels X, M, D, T, and Q refer to the number of bridging O atoms that surround the Si atom, i.e., $SiC_{4-x}O_x$ units with x = 0, 1, 2, 3, and 4, respectively. These redistribution reactions (very common in organosilicon chemistry) have been well-documented in the literature.[22,34,35]

This redistribution of oxygen and carbon atoms is found to lead to a change in the macroscopic property, density,[36] as shown in Figure 4. It is interesting to see the densification of the sample following closely the changes observed with IR spectroscopic data. Therefore, we conclude that the increases in the IR wavenumbers of these Si−O modes appear to be due first to the cross-linking during the gel to glass transformation from 120 to ca. 1000 °C, with a strengthening of the structure; then from ca. 1000 to 1400 °C, there is a densification of the glass. Finally, from ca. 1200 to 1500 °C, during the carbothermal reduction,[37] there

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is the introduction of the lighter carbon atoms to the network, thus replacing the heavier oxygen atoms, which leads to further strengthening of the glass bonds. However, the carbothermal reduction involves the evolution of gaseous CO, which results in the creation of inhomogeneities such as defects and voids in the sample, an effect which acts to reduce the density. This becomes more important above a temperature of about 1400 °C, and the few density measurements around this temperature are in keeping with such an expectation.

Moreover, previous studies by Raman and infrared spectroscopies on silica monoliths produced by the sol−gel route[38] have also shown that, with increasing thermal treatment temperature, there is a shift to higher frequencies for the Si−O−Si vibrations. The authors explain these observations by suggesting that the gel−glass matrix is progressively strengthened by bond shortening and a small reduction in mean Si−O−Si bond angle and angular distribution. Another study by infrared spectroscopy[39] reports that the Si−O−Si bridging sequences present in the gel are strained at the surface of the pores, with larger bridging angles and longer Si−O bonds, in comparison to bulk vitreous silica. As is well-known that the porosity and stress can affect the precise position of infrared absorption bands in thin films of noncrystalline silica,[40,41] it is not surprising to observe an increase of the Si−O−Si wavenumbers in the present system, in parallel with an increase in density and the collapse of the pore volume from 600 to 1200 °C.[36] This drop in pore volume is accompanied by a decrease almost to a quasi-null surface area at 800 °C,[36] where it is shown here that there is condensation of Si−CH_3 groups. This condensation process has very probably increased the surface energy and enhanced pore collapse, similar to that observed during the condensation of Si−OH groups into Si−O−Si bonds for SiO_2 gels.[42]

The shift to higher wavenumbers of the ν^{asym}(Si−O−Si) vibration has also been correlated to an increase of the Si−O−Si bridging angle, using a force field model.[43,44] However, even if a relationship exits between the IR absorption frequency and the density of the network, its evolution is complex because it depends on the structural form of the network, whether crystalline or amorphous.[43,45]

The densification may also result from a transformation of a gel network composed of silsesquioxane units to a polysiloxane structure similar to that in silica glass. Such a proposal was considered for tetraethoxysilane-derived silica gel.[46] Figures 1 and 2 show the significant decrease in intensity of all the bands assigned to the silsesquioxane structural unit, between 600 and 800 °C, supporting such a conclusion.

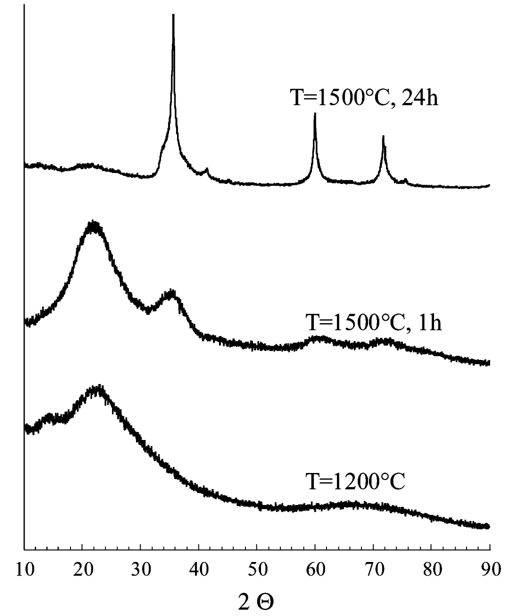

Figure 5. X-ray powder diffraction measurements of MTES samples pyrolyzed at different temperatures and with different isothermal hold times. Cu Kα radiation was used with the samples held at ambient temperature.

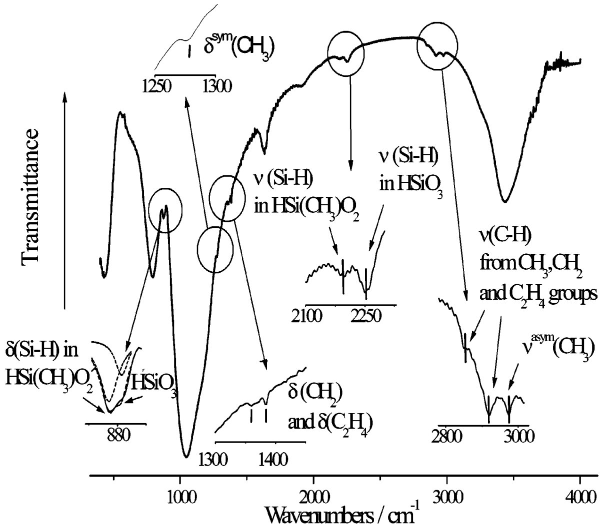

Figure 6. IR spectrum of the MTES sample fired at 800 °C. Weak peaks expanded for clarity.

Powder X-ray diffraction work carried out on samples with different isothermal hold times show the glassy nature of the material, and that the glass-to-crystalline transformations need long isothermal hold times, around 24 h, even at a temperature of ca. 1500 °C, Figure 5.

There is also some evidence from the infrared spectrum that small quantities of $SiCH_2Si$ and $SiCH_2CH_2Si$ groups are formed. An expansion of the IR spectrum, around 1400 cm^{-1} of the 800 °C sample (Figure 6), shows two very weak but interesting features. First the $\delta^{asym}(CH_3)$ expected at ca. 1415 cm^{-1} has disappeared and been replaced by two new bands, a sharp band at 1385 cm^{-1} and a broad band at ca. 1350 cm^{-1}. These bands may be assigned to the IR active CH_2 scissors of respectively $SiCH_2CH_2Si$[26] and $SiCH_2Si$[26,28] units. The CH_2 wagging and rocking modes,[26,28] which would have confirmed the presence of these groups, are not observable due to the presence of the strong SiOSi vibrations at respectively ca. 1080 and 795 cm^{-1}. However, first, the

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expansion of the IR spectrum at ca. 1250 cm^{-1} shows a very weak band at 1274 cm^{-1}, assignable to $\delta^{sym}(CH_3)$ of CH_3 residual groups. Second, the expansion of the IR spectrum around 2900 cm^{-1} shows three weak bands at ca. 2850, 2919, and 2971 cm^{-1} assignable to C−H stretching modes of CH_2 and CH_3 units, and the 2971 cm^{-1} vibration corresponding to the C−H asymmetric stretching mode of residual Si−CH_3 units.[26,27]

$SiCH_2Si$ and $SiCH_2CH_2Si$ groups are likely to be formed in a manner similar to the reactions postulated by Horn and Marsmann[47]and may ultimately be responsible for the insertion of some of the carbon into the silica network, before 1000 °C, as also suggested by Bahloul-Hourlier et al.[48]

With the new insight in to the structure of this material, it is now possible to speculate as to the cause of the changes in the numbers of Si−O and Si−C bonds during pyrolysis, as observed using NMR spectroscopy,[22] Figure 4. At the temperatures below ca. 500 °C the network structure is dominated by polyhedralsilsesquioxanes embedded in a 3-D network. The gradual conversion to a silica-type network will initially involve a replacement of the Si−C bonds by Si−O bonds.

Kamiya et al.[15] have reported a Raman spectrum of free carbon for a sample pyrolyzed at 1100 °C under an atmosphere of nitrogen. The samples made for the present study were pyrolyzed in an atmosphere of helium and the spectra at three temperatures, 1200, 1400, and 1500 °C, clearly show the organization and crystallization of free carbon with a rise in temperature of pyrolysis, as a decrease of the width of the bands at ca. 1350 and 1600 cm^{-1} accompanied by an increase in the intensity ratio I_{1600}/I_{1350}, Figure 7.

The carbothermal reduction of SiO_2, which is accompanied by the formation of CO,[49] above ca. 1100 °C will increase the Si−C bonds at the expense of Si−O bonds.

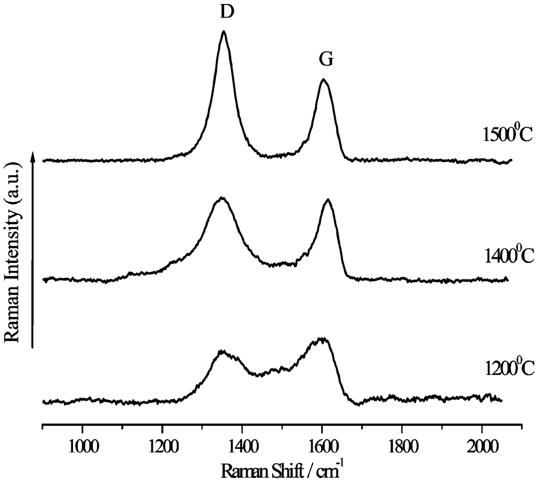

Figure 7. Raman spectra of the high-temperature MTES samples showing the vibrations of free carbon. D = disordered and G = graphitic bands.

Conclusion

The present vibrational spectroscopic investigation of the gel to glass transformation of methyltriethoxysilane provides results compatible with the assertion by earlier workers of the presence of polyhedralsilsesquioxane structural moieties embedded in a 3-D network. Infrared spectroscopy is also shown to be a sensitive probe of the glass formation with a gel to glass transition temperature of ca. 950 °C for the present system under the experimental condition used as described earlier. Detailed examinations of the IR spectra also provide evidence for the formation of Si−CH_2−Si and Si−CH_2−CH_2−Si units during the pyrolysis process, a probable mechanism for the introduction of some of the carbon atoms into the silicon oxygen network.

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