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Journal of MOLECULAR STRUCTURE

Journal of Molecular Structure 887 (2008) 152-158

www.elsevier.com/locate/molstruc

Spectroscopic study of ceramic precursors obtained by hydrolytic condensation of ethoxycyclotetrasiloxane

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> Received 16 November 2007; received in revised form 19 December 2007; accepted 24 December 2007 Available online 13 January 2008

Abstract

Hydrolytic polycondensation process, also called sol-gel process, leads to formation of xerogels from simple molecules e.g. most widely used tetraethoxysilane (TEOS). In the presented work 2,4,6,8-tetraethoxy-2,4,6,8-tetramethylcyclotetrasiloxane – $D_4(OEt)_4$ was applied as the molecular precursor. Polycondensation reactions were performed in the presence of Bu_4NF or HCl/NH_4OH as the catalysts.

The obtained xerogels were studied by FT-IR, MAS-NMR and XRD methods. Depending on the condensation process conditions, structure of the resulting materials varied from octahedral cage unit (T_8) through a ladder chain to random structure.

Dried xerogels were heated at the temperature of 800 and 1000 °C in argon or air atmosphere (pyrolysis or ceramization). In the atmosphere of argon SiC_xO_y glass materials were obtained, while in air silica glass was formed. Their properties depended on the pyrolysis conditions as well as on the xerogel structure. IR spectroscopy results allowed to conclude about the short range order in amorphous xerogel and glass materials.

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Keywords: Vibrational spectra; Silsesquioxanes; Ceramics precursors

1. Introduction

Sol-gel method of ceramics preparation has been known for many years, but recently it has developed as a method for the synthesis of nanostructural materials [1]. In this process various alkoxysilane or alkoksysiloxane precurosors can be condensed to form polysiloxane macromolecules [2]. The type of precursor and the process conditions determine the structure of the synthesized material [3].

Polysilsesquioxanes (POSS) are usually formed during the reaction of hydrolytic condensation of relatively simple molecules - metyltriethoxsilanes (T unit source) and dimetyldietoxysilanes (M unit). Alkoxy groups can be hydro-

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lyzed to Si–OH in the presence of water, which is followed by their condensation with the formation of Si–O–Si bridges. The resulting silsesquioxane material can contain macromolecules of distinct random, ladder and cage or partial cage structure [4]. In order to obtain well defined silsesquioxanes it is preferred to start the hydrolytic condensation process with more complex molecules, bringing in a specific structure, that can govern the structure of the product. Depending on the reaction conditions, polycondesation can result then in the formation of well-defined ladder-type polysilsesquioxanes [5].

Tetracyclic ladder polysilsesquioxanes are well defined precursors for silicon-based ceramics such as silicon oxycarbide (SiC_xO_y) [6] or silica glass with nanoporous structures [7]. Synthesis of such ladder-type polysilsesquioxanes and their use as precursors for SiC_xO_y ceramics and silica glass has been also the main aim of the present work. 2,4,6,8-tetraethoxy-2,4,6,8-tetramethylcyclotetrasiloxane

has been chosen as the precursor. The molecule contains four alkoxy groups at each silicon atom of 4-fold siloxane ring and thus the structure impels the formation of ladderlike POSS.

2. Experimental

2.1. Samples preparation

Samples: K1, K3 and K4 were prepared in a similar way from (2,4,6,8-tetraethoxy)-2,4,6,8-tetramethylcyclotetrasiloxane.

K1. (2,4,6,8-Tetraethoxy)-2,4,6,8-tetramethylcyclotetrasiloxane (2.10 g, 5.0×10^{-3} mol) was mixed with H₂O (0.4 ml) in a flask equipped with a magnetic stirrer and inlet of argon. 2 N solution of HCl (0.002 ml) was added and the mixture was stirred at room temperature for 1 h. After that time NH₄OH was added to the reaction mixture (0.004 ml, pH of the mixture was close to 9). The reaction mixture was stirred for 3 days at room temperature. The insoluble fraction formed during the reaction was filtered off and washed with large quantities of EtOH, toluene and acetone. The product was dried under high vacuum to give 1.19 g of the xerogel (a white solid) with average 88.0% yield.

K3. (2,4,6,8-Tetraethoxy)-2,4,6,8-tetramethylcyclotetrasiloxane (20.37 g, 49.0×10^{-3} mol) was mixed with H₂O (3.88 ml) in a flask equipped with a magnetic stirrer and inlet of argon. 2 N solution of HCl (0.02 ml) was added and the mixture was stirred at room temperature for 1 h. After that time NH₄OH was added to the reaction mixture (4.0 ml, pH of the mixture was close to 11). Gelation under such more alkaline conditions began much faster than it was observed for K1 and K4. Fine solid particles were formed soon after alkalization. The reaction mixture was stirred for 3 days at room temperature. The insoluble fraction formed during the reaction was filtered off and washed with large quantities of EtOH, toluene and acetone. The product was dried under high vacuum to give 15.16 g of xerogel (115.6% yield, calculated for the expected completely condensed product). Additionally, xerogel (K3) was calcinated at 230 °C for 3 h under flow of argon to give 12.36 g of completely condensed product (Y = 94.2%).

K4. (2,4,6,8-Tetraethoxy)-2,4,6,8-tetramethylcyclotetrasiloxane (34.34 g, 82.5×10^{-3} mol) was mixed with H₂O (6.5 ml) in a flask equipped with a magnetic stirrer and inlet of argon. 2 N solution of HCl (0.034 ml) was added and the mixture was stirred at room temperature for 1 h. After that time NH₄OH was added to the reaction mixture (0.07 ml, pH of the mixture was close to 9). The reaction mixture was stirred for 3 days at room temperature. The insoluble fraction formed during the reaction was filtered off and washed with large quantities of EtOH, toluene and acetone. The product was dried at room temperature under high vacuum to give 16.38 g of solid xerogel (74.1% yield).

K2. Sample was obtained from a solution of (2,4,6,8-tetraethoxy)-2,4,6,8-tetramethylcyclotetrasiloxane (3.3 g, $7.9 \times$ 10^{-3} mol) in dry EtOH (10 ml). The solution was prepared in a flask equipped with a magnetic stirrer and inlet of argon. Bu₄NF (1.9 ml, 1 M solution in THF) was added at room temperature. After 1 h the reaction mixture became turbid. It was then stirred for 72 h at room temperature. The insoluble fraction was filtered off and washed with large quantities of EtOH and acetone. The product was dried under high vacuum to give 1.52 g of a white solid being irregular polymeric silsesquioxane material (71.5% yield, calculated for the expected, completely condensed product).

Pyrolytic polycondensation (ceramization) was carried out under argon (SiC_xO_y) or air atmosphere (SiO₂) at the temperature of 800 and 1200 °C.

2.2. Measurements

Solid state NMR spectra were recorded at 300 K on a Bruker MSL-300 MHz spectrometer (59.6 MHz for ²⁹Si and 75.5 MHz for ¹³C) using a Bruker CP MAS probe with a 4 mm zirconium rotor. The peak positions were referenced to the signal of Q_8M_8 (trimethylsilyl ester of cubic octameric silicate) standard. ¹H–²⁹Si CP MAS and ¹H-¹³C CP MAS NMR experiments were performed at sample spinning rates of 6 and 8 kHz, respectively. Contact times (t) were 3 ms for ²⁹Si and 2.5 ms for ¹³C with recycling delay of 6 s.

Infrared spectra were measured on a Bio-Rad FTS-60 spectrometer. Spectra were collected in the mid and far infrared region (4000–100 cm⁻¹) after 256 scans at 2 cm⁻¹ resolution. Samples were prepared by the standard KBr and polyethylene (Merck) pellets method. Raman spectra were collected after 10000 scans at 4 cm⁻¹ resolution using FTS 6000 Bio-Rad Spectrometer with Raman section (with Nd:YAG Spectra Physic T10 106 4c laser). The laser power on the samples was maintained at 300 mW.

X-ray diffraction (XRD) data were collected by Philips X'Pert Pro MD powder diffractometer using K α_1 radiation from Cu anode. The configuration was standard Bragg-Brentano setup with Ge(111) monochromator at the incident beam. All measurements were carried out at room temperature with the 0.008° step size at 2 Θ scanning range and the 64 s of measurement time for each step. Data analysis and the peak profile fitting procedure were carried out using Philips X'Pert HighScore Plus (PW3212) Release 2.1 software.

3. Results and discussion

2,4,6,8-Tetraethoxy-2,4,6,8-tetramethylcyclotetrasiloxane is a mixture of four conformers: one with *cis* only positions of ethoxy groups and three *trans* isomeric forms. Each type of isomeric 2,4,6,8-tetraethoxy-2,4,6,8-tetramethylcyclotetrasiloxane molecules can give different condensation products, therefore the xerogel material obtained as a result of its hydrolytic condensation can be composed of silsesquioxanes of different forms. Recently, we have found that tetrabutylammonium fluoride catalyzed hydrolytic condensation of 2,4,6,8-tetraethoxy-2,4,6,8-tetramethylcyclotetrasiloxane gives almost completely pure, crystalline octamethyloctasilsesquioxane (T₈) [8]. In this work we have used 2,4,6,8-tetraethoxy-2,4,6,8-tetramethylcyclotetrasiloxane in order to find an effective synthetic route for polysilsesquioxanes of ladder structure:



In the ladder-type of structure $CH_3Si(OSi)_3$ (T³ units) dominate, with the ratio between T units and terminal groups (CH₃)₂Si(OSi)₂ (D units) depending on the ladder length. In our case CH₃Si(OSi)₂(OEt) (T²) segments replace typical D units. In ²⁹Si CPMAS NMR spectra of xerogels (Fig. 1) two bands at chemical shift -65.0 ppm and -58.0 ppm, due to T^3 and T^2 units, respectively [9], are very intensive. In the samples K4, K2 and K1 the band around -65.0 ppm is the most intensive one, while in the spectrum of sample K3 before calcination the peak at -58.9 ppm dominates. showing that the polycondesation process has not been complete. After calcination the ratio of T^3/T^2 units resembles that found for K4. Low intensity peaks around -35 ppm and -110 ppm indicate the presence of the D units and Si(OSi)₄ (Q⁴ unit) respectively [10]. The peak at about -86 ppm is probably due to $(\text{EtO})_3 \text{Si}(\text{OSi})_1$ (Q¹ unit). It suggests rearrangement of substituents at silicon atom during the reaction. In the NMR spectra of samples K2 and K1 mostly the bands due to T^3 and T^2 bonding sequence are present, with only traces of Q^4 at about -104 ppm. The ¹³C CPMAS NMR spectra (not shown here) have indicated the presence of SiCH₃ and SiOEt groups only.

FT-IR and FT-Raman spectra (Fig. 2) of xerogel samples: K4, K3, K2 and K1 are very similar. Bands in the ranges: 430–445, 570–585 and 10301–1144 cm⁻¹ are due to Si—O vibrations in polysilsesquioxanes of ladder-type structure [11]. Characteristic double band at about 1130–1033 cm⁻¹ is due to asymmetric stretching vibrations of Si—O, low intensity band at 570–585 cm⁻¹ is due to 4-membered ring vibration [12].

The bands occurring at about 800 cm^{-1} are due to Si–C and those at ca. 900 and 2200 cm⁻¹ are ascribed to Si–H. The remaining bands originate from characteristic vibrations of methyl and ethyl groups. IR spectra assignments of all xerogel samples are presented in Table 1.

In FT-Raman spectra the most intensive bands at around 2900 and 1400 cm^{-1} are due to alkyl groups, other less intensive ones can be assigned correspondingly to those found in IR spectra.



Fig. 1. ²⁹Si CPMAS-NMR spectra of xerogels obtained by hydrolytic polycondensation of 2,4,6,8-tetraethoxy-2,4,6,8-tetramethylcyclotetrasiloxane.

Fig. 3 shows X-ray diffraction patterns taken for samples K4, K3, K2 and K1 (Note, scan intensities are not normalized and each one has its own intensity scale in order to visualize all interesting features.). Diffraction patterns of amorphous xerogels K4 and K3 contain no sharp reflections (see XRD data in Fig. 3) and show the presence of polycondensed POSS of random ladder-like structure. Low intensity, broad peaks around 10° and $20^{\circ}[2\Theta]$ could be interpreted as some degree of ordering in one direction for possibly two, but definitely not crystalline components.

XRD scan for sample denoted as K2 shows similar peaks around 10° and 20° [2 Θ] but there is also a set of



Fig. 2. FT-IR (a) and FT-Raman (b) spectra of xerogels obtained by hydrolytic polycondensation of 2,4,6,8-tetraethoxy-2,4,6,8-tetramethylcyclotetrasiloxane.

Table 1 Assignments of bands in infrared spectra of synthesized xerogels $[\mathrm{cm}^{-1}]$

	K4	K3	K2	K1
δ (OSiO)	432	445	445	_
v _s (SiOSi)	570	586	557	562
v (SiC)	777	780	774	779
δ (SiH)	897	_	_	_
vas(SiOSi)	1032, 1133	1031, 1130	1033, 1130	1030, 1127
δ (CH ₃)	1277	1275	1274	_
δ (CH ₂)	1413	1394	1394	$\sim \! 1400$
v (SiH)	2236-2177	_	_	_
v (CH)	2976, 2915	2929, 2977	2890, 2930, 2977	2929, 2978

intensive reflections. In Fig. 3. five pairs of peaks can be clearly seen. We have fit pseudo-Voight profiles to each peak. From the fitting results we have found that every second peak starting from 42° [2 Θ] angle has almost identical Full Width at Half Maximum (FWHM). This leads to the conclusion that there are two sets of diffraction patterns for two components. One with the average FWHM of 0.418 $[2\Theta]$ and the second FWHM of 0.772 $[2\Theta]$. Moreover, the number of peaks as well as the peaks intensity ratio for each pattern are similar. Therefore, we can conclude that, apart from two amorphous phases, sample K2 consists also of two phases of analogous crystal structure but with different sizes of the unit cell. The exact crystalline phase of both components has not been distinguished and it has no match in the existing powder diffraction data base. Similar XRD pattern analysis has been performed for the scan taken for sample K1. Identical reasoning have led us to the conclusion that this sample contains one crystalline component (besides the amorphous one), comparable to that observed of the largest FWHM in sample K2. Peak positions as well as FWHM and intensity ratios are identical.

As it appears from K1 and K2 diffraction pattern comparison, the reflection around 10° probably belongs to the one of the two phases with smaller FWHM. Most likely, very large broadening of the peak width is due to the fact that for this particular direction large distribution of the crystal plane distances can be observed. Similar effect is common for compounds which structural "building blocks" which have well defined parallel planes of atoms but the distances between them varies within the certain range (e.g. montmorillonite). Similar broad peaks at the lower angles are also observed for the K3 and K4 samples. This same reasons leads us to the conclusions that there is one distinct direction (plane distance) for each of two possible phases, but the parallel planes have no inner structure because of lack of reflections at higher angles.

The aim of the present work has been to obtain silsequioxane precursors for the oxycarbide (SiC_xO_y) and silica glass materials with nanostructure determined by xerogel precursors. For this reason, samples K4 and K3 have been selected for further pyrolysis (ceramization). Both samples are structurally similar, amorphous ladderlike polysilsesquoxanes with theoretical Si/C ratio close to 1:1. Pyrolysis process has been performed in the argon



Fig. 3. X-ray diffraction patterns of xerogels.

or air atmosphere at the temperature of 800 and 1000 °C. In the case of argon atmosphere, amorphous silicon oxycarbide (SiC_xO_y) formation has been expected. Ladder terminal methyl groups should decompose resulting in new Si—C bonds. Theoretically the Si/C ratio should be 1:1, but a part of carbon (not only due to ethoxy groups) can appear also in the form of amorphous carbon. When pyrolysis of polysilsesquioxanes is performed under air atmosphere all methyl and ethoxy groups are eliminated with the formation of pure amorphous silica of specific nanostructure.

IR spectra presented in Figs. 4 and 5 confirm the expected results. The spectra of the sample heated in air (Figs. 4 and 5b) are typical of silica glass [13] while in the spectra of the samples heated in argon (Figs. 4 and 5a),

some additional bands can be observed. Three main bands at about: 1100, 800 and 450 cm^{-1} due to Si—O vibrations are complex and relatively broad, but their numeric deconvolution makes it possible to acquire the important information on the structure of pyrolysed, glassy materials. The deconvoluted spectra from Figs. 4 and 5 are presented in Fig. 6.

Win-IR[™] program has been applied for the IR spectra deconvolution. The bell-type curves of the pre-determined shape (Gaussian, Loretzian or mixed) have been used in order to obtain the best fit of the complex band. The following starting parameters have been set first: number of peaks, their positions and widths at half-maximum (FWHM), relative intensities and shapes as determined by the selected function. These parameters have been



Fig. 4. FT-IR spectra of sample K4 after pyrolysis in argon (a) and air (b) atmosphere.



Fig. 5. FT-IR spectra of sample K3 after pyrolysis in argon (a) and air (b) atmosphere.



Fig. 6. Decomposed IR spectra of sample K4 (a) and K3 (b).

determined by calculation of second derivative of the spectrum. This allows to determine inflection points and peak maxima. Having preliminary data concerning spectrum topology, one should start with the smallest possible number of bands and increase it in the next iterational cycle. The procedure of deconvolution is based on synthetic curve fitting, which is a superposition of component peaks on the original spectrum. The "fitting level" is determined by the coefficient χ^2 (minimum square method) [14]. The resulting deconvoluted spectra (bottom) and curvefit spectra (upper) are shown in Fig. 6.

Spectra of different samples, K4 and K3, heated in the same atmosphere, are practically identical, while the spectra of the same sample but heated in argon or air atmosphere are significantly different. In the spectra of samples pyrolysed in argon, apart from the bands characteristic for glassy silica, the bands in the range of $800-900 \text{ cm}^{-1}$ due to Si–C stretching vibrations can be also observed. In the case of air-pyrolysed samples only the bands due to glassy silica are seen. However, distinct differences can be found on their careful comparison with the spectra of silica glass typically obtained at high tempera-

ture from the liquid phase. This means that the "short range" structure of these silica glasses is different.

To summarize, we can conclude that oxycarbide $(SiC_x - O_y)$ and SiO₂ glasses with specific nanostructure can be obtained from polysilsesquioxane precursors of special siloxane bonds arrangement.

Acknowledgment

This work was supported by Polish Ministry of Science and Higher Education under Grant N507 093 31/2271.

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