

Contents lists available at [SciVerse ScienceDirect](http://www.sciencedirect.com)

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

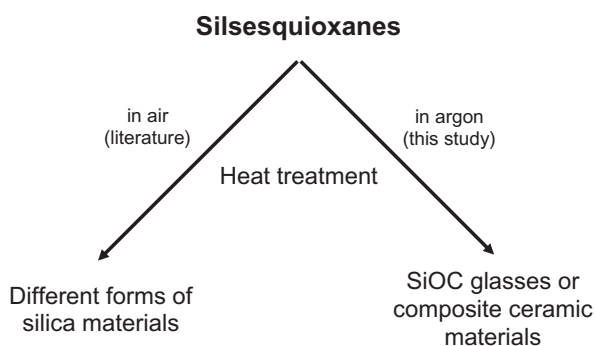
SiOC glasses produced from silsesquioxanes by the aerosol-assisted vapor synthesis method

M. Sitarz^{a,*}, C. Czosnek^b, P. Jeleń^a, M. Odziomek^a, Z. Olejniczak^c, M. Kozanecki^d, J.F. Janik^b^aAGH University of Science and Technology, Faculty of Materials Science and Ceramics, Al. Mickiewicza 30, 30-059 Krakow, Poland^bAGH University of Science and Technology, Faculty of Energy and Fuels, Al. Mickiewicza 30, 30-059 Krakow, Poland^cInstitute of Nuclear Physics, Polish Academy of Sciences, ul. Radzikowskiego 152, 31-342 Krakow, Poland^dLodz University of Technology, Faculty of Chemistry, Department of Molecular Physics, ul. Zeromskiego 116, 90-924 Lodz, Poland

HIGHLIGHTS

- Aerosol-assisted vapor synthesis method allows to obtain amorphous Si_xO_y materials from silsesquioxanes.
- $^{29}\text{Si}/^{13}\text{C}$ MAS NMR, MIR and Raman spectroscopic studies have shown that for selected silsesquioxanes the amorphous materials have $\nu\text{-SiO}_2$ structure.
- MIR and Raman spectroscopic studies showed that black glasses can be obtained.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 12 March 2013

Received in revised form 27 April 2013

Accepted 2 May 2013

Available online 16 May 2013

Keywords:

Aerosol synthesis
Silsesquioxanes
Pyrolysis
Silica glass
Black glasses

ABSTRACT

In this paper, we describe a new method based on aerosol-assisted vapor synthesis for making glass materials by pyrolysis of readily available silsesquioxanes $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ and $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$. Combined powder X-ray diffraction (XRD) and spectroscopic studies in the far infrared region (FIR) showed that under applied conditions the method yielded amorphous materials. Subsequent structural studies with the application of the ^{29}Si and ^{13}C MAS NMR, Raman, and middle infrared (MIR) techniques led to the conclusion that the pyrolysis of the silsesquioxane precursors resulted in glass materials with a structure of amorphous silica $\nu\text{-SiO}_2$. In the case of certain glasses prepared from $\text{CH}_3\text{Si}(\text{OCH}_3)_3$, they were also shown to possess in the structure some Si–C bonds (black glasses), whereas those originated from $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ were composites that in addition to the silica glass phase contained domains of free/unbound carbon.

© 2013 Elsevier B.V. All rights reserved.

Introduction

Preparations of black glasses by classical melting of a mixture of solid silica SiO_2 and carbon C are very difficult or even impossible due to feasible oxycarbide decomposition to silicon carbide SiC and silica SiO_2 , and a loss of some carbon caused by accompanying oxidation processes. Such obstacles, potentially, can be overcome by

* Corresponding author. Tel.: +48 126172395; fax: +48 126337161.

E-mail address: msitarz@agh.edu.pl (M. Sitarz).

pyrolysis of precursors already containing Si–C bonds with the latter remaining in the resulting glass. In silicon oxycarbides SiOC, carbon is incorporated into amorphous silica structure modifying the glass network. The structure strengthening occurs as a result of replacing two-coordinated oxygen centers by four-coordinated carbon ones. Gradual changes of many properties of the oxycarbide glasses make these materials advantageous for many modern applications. Among numerous and diverse applications, of special interest are those in emerging new energy technologies. For example, an attempt to use the mesoporous SiOC ceramics of high sur-

face area for hydrogen storage has been made [1]. Another area of interest involves the use of silicon oxycarbides as anode material in lithium ion batteries. Indeed, several attempts to increase the anode capacity have been made. A SiOC composite anode material obtained by electrochemical co-deposition in the Si–C–O system was used for the production of Li battery achieving a capacity value over 1000 mAh per gram of Si [2]. The employment of single wall carbon nanotubes as a conducting agent instead of carbon black led to the capacity increase of silicon oxycarbide anodes [3]. The production of silicon oxycarbide films free of deformations and cracks that were obtained by pyrolysis of polyvinylsilsesquioxane up to 1400 °C, has been reported [4]. In this case, the films appeared to contain free carbon, mainly, in the amorphous form with some quantity of graphitic carbon. Recently, the formation of hermetic SiOC coatings by pyrolysis of polysiloxane and/or polysilsesquioxane polymers was confirmed in our laboratory [5]. Additionally, fully dense and crack-free SiOC ceramics containing free carbon were obtained via direct photo-crosslinking and pyrolysis of polysiloxane [6]. In that case, according to the XRD investigations, the materials prepared at 1100 °C were amorphous, whereas the ceramics pyrolyzed at 1400 °C contained the turbostratic graphite-like carbon and silicon carbide as crystalline phases. Silicon oxycarbide glass fibers have been also drawn from organically modified silicates by the sol–gel method [7]. Yet another study suggests that SiOC may offer unique opportunities as a substitute of pyrolytic carbon in medical device applications requiring excellent tribological properties such as artificial heart valves [8]. In summary, the oxycarbide glasses could be related to the amorphous/glassy silica matrix in which some oxygen atoms are replaced by atoms of carbon. In the reported syntheses of such glasses, the oxycarbide phase has often been accompanied by variable quantities of finely distributed free carbon contributing to the common name of such products – black glasses. However this description includes also such related glass systems as amorphous silica/free carbon and amorphous silica/oxycarbide/free carbon which may be formed as final or transient products in pyrolytic conversions of many Si–O–C containing precursor systems.

In this study, presented is an alternative way for the preparation of glass powders from selected organosilicon precursors by the aerosol-assisted synthesis method. The products were characterized with IR, Raman, ^{13}C and ^{29}Si MAS NMR spectroscopy, and powder XRD diffraction.

Materials and methods

All powder materials were prepared by the aerosol-assisted synthesis method of which details were published elsewhere [9]. The preparation of powders was carried out in the set-up that consisted of three major sections, i.e., (i) an ultrasonic aerosol generator, (ii) an alumina tube reactor (76 mm ID, 1500 mm in length) placed in a furnace pre-heated to the appropriate temperature, and (iii) a nylon filter for solid particle collection. Three different reaction temperatures, i.e., 1000 °C, 1200 °C, and 1400 °C were applied. The neat substrates, methyltrimethoxysilane $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ (MTMS) and triethoxymethylsilane $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ (TEMS) were purchased from Sigma–Aldrich and used as received. The aerosol mist of a precursor produced in the ultrasonic generator was transported with flowing argon (4 L/min) to the ceramic reactor pre-heated to the selected temperature. Solid products were collected on an exit nylon filter. The free-flowing black powder materials were appropriately characterized (Table 1).

FT-IR spectra were recorded with a Bruker Company Vertex 70v spectrometer. Spectra were collected in the middle (MIR) and far infrared (FIR) regions ($4000\text{--}50\text{ cm}^{-1}$) after 128 scans at 4 cm^{-1} resolution. Samples were prepared by the standard KBr (MIR)

Table 1
Obtained glasses.

Name/temperature	1000 °C	1200 °C	1400 °C
$\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ (TEMS)	TEMS1	TEMS2	TEMS3
$\text{CH}_3\text{Si}(\text{OCH}_3)_3$ (MTMS)	MTMS1	MTMS2	MTMS3

and polyethylene (FIR) pellet methods. Spectra deconvolution have been carried out according to the method proposed by Handke et al. [10].

Raman spectra were acquired with use of JobinYvon T64000 triple-gratings spectrometer equipped with the Olympus BX40 confocal microscope. Ar-ion laser (LEXEL) line 514.5 nm was used for samples excitation. Laser power (4–6 mW at a sample) and time of a single measurement (240–360 s) were adjusted to obtain Raman spectra and to avoid overheating of the samples.

X-ray powder diffraction measurements were performed using Philips X'Pert Pro MD diffractometer $\text{Cu K}\alpha_1$ line monochromatized by $\text{Ge}(111)$ monochromator. Standard Bragg–Brentano geometry with θ – 2θ setup was applied (0.008° step size and $5\text{--}90^\circ$ 2θ range).

Solid state NMR spectra were recorded at 27 °C on a Bruker MSL-300 MHz spectrometer (59.6 MHz for ^{29}Si) 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.

Results and discussion

As previously mentioned, the black glasses have the amorphous silica structure in which two O^{2-} oxygen ions are replaced by one C^{4-} anion. From the point of view of the advantageous physical and chemical resistance properties, it is desirable to make homogeneous black glasses. Since the silica matrix is able to accommodate only a limited number of carbon ions, the use of silsesquioxanes as precursors is highly favorable. In this regard, these compounds contain mostly the so-called T units (3 oxide ions, 1 carbon ion by 1 silicon ion) and, therefore, constitute a strictly defined C–Si–O chemical environment.

The powder materials obtained in this study from $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ and $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ were examined with XRD to determine a degree of their crystallinity. The high intensity background (halo) in the 2θ range of $10\text{--}30^\circ$ in the diffraction patterns (not shown) suggests that these materials are highly amorphous. In agreement with this, no sharp bands in the far infrared (FIR) spectra were detected. After corroborating the amorphous nature of the products, the occurrence of Si–C bonds, i.e., the presence of carbon in the black glass, and/or free carbon domains unbound in the silica matrix was examined by NMR and Raman spectroscopy.

The solid state NMR probes short range chemical environments of all silicon atoms independent on their long range ordering while local differences in chemical make-up result in various chemical shifts for different silicon-based species. In our systems, the elements Si, C, and O can be spatially configured in a more or less random way. For example, the four-valent Si centers may be involved in such close neighbor groups as SiO_4 (in silica), SiCO_3 , SiC_2O_2 , SiC_3O , and SiC_4 (in silicon carbide). In the last case, each silicon atom is surrounded by four carbon atom and vice versa. The ^{29}Si and ^{13}C MAS NMR spectra of all materials prepared at the selected temperatures are shown in Figs. 1–4. All ^{29}Si MAS NMR spectra included a strong prevailing band at ca. -110 ppm which is related to SiQ_4 groups (where Q is the number of oxygen bridging atoms) [11]. For powders obtained from TEMS (Fig. 1), the spectra showed only this band whereas in the spectra for the products from MTMS (Fig. 2) an additional band at about -70 ppm assigned to CSiO_3

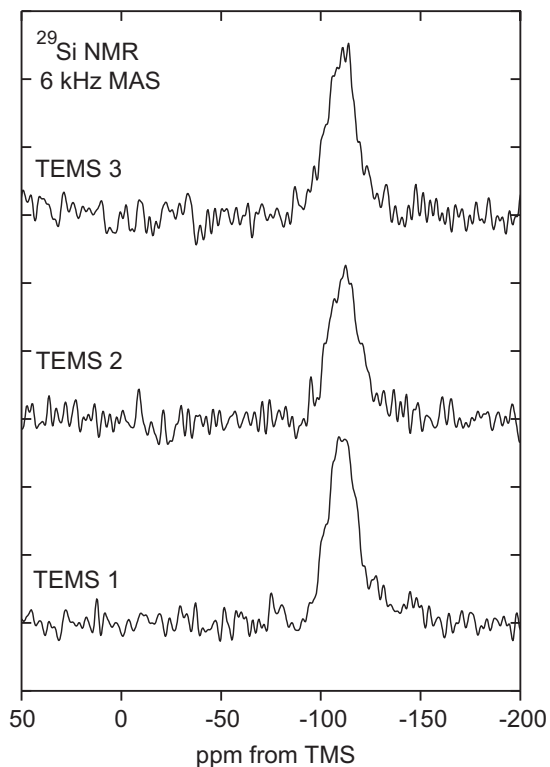


Fig. 1. ^{29}Si MAS NMR spectra of glasses obtained from triethoxymethylsilane (TEMS) at different temperatures; TEMS1 at 1000 °C, TEMS2 at 1200 °C, TEMS3 at 1400 °C.

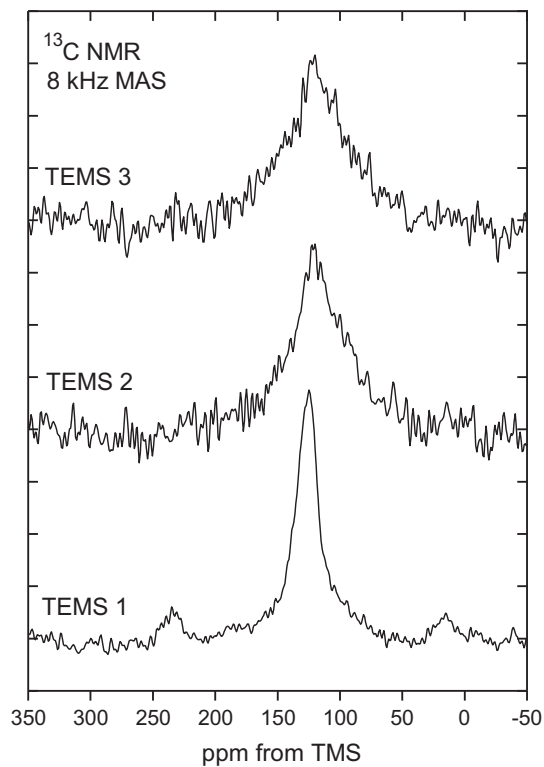


Fig. 3. ^{13}C MAS NMR spectra of glasses obtained from triethoxymethylsilane (TEMS) at different temperatures; TEMS1 at 1000 °C, TEMS2 at 1200 °C, TEMS3 at 1400 °C.

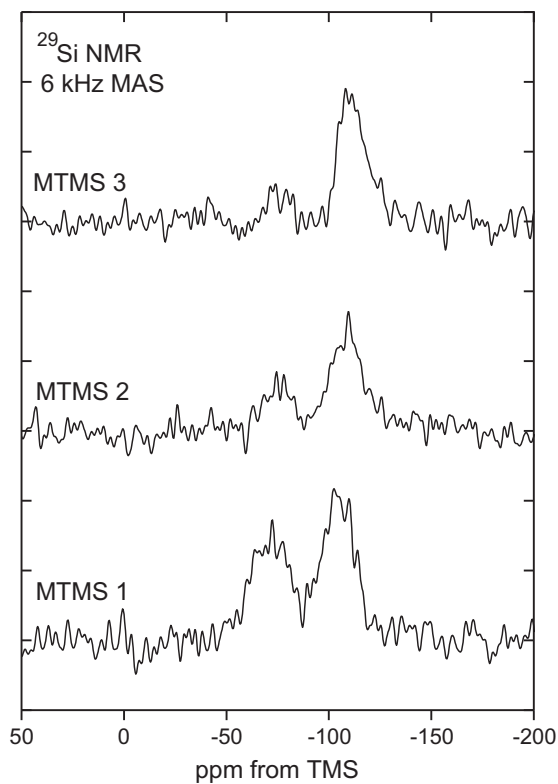


Fig. 2. ^{29}Si MAS NMR spectra of glasses obtained from methyltrimethoxysilane (MTMS) at different temperatures; MTMS1 at 1000 °C, MTMS2 at 1200 °C, MTMS3 at 1400 °C.

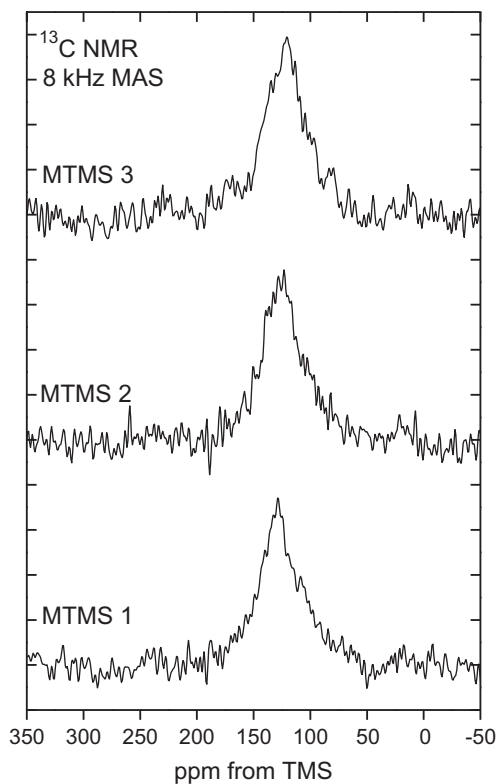


Fig. 4. ^{13}C MAS NMR spectra of glasses obtained from methyltrimethoxysilane (MTMS) at different temperatures; MTMS1 at 1000 °C, MTMS2 at 1200 °C, MTMS3 at 1400 °C.

groups with the Si–C bonds was present [12]. The ^{29}Si MAS NMR results indicate that in each case the silicon oxide matrix was synthesized. However, the black glasses containing also the Si–C bonds were most likely obtained only when MTMS was used as precursor. From the comparison of these NMR results, the higher was the pyrolysis temperature the lower was the content of the CSiO_3 groups as judged by relative changes of the -70 ppm peak's intensities (Fig. 2).

The results of the ^{13}C MAS NMR determinations do not unambiguously support the presence of the black glass, i.e., Si–C bonds incorporated in the silica matrix, since the spectra for all glasses are almost identical (Figs. 3 and 4) and display an exclusive band at about $+130$ ppm. This band, potentially, could be associated with poorly ordered graphitic carbon species and/or carbon structure units having double or triple bonds which may be bonded to silicon atoms [13]. Furthermore, the characteristic band for C– Si_4 groups (ca. $+25$ – 15 ppm, [14]) is not visible in the ^{13}C MAS NMR spectra. Given this evidence, the presence of phase-separate particles of graphitic carbon seems to be well substantiated. One has to stress the fact, though, that the expected number of the Si–C bonds in the glasses from the pyrolysis of the silsesquioxanes would be relatively small and could go undetected. In this regard, according to a relevant literature report, the lack of this band in the ^{13}C MAS NMR spectra of some black glasses can be explained by such factors as (i) small concentrations of C– Si_4 groups, (ii) T_1 relaxation times of these units being much longer in oxycarbide glasses compared to relaxation times in silicon carbide, and (iii) T_2 relaxation times in oxycarbide glasses being short enough to cause the signal to be broadened beyond detection [14].

Raman spectroscopy was applied as yet another method to determine the structural role of carbon in the materials. In the Raman spectra of the TEMS-derived powders, two bands at about 1550 and 1270 cm^{-1} are present (Fig. 5) which are characteristic of strongly defective graphite domains (G and D bands [15–17]). These results confirm the findings by ^{29}Si MAS NMR that support the presence of a separate carbon phase in such products. In the

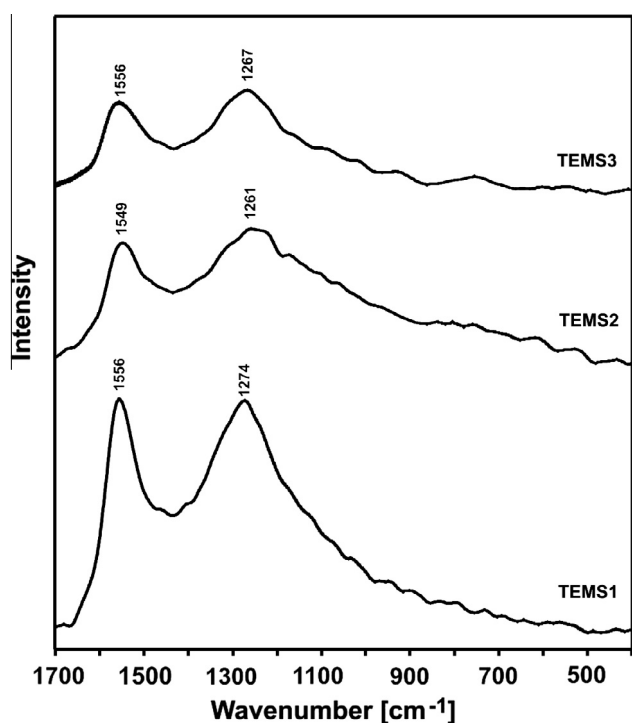


Fig. 5. Raman spectra of glasses obtained from triethoxymethylsilane (TEMS) at different temperatures; TEMS1 at 1000°C , TEMS2 at 1200°C , TEMS3 at 1400°C .

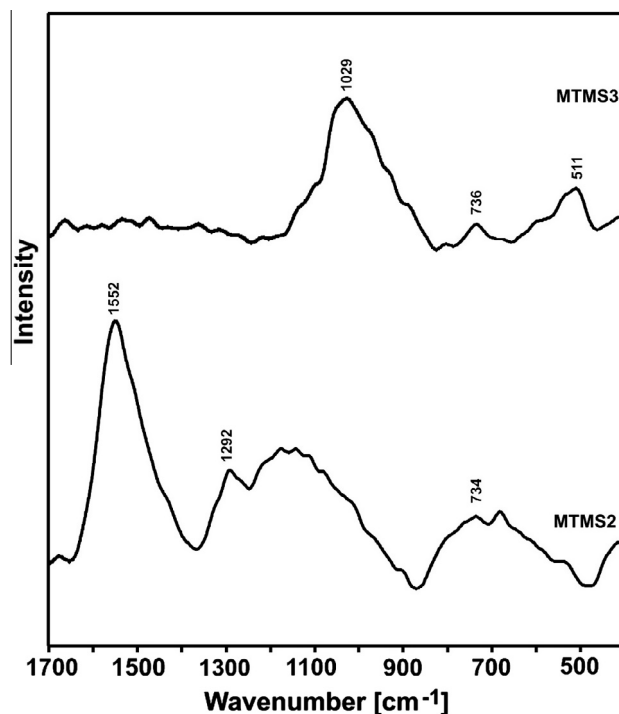


Fig. 6. Raman spectra of glasses obtained from methyltrimethoxysilane (MTMS) at different temperatures; MTMS2 at 1200°C , MTMS3 at 1400°C .

case of the materials prepared from MTMS, good quality Raman spectra could be obtained only for samples MTMS2 and MTMS3 (Fig. 6). Specifically, in the MTMS2 spectrum, similarly to the TEMS-derived materials the high intensity bands at about 1550 and 1290 cm^{-1} are present, indicating mostly separate phase carbon domains. In a marked contrast with this, spectrum for MTMS3 lacks the bands characteristic for graphitic carbon and, consequently, provides an indirect evidence for carbon incorporated in the silica matrix. There are three bands at about 1030 , 740 , 510 cm^{-1} that are observed in this spectrum. The Raman spectrum of pure silica glass ($\nu\text{-SiO}_2$) includes the characteristic bands at about 450 cm^{-1} (bending vibrations Si–O–Si), 500 cm^{-1} (four-membered ring vibrations), 600 cm^{-1} (three-membered ring vibrations), and 800 cm^{-1} [18]. On the other hand, the bands associated with the Si–C bonds have been reported to appear near 780 cm^{-1} (transversal TO) and 970 cm^{-1} (longitudinal LO) [19–21]. Therefore, it can reasonably be assumed that the two bands (1030 and 740 cm^{-1}) appearing in the MTMS3 spectrum can be attributed to the presence of the Si–C bonds supporting its black glass features. These bands (734 cm^{-1} and very broad band at 1200 – 1110 cm^{-1}) are also visible in the spectrum of MTMS2 (Fig. 6). But in the case of this glass, the spectrum is dominated by the bands associated with graphite (1552 and 1292 cm^{-1}), which clearly indicates a lack of homogeneity.

All powder materials were also studied by mid-infrared spectroscopy MIR (Figs. 7 and 8). The analysis of the MIR spectra indicates that only in the case of the MTMS3 precursor, the resulting glass was free of post-organic residues and hydroxyl groups. All other spectra show bands indicating the presence of Si–H bonds a typical feature in incomplete thermal conversions of SiCH_x groups. The predominant bands associated with the stretching vibration of Si–O and silicon oxide bending modes [22–25] are observed in all the MIR spectra. Earlier MIR studies have demonstrated that the absorptions associated with Si–C bond vibrations appear at approximately 940 and 840 cm^{-1} [5]. However, because

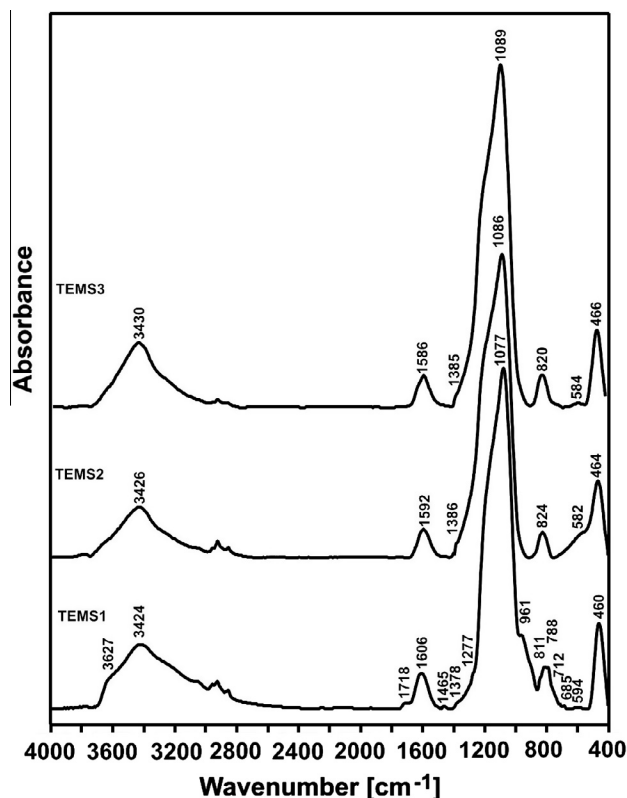


Fig. 7. MIR spectra of glasses obtained from triethoxymethylsilane (TEMS) at different temperatures; TEMS1 at 1000 °C, TEMS2 at 1200 °C, TEMS3 at 1400 °C.

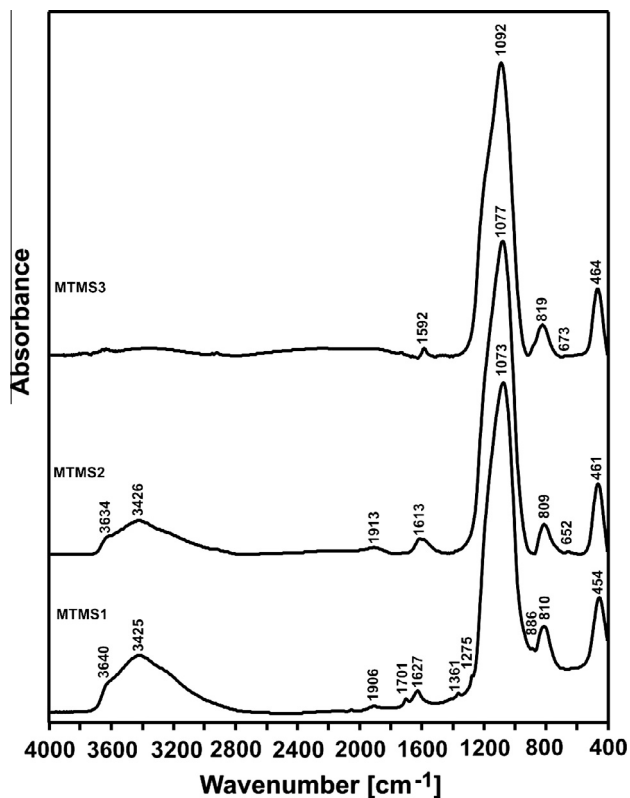


Fig. 8. MIR spectra of glasses obtained from methyltrimethoxysilane (MTMS) at different temperatures; MTMS1 at 1000 °C, MTMS2 at 1200 °C, MTMS3 at 1400 °C.

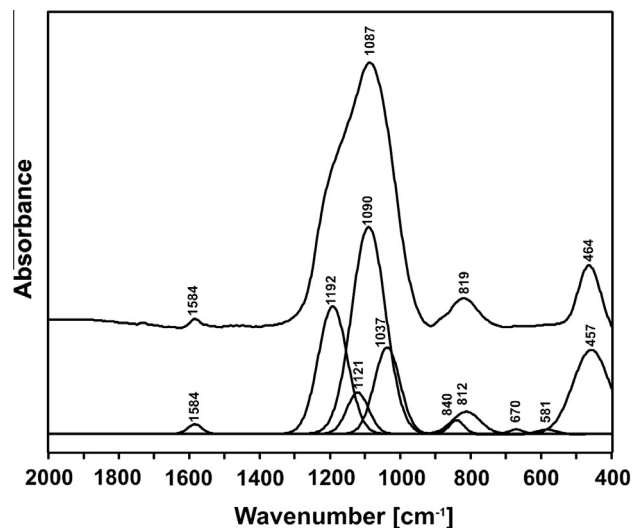


Fig. 9. Deconvoluted MIR spectrum of glass obtained from methyltrimethoxysilane at 1400 °C (MTMS3).

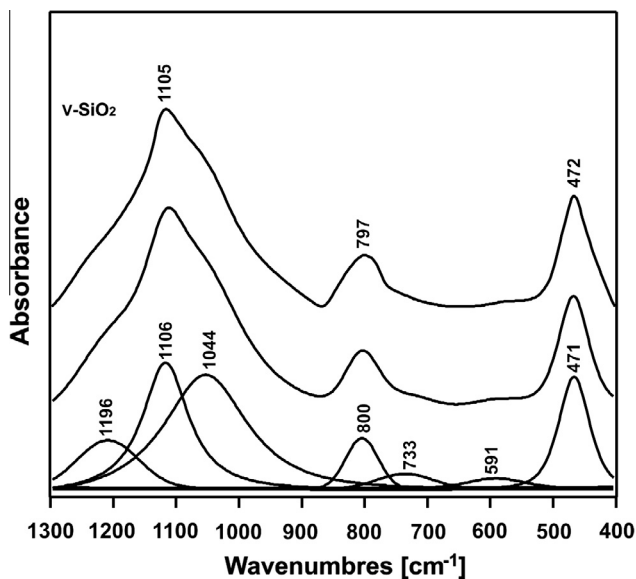


Fig. 10. Deconvoluted MIR spectrum of amorphous silica ($v\text{-SiO}_2$) [5].

of the large half-width MIR spectra for obtained glasses and overlapping bands characteristic of the Si–O and Si–C it is practically not possible to determine the presence of Si–C bonds. In order to remedy band overlap obstacles, deconvolution of the MIR spectrum for MTMS3 was done and the results are shown in Fig. 9. They are compared with the results of the MIR spectrum deconvolution for $v\text{-SiO}_2$ (Fig. 10) and MIR spectrum of SiC (Fig. 11) [5]. Comparison of these results and literature data [5] allow us to assign the band observed at about 840 cm^{-1} to Si–C bond presence.

Conclusions

The comprehensive structural studies (powder XRD, ^{29}Si and ^{13}C MAS NMR, Raman spectroscopy, FIR and MIR) of the powder materials prepared from pyrolysis of the silsesquioxanes $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ and $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ confirm that the applied aerosol-assisted vapor synthesis method yields amorphous materials

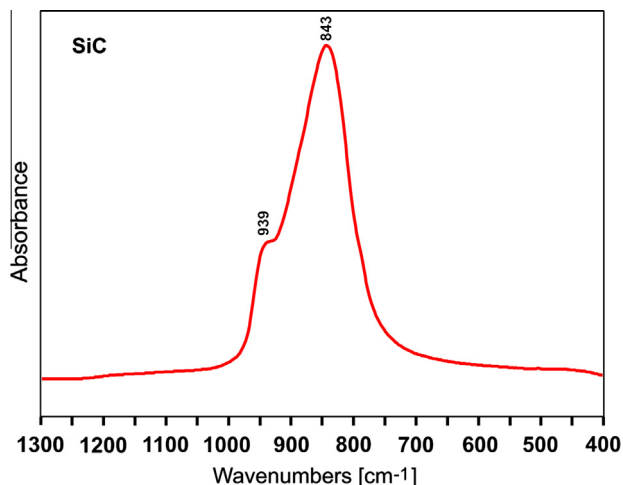


Fig. 11. MIR spectrum of silicon carbide (SiC) [5].

based on the silica v -SiO₂ glassy structure. In the case of the CH₃Si(OCH₃)₃ precursor, it is possible to obtain black glasses in which some carbon is chemically bound to the prevailing silica matrix. The homogeneity of such glasses is mainly dependent on synthesis temperature. The increase of pyrolysis temperature leads to an increase in the homogeneity of black glasses obtained on the basis of MTMS. The pyrolysis of CH₃Si(OC₂H₅)₃ leads to non-homogeneous glasses in which carbon is a common separate phase, unbounded with silicon oxide network.

On the basis of this study it can be concluded that the proposed aerosol-assisted vapor synthesis method can be used for the preparation of homogeneous black glasses, i. e., amorphous oxycarbide phases based on silica matrix containing Si–C bonds.

Acknowledgements

M. Sitarz acknowledges a support by the Polish Ministry of Science and Higher Education under the project “Silsequioxanes as ceramic precursors”, N N507 265940. C. Czosnek and J.F. Janik want to thank for the financial support by AGH-UST, task No. 11.11.210.213.

References

- [1] Q.D. Nghiem, S.J. Chob, D.P. Kim, *J. Mater. Chem.* 16 (2006) 558.
- [2] T. Momma, S. Aoki, H. Nara, T. Yokoshima, T. Osaka, *Electrochem. Commun.* 13 (2011) 969.
- [3] J. Shen, D. Ahn, R. Raj, *J. Power Sources* 196 (2011) 2875.
- [4] N. Takamura, K. Taguchi, T. Gunji, Y. Abe, *J. Sol–Gel Sci. Technol.* 16 (1999) 227.
- [5] M. Handke, M. Sitarz, E. Długoń, *J. Mol. Struct.* 993 (2011) 193.
- [6] S. Martínez-Crespiera, E. Ionescu, H.J. Kleebe, R. Riedel, *J. Eur. Ceram. Soc.* 31 (2011) 913.
- [7] Y. Hu, *J. Mater. Sci.* 35 (2000) 3155.
- [8] R. Zhuo, P. Colombo, C. Pantano, E.A. Vogler, *Acta Biomater.* 1 (2005) 583.
- [9] C. Czosnek, J.F. Janik, *J. Nanosci. Nanotechnol.* 8 (2008) 907.
- [10] M. Handke, W. Mozgawa, M. Nocun, *J. Mol. Struct.* 450 (1998) 229.
- [11] G.D. Cody, B. Mysen, G. Saghi-Szabo, J.A. Tossell, *Geochim. Cosmochim. Ac.* 65 (2001) 2395.
- [12] C.G. Pantano, A.K. Singh, H. Zhang, *J. Sol–Gel Sci. Technol.* 14 (1999) 7.
- [13] H.O. Kalinowski, S. Berger, S. Braun, *Carbon-13 NMR Spectroscopy*, Wiley, 1988.
- [14] J. Brus, F. Kolar, V. Machovic, J. Svitilova, *J. Non-Cryst. Solids* 289 (2001) 62.
- [15] F. Tuinstra, J.L. Koenig, *J. Phys. Chem.* 53 (1970) 1126.
- [16] F. Tuinstra, J.L. Koenig, *J. Compos. Mater.* 4 (1970) 492.
- [17] S. Costa, E. Borowiak-Palen, M. Kruszyńska, A. Bachmatiuk, R.J. Kaleńczuk, *Mater. Sci. – Poland* 26 (2008) 2.
- [18] M. Ivanda, R. Clasen, M. Hornfeck, W. Kiefer, *J. Non-Cryst. Solids* 322 (2003) 46.
- [19] G. Gouadec, P. Colomban, *J. Eur. Ceram. Soc.* 21 (2001) 1249.
- [20] M. Gadzira, G. Gnesin, O. Mykhaylyk, O. Andreyev, *Diamond Relat. Mater.* 7 (1998) 1466.
- [21] S. Nakashima, Y. Nakatake, Y. Ishida, T. Talkahashi, H. Okumura, *Physica B* 308–310 (2001) 684.
- [22] B. Toury, F. Babonneau, *J. Eur. Ceram. Soc.* 25 (2005) 265.
- [23] M. Sitarz, M. Handke, W. Mozgawa, *J. Mol. Struct.* 511–512 (1999) 281.
- [24] M. Sitarz, *J. Non-Cryst. Solids* 357 (2011) 1603.
- [25] M. Sitarz, M. Handke, W. Mozgawa, *Spectrochim. Acta Part A* 56 (2000) 1819.