

LAYER ARRANGEMENT IN THE STRUCTURE OF OCTAKIS-(TRIMETHYLSILOXY)OCTASILSESQUIOXANE AND DODECAKIS-(TRIMETHYLSILOXY)CYCLOHEXASILOXANE

S. A. Gromilov,¹ T. V. Basova,¹ D. Yu. Emel'yanov,²
A. V. Kuzmin,² and S. A. Prokhorova¹

UDC 541.49+548.734

Layers of $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ and $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$ organosilicon compounds obtained by chemical vapor deposition were investigated by X-ray diffraction (DRON-RM4, $R = 192$ mm, CuK_α radiation) and Raman spectroscopy (Triplemate, SPEX). The layers were found to be ideally oriented polycrystalline films. The octakis-(trimethylsiloxy)octasilsesquioxane polycrystals are oriented in one crystallographic direction — $[001]$, while the dodecakis-(trimethylsiloxy)cyclohexa-siloxane polycrystals are oriented in the $[\bar{1}20]$ and $[\bar{1}11]$ directions. Crystal structure analysis in these directions yielded the type of the planar lattice followed by the molecules and their orientation relative to the support.

Keywords: organosilicon compounds, X-ray diffraction study, Raman spectroscopy, oriented layers.

Organosilicon compounds such as octaorganylsilsesquioxanes are promising materials for vacuum lithography; they are also used as photo, electron, and X-ray resists [1, 2]. They can be deposited on various supports by thermal evaporation in vacuum (sublimation). They are sensitive to various types of radiation and have the best (for electron resists) resolution (50 nm) [3].

Despite the numerous publications on oligoorganylsilsesquioxanes and the wide spectrum of their applications, crystal structure organization of the layers has not been discussed in relation to the physicochemical properties of the compounds. A study of this kind will help to clarify the mechanisms of surface processes at the molecular level to use them in developing physicochemical principles for obtaining articles with given characteristics.

This work is devoted to a study of octakis-(trimethylsiloxy)octasilsesquioxane $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ and dodecakis-(trimethylsiloxy)cyclohexasiloxane $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$. The molecular formulas of these compounds are $\text{C}_{36}\text{H}_{24}\text{O}_{20}\text{Si}_{16}$ and $\text{C}_{36}\text{H}_{108}\text{O}_{18}\text{Si}_{18}$. We prepared oriented polycrystalline samples of these compounds and investigated them by X-ray diffraction and Raman spectroscopy. By analyzing these samples we passed from the 3D crystal structure to a 2D section (preferred crystallographic plane). Previously, we showed that the $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ layers are oriented in the same direction (i.e., they are ideally oriented) [4]. It was interesting to study orientation in the cyclic $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$ complex.

EXPERIMENTAL

Synthesis of $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ and $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$ is described in [5]. Layers of these compounds were obtained by vapor condensation (HBA-1 Carl Zeiss Jena vacuum apparatus, vacuum $\sim 10^{-5}$ torr, open type source, temperature

¹A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk; grom@che.nsk.su. ²Novosibirsk State University. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 45, No. 3, pp. 497-501, May-June 2004. Original article submitted April 22, 2003.

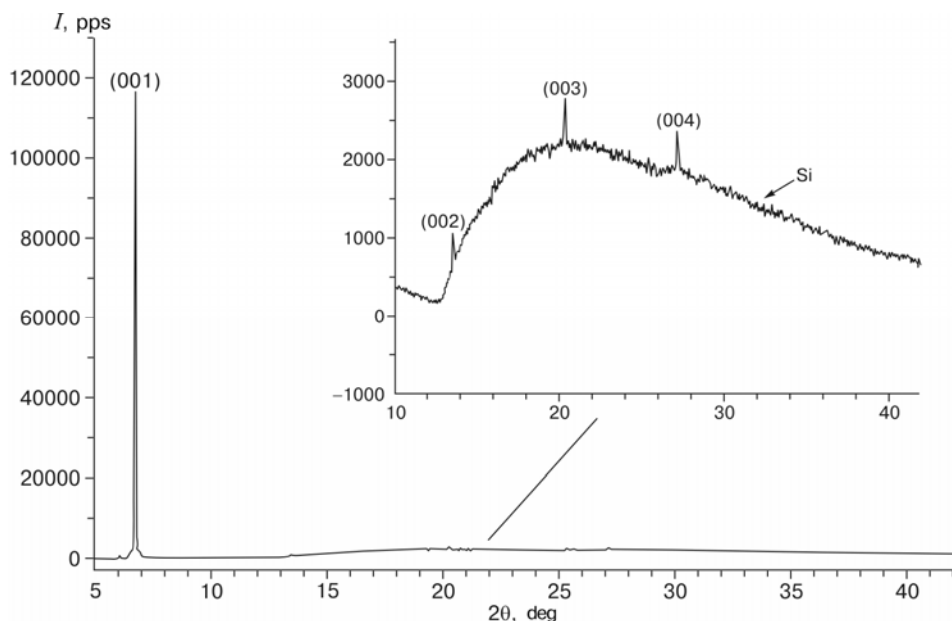


Fig. 1. Diffractogram of the $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ sample on the polished side of the surface of the Si support. Insert: region of 2θ 10° – 40° .

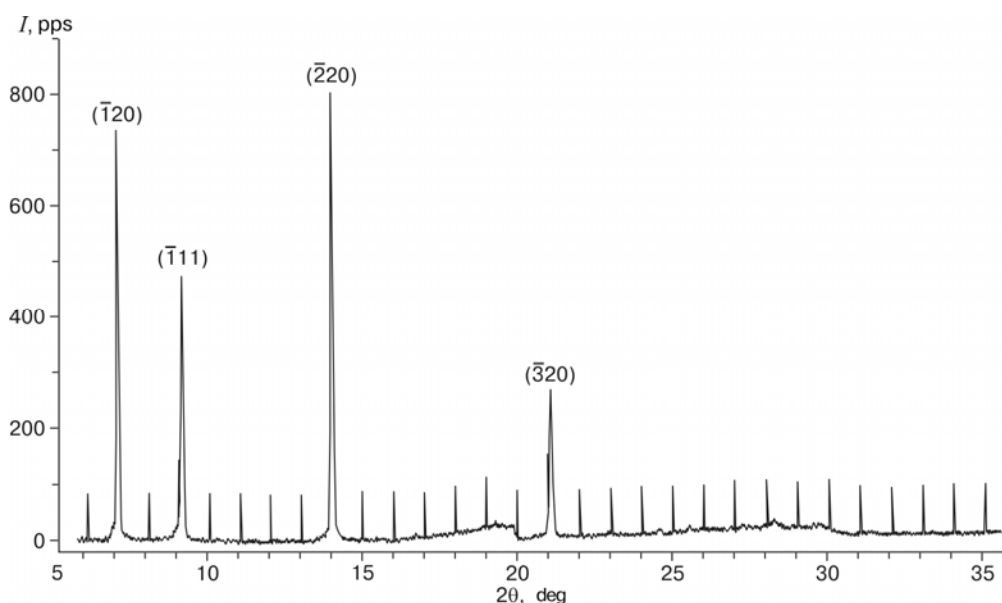


Fig. 2. Diffractogram of the $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$ sample.

140°C – 180°C) on various supports (Si plates, melted quartz, etc.). The supports were kept at room temperature. The rate of application was 10 \AA/s – 30 \AA/s , the final layer thickness $0.5\text{ }\mu\text{m}$ – $1\text{ }\mu\text{m}$.

The samples were applied to the above-indicated supports as uniform and transparent colorless layers (spot diameter $\sim 1\text{ cm}$). The supports were fixed with plasticine in the recess of the quartz cell from the GUR-8 goniometer kit. The plane of the sample was superimposed on the plane of the upper surface of the cell using a glass plate.

X-ray diffraction study was performed on a DRON-RM4 diffractometer ($R = 192\text{ mm}$, CuK_α radiation, Ni filter, scintillation detector with amplitude discrimination) in the 2θ range from 5° to 40° at room temperature. The diffractograms are shown in Figs. 1 and 2. As can be seen, the diffractogram of $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ is represented by reflections from only one

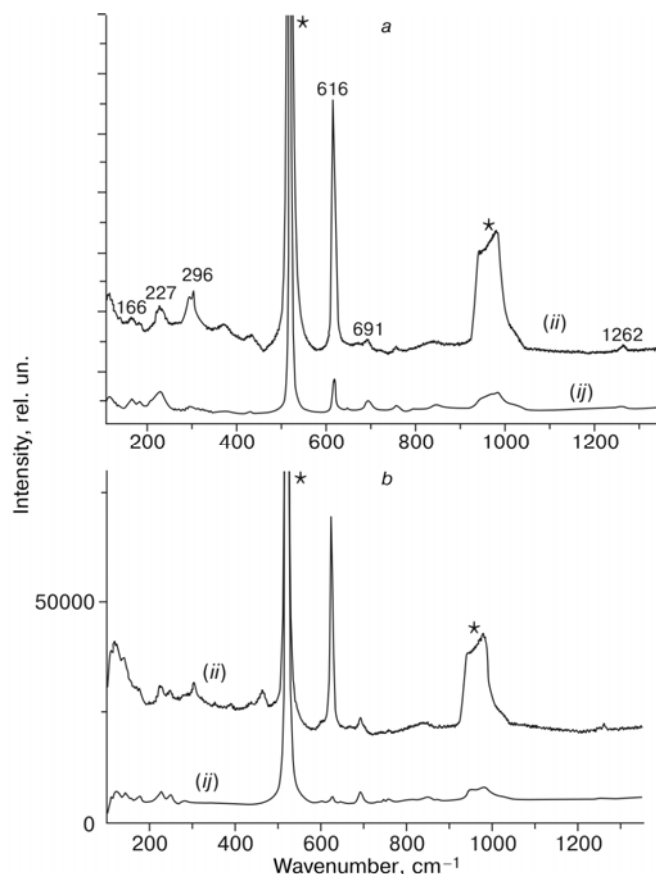


Fig. 3. Polarized Raman spectra of $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ (a) and $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$ (b) films recorded with parallel (ii) and cross (ij) polarizations of incident and scattered light.

crystallographic plane. The diffractogram of $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$ contains reflections from two plane families. This points to the ideal orientation of all crystallites relative to the support in $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ and to doubly composite orientation of crystallites in $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$.

Polarized Raman spectra of the films were obtained on a Triplemate SPEX instrument equipped with a CCD detector and a microscope for recording backscattering spectra excited with a 488 nm argon laser line. The plane of polarization of scattered light was set by a polaroid placed in the inlet channel of the spectrometer.

Figure 3a shows polarized Raman spectra of $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ films recorded with parallel (ii) and cross (ij) polarizations of incident and scattered light. Band assignment and calculations for the vibrational spectra of this compound are reported elsewhere [6]. The intensity ratio I_{ii}/I_{ij} was measured for each type of symmetry in the spectra recorded with parallel (ii) and cross (ij) polarizations of incident and scattered light.

The 296 cm^{-1} and 616 cm^{-1} modes are totally symmetric vibrations, whose intensity decreases abruptly in the (ij) compared to the (ii) spectra (Fig. 3a). For F_{1g} type vibrations in the regions 166 cm^{-1} , 227 cm^{-1} , and 691 cm^{-1} , the intensity ratio I_{ii}/I_{ij} is close to 1. This intensity ratio in the spectra of the film differs from that in the spectra of finely disperse powders or solutions, indicating that the $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ film is oriented. The Raman spectra presented in Fig. 3b indicate that the $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$ film has no ideal orientation of crystallites.

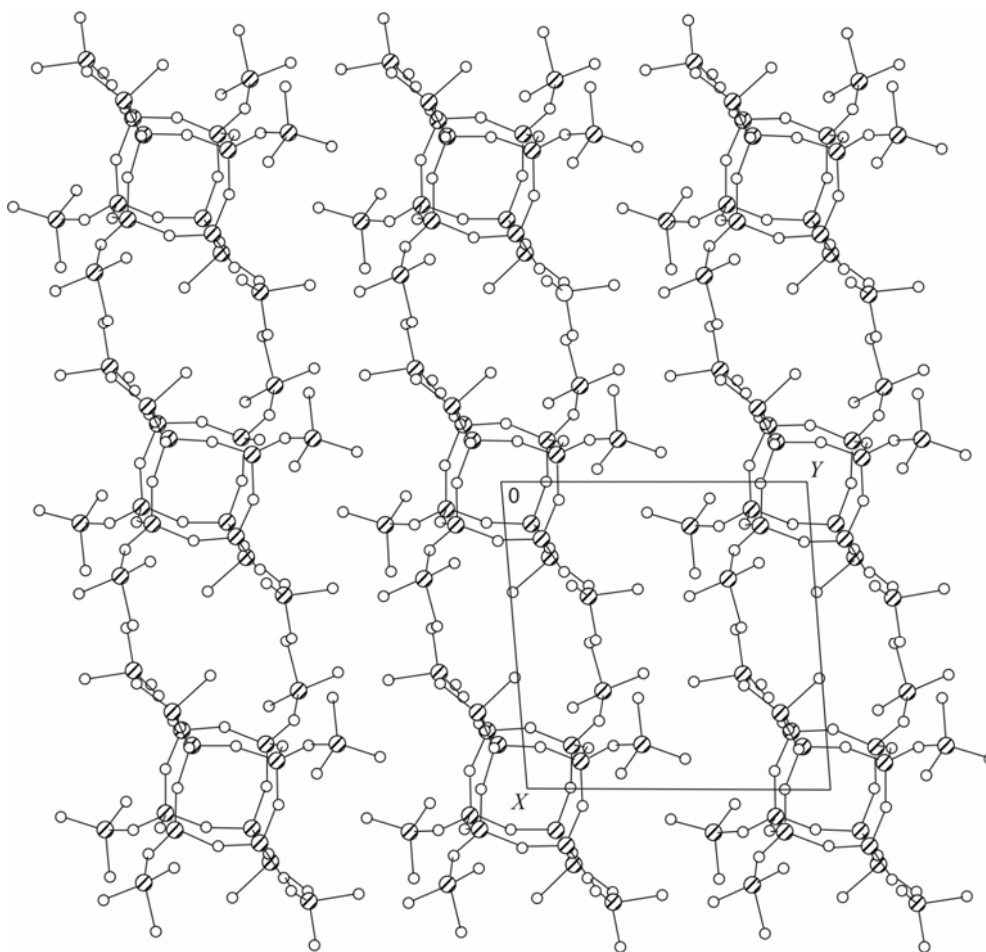


Fig. 4. Arrangement of isolated layers in the crystal structure of $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ in a direction perpendicular to $[001]$.

DISCUSSION OF RESULTS. CONCLUSIONS

The diffractograms were indexed using the data of [6]. Based on the results of this work for $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ ($a = 11.046 \text{ \AA}$, $b = 11.104 \text{ \AA}$, $c = 13.554 \text{ \AA}$, $\alpha = 77.68^\circ$, $\beta = 82.08^\circ$, $\gamma = 84.04^\circ$, space group $P\bar{1}$) we calculated (using the XPOW program) the theoretical diffractogram. Comparing it with the experimental diffractogram, we concluded that $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ crystallites are ideally oriented in the $[001]$ direction. This direction is characterized by the largest interplanar distance $d = 13.15 \text{ \AA}$ of all interplanar distances in the crystal lattice; accordingly, the layers have the largest atomic occupancies.

Based on the established orientation of crystallites and X-ray data [7] for $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ we analyzed the structural organization of the most developed upper faces. For this, in the crystal structure of $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ we isolate a plane the normal to which is close to, or coincident with, the isolated $[001]$ direction. Figure 4 shows a layer parallel to the (001) family of crystallographic planes, the preferred direction being perpendicular to the plane of the drawing. It can readily be seen that the terminal methyl groups are oriented toward the surface of the support. Layer growth occurs by repetition of these layers after the interplanar distance d_{001} .

A comparison of the theoretical and experimental diffractograms for $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$ ($a = 25.338 \text{ \AA}$, $c = 10.907 \text{ \AA}$, space group $R\bar{3}$) indicated that in the sample, the crystallites have two orientations, $[\bar{1}20]$ and $[\bar{1}11]$. Molecular arrangement in the crystal lattice in these directions can be seen in Fig. 5.

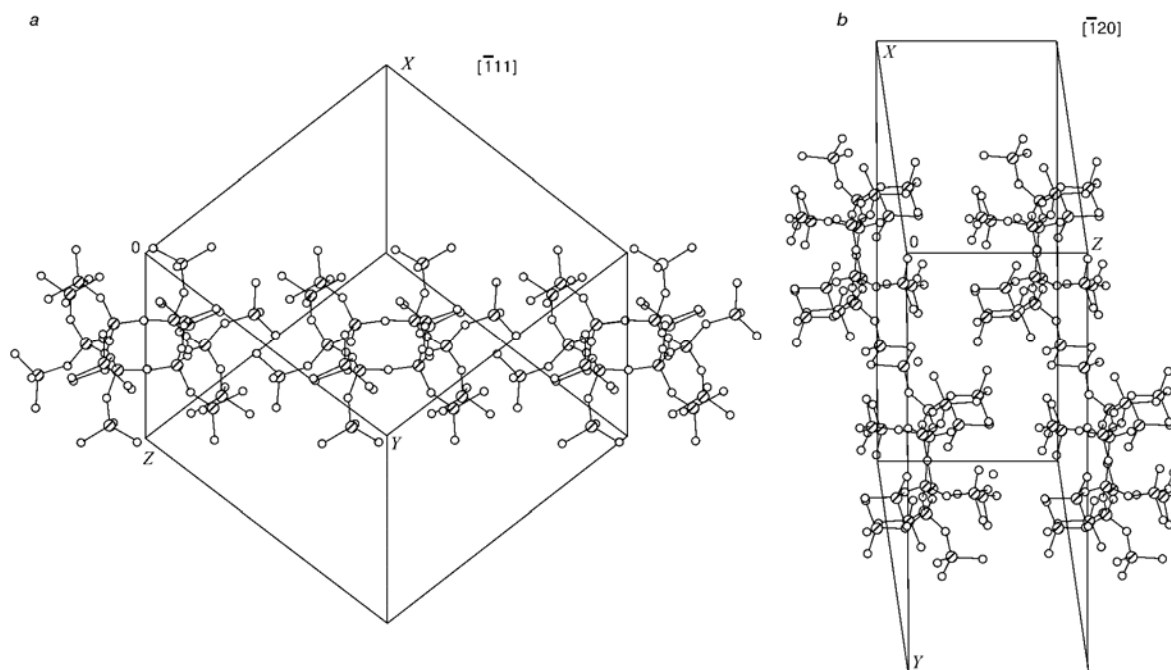


Fig. 5. Organization of the crystal structure of $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$ in $[\bar{1}11]$ and $[\bar{1}20]$ directions.

Raman spectroscopy data confirmed that all crystallites in the $[(\text{CH}_3)_3\text{SiO}]_8(\text{SiO}_{1.5})_8$ sample are oriented in the same direction. Polarized Raman spectra of the $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$ film do not unambiguously reveal the preferable orientation of crystallites in the sample. Indeed, X-ray data indicate that there are two preferable orientations. In the $[\bar{1}20]$ direction, $[(\text{CH}_3)_3\text{SiO}]_{12}(\text{SiO})_6$ molecules lie perpendicularly to the plane of the sample; in the $[\bar{1}11]$ direction, they make with it an angle of 26.4° .

We are grateful to R. G. Mirskov for providing us with the samples.

REFERENCES

1. F. A. Kuznetsov (ed.), *Problems in Electronic Materials Science* [in Russian], Novosibirsk, Nauka (1986).
2. B. A. Trofimov, Yu. D. Tsvetkov, T. V. Leshina, et al., *Fundamental Research Integration Programs* [in Russian], Siberian Branch, Russian Academy of Sciences, Novosibirsk (1998), pp. 468-477.
3. L. V. Litvin, T. A. Gavrilova, and A. E. Plotnikov, *Mikroelektronika*, **26**, No. 6, 451-457 (1997).
4. S. A. Gromilov, D. Yu. Emel'yanov, A. V. Kuzmin, and S. A. Prokhorova, *Zh. Strukt. Khim.*, **44**, No. 4, 766-768 (2003).
5. G. V. Kalmychkov, V. I. Rakhlin, B. A. Gostevskii, et al., *Dokl. Akad. Nauk*, **362**, No. 3, 359-361 (1998).
6. B. A. Kolesov, T. N. Martynova, and T. I. Chupakhina, *Zh. Strukt. Khim.*, **29**, No. 6, 77-81 (1988).
7. K. Larson, *Arkiv Kemi*, **16**, 203 (1960).
8. N. Auner, B. Ziemer, B. Herrschaft, et al., *Eur. J. Inorg. Chem.*, 1087-1094 (1999).

Copyright of Journal of Structural Chemistry is the property of Kluwer Academic Publishing / Academic and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.