

SYNTHESIS OF PRECERAMIC ORGANOMAGNESIUM OXANEALUMOXANE SILOXANES

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Organomagnesiumoxane alumoxane siloxane oligomers with different Al:Mg and Al:Si molar ratio have been synthesized through ethylacetoacetate alkoxyhydroxyalumoxane oligomers co-condensation with magnesium acetylacetonate and oligoethoxysiloxanes in organic solvents (alcohol, toluene) at a temperature of 70 – 100 °C within 3 – 6 hours with the following solvent distillation. The physicochemical properties of the synthesized oligomers were studied. It is shown that with a molar ratio of Al:Mg \approx 2 and Al:Si \approx 1, oligomers have fiber-forming properties. The process of thermotransformation of organomagnesiumoxane alumoxane siloxanes into ceramic phases is investigated. It is found that pyrolysis results in the formation of multicomponent ceramics based on magnesium, aluminum, and silicon oxides, in particular, ceramics with a composition close to that of cordierite $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) or a mixed composition: magnesium-aluminum spinel and mullite.

Therefore, the synthesized organomagnesiumoxane alumoxane siloxanes are preceramic oligomers and can be used as precursors for the preparation of various components (binders, impregnating compositions, fibers, ceramic powders) of high-purity ceramic composites based on magnesium, aluminum and silicon oxides.

Keywords: organomagnesiumoxane alumoxane siloxane, oligomers, synthesis, thermal transformation, cordierite, spinel, mullite

1. Introduction

Among the various ceramic materials, three-component ceramics based on magnesium, aluminum and silicon oxides, in particular mixed spinel-mullite composition ($(\text{MgAl}_2\text{O}_4 + 3\text{Al}_2\text{O}_3 - \text{SiO}_2)$ or cordierite - $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$, occupy a special position. Such materials have a low coefficient of thermal expansion and high heat resistance, which allows them to be used in various fields of engineering, for example, as a thermostable carrier of catalytic systems, lining plates in thermal devices operating up to 1400 ° C, etc. In addition, such materials have high resistivity and low dielectric constant [1-3].

According to conventional technology, cordierite is produced from oxides, which requires high temperatures for the synthesis of ceramic powders (above 1250 °C) and a narrow sintering range (1520 °C). This technology does not allow obtaining dense fine crystalline ceramics, therefore, expensive finely dispersed and ultrafine powders are used, which limits their widespread practical application [4, 5].

In addition, ceramic cordierite composition can be obtained by sol-gel technology [6, 7].

However, the most promising approach to preparing advanced ceramic materials with desired properties is the use of pre-ceramic organoelement oligomers as initial compounds. The preparation of ceramics through such oligomers makes it possible to control the composition and structure of ceramic compositions at all levels (microcrystalline, nanostructured or amorphous), which is impossible by any other known methods [8, 9].

We are the first to synthesize hydrolytically stable and soluble in organic solvents organomagnesiumoxane alumoxane siloxane oligomers, the thermal transformation of which leads to the formation of highly pure fine crystalline multicomponent ceramics based on aluminum, magnesium and silicon oxides [10].

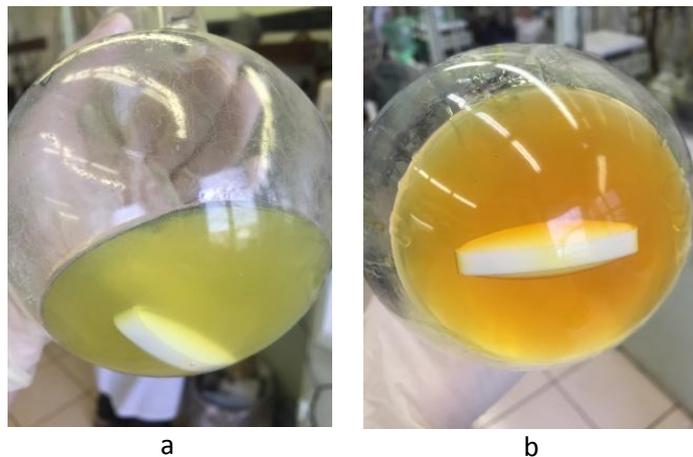
2. Methods

2.1 General Procedure for the Preparation of Organomagnesiumoxane Alumoxane Siloxane

The synthesis is performed as follows: to a solution of organoalumoxane (ethyl acetoacetate ethoxyhydroxyalumoxane) oligomer [11] in an organic solvent (ethyl alcohol, toluene), a predetermined amount of $(\text{acac})_2\text{Mg}$ is added batch wise for an hour under continuous stirring and a temperature of 60-100 °C. Next, the reaction mass is held under continuous stirring for 6 hours at 70-100 °C. Then ethyl silicate-40 is dosed for 1.5 hours under stirring at a temperature of 60-70 °C. It is held under stirring and a temperature of 60-100 °C for 7 hours. The solvent is distilled at atmospheric pressure. Light yellow viscous mass is produced (**Fig. 1a**). The product is dried at a residual pressure (2-4 mm Hg) under heating to 150 °C for 3 hours. An orange glassy oligomer is obtained (**Fig. 1b**). Samples of synthesized oligomers are taken for physicochemical studies.

Fig. 1 Oligomer appearance after solvent distillation:

a – at atmospheric pressure; b – at residual pressure of 2-4 mm Hg



The synthesized samples of organomagnesiumoxane alumoxane siloxanes were studied by the following methods: NMR, IR spectroscopy, SEM, TGA, X-ray phase analysis, elemental analysis.

IR spectra were recorded on «Nicolet» iS50R in the range of 400–4000 cm^{-1} by a Smart iTR single attenuated total reflection (ATR) multipurpose accessory (diamond crystal).

^1H , ^{13}C , ^{17}O , ^{27}Al , ^{29}Si NMR spectra of organomagnesiumoxane alumoxane siloxanes were determined for solutions in deuteriochloroform - CDCl_3 by AVANCE-600 (BRUKER).

The proton operating frequency is 600.13 MHz, the external standard is $[\text{Al}(\text{H}_2\text{O})_6]_3^+$, and the internal standard is tetramethylsilane.

Thermal gravimetric analysis (TGA) was conducted on TGA/SDTA 851 Mettler Toledo at the rate of 10 deg/min in air up to 1100 °C.

Organomagnesiumoxane alumoxane siloxanes pyrolysis was conducted in an electric resistance furnace SNOL 12/16 at 750 °C, 900 °C and 1500 °C in air, $x\text{MgO}\cdot y\text{Al}_2\text{O}_3\cdot z\text{SiO}_2$ ceramic samples were produced.

The morphology of the surface and elemental composition were studied using FEI Quanta 250 and Philips SEM505 scanning electron microscopes, the latter equipped with an SAPHIRE Si (Li) energy dispersive detector type SEM10 and Micro Capture SEM3.0M image capture system.

Elemental mapping with overlay elements on the same map was carried out on a scanning electron microscope Tescan Mira LMU, equipped with an energy dispersive X-ray spectrometer INCA X_MAX-50 Oxford Instruments. Due to the good dielectric properties of the synthesized oligomers, they were studied in a low vacuum mode (nitrogen, vapor pressure 30 Pa). Ceramic

samples were analyzed in a high vacuum mode without sputtering, using low values of probe currents and accelerating voltages (up to 5-10 kV).

Phase compositions were determined by X-ray diffraction at room temperature on a Shimadzu XRD-6000 vertical X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda_{\text{K}\alpha\text{cp}}=(2\lambda_{\text{K}\alpha1}+\lambda_{\text{K}\alpha2})/3=1.54178$ [Å]). The crystalline and amorphous phases present were identified using ICDD PDF Release 2003 data.

The aluminum content was determined by trilonometry. Magnesium content was determined on the Spectr AA 240 FS KBr atomic absorption spectrophotometer. The silicon content was determined spectrophotometrically as a silicon-molybdenum complex at a wavelength of 400 nm. Carbon and hydrogen contents were determined gravimetrically by burning a weighed sample in oxygen flow on Eurovector EA3000 gas analyser .

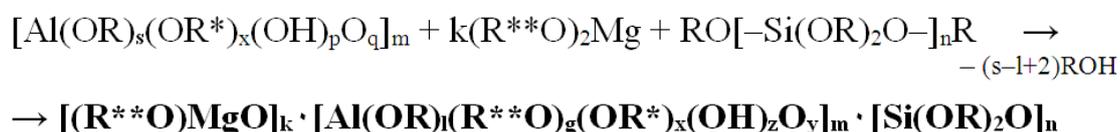
The content of hydroxyl groups in the organoalumoxanes and organomagnesiumoxane alumoxanes was found by a gasometric method.

3. Results and discussion

We were faced with the task of synthesizing pre-ceramic oligomers, the pyrolysis of which allows the preparation of cordierite ceramics $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$. That is why organomagnesiumoxane alumoxane siloxanes with molar ratio $\text{Al}:\text{Mg} \approx 2$ and $\text{Al}:\text{Si} \approx 0.8$ were synthesized.

Organomagnesiumoxane alumoxane siloxane oligomers were synthesized through ethylacetoacetate alkoxyhydroxyalumoxane oligomers co-condensation with magnesium acetylacetonate and oligoethoxysiloxanes in organic solvents (alcohol, toluene) according to scheme (1):

Scheme 1. Synthesis of Organomagnesiumoxane Alumoxane Siloxane



Where, $k \approx 2$, $m = 4-5$, $n \approx 5-6$;

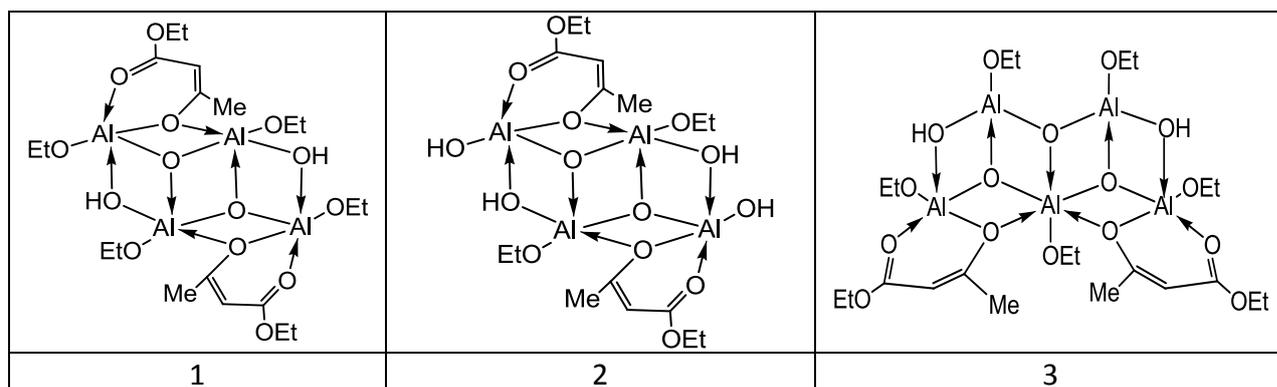
$s+x+2q+p=3$; $k/m+1+g+x+2y+z=3$;

$\text{R} - \text{C}_2\text{H}_5$; $\text{R}^* - \text{C}(\text{CH}_3)=\text{CHC}(\text{O})\text{OC}_2\text{H}_5$;

$\text{R}^{**} - \text{C}(\text{CH}_3)=\text{CHC}(\text{O})\text{CH}_3$.

It was previously shown that chelated alkoxyalumoxanes were a mixture of oligomers of different molecular weights (mainly Mn = 600 – 900). The probable structure of the main oligomeric fragments of chelated alkoxyalumoxanes was proposed (**Fig. 2**) [11, 12].

Fig. 2 Probable structures of the main oligomeric fragments of ethyl acetoacetate ethoxyhydroxyalumoxanes



Taking into account the probable structure (Fig. 2) and elemental analysis data, the basic empirical formulas of ethyl acetoacetate alkoxyhydroxyalumoxanes used in this work were calculated (**Table 1**).

Table 1. The results of elemental and thermogravimetric analyses of ethyl acetoacetate ethoxyhydroxyalumoxane and empirical formulas of the main oligomeric fragments

| No | | Chemical composition, | | | | C wt %(TGA) |
|----|---|-----------------------|------|-------|-------|--------------------------------|
| | | wt % | | | | |
| | | C | H | Al | OH | Al ₂ O ₃ |
| | Initial ethyl acetoacetate ethoxyhydroxyalumoxane | | | | | |
| | | 38.08 | 6.78 | 18.52 | 6.20 | 35.09 |
| | Calculated empirical formulas | | | | | |
| 1 | C ₂₀ H ₄₀ O ₁₄ Al ₄ | 39.22 | 6.54 | 17.65 | 5.56 | 33.33 |
| 2 | C ₁₆ H ₃₂ O ₁₄ Al ₄ | 34.53 | 5.76 | 19.42 | 12.23 | 36.69 |
| 3 | C ₂₂ H ₄₅ O ₁₆ Al ₅ | 37.71 | 6.43 | 19.29 | 4.86 | 36.43 |

At the first stage, ethyl acetoacetate ethoxyhydroxyalumoxane is co-condensed with magnesium acetylacetonate.

It was previously found that the interaction of ethyl acetoacetate alkoxyhydroxyalumoxanes [12] with magnesium acetylacetonate proceeds primarily along

hydroxyl groups with the formation of Mg–O–Al bonds and the release of acetylacetone. The resulting acetylacetone reacts with ethoxy groups of ethyl acetoacetate ethoxyhydroxyalumoxanes, C₂H₅O– are partially replaced by –OC (CH₃) = CHC (O) CH₃ to produce alcohol, which is confirmed by the absence of the distillate obtained after the synthesis of organomagnesiumoxane alumoxane in toluene in ¹³C NMR spectra, ¹³C signals typical for acetylacetone functional groups. We found that organomagnesiumoxane alumoxanes are alumoxanes with organomagnesiumoxane groupings in the side chain at aluminum. Therefore, at the interaction of ethyl acetoacetate alkoxyhydroxyalumoxanes and (acac)₂Mg, opening of alumoxane bonds is not observed [12].

At the second stage, ethyl silicate-40 is added to the reaction mixture, it reacts with the hydroxyl groups of organomagnesiumoxane alumoxane and unreacted organoalumoxane. Glassy yellow-orange oligomers are obtained (Fig. 1b) with a given molar ratio of Al:Mg ≈ 2 and Al:Si ≈ 0.8 (Tables 2,3).

X-ray amorphism of organomagnesiumoxane alumoxane siloxanes does not allow to determine their real structure, however, the presence of the given structural units in the general formula is confirmed by the data of ¹H, ¹³C, ²⁷Al, ²⁹Si NMR, IR spectroscopy, TGA, SEM and elemental analysis.

Table 2 presents experimentally found values according to elemental analysis and TGA.

Table 2. The results of elemental and thermal gravimetric analysis of the synthesized organomagnesiumoxane alumoxane siloxanes.

| № | Molar ratio | | Chemical composition of organomagnesiumoxane alumoxane | | | | | | C wt % (TGA) |
|---|-------------|-------|--|-----|------|------|-------|------|--------------|
| | Al:Mg | Al:Si | Found, wt % | | | | | | |
| | | | C | H | Al | Mg | Si | OH | |
| 1 | ≈ 2 | ≈ 0.8 | 34.8 | 5.3 | 8.16 | 3.63 | 10.58 | 1.54 | 43.90 |
| 2 | ≈ 2 | ≈ 0.8 | 36.2 | 5.2 | 7.39 | 3.30 | 9.58 | 1.75 | 39.84 |
| 3 | ≈ 2 | ≈ 0.8 | 40.4 | 5.5 | 5.82 | 2.55 | 7.55 | 1.67 | 34.07 |

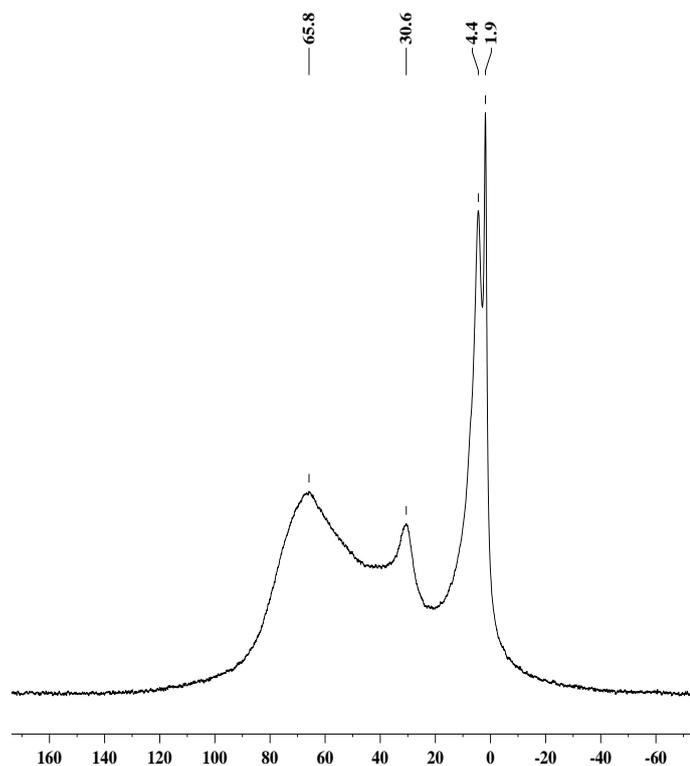
The probable empirical formulas presented in Table 3 are confirmed by a good agreement between the calculated elemental composition values for the empirical formulas and the experimentally found values based on elemental analysis data (Table 2).

Table 3. Empirical formulas of main oligomeric fragments of organomagnesiumoxane alumoxane siloxanes with Al:Mg \approx 2, Al:Si \approx 0.8.

| Empirical formulas of main oligomeric fragments of organomagnesiumoxane alumoxane siloxanes | Chemical composition of organomagnesiumoxane alumoxane siloxane, wt % | | | | | | C wt % |
|---|---|------|------|------|-------|------|--------|
| | C | H | Al | Mg | Si | OH | |
| $C_{44}H_{87}O_{30}Al_4Mg_2Si_5$ | 37.96 | 6.25 | 7.76 | 3.45 | 10.06 | 0.00 | 41.98 |
| $C_{42}H_{83}O_{30}Al_4Mg_2Si_5$ | 36.98 | 6.09 | 7.92 | 3.52 | 10.27 | 1.25 | 42.85 |
| $C_{47}H_{89}O_{31}Al_4Mg_2Si_5$ | 39.03 | 6.16 | 7.47 | 3.32 | 9.69 | 0.00 | 40.41 |
| $C_{46}H_{93}O_{33}Al_4Mg_2Si_6$ | 36.87 | 6.21 | 7.21 | 3.21 | 11.22 | 1.14 | 43.02 |
| $C_{51}H_{99}O_{34}Al_4Mg_2Si_6$ | 38.76 | 6.27 | 6.84 | 3.04 | 10.64 | 0.00 | 40.78 |
| $C_{42}H_{82}O_{30}Al_5Mg_2Si_5$ | 36.29 | 5.90 | 9.72 | 3.46 | 10.08 | 0.00 | 45.72 |
| $C_{56}H_{107}O_{38}Al_5Mg_2Si_6$ | 38.67 | 6.16 | 7.77 | 2.76 | 9.67 | 0.98 | 39.99 |
| $C_{46}H_{92}O_{33}Al_5Mg_2Si_6$ | 36.24 | 6.04 | 8.86 | 3.15 | 11.03 | 0.00 | 45.63 |
| $C_{53}H_{105}O_{37}Al_5Mg_2Si_6$ | 37.77 | 6.24 | 8.02 | 2.85 | 9.98 | 1.01 | 41.27 |

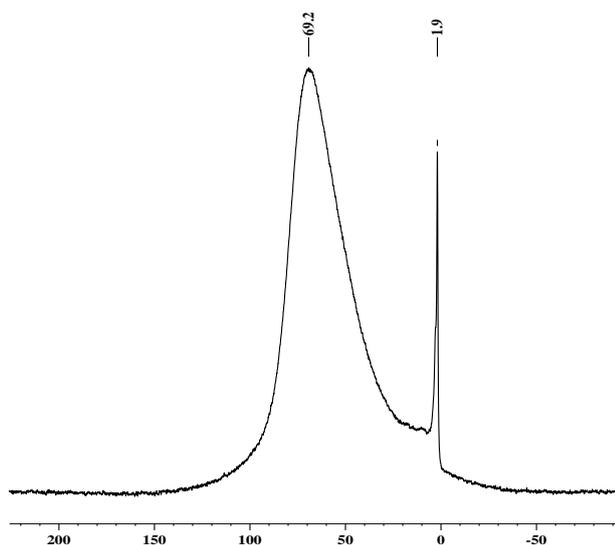
In ^{27}Al NMR spectra (600.13 MHz, $CDCl_3$) of the concentrated oligomer solutions in $CDCl_3$ three types of signals of almost the same intensity are recorded: 70.0–80.0 ppm (4-coordinated), 30.0–45.0 (5-coordinated), 1.8–7.5 ppm (6-coordinated) (**Fig. 3**).

Fig. 3 ^{27}Al NMR spectra of the concentrated solutions of organomagnesiumoxane alumoxane siloxanes



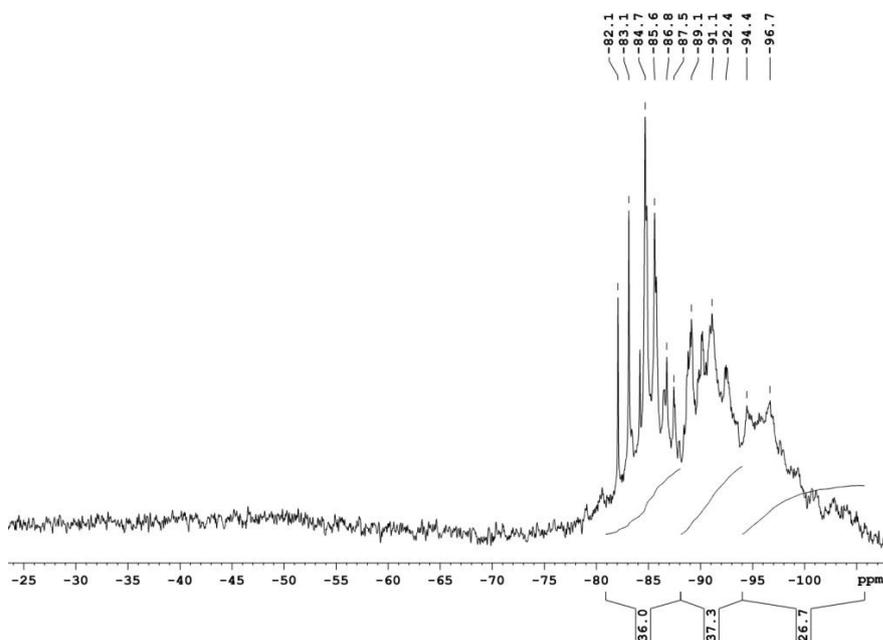
In ^{27}Al NMR spectra of the diluted solutions in CDCl_3 very intensive signal of 40.0–90.0 ppm (4-coordinated) and weak signal of 0.0–5.0 ppm (6-coordinated) are observed. This, apparently, is related to a rupture of coordination bonds between the aluminum atom and carbonyl groups (**Fig. 4**).

Fig. 4 ^{27}Al NMR spectra of diluted solutions of organomagnesiumoxane alumoxane siloxanes



The ^{29}Si NMR spectra contain a number of signals characteristic of silicate glass in the region from (-) 100 to (-) 80 ppm. In all spectra, three groups of signals at (-)82-(-)89, (-)90-(-)94, (-)96-(-)100 ppm, corresponding to $(\text{EtO})_3\text{SiO}$, $(\text{EtO})_2\text{SiO}_2$ и SiO_4 groups can be identified (**Fig. 5**).

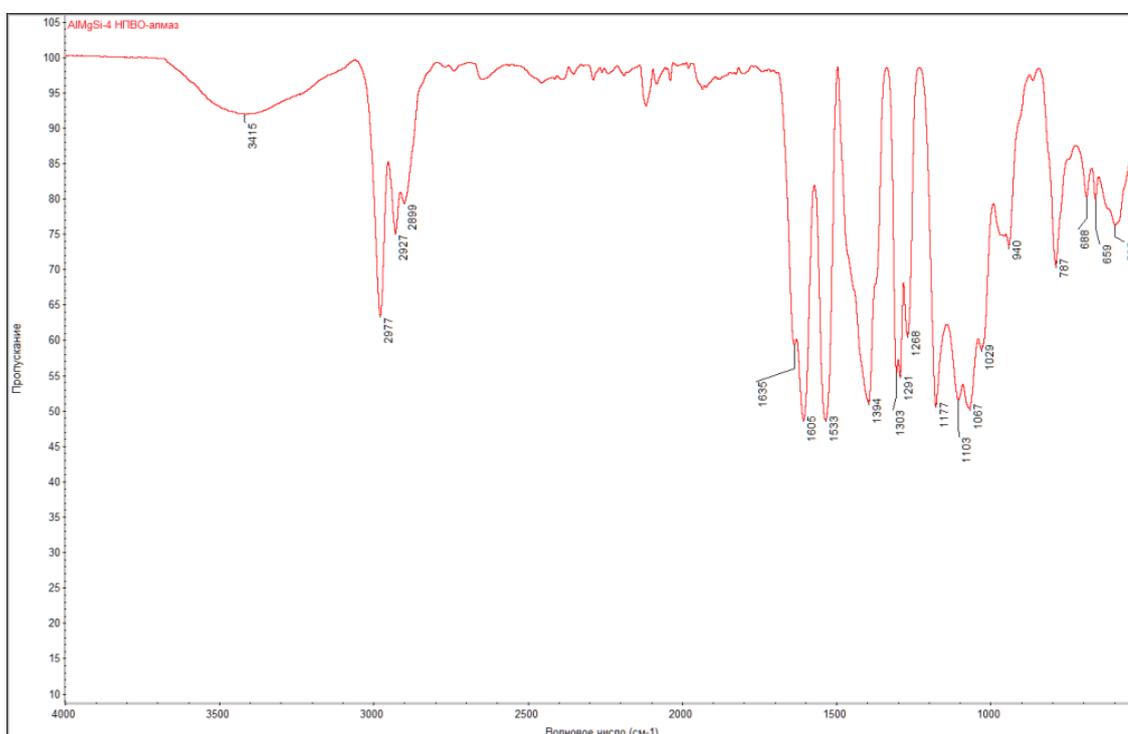
Fig. 5 ^{29}Si NMR spectra of organomagnesiumoxane alumoxane siloxanes



In ^1H , ^{13}C NMR spectra of organomagnesiumoxane alumoxane siloxanes the following signals are recorded: ^1H -NMR (600,13 MHz, CDCl_3) broad 0.7-1.5 ppm CH_3 ($\text{C}_2\text{H}_5\text{O}-$); broad 1.5-2.4 ppm CH_3 of acetoxy group; broad 3,5-4,5 ppm CH_2 ($\text{C}_2\text{H}_5\text{O}-$); broad 4,5-5.6 ppm CH ($\text{CH}=\text{}$); ^{13}C -NMR (600,13 MHz, CDCl_3) broad 13-20 ppm CH_3 ($\text{C}_2\text{H}_5\text{O}-$); broad 24-27 ppm CH_3 of acetoxy group; broad 57-61 ppm CH_2 ($\text{C}_2\text{H}_5\text{O}-$); broad 99-103 ppm CH ($\text{CH}=\text{}$); broad 170-175 ppm $\text{CO}(\text{O})$; broad 184-195 ppm $\text{C}=\text{O}$.

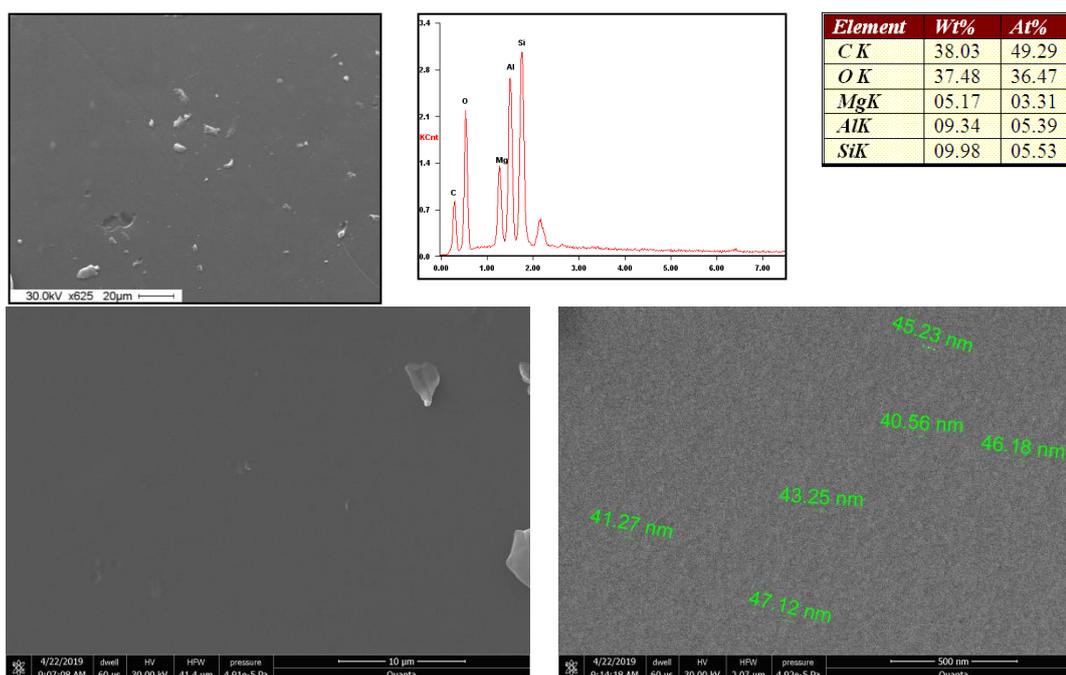
The interpretation of the absorption bands of organomagnesiumoxane alumoxane siloxanes observed in the IR spectrum (**Fig. 6**) is as follows: IR (cm^{-1}), 595 $\nu(\text{Mg}-\text{O}-\text{Al})$, 659, 688 $\nu(\text{Mg}-\text{O}; \text{Al}-\text{O}; \text{Si}-\text{O})$, 863 $\nu(\text{Al}-\text{O}-\text{Al})$, 940 $\nu(\text{Mg}-\text{O})$, 967 $\nu(\text{Al}-\text{O}_4; \text{Si}-\text{O})$, 1030, 1071, 1101, 1176 $\nu(\text{Mg}-\text{O}-\text{C}; \text{Al}-\text{O}-\text{C}; \text{Si}-\text{O}-\text{C})$, 787, 1268, 1291, 1303, 1398 $\delta\{\text{CH}, \text{C}(\text{CH}_3)\}$ and $\nu(\text{C}-\text{O})$, 1533 $\nu(\text{C}=\text{C})$, 1602 $\nu(\text{C}=\text{O}$ from $[\text{CH}_3(\text{O})\text{CCH}=\text{C}(\text{CH}_3)\text{O}]$), 1635 $\nu(\text{C}=\text{O}$, bonded by coordination bond with Al atom), 2899, 2927, 2977 $\nu(\text{CH})$, 3415 $\nu(\text{OH})$; it somewhat difficult due to the similarity of the spectra of the starting organoalumoxanes, $(\text{acac})_2\text{Mg}$ and ethylsilicate-40.

Fig. 6 IR of organomagnesiumoxane alumoxane siloxanes



The surface morphology and elemental composition of organomagnesium oxane alumoxane siloxanes are shown in **Fig. 7**.

Fig. 7 SEM micrographs and X-ray elemental analysis of organomagnesiumoxane alumoxane siloxanes



It should be emphasized that organomagnesiumoxane alumoxane siloxanes may have fiber-forming properties (characteristic temperatures [13] are presented in **Table 4**. **Figure 8** presents photos of manually produced fibers.

Table 4. Characteristic temperatures* of fiber-forming organomagnesiumoxane alumoxane siloxanes

| Oligomer Table 2 | T ₁ , °C | T ₂ , °C | T ₃ , °C |
|---------------------|---------------------|---------------------|---------------------|
| 3 | 74 | 79-96 | 101 |

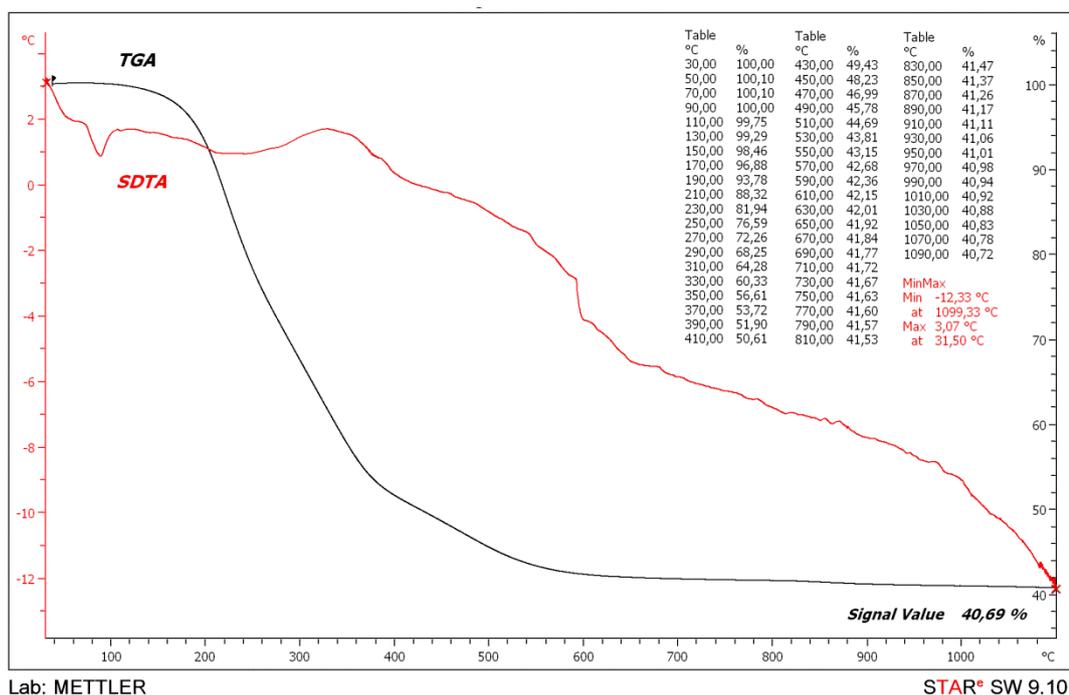
* T₁ -softening point, T₂ – fiberization temperature, T₃ – melting or solidifying points

Fig.8 A picture of manually produced fibers



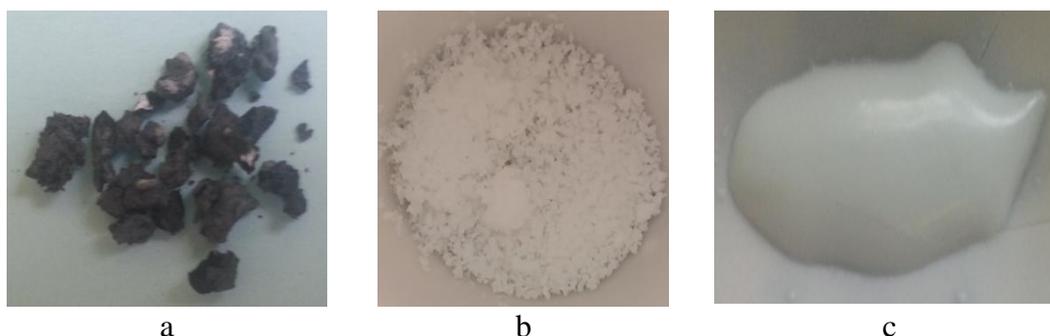
Figure 9 presents a typical thermogram of organomagnesiumoxane alumoxane siloxanes. The TGA curve shows that the oligomer is stable when heated to a temperature of ≈ 200 °C. The main weight loss occurs in the temperature range of 200–500 °C (the remainder is about 45 weight %). Further, the removal of residual hydroxyl groups in the form of H₂O vapor is observed, the ceramic residue is 40.69 wt %, which corresponds to the theoretical values (**Table 3**). This suggests that the thermal transformation of organomagnesiumoxane alumoxane siloxanes results in the formation of ceramics of the desired composition – 2MgO·2Al₂O₃·5SiO₂.

Fig. 9 TGA и SDTA curves



We investigated a ceramization process of organomagnesiumoxane alumoxane siloxanes in air at temperatures of 800, 1300 and 1500 °C (**Fig. 10**).

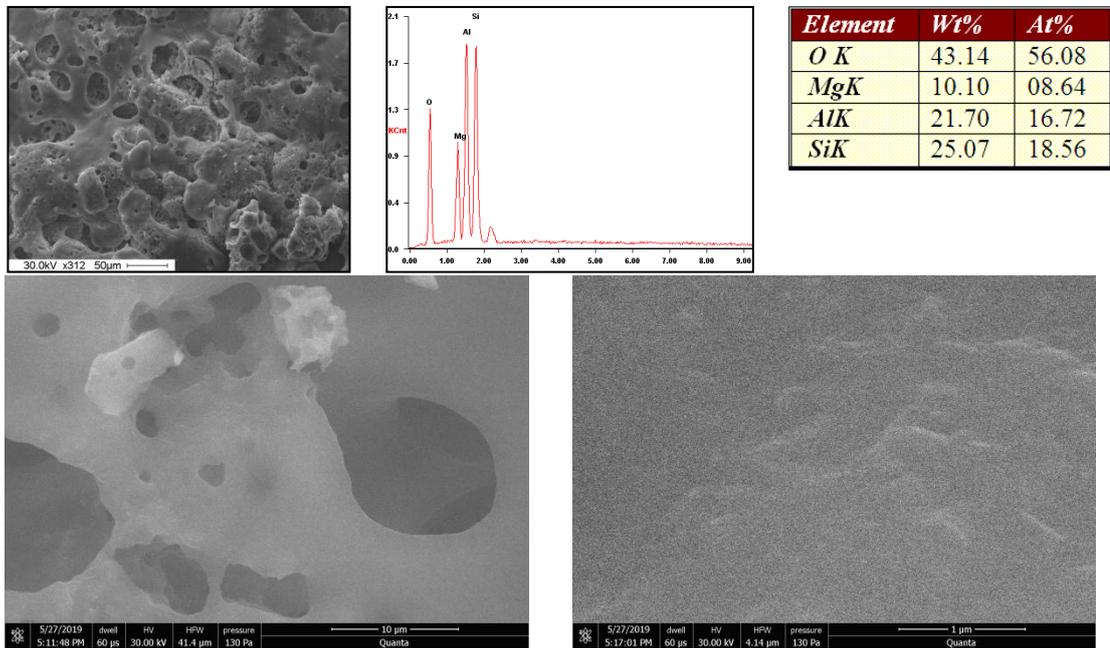
Fig. 10 Samples of ceramics: a – 800 °C; b – 1300 °C; c – 1500 °C



Obtained ceramics samples were studied by SEM and X-ray phase analyses (**Fig. 10**).

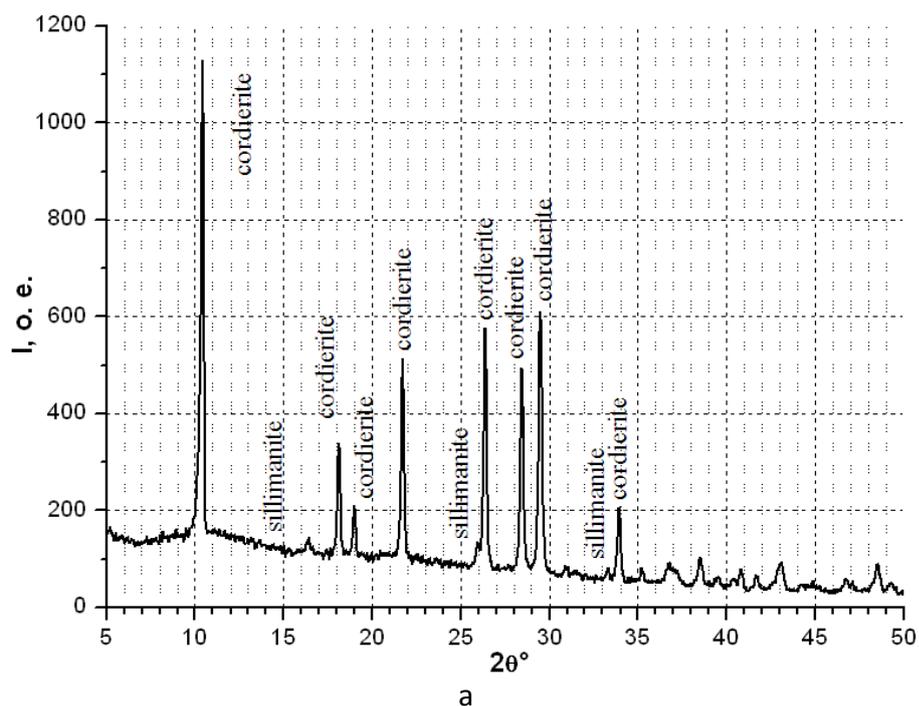
Surface morphology and elemental composition of the ceramics at 1300 °C are presented in **Fig. 11**.

Fig. 11 SEM micrographs and X-ray elemental analysis of ceramics sample at 1300 °C



It is shown by diffractometry that after the pyrolysis of organomagnesiumoxane alumoxane siloxanes at 1300 - 1500 °C, ceramic phases: cordierite, sillimanite, mullite, sapphire are formed (**Fig. 12**).

Fig. 12 Diffractograms of ceramics sample (a) and ceramic fibers (b)



Conclusion

Hydrolytically stable in air, ceramic-forming organomagnesiumoxane alumoxane siloxanes soluble in organic solvents were synthesized, they compound may have fiber-forming properties. The process of thermal transformation of organomagnesiumoxane alumoxane siloxanes into ceramic phases was studied. It was found that the pyrolysis of organomagnesiumoxane alumoxane siloxanes at a temperature of 1300 - 1500 °C results in the formation of cordierite, sillimanite, mullite, sapphirine.

Therefore, the synthesized organomagnesiumoxane alumoxane siloxanes are preceramic oligomers and can be used as precursors for the preparation of various components (binders, impregnating compositions, fibers, ceramic powders) of high-purity ceramic composites based on magnesium, aluminum and silicon oxides.

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