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molecules
MDPI

SYNTHESIS OF PRECERAMIC ORGANOMAGNESIUM OXANEALUMOXANE SILOXANES

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Introduction

Among the various ceramic materials, three-component ceramics based on magnesium, aluminum and silicon oxides, in particular mixed spinel-mullite composition ($MgAl_2O_4 + 3Al_2O_3$ SiO_2) or cordierite - $Mg_2Al_4Si_5O_{18}$, occupy a special position.

- low coefficient of thermal expansion
- high resistivity
- low dielectric constant

Such materials to be used in various fields of engineering, for example, as a thermo stable carrier of catalytic systems, lining plates in thermal devices operating up to 1400 ° C, etc.

Introduction

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.

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 .

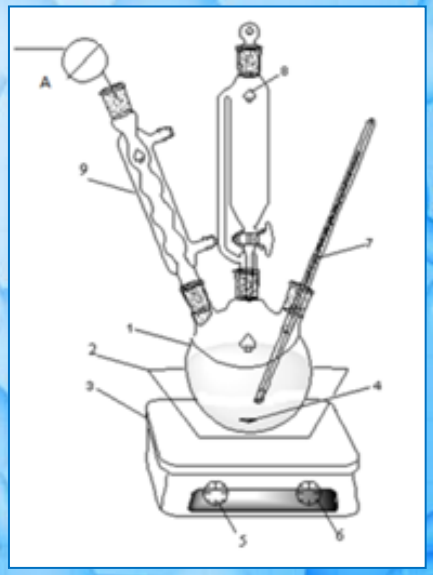
Methods

The synthesis is performed as follows: to a solution of organoalumoxane (ethyl acetoacetate ethoxyhydroxyalumoxane) oligomer in an organic solvent (ethyl alcohol, toluene), a predetermined amount of $(acac)_2Mg$ is added batch wise for an hour under continuous stirring and a temperature of 60-100 ºC. Next, the reaction mass is held under continuous stirring for 6 hours at 70-100 ºC. Then ethyl silicate-40 is dosed for 1.5 hours under stirring at a temperature of 60-70 ºC. It is held under stirring and a temperature of 60-100 ºC 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 ºC for 3 hours. An orange glassy oligomer is obtained

Oligomer appearance after solvent distillation:
a – at atmospheric pressure; b – at residual pressure of 2-4 mm Hg

a

b



Results and discussion

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

Scheme 1. ***Synthesis of Organomagnesiumoxane Alumoxane Siloxane***

$$[Al(OR)_s(OR^*)_x(OH)_pO_q]_m + k(R^{**}O)_2Mg + RO[-Si(OR)_2O-]_nR \rightarrow$$

$$- (s-l+2)ROH$$

$$\rightarrow [(R^{**}O)MgO]_k \; [Al(OR)_l(R^{**}O)_g(OR^*)_x(OH)_zO_y]_m \; [Si(OR)_2O]_n$$

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

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

$R - C_2H_5$; $R^* - C(CH_3)=CHC(O)OC_2H_5$;

$R^{**} - C(CH_3)=CHC(O)CH_3$.

Results and discussion

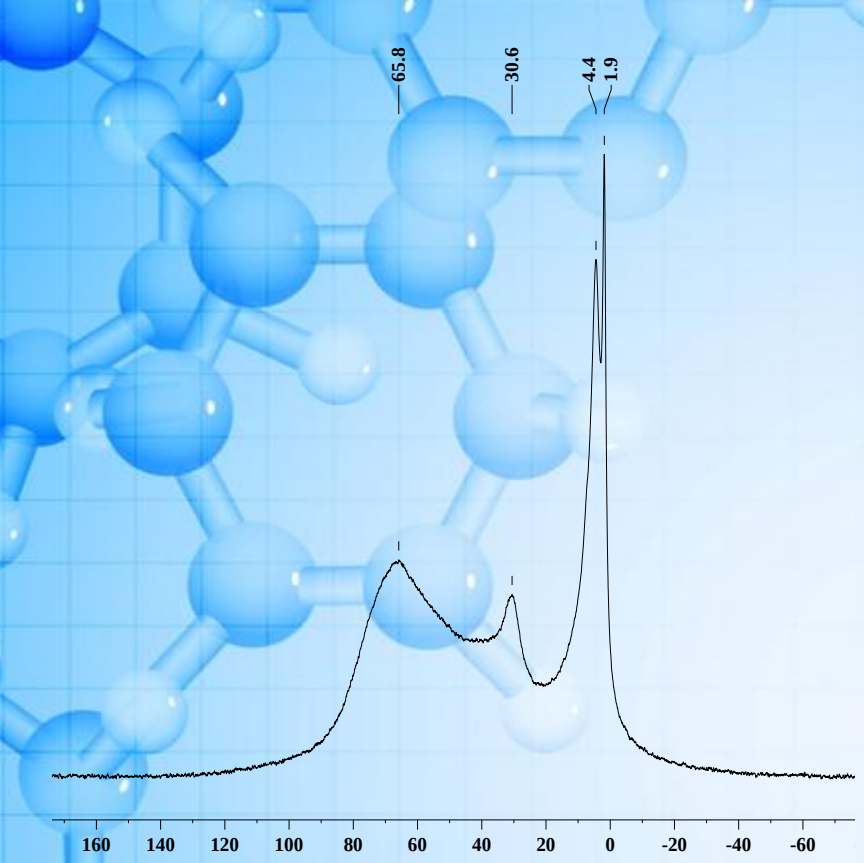
The results of elemental and thermal gravimetric analysis of the synthesized organomagnesiumoxane alumoxane siloxanes

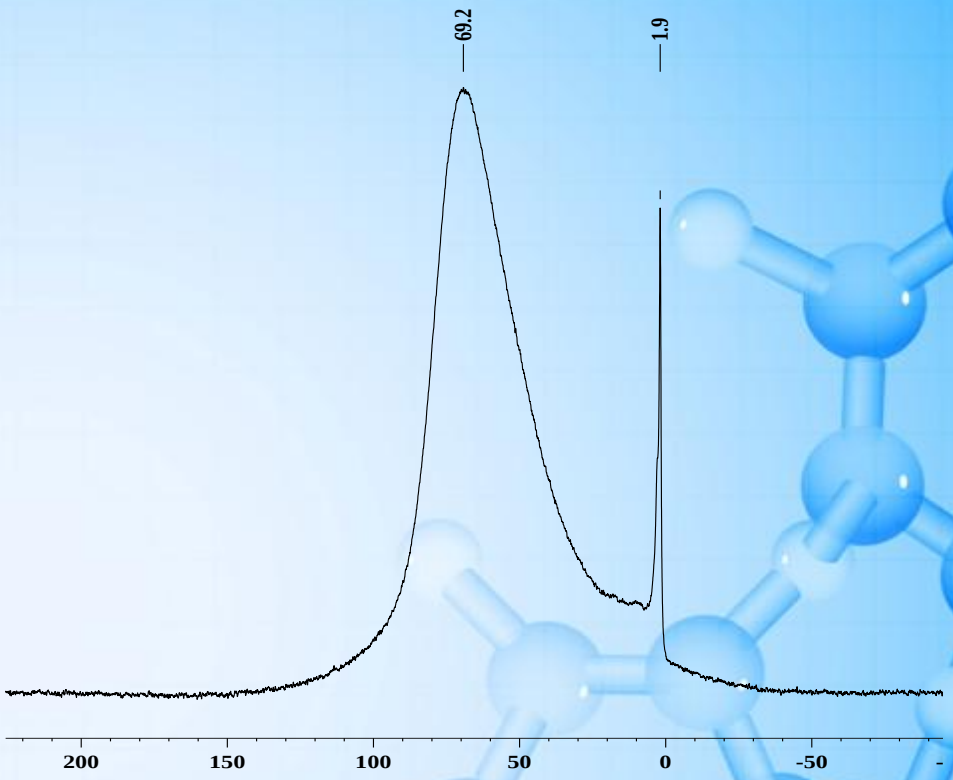
№	Molar ratio		Chemical composition of organomagnesiumoxane alumoxane Found, wt %						C wt % (TGA)
	Al:Mg	Al:Si	C	H	Al	Mg	Si	OH	
1	≈ 2	≈ 0.8	34.8	5.3	8.16	3.63	10.58	1.54	43.90
2	≈ 2	≈ 0.8	36.2	5.2	7.39	3.30	9.58	1.75	39.84
3	≈ 2	≈ 0.8	40.4	5.5	5.82	2.55	7.55	1.67	34.07

Empirical formulas of main oligomeric fragments of organomagnesiumoxane alumoxane siloxanes with Al:Mg ≈ 2, Al:Si ≈ 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

Results and discussion



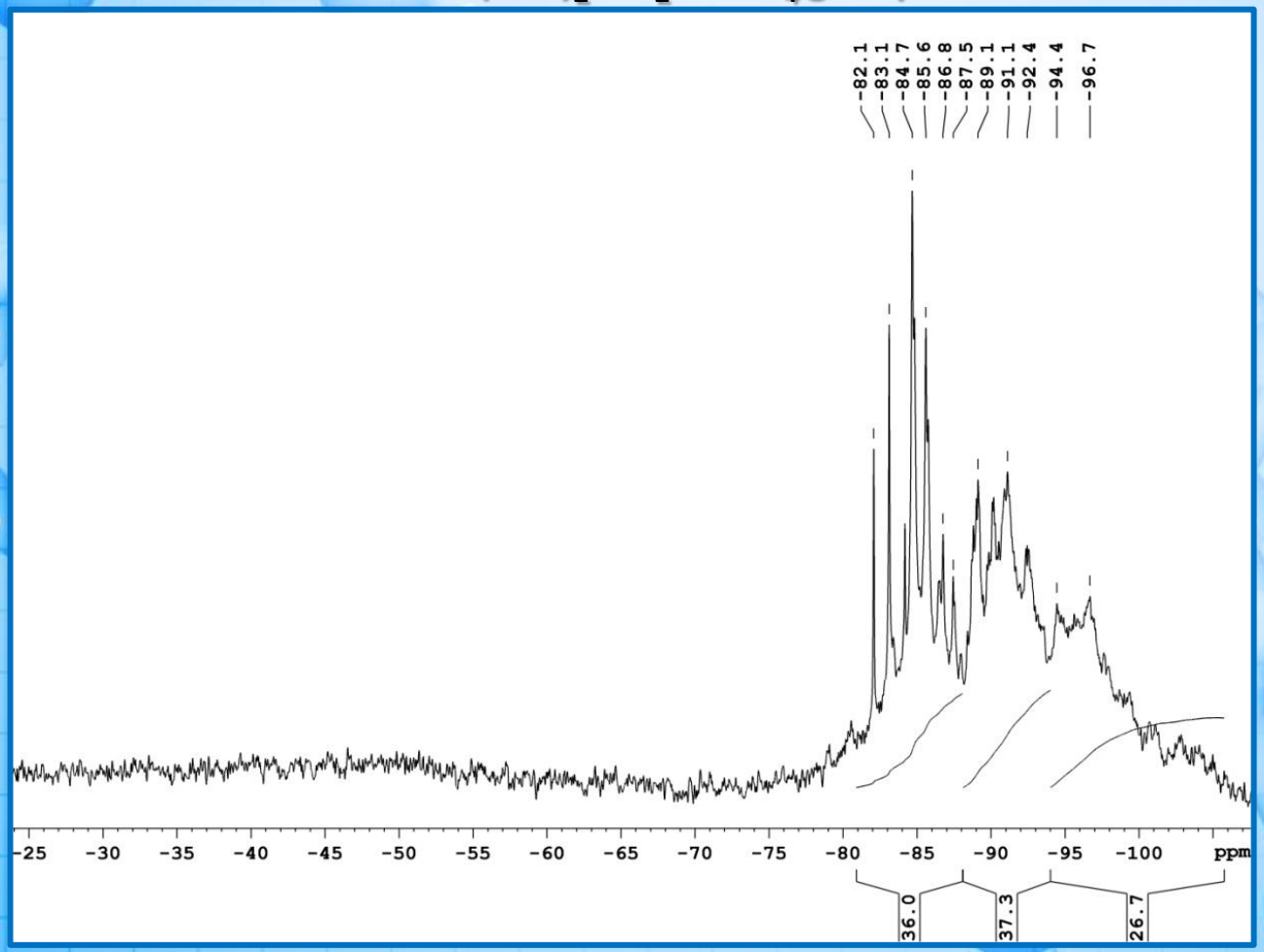


In ^{27}Al NMR spectra (600.13 MHz, $CDCl_3$)of the concentrated oligomer solutions in $CDCl_3$ three types of signals of almost the same intensity are recorded: 70.0–80.0 ppm (4-coordinated), 30.0–45.0 (5- coordinated), 1.8-7.5 ppm (6- coordinated) .

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

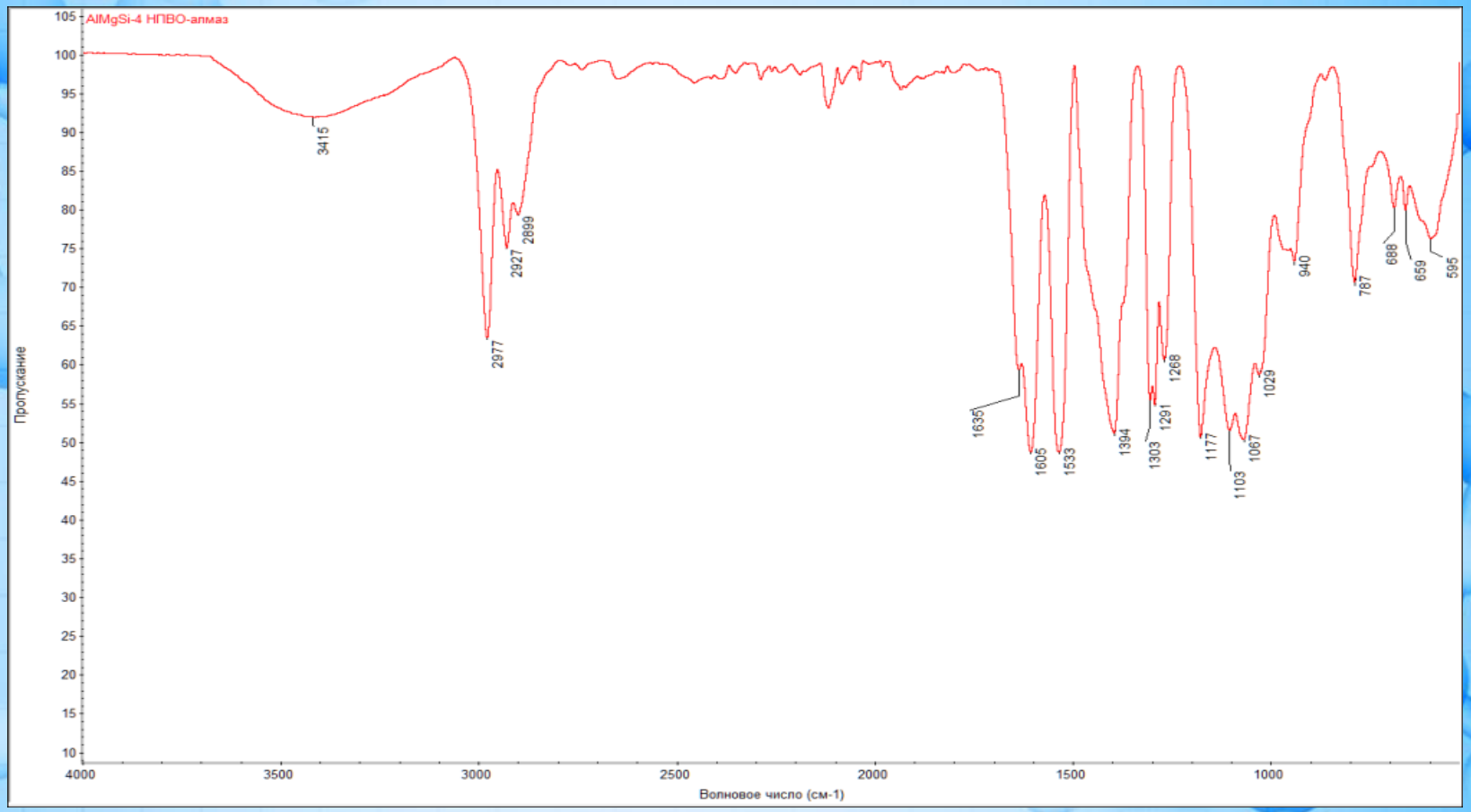
Results and discussion

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 $(EtO)_3SiO$, $(EtO)_2SiO_2$ и SiO_4 groups can be identified



Results and discussion

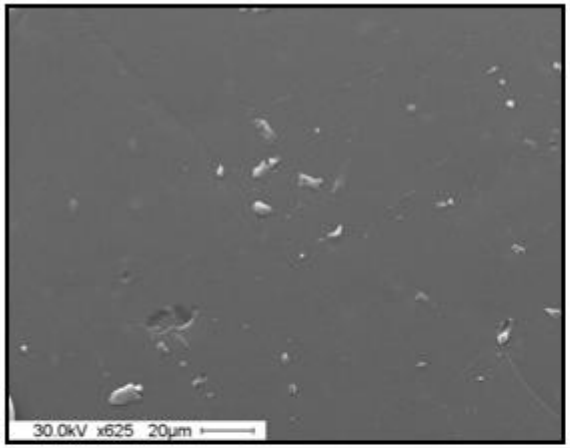
IR of organomagnesiumoxane alumoxane siloxanes

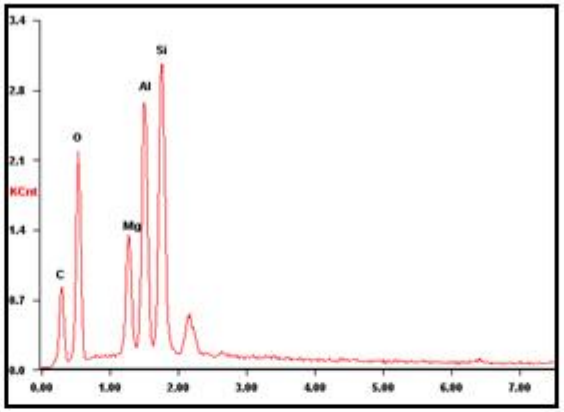


IR (cm^{-1}): 595 ν(Mg–O–Al), 659, 688 ν(Mg–O; Al–O; Si–O), 863 ν(Al–O–Al), 940 ν(Mg–O), 967 ν(Al–O_4; Si–O), 1030, 1071, 1101, 1176 ν(Mg–O–C; Al–O–C; Si–O–C), 787, 1268, 1291, 1303, 1398 δ{CH, C(CH_3)} and ν(C–O), 1533 ν(C=C), 1602 ν(C=O from [CH_3(O)CCH=C(CH_3)O]), 1635 ν(C=O, bonded by coordination bond with Al atom), 2899, 2927, 2977 ν(CH), 3415 ν(OH)

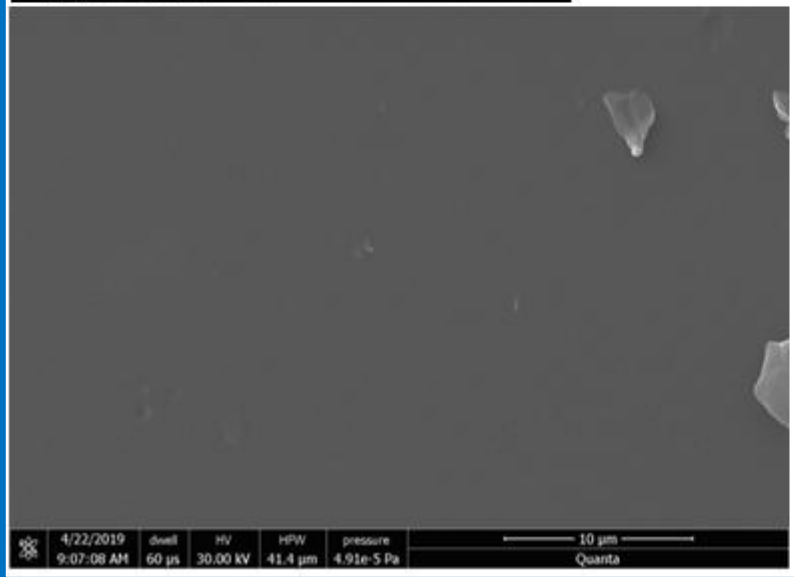
Results and discussion

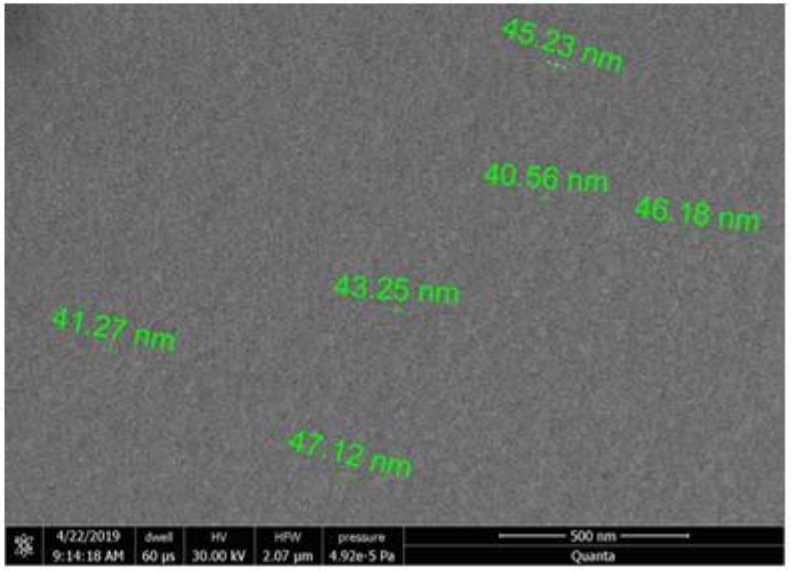
SEM micrographs and X-ray elemental analysis of organomagnesiumoxane alumoxane siloxanes





Element	Wt%	At%
C K	38.03	49.29
O K	37.48	36.47
MgK	05.17	03.31
AlK	09.34	05.39
SiK	09.98	05.53





Results and discussion

Characteristic temperatures* of fiber-forming organomagnesiumoxane alumoxane siloxanes

Oligomer	T_1, °C	T_2, °C	T_3, °C
3	74	79-96	101

** T_1-softening point, T_2 – fiberization temperature, T_3 – melting or solidifying points*

A picture of manually produced fibers

Results and discussion

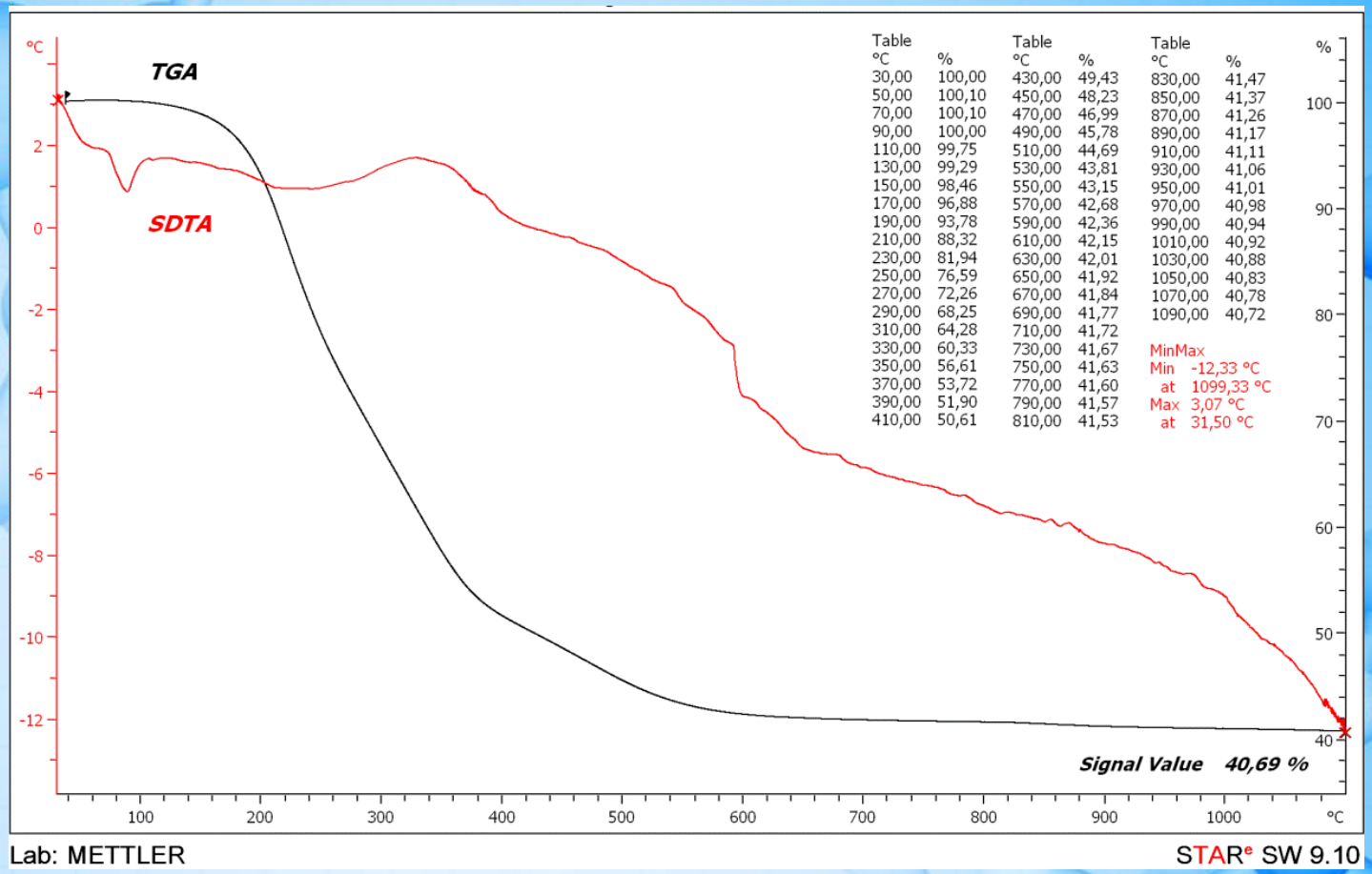


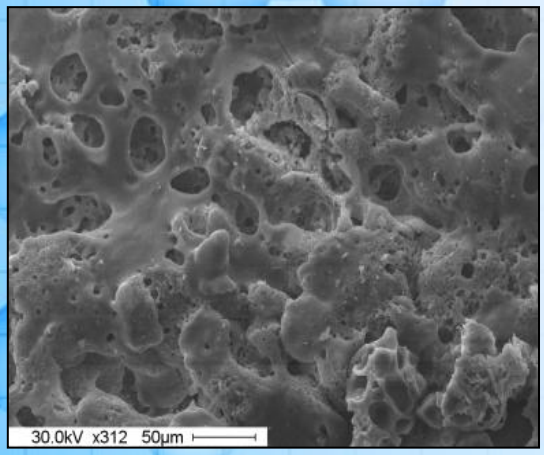
Table °C	%	Table °C	%	Table °C	%
30,00	100,00	430,00	49,43	830,00	41,47
50,00	100,10	450,00	48,23	850,00	41,37
70,00	100,10	470,00	46,99	870,00	41,26
90,00	100,00	490,00	45,78	890,00	41,17
110,00	99,75	510,00	44,69	910,00	41,11
130,00	99,29	530,00	43,81	930,00	41,06
150,00	98,46	550,00	43,15	950,00	41,01
170,00	96,88	570,00	42,68	970,00	40,98
190,00	93,78	590,00	42,36	990,00	40,94
210,00	88,32	610,00	42,15	1010,00	40,92
230,00	81,94	630,00	42,01	1030,00	40,88
250,00	76,59	650,00	41,92	1050,00	40,83
270,00	72,26	670,00	41,84	1070,00	40,78
290,00	68,25	690,00	41,77	1090,00	40,72
310,00	64,28	710,00	41,72		
330,00	60,33	730,00	41,67	MinMax	
350,00	56,61	750,00	41,63	Min -12,33 °C	
370,00	53,72	770,00	41,60	at 1099,33 °C	
390,00	51,90	790,00	41,57	Max 3,07 °C	
410,00	50,61	810,00	41,53	at 31,50 °C	

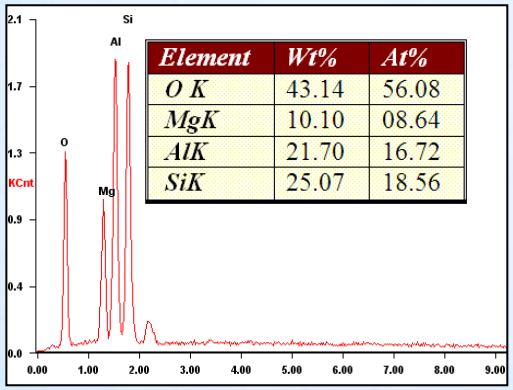
The TGA curve shows that the oligomer is stable when heated to a temperature of ≈200 ºC. The main weight loss occurs in the temperature range of 200–500 ºC (the remainder is about 45 weight %). Further, the removal of residual hydroxyl groups in the form of H_2O vapor is observed, the ceramic residue is 40.69 wt %, which corresponds to the theoretical values (slide 6).

Results and discussion

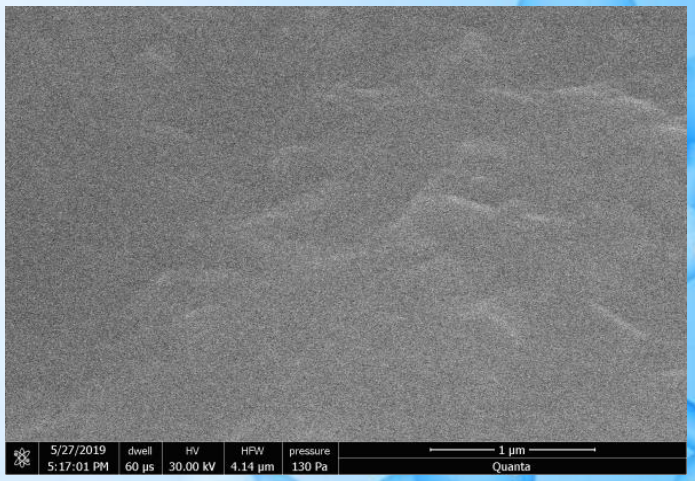
Samples of ceramics: **a – 800 ºC;** **b – 1300 ºC;** **c – 1500 ºC**

SEM micrographs and X-ray elemental analysis of ceramics sample at 1300 ºC





Element	Wt%	At%
O K	43.14	56.08
MgK	10.10	08.64
AlK	21.70	16.72
SiK	25.07	18.56



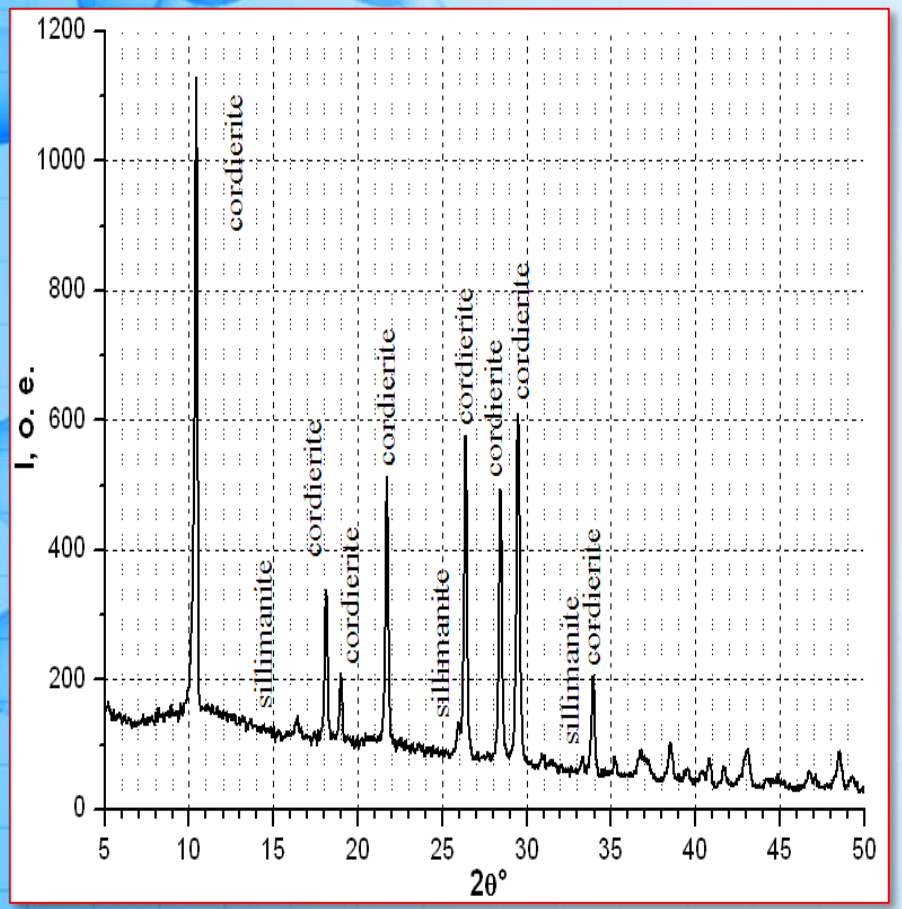
Pyrolysis of organomagnesiumoxane alumoxane siloxane

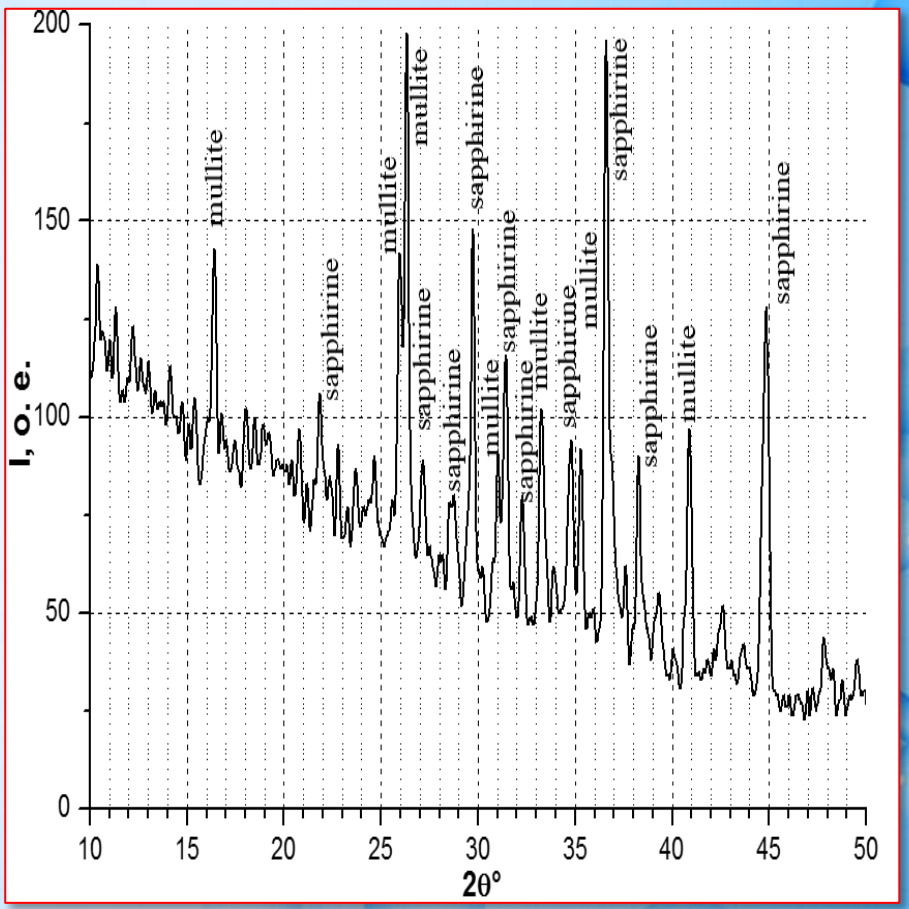
$$[Mg(OR^{**})O]_k\cdot[Al(OR)_l(OR^{**})_g(OR^{*})_x(OH)_zO_y]_m\cdot[Si(OR)_2O]_n \xrightarrow{20\text{-}900\ ^\circ C} \underset{\text{amorphous}}{kMgO\cdot mAl_2O_3\cdot nSiO_2} \xrightarrow{1300\text{-}1500\ ^\circ C}$$

$$\xrightarrow{1300\text{-}1500\ ^\circ C} \underset{\text{cordierite}}{x(Mg_2Al_4Si_5O_{18})}\cdot \underset{\text{sillimanite}}{y(Al_2SiO_5)}\cdot \underset{\text{mullite}}{z(3Al_2O_3\cdot 2\,SiO_2)}\cdot \underset{\text{sapphirine}}{p(Mg_7Al_{18}Si_3O_{40})}$$

Results and discussion

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 ºC 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.