

Dependence of kinetics of composite material gel formation in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ on the conditions of technological process

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The paper deals with the influence of the technological process conditions on the kinetics of formation of the composite material of the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ using sol-gel method. The optimal amounts of catalyst and water for gel formation in the system of a given composition have been established. The physical and chemical processes occurring during heat treatment of the obtained glasslike material have been studied in order to ensure the conditions for maintaining its stable state. It is found that the composite semi-finished product fired at the temperature of 780–800°C does not require special conditions of storage for a long time. The obtained composite material can be used for the manufacturing of structural glass ceramics using the ceramic powder technology. However, sintering of such lithium-aluminosilicate glass ceramics takes place at the temperatures being 90–100°C lower compared to glass ceramics of similar composition, which is traditionally obtained from specially made glass. The proposed technology significantly reduces energy costs related to production of eucryptite and spodumene glass ceramics.

Keywords: glass-ceramics, sol-gel method, firing, water absorption, linear coefficient of thermal expansion, eucryptite.

Залежність кінетики гелеутворення композиційного матеріалу у системі $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ від умов технологічного процесу. *О.С.Хоменко*

Розглянуто вплив умов технологічного процесу на кінетику утворення композиційного матеріалу системи $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ золь-гель способом. Встановлено оптимальні кількості катализатора та води для гелеутворення системи заданого складу. Досліджено фізико-хімічні процеси, що відбуваються при термообробці отриманого склоподібного матеріалу, задля забезпечення умов збереження його стабільного стану. Встановлено, що у прожареному при температурі 780–800°C стані композиційний напівфабрикат не вимагає спеціальних умов зберігання протягом тривалого часу. Одержаний композиційний матеріал може бути використаний для виготовлення склокераміки конструкційного призначення за порошковою керамічною технологією. Але спікання такої літійалюмосилікатної склокераміки відбувається при температурах на 90–100°C нижче у порівнянні із склокерамікою аналогічного складу, яку традиційно одержують із спеціально звареного скла. Запропонована технологія суттєво знижує енергетичні витрати на виробництво евкриптитової та сподуменової склокераміки.

Рассмотрено влияние условий технологического процесса на кинетику образования композиционного материала системы $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ золь-гель способом. Установлены оптимальные количества катализатора и воды для гелеобразования системы заданного состава. Исследованы физико-химические процессы, происходящие при термообработке полученного стекловидного материала, для обеспечения условий сохранения его стабильного состояния. Установлено, что в прокаленном при температуре 780–800°C состоянии композиционный полуфабрикат не требует специальных условий хранения в

течение длительного времени. Полученный композиционный материал может быть использован для изготовления стеклокерамики конструкционного назначения по порошковой керамической технологии. Но спекание такой литийалюмосиликатной стеклокерамики происходит при температурах на 90–100°C ниже по сравнению с стеклокерамикой аналогичного состава, которую традиционно получают из специально сваренного стекла. Предложенная технология существенно снижает энергетические затраты на производство евкриптитовой и сподуменовый стеклокерамики.

1. Introduction

Glass ceramics of the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LAS) became widely used in the manufacture of heat-resistant materials for the most critical industries, such as rocket and space, defense, and chemical industries [1–3]. Such products have the long service life and are capable of working at high temperatures. Today the scientific papers relating to the search of new fields of use, improvement of performance characteristics and reliable methods of these materials' manufacturing, as well as their study, are relevant.

Obtaining of glass ceramics based on the triple LAS system is based on the presence of two crystalline phases in it: β -eucryptite and β -spodumene [2, 4], which have low (and even negative, among the limited number of existing crystalline compounds [5]) indicators of the linear coefficient of thermal expansion.

Glass ceramics of the LAS system with high resistance to thermal shocks has been successfully obtained by the traditional method [4], i.e. melting of glass of the specified composition with its further crystallization. The value of the linear coefficient of thermal expansion of the material is from $-0.370 \cdot 10^{-6}$ to $4.501 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$ in the range of 22–700°C. Raw materials for glassmaking are the alumina (Al_2O_3), quartz (SiO_2), lithium carbonate (Li_2CO_3) or spodumene concentrate (as the lower cost option), which is at the same time a source of Li_2O , Al_2O_3 and SiO_2 . Besides, the compound $\text{TiO}_2 \cdot 2\text{ZrO}_2$ has a positive effect on the bulk crystallization capacity of glass ceramics. However, this method for obtaining of glass crystalline materials is associated with high energy costs, since the temperature of 1550°C is required for the making of basic glass.

The authors of [6] developed glass ceramics with the low coefficient of thermal expansion in the LAS system using non-isothermal sintering with simultaneous crystallization. It is reported that sintered material with the optimal composition reaches 98 % of the theoretical density of the parent glass and has the extremely low

linear coefficient of thermal expansion ($0.02 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$) in the temperature range of 40–500°C. It should be pointed out that this figure is even lower than the indicator of the commercial product Ceran®, made by the traditional method of directional crystallization. Sintered glass-ceramics features four-point bending strength of 92 ± 15 MPa, despite the porosity of 2 %. It is white, opaque material with no significant transmission of infrared radiation. Maximum operating temperature is 600°C. Therefore, it can be used for the modern induction heating panels. High tribological indicators of similar materials are mentioned in [7]. In this manufacturing method, high temperatures of melting of the parent glasses also pose a problem.

Manufacturing of glass ceramics in the LAS system by the method of melt hardening with the use of modifying additives ZrO_2 and MgO is proposed in [8]. It is found that the compound $(\text{Li}, \text{Mg}, \text{Zn})_{1.7} \text{Al}_2\text{O}_4 \text{Si}_6\text{O}_{12}$ is the first crystalline phase which is formed in glass ceramics and converted into the phase $\text{LiAlSi}_3\text{O}_8$ at 800°C. The other two crystalline phases ZrO_2 and $\text{CaMgSi}_2\text{O}_6$ settle out at 700 and 750°C accordingly. Compaction of this LAS glass ceramics begins at about 730°C and stops at nearly 805°C. The coefficient of thermal expansion increases with the growth of sintering temperature. The sample sintered at 800°C during 30 minutes shows high performance characteristics. Non-isothermal energy of crystallization activation energy is 149 kJ/mol, and the values of the Avrami constant are in the range from 3.2 to 3.9. It makes this material suitable in the LTCC (Low Temperature Co-Fired Ceramic) technology for the creation of microwave radiating devices, including Bluetooth and WiFi-modules in many smartphones. However, difficulties of the manufacturing process are associated with the sensitivity of the hardened melt to the technological factors.

The paper [9] contains the information that extra-fine powders of glass ceramics of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ can be prepared by sol-gel method with the use of tetraethoxysilane, titanium butoxide, inorganic salts of lith-

ium, magnesium, aluminum (and zinc) as the source materials. The results show that the process of nucleation on the surface intensively occurs for over-dispersed powders, due to which glass ceramics has the low coefficient of thermal expansion ($\alpha < 10 \cdot 10^{-7} \text{ } ^\circ\text{C}^{-1}$).

The authors of [10] studied the possibility of introduction to LAS glass ceramics obtained by sol-gel method of the additives of Er and different amounts of ZrO_2 . Studying of the microstructure of the resulting product, as well as its three-dimensional reproduction from HAADF-STEM images, allowed establishing the temperatures of crystallization of cubic and lamellar crystals (900°C and 1000°C).

Sol-gel technology is one of the most promising technologies for the production of composite materials. It allows obtaining a homogeneous and reactive semi-finished product for the further sintering [11, 12]. This technology is implemented at the expense of the hydrolysis of the corresponding compounds of elements being a part of the oxide system. As a result of hydrolysis and subsequent condensation, the particles comprising oxides in the specified ratios are obtained. Thus, fragments of the future material of the composite composition appear already in the gel, and it minimizes the diffuse interference during sintering of such material. One of significant disadvantages of this technology is the increased cost of certain components, as well as sensitivity to the environmental technological factors.

Consequently, there are many relevant and diverse scientific papers on the development of LAS glass ceramics, with sol-gel technology being increasingly popular. At the same time, the existing scientific literature on the development of sol-gel method for obtaining of LAS composite does not describe a comprehensive approach that would allow establishing the optimal parameters of technology factors affecting the rate of gel formation, composite quality and nature of thermal transformations. The above formed the purpose and objectives of our research.

2. Experimental

The subject of research is the technological process for obtaining of the composite material of the oxide system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ by sol-gel method with the prospect of using these materials in the production of heat-resistant glass ceramics.

Our purpose is to study the influence of the technology factors on sol-gel process for obtaining of the composite material for heat-resistant glass ceramics.

Below listed are the objectives of the work:

- studying of the impact of the amounts of water and acid catalyst on sol-gel process for obtaining of the composite material of the specified system;

- studying of the nature of thermal transformations of the composite material to ensure its stable state and processability;

- studying of the properties of obtained glass crystalline material and drawing of a conclusion about the possibility of its application in the production of heat-resistant materials.

Ethyl silicate ETS-40 and soluble salts of the corresponding elements were taken as the main raw materials for the research; enriched kaolin KFN-2 was chosen as a suspending additive to the slip.

Standard methods of measuring the flowability of the slip with the use of the Ford cup with the drain hole of 4 mm in diameter and water absorption of glass ceramic samples according to the indicators of weight gain during water saturation in vacuum were used.

Phase composition was determined by means of DRON-3M unit with X-ray tube with the copper electrode.

The behavior of glass composite during heating was determined by the differential thermal analysis on the derivatograph Q-1500 D.

The linear coefficient of thermal expansion (LCTE) was measured on the quartz dilatometer DKV-5.

Microstructure was examined using MBC-10 optical microscope in the reflected light.

The experiment was planned and the results were processed using the complete factorial experiment by means of MathCad program.

3. Results and discussion

3.1. Features of synthesis of composite materials in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ by sol-gel method

With all the advantages of sol-gel technology for obtaining of composite materials [8, 10], this method has certain peculiar features. It is significantly dependent on the solubility of the components, ambient temperature, amount of water for hydrolysis, acid catalyst, sequence of introduction of the components of the composition, etc.

Table 1. Plan of the experiment

No.	Plan in coded coordinates						Plan in real coordinates	
	x_0	x_1	x_2	x_1x_2	x_1^2	x_2^2	Amount of water, ml	Amount of nitric acid, ml
1	+1	+1	+1	+1	+1	+1	30	5
2	+1	+1	-1	-1	+1	+1	10	5
3	+1	-1	+1	-1	+1	+1	30	1
4	+1	-1	-1	+1	+1	+1	10	1
5	+1	+1	0	0	+1	0	20	2.5
6	+1	-1	0	0	+1	0	20	1
7	+1	0	+1	0	0	+1	30	2.5
8	+1	0	-1	0	0	+1	20	5
9	+1	0	0	0	0	0	10	2.5

[12]. Therefore, for this LAS system we studied the dependence of gel formation time on two most important parameters at the same time, i.e. the amounts of water and acid catalyst. The matrix for planning of the experiment is given in Table 1. The amounts of water and catalyst are shown relative to 10 g of dry matter of the composition.

Ethyl silicate ETS-40 ($\text{Si}(\text{OC}_2\text{H}_5)_4$) which is effective to ensure the hydrolysis process was used as a gel-forming agent [13]. Soluble salts $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Al}_2(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were chosen for the introduction of the oxide component. The choice of these salts is conditioned by their sufficiently high solubility in water (Table 2), which allows introducing salts into the composition in the form of solutions and improves the averaging of the poly-oxide system. Relatively low toxicity of the salts during heat treatment was also taken into account.

The calculation of the quantity of components was made in accordance with the stoichiometric ratio of oxides corresponding to the eucryptite $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, wt. %: $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ — 32.0; $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ — 28.8, ethyl silicate ETS-40 — 39.2.

The process of sol formation is carried out with constant long-term mixing of the abovementioned components in the aqueous medium. The objective of the mixing process is to ensure transition of the system from sol to gel state. Gels are solid colloidal systems, which are formed when there is such an association between sol particles, and the system as a whole acquires the properties of a solid, i.e. shows elasticity during deformation. Due to binding of the initially separated particles into an aggregate, the dispersed phase forms a three-di-

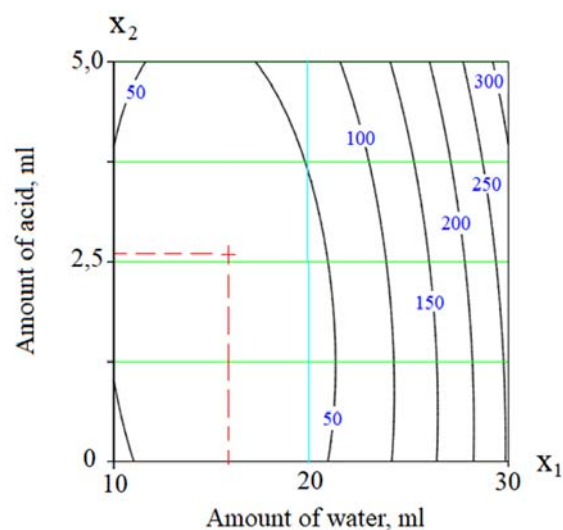


Fig.1. Influence of the amounts of water and acid on the time of gel formation of the experimental system, h.

mensional grid, in the intervals of which there is the dispersion medium.

Water is a stimulator of hydrolysis of ethyl silicate into alcohol and polysilicic acids. The initial amount of water was chosen taking into account [12], studying the effect of water on the silicic acid polymerization process. It is noted that, from the point of view of gel formation, the hydrolysis with excess water is the most advantageous process; in this case, the formed solutions of silicic acids have high viscosity and are capable of turning into gel state.

However, as it turned out in the course of our experiment, process parameters should be selected strictly individually for each oxide system, and the first attempts to obtain a gel of certain composition led to the large number of defects (delaminations,

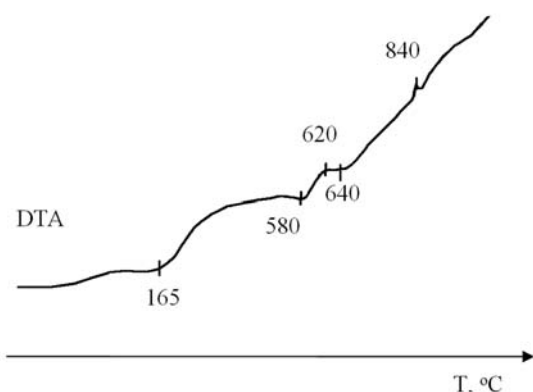


Fig. 2. Curve of differential thermal analysis of the composite heated to 1000°C.

local compactions, turbidity). At the same time, the transparent and homogeneous gel is formed during the normal course of the technological process.

After working on the reproducibility of research results, according to the plan of the complete factorial experiment given in Table 1, we studied the dependence of gel formation time on two factors — the amounts of water and acid catalyst (Fig. 1).

The graph clearly shows the optimal area, i.e. conditions where the gel formation time is minimal. That is, increase in the amount of water in the system above 20 ml will extend the gel formation under the other conditions being the same. The calculation allowed establishing the optimal amounts of acid (2.5 ml) and water (15.4 ml), with the gel formation time of 10.5 h.

Therefore, the gel in the process of solidification turns into glasslike state and represents a homogeneous monolithic composite. Since at this stage interconnected hydroxyl groups and acid residues form almost half of the volume in the structure of the gel [14], further formation of the dense material requires heat treatment of the gel. In order to determine the nature of the thermal transformations of the experimental composite, the differential thermal analysis was performed; the results are shown in Fig. 2.

The thermogram demonstrates three endoeffects with the maxima at 165°C, 580°C and 640°C, which are associated with the destruction of polymer bonds in the composite, as well as decomposition of salt nitrates and release of crystallization water from them.

We paid attention to the fact that the temperatures of removal of nitrogen oxides from the resulting composite material may

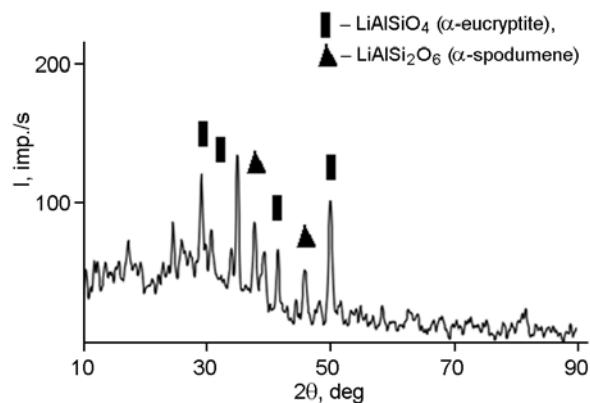


Fig. 3. X-ray pattern of the experimental composite after firing at 850°C.

be higher (the maximum of the third endoeffect is 640°C), than decomposition temperatures of conventional nitrates: $\text{Al}(\text{NO}_3)_3$ — 150–200°C and LiNO_3 — 475–600°C [15]. Probably, this is due to the fact that nitrate component during gel formation is "bound" in the structure of the composite. Total weight loss of 48 % was recorded on the thermogravimetric curve during the heating time.

Exoeffects with the maximum at 840°C indicates the appearance of crystalline phases — low-temperature α -spodumene $\text{LiAlSi}_2\text{O}_6$ and α -eucryptite LiAlSiO_4 , because in samples fired at 850°C X-ray phase analysis records their presence (Fig. 3).

Besides, according to the thermogram it is possible to conclude on the dominating amorphous state of the composite as the X-ray amorphous halo appears, and intensity of the formed phases is rather small (120–130 imp./s).

As a result of research using sol-gel method, composite material in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ on the basis of ethyl silicate and soluble salts of the corresponding oxides is obtained.

3.2. Study of the nature of thermal transformations of composite materials during heating

It is obvious that for the further use of the obtained LAS composite material it is necessary to stabilize its aggregate state by heat treatment [11, 16]. According to the thermogram curve (Fig. 2), the maximum of the last endoeffect is recorded at 640°C and theoretically all destructive processes should be completed before 650–670°C. However, in the course of research it was found that the composite fired even at 700°C was capable of adsorbing moisture

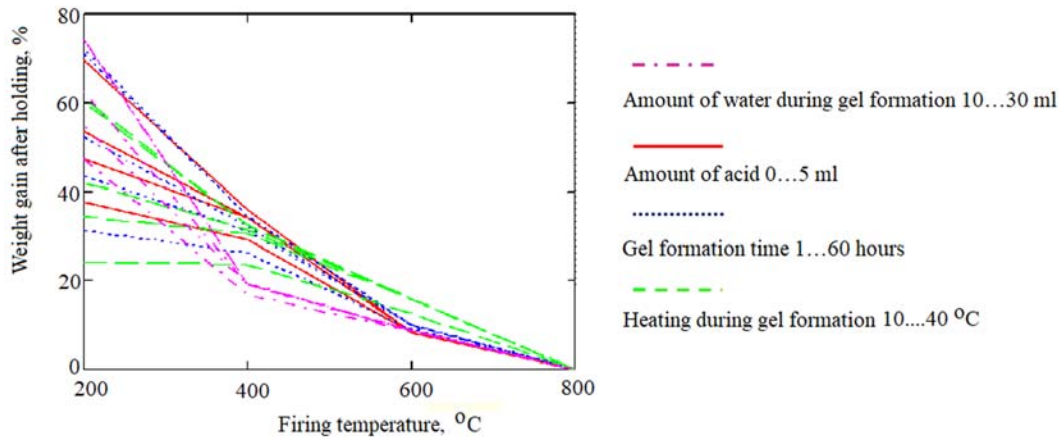


Fig. 4. Effect of firing temperature on the ability of the composite to absorb moisture from the air, taking into account the initial factors during gel formation.

and increasing in weight, i.e. retained hygroscopic properties. It significantly complicated the processability of the composite material during storage, quantitative calculations, and reproduction of results. In addition, the presence of adsorbed water may cause cracking of the glass crystalline material, or increased shrinkage when heated [17].

At the same time, X-ray phase analysis showed (Fig. 2) that after heat treatment at 850°C crystalline phases of eucryptite and spodumene were recorded in the experimental composite; therefore, their destruction during subsequent grinding of the fired composition to create glass ceramic material is impractical.

Therefore, in order to establish the optimal processing temperature for the composite, at which the system does not adsorb moisture, and at the same time retains the amorphous state with high reactivity, we conducted a number of firings of the obtained composite material at temperatures of 200–800°C. After firing, the samples were held in the air for 24 h. Then the degree of water adsorption by the material was determined by the weight method.

From the above data (Fig. 4) it is seen that weight gain less than 1 % is observed after heat treatment at 780°C, whereas at 800°C the process of formation of the stable solid aggregate state of the composite becomes irreversible. Besides, X-ray phase studies confirmed the dominance of the amorphous phase in the obtained glass composite (Fig. 5).

Thus, after heat treatment at 780–800°C glasslike composite material does not require special storage conditions for a long time. In the future, it can be used as a basis for the manufacturing of heat-resistant glass crystalline materials of the LAS system, or as a binder in the production of other densely sintered materials [11, 18], including those with low linear coefficient of thermal expansion [19].

3.3. Study of glass ceramics performance characteristic

The purpose of the next stage of work was to obtain lithium-aluminosilicate glass ceramics on the basis of glass composite fired at 780°C. The composite material was subjected to fine wet grinding in the porcelain drum for 6 h until complete passage through the sieve No.0063. Moisture con-

Table 2. Physical and chemical properties of the main components

Name of the component	Purpose in the composition	Solubility in water under n.c., g/100 ml	Dehydration temperature, °C	Temperature of removal of the nitrate component, °C
LiNO ₃ ·3H ₂ O	Introduction of Li ₂ O	90	70	475–600
Al(NO ₃) ₃ ·9H ₂ O	Introduction of Al ₂ O ₃	73.9	73.5	150–200
Si(OC ₂ H ₅) ₄	Introduction of SiO ₂ and creation of a basis for hydrolysis	–	169	–

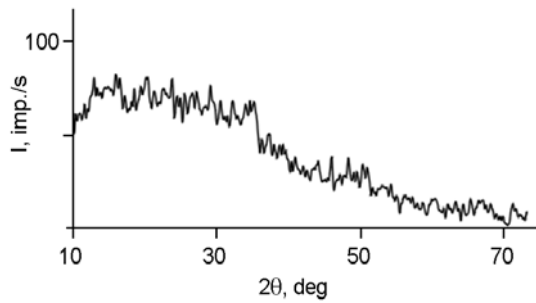


Fig. 5. X-ray pattern of the experimental composite after heat treatment at 780°C.

tent of the suspension was equal to 32 %. As a suspending additive to reduce the tendency of the molding slip to delamination 5 % kaolin was added. Samples for research were formed by casting into plaster molds.

It should be noted that during the preparation of the molding slip there were difficulties with its fluidity; the figure was 45 s (at the recommended values of 15–20 s), which was connected with the leaching of Li^+ (pH reached 10–11). Unfortunately, this phenomenon typical for lithium-aluminosilicate glass obtained by the traditional method of glassmaking also occurs in sol-gel technology for obtaining materials of the experimental system. Therefore, for the formation of glass ceramics in the future it is recommended to use the method of semi-dry molding.

To compare the properties and efficiency of the developed glass composite, samples of glass ceramics were also made following the classical powder technology, which included [4]: melting of glass of similar composition at 1550°C, fritting, fine wet grinding, formation of samples by plaster-mold casting and sintering.

Samples of both series were fired at 1250, 1300 and 1350°C; obtained properties are given in Table 3.

As can be seen from the presented data, the reactive capacity to sintering in the glass composite obtained by sol-gel method is much higher than in glass powder. For example, the samples of series 1 already after firing at 1250°C have water absorption of 0.5–0.6 %, whereas for samples of series 2 this temperature is clearly not enough for sintering of the material (water absorption is 19.2–19.8 %). Only firing at 1350°C allows obtaining dense samples of series 2 with water absorption of 0.5–0.7 %, while the samples of series 1 after firing at this temperature are swollen and deformed (Fig. 6).

The developed material refers to heat-resistant ones, because after firing at 1250°C it has the low linear coefficient of thermal expansion — $9.2 \cdot 10^{-7}$ 1/°C, which corresponds to eucryptite-spodumene glass ceramics [4, 5, 20]. According to the indicator of the volume resistivity (at 350°C) — $2.4 \cdot 10^{10}$ Ohm·m, the obtained material can be referred to dielectrics, for which this indicator should be $\rho_{diel} > 10^8$ Ohm·m [21].

Thus, due to increased activity of the glass composite obtained by sol-gel method, the manufacturing of glass ceramics of the specified composition becomes possible at lower temperatures with the maintenance of its basic performance.

The recommended flow diagram of the process of manufacturing of $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ glass ceramics with the use of sol-gel technology is shown in Fig. 7.

5. Conclusions

As a result of our study, we considered the influence of the technological process conditions on the kinetics of formation of

Table 3. Properties of experimental glass ceramics after firing

Material	Firing temperature, °C	Water absorption, %	LCTE.	$\alpha \cdot 10^7$, 1/°C
Series 1 (glass-ceramics obtained from the composite by sol-gel method)	1250	0.5–0.6	9.2	–
	1300	0.1–0.2	15.5	2.4
	1350	the samples are swollen and deformed		
Series 2 (glass-ceramics obtained by ceramic technology through sintering of glass powder)	1250	19.2–19.8	–	–
	1300	3.4–4.2	–	–
	1350	0.5–0.7	7.5	3.0

" – " Indicator was not measured

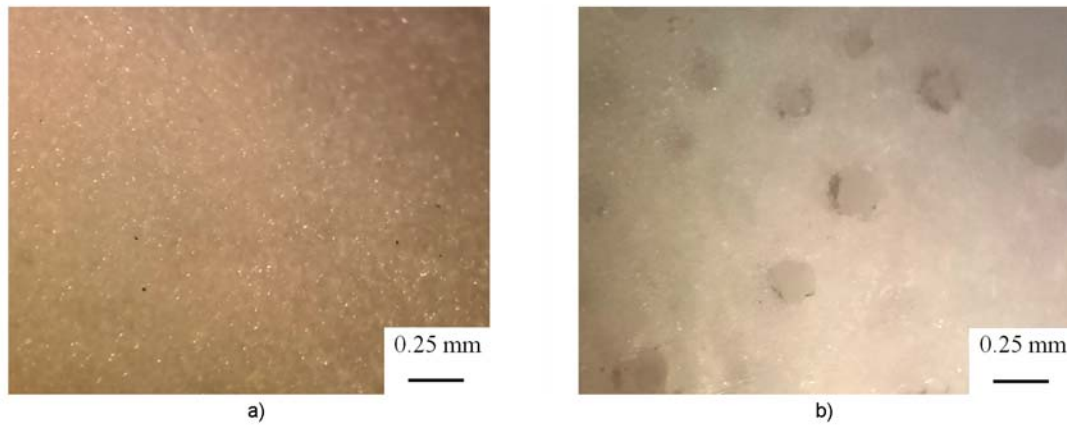


Fig. 6. Outer surface of experimental samples of series 1 after firing at 1250°C (a) and 1350°C (b).

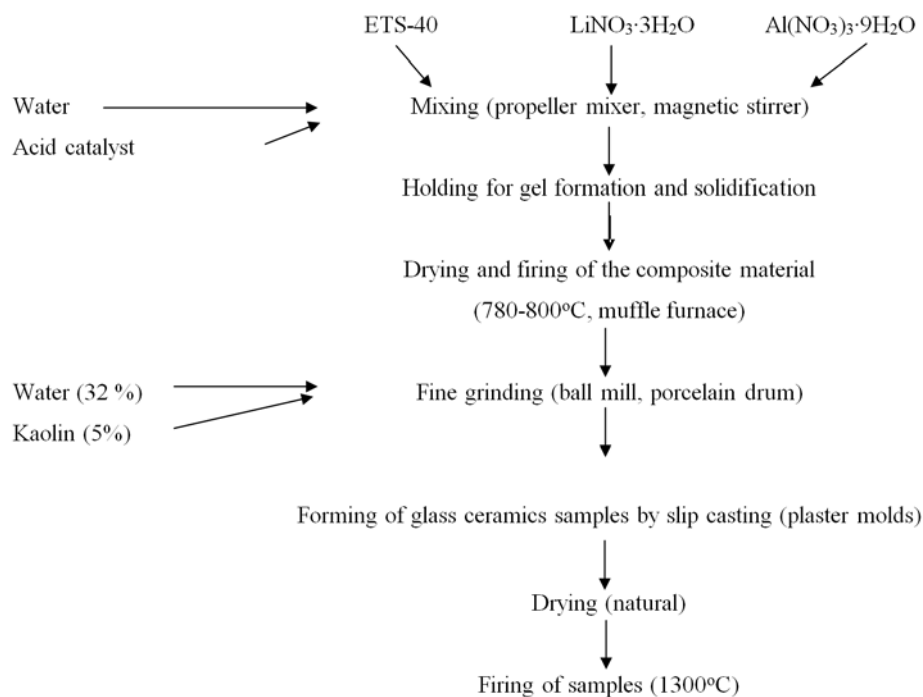


Fig. 7. Flow diagram of the process of obtaining $\text{Li}_2\text{O}\text{-Al}_2\text{O}_3\text{-2SiO}_2$ glass ceramics with the use of sol-gel technology.

the composite material of the system $\text{Li}_2\text{O}\text{-Al}_2\text{O}_3\text{-SiO}_2$ using sol-gel method, and validated the technology of obtaining, reproduction and storage of composite glasslike materials of the experimental system.

Studies of the kinetics of gel formation allowed determining the influence of the main technology factors, i.e. the amounts of water and acid catalyst, on the time of obtaining of the gel composite and composite material as a whole. Based on the results, a process model is built for the first time, and it is established that the minimum gel

formation time of the composition (10.5 h) can be achieved by introducing the amounts (ml) of: acid — 2.5; water for hydrolysis — 15 (per 10 g of dry raw material mixture).

The physical and chemical processes occurring during heat treatment of the obtained glasslike material have been studied in order to ensure the conditions for maintaining its stable state, which increases both the scientific and practical value of the research. It is found that regardless of the kinetics of gel formation and quantitative characteristics of technology factors of sol-

gel process, the temperature of firing of the composite materials should be 780–800°C; the composite semi-finished product in this state only does not require special storage conditions for a long time.

The above glasslike material can be further used for the manufacturing of structural ceramics with the low linear coefficient of thermal expansion. However, sintering of such lithium-aluminosilicate glass ceramics takes place at the temperatures being 90–100°C lower compared to glass ceramics of similar composition, which is traditionally obtained from specially made glass. The proposed technology significantly reduces energy costs related to production of eucryptite and spodumene glass ceramics.

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