

UDC 666.266.6

*O.V. Savvova*<sup>a</sup>, *O.I. Fesenko*<sup>a</sup>, *G.K. Voronov*<sup>a</sup>, *V.D. Tymofieiev*<sup>b</sup>, *O.V. Babich*<sup>c</sup>**INVESTIGATION OF THE STRUCTURE GLASS-CERAMIC MATERIALS ACCORDING TO DATA OF IR SPECTROSCOPY**<sup>a</sup> O.M. Beketov National University of Urban Economy in Kharkiv, Kharkiv, Ukraine<sup>b</sup> Military Institute of Armored Forces of National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine<sup>c</sup> Research Institution «Ukrainian Research Institute of Environmental Problems», Kharkiv, Ukraine

The efficiency of the use of IR spectroscopy in studying the structure of magnesium-aluminosilicate glass-ceramic materials was analyzed. It was established that the formation of the structure of these glass-ceramic materials during the heat treatment is associated with a distortion of the cordierite structure. The presence of solid solutions, high and low cordierite in the structure of the materials under study was detected according to the systems of bands F<sub>2</sub>, E<sub>2</sub>, C<sub>2</sub> and D<sub>2</sub>, depending on the temperature of their heat treatment. The mechanism of phase formation in magnesium-aluminosilicate glass-ceramic materials has been determined, which consists in the formation of future crystals of β-cordierite and spinel at the initial stages of nucleation, and crystals of α-cordierite and mullite at the stage of crystallization. Formation of a finely dispersed glass-ceramic structure with a predominant content of α-cordierite or mullite under conditions of low-temperature heat treatment is a decisive factor in ensuring high thermal and mechanical properties of glass-ceramic materials. This allows them to be used as structural elements of devices and equipment under thermal and mechanical loads.

**Keywords:** IR spectroscopy, high strength magnesium-aluminosilicate glass-ceramic material, structure, cordierite, mullite.

**DOI:** 10.32434/0321-4095-2021-139-6-71-78

**Introduction**

Intensive development of instrumentation with the introduction of mathematical methods for processing a significant amount of experimental data has created conditions for the use of infrared spectroscopy (IR spectroscopy) methods for the operational analysis of silicate materials. IR spectroscopy is one of the most effective methods for studying the phase composition of raw materials and the structure of ceramics, glasses and glass-ceramic materials [1,2]. The use of IR spectroscopy in a complex of complementary methods of physicochemical analysis and in the development of innovative refractory non-metallic and silicate materials gives a powerful impetus to expand their field of application by modifying their composition, structure and properties, including at the nanoscale [3,4].

The IR spectroscopy method allows diagnosing minerals, especially the presence of small impurities

in them, the determination of which is not available by chemical analysis. A significant amount of minerals and rocks, including most of the rock-forming minerals such as quartz, clay, calcite, dolomite, and gypsum, which are the basic raw material in the silicate materials production, can be clearly distinguished by their spectra in the mid-IR range (400–4000 cm<sup>-1</sup>) [5,6]. Thus is important when choosing raw materials and developing ceramic and glass materials compositions. The use of the IR spectroscopy method makes it possible to establish the features of the kinetics of phase formation processes in materials where IR spectra can detect compounds and their modifications [7].

The use of IR spectra is especially valuable when studying the mechanism of nucleation in glass materials at the initial stages of their ceramization. Together with the use of the method of electron microscopy, this method makes it possible to clearly determine the temperature of the first stage of heat

treatment, which is the key to effective design of glassceramics with specified physicochemical and service properties. Thus, Guo et al. [8] and Savvova et al. [9] investigated the mechanism of nucleation of lithium aluminosilicates in glasses of the system  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  containing combined crystallization catalysts ( $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ ,  $\text{La}_2\text{O}_3$ , and fluorides). The presence in the glass melt of the cybotactic groups  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$ , which are observed in the IR spectrum, makes it possible, upon cooling, to form a heterogeneous microstructure by the liquation mechanism with the presence of a nucleator and subsequent crystal growth under low-temperature heat treatment conditions.

The IR spectroscopy method can be effectively used to study the surface properties of dispersed oxide systems. The main advantage of the method is the ability to obtain information about almost all possible states of substances present on the material surface: surface hydroxyl groups, oxygen, and coordination unsaturated cations. The study of the spectra of surface vibrations of both the intrinsic nature of the M–O bond and the impurity nature (OH-vibrations) as well as their comparison with data on the crystal-chemical structure of oxides provides important information on the coordination and ligand heterogeneity of compounds. IR spectroscopy has the advantage of determining volatile compounds in glasses (for example,  $\text{OH}^-$ , molecular  $\text{H}_2\text{O}$ , molecular  $\text{CO}_2$  and  $\text{CO}_3^{2-}$ ) [10] and differentiation of the structure with the formation of nanoscale spherical irregularities with their subsequent ordering [11] for the synthesis of functional glass-ceramic materials with hardened structure.

It is useful to use the method of IR spectroscopy in the development of glass-ceramic materials based on the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , which are characterized by high thermo-mechanical properties due to the peculiarities of their structure. However, structure formation in glass materials during heat treatment is realized due to a complex mechanism of phase transformations, and the effect of the matrix glass on these processes is very difficult to predict and take into account when providing a ceramized structure, especially at the stage of nucleation [12,13]. Therefore, the study of the structure of magnesium-aluminosilicate glass-ceramic materials according to IR spectroscopy data is an important component in the development of nanostructured materials for special purposes, which was the goal of this work.

#### **Experimental**

Experimental glasses in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  were melted in corundum crucibles at the temperature of 1550–1600°C in

condition of oxidizing atmosphere and heat-treated at the temperature of 800–1100°C.

The structure of the glass-ceramics was studied using IR spectroscopy by the method of deposited films in the range of 4000–400  $\text{cm}^{-1}$  on a Specord 80 spectrometer. Petrographic studies of materials were carried out using an optical polarizing microscope NU-2E. The nature of the surface of the material was assessed using the direct method of electron microscopy on a scanning electron microscope-microanalyzer with wavelength dispersion spectrometer. Vickers hardness (HV) and fracture toughness index ( $K_{IC}$ ) were determined using a TMB-1000 device by indenting a Vickers pyramid (with a load on the pyramid of 5000 g) in 10 measurements. Fire resistance was determined by the pyrometric cone method.

The preparation of glass-ceramics based on glasses of the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  with the required performance characteristics was realized by ensuring the process of structure formation of glasses during the melting process, cooling the melt followed by finely dispersed catalyzed crystallization of the amorphous matrix, with the formation of a volumetric-crystallized glass-ceramic structure during a low-temperature heat treatment.

Based on these conditions, the following requirements for a glass matrix as a basis for obtaining magnesium-aluminosilicate glass-ceramic materials were established:

- formation of cybotactic groups  $[\text{AlO}_4]$  in the glass melt;
- formation of a crystallization nucleator upon cooling due to phase separation by the spinodal mechanism;
- flow of finely dispersed bulk crystallization for the formation of a high-strength phase  $<1 \mu\text{m}$  in size in an amount of 80 vol.% under conditions of low-temperature heat treatment.

Taking into account previous studies on the peculiarities of changes in the phase composition of magnesium-aluminosilicate glass-ceramic materials (KSK series) during heat treatment [12], the compositions KSK-4, KSK-6 and KSK-10 were chosen for a detailed study of structure formation, which are characterized by different types and contents of the crystalline phase at different stages of heat treatment, according to petrographic analysis (Table).

#### **Results and discussion**

The structure of cordierite can be identified using absorption spectra [14]. For the crystalline phase of cordierite, which is represented by six-membered silicon-oxygen rings  $[\text{Si}_6\text{O}_{18}]$ , the first main

## Specified chemical composition of the studied glasses, their structure, melting and heat treatment temperatures

Brand	Chemical composition of model glasses, wt.%			Crystallization catalysts	Melting temperature, °C	Glass structure after melting	Heat treatment stage temperature, °C		Type and content of crystal phase after heat treatment vol.%
	Phase-formation components						I	II	
	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>						
KSK-4	14	28	45	TiO <sub>2</sub> , CeO <sub>2</sub> (5.5)	1600	amorphous	800	1100	α-cordierite 4%; mullite 2%; spinel quartz, corundum (traces)
KSK-6	13	22	49	TiO <sub>2</sub> , P <sub>2</sub> O <sub>5</sub> , ZrO <sub>2</sub> (12)	1550	amorphous	800	1100	α-cordierite 25%; mullite 10%; quartz
KSK-10	9	29	51	TiO <sub>2</sub> , ZrO <sub>2</sub> , CeO <sub>2</sub> , P <sub>2</sub> O <sub>5</sub> (6)	1550	microheterogeneous	850	1150	mullite 80%; cordierite 2%

band is observed in the range of 1250–952 cm<sup>-1</sup>. It is a complex doublet. The second band at 806–769 cm<sup>-1</sup> is specific for ring silicates. For doubled six-membered rings, the «increased» wavelength of the circular band of cordierite [Si<sub>3</sub>AlO<sub>18</sub>] (at 770 cm<sup>-1</sup>), when compared with beryl, diopside and tourmaline (805; 781; 783 cm<sup>-1</sup>, respectively) is possible to explain by the replacement of a part of silicon in a ring on aluminum.

A feature of the formation of the structure of magnesium-aluminosilicate materials is associated with the distortion of the cordierite structure, which is a consequence of the redistribution of Si and Al atoms in cordierite rings Si<sub>3</sub>AlO<sub>18</sub>. According to Miashiro's classification, its stable at high temperatures form of cordierite is called α-cordierite

and can be attributed to high, slightly distorted cordierite or to high indialyte. The change in the composition of metastable phases formed during the crystallization of materials to the intense appearance of α-cordierite (M<sub>2</sub>A<sub>2</sub>S<sub>5</sub>) and/or mullite (A<sub>3</sub>S<sub>2</sub>), the vibration frequencies of which are clearly recorded in the IR spectra, significantly affects the performance characteristics of the glass-ceramic materials under study.

The interpretation of the absorption spectra of cordierite solid solutions, which are formed during the heat treatment at a temperature of 1100–1150°C in the investigated materials of the KSK series, is also complicated (Figs. 1–3, curve a).

Strong absorption bands in the regions of about 500 and 1000 cm<sup>-1</sup>, characteristic of all studied

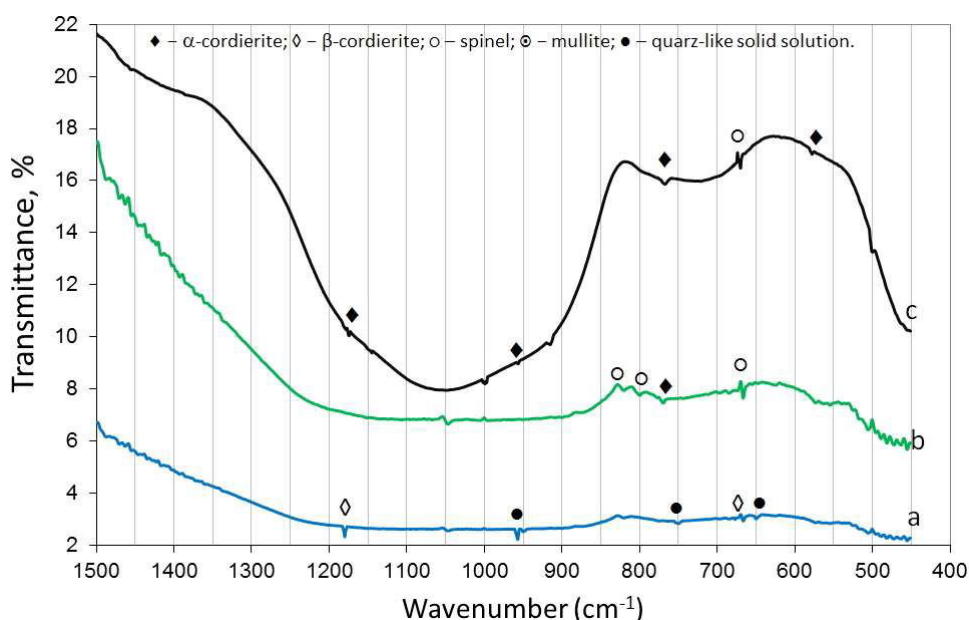


Fig. 1. Absorption spectra of investigated material KSK-4 at different temperatures: a – 900°C; b – 1000°C; c – 1100°C

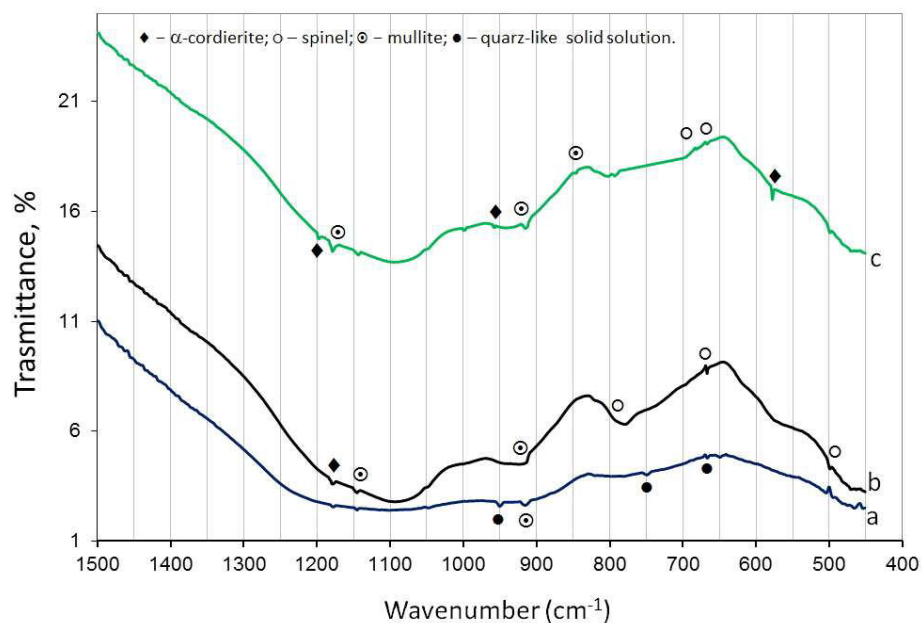


Fig. 2. Absorption spectra of investigated material KSK-6 at different temperatures: a – 900°C; b – 1000°C; c – 1100°C

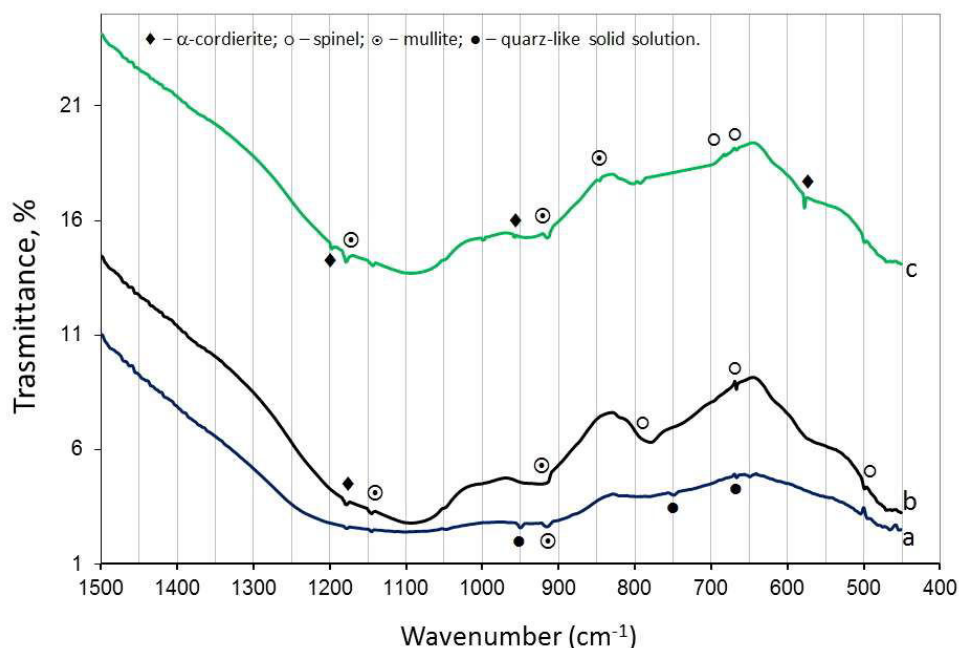


Fig. 3. Absorption spectra of investigated material KSK-10 at different temperatures: a – 900°C; b – 1000°C; c – 1150°C

materials, are traditionally interpreted as active vibrational modes of tetrahedral configurations  $[\text{SiO}_4]$ ; of loosening of Si–O bonds and of bonding of Si–O at  $1000 \text{ cm}^{-1}$  and at  $500 \text{ cm}^{-1}$ , respectively. However, tetrahedra  $[\text{SiO}_4]$  are difficult to identify due to the presence of stretching vibrations of polyhedra  $[\text{PO}_4]^{3-}$  and  $[\text{BO}_4]^{5-}$  at  $1050\text{--}1300 \text{ cm}^{-1}$  and at  $1000\text{--}1100 \text{ cm}^{-1}$ , respectively, which is specific of glass KSK-4.

The F2 and E2 bands in the vibration regions

of  $1175$  and  $957 \text{ cm}^{-1}$  are observed in the IR spectra of all materials; they are characteristic of high cordierite. The presence of high cordierite is also evidenced by the oscillation strength of the C2 band at the frequency of  $680 \text{ cm}^{-1}$  and the D2 band at the frequency of  $770 \text{ cm}^{-1}$ , which is characteristic of the circular  $[\text{Si}_3\text{AlO}_{18}]$  band. This is more clearly observed for the studied materials KSK-4 and KSK-6, which are characterized by the ratio  $\text{MgO}:\text{Al}_2\text{O}_3:\text{SiO}_2 = 1:(1.7\text{--}2.0):(3.2\text{--}3.7)$  (Table). The D band was

previously assigned to six-fold rings in the cordierite structure. However, due to the presence of such bands in a quartz-like solid solution, where there are no such rings, it is arguably attributed to the symmetric vibrations of tetrahedral modes activated by the deviation of tetrahedra from cubic symmetry [14].

Bands B correspond to octahedral positions  $[\text{MgO}_6]$  at the frequency of  $578\text{ cm}^{-1}$ , which is explained by the mutual influence of C bands and the inclusion of octahedral positions in the ordering mechanism of cordierite. The transition from high to low cordierite, which is characterized by an increase in the splitting of absorption bands and an increase in the intensity of the absorption band C, is not observed for the studied glasses.

The highest intensity of cordierite vibrations is characteristic of KSK-4 material, for which the content of the crystalline phase is 40 vol.%, and the least intensity is observed for KSK-10, which is confirmed by experimental data [12]. For the KSK-10 material with the ratio  $\text{MgO}:\text{Al}_2\text{O}_3:\text{SiO}_2 = 1:3.3:5.7$  (Table), there is an interaction of cordierite with alumina at  $1150^\circ\text{C}$  to form mullite and spinel according to the reaction:  $15\text{A} + 2\text{M}_2\text{A}_2\text{S}_5 = 4\text{MA} + 5\text{A}_3\text{S}_2$ . Despite the reversibility of this reaction, the presence of crystalline phases of mullite and spinel along with high cordierite is also characteristic of the investigated materials in the IR spectra. X-ray analysis cannot fix crystal phases of spinel (in KSK-6 and KSK-10) and  $\alpha$ -cristobalite (in KSK-10) under heat treatment at  $1100^\circ\text{C}$ , since the dimensions of crystalline phases are less than  $1\text{ }\mu\text{m}$ . The presence of these crystalline phases is confirmed only by IR spectroscopy data (Figs. 2 and 3).

For the KSK-10 material, the vibration bands at  $815$ ,  $915$ ,  $1145$ , and  $1178\text{ cm}^{-1}$  correspond to the mullite structure. In the regions of  $1200$ – $1100\text{ cm}^{-1}$  and  $670$ – $700\text{ cm}^{-1}$ , mullite is weakly absorbed (Fig. 1, curve a). The identification of mullite for the studied materials KSK-4 and KSK-6 with its insignificant intensity indicates the formation of a continuous solid solution of  $\alpha$ -cordierite in mullite. The B band is observed at  $580\text{ cm}^{-1}$  for  $[\text{MgO}_6]$ , which is explained by the mutual influence of the C bands and the inclusion of octahedral positions in the ordering mechanism of cordierite.

Cristobalite is fixed at the  $793\text{ cm}^{-1}$  vibration band only for the KSK-10 material. The spectrum of quartz differs from that of cristobalite by the presence of doublets of the  $796\text{ cm}^{-1}$  and  $778\text{ cm}^{-1}$  bands, while there is only a  $793\text{ cm}^{-1}$  band for cristobalite. For the materials under study, vibrations corresponding to magnesium aluminate spinel are observed at  $800$ ,  $700$ , and  $675\text{ cm}^{-1}$  bands. The

simultaneous presence of  $\alpha$ -cordierite, spinel and  $\alpha$ -cristobalite in the KSK-10 material indicates the reversibility of the reaction  $\text{A}_3\text{S}_2 + 2\text{MA} + 3\text{S} = 3\text{A} + \text{M}_2\text{A}_2\text{S}_5$  (at the temperature of  $1000$ – $1050^\circ\text{C}$ ). This is confirmed by the results of electron microscopy, which indicate the simultaneous presence of mullite, represented by columnar crystals of about  $1\text{ mm}$  in size with a sufficiently high aspect ratio of type II (3–10:1) and an insignificant amount of cubic spinel crystals (Fig. 4,a) [15]. At higher magnification, branching of crystals of secondary mullite and reinforcement of the structure for the KSK-10 material are observed (Fig. 4,b).

To establish the features of the structure formation of the materials during heat treatment, a study was made on changes in their phase composition at the temperatures of  $900$  and  $1000^\circ\text{C}$ , which are characteristic of the M–A–S system.

For the prototypes KSK-4 and KSK-6, which were kept at the temperature of  $900^\circ\text{C}$ , we observed the formation of solid solutions in the C, D, and E bands with frequencies of  $650$ ,  $750$ , and  $950\text{ cm}^{-1}$ , respectively, and low cordierite ( $\beta$ -cordierite) in the bands F2, E2 and C2 with frequencies of  $1180$ ,  $958$ , and  $677\text{ cm}^{-1}$ , respectively. It is the presence of the cybotactic groups of  $\beta$ -cordierite at low temperatures in the structure of the prototypes that makes it possible to form  $\alpha$ -cordierite crystals with increasing temperature. For the KSK-10 material, slight vibrations of mullite are observed at frequencies of  $1178$ ,  $1145$ , and  $915\text{ cm}^{-1}$ . This is due to the presence of mullite crystals after melting, which is the nucleating agent for this material. The results of electron microscopy confirm the presence of a significant amount of nanosized nucleations, which are represented by spheres of  $50\text{ nm}$  in size and densely located around them of smaller nucleations (Fig. 4,c).

Heat treatment at  $1000^\circ\text{C}$  leads to the formation of  $\alpha$ -cordierite, the vibrations of the C2 and D2 bands of which are observed at frequencies of  $680$  and  $770\text{ cm}^{-1}$ , respectively, for all prototypes and spinel at frequencies of  $800$  and  $700\text{ cm}^{-1}$ . The presence of insignificant vibrations at the frequency of  $770\text{ cm}^{-1}$  (band D2) is associated with symmetric vibrations of tetrahedral modes activated by the deviation of tetrahedra from cubic symmetry. The structure of the KSK-10 material is represented by  $\alpha$ -cordierite crystals in the form of isometric prisms (Fig. 4,d), which have the form of a hexagon in the section of the microsection. Crystals of high-temperature  $\alpha$ -cordierite are short-prismatic; they belong to the rhombic system and are doubled in such a way that they seem to be hexagonal.

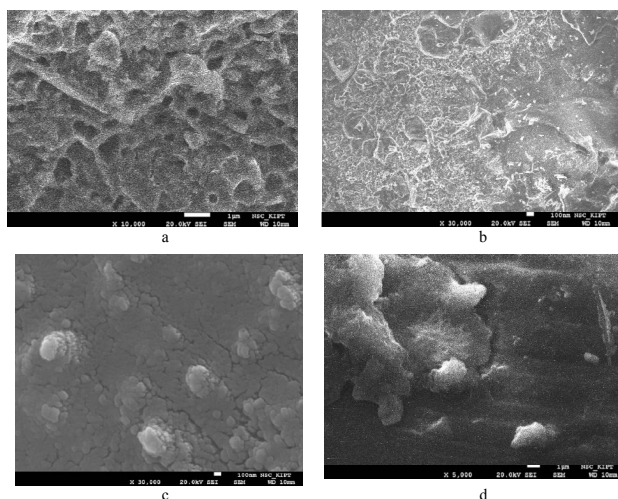


Fig. 4. Structure of glass-ceramic material KSK-10 according to SEM data

The results of petrographic analysis showed that solid solutions are formed based on  $\alpha$ -cordierite with a crystalline phase content of 25–40 vol.% for materials KSK-4 and KSK-6 at the indicated temperatures, which is due to the chemical interaction of  $\alpha$ -cristobalite and spinel according to the reaction  $2MA+5S=M_2A_2S_5$ . For KSK-10 material based on mullite, cordierite is formed as a result of the reaction:  $A_3S_2+2MA+3S=3A+M_2A_2S_5$  (at the temperatures of 1000–1050°C), which interacts with alumina when the temperature rises to 1150°C, leading to the formation of mullite and spinels according to the reaction  $15A+2M_2A_2S_5=4MA+5A_3S_2$ . Subsequent heat treatment at 1150°C leads to the formation of a continuous solid solution of  $\alpha$ -cordierite in mullite in the amount of 80 vol.%.

Consequently, the presence of solid solutions of spinel,  $\alpha$ -cristobalite and mullite at the initial stages of nucleation, the identification of which is possible from the data of IR spectroscopy, is a determining factor in the formation of a reinforced ceramized structure at the stage of crystallization of the studied glass materials.

The developed glass-ceramic materials under the conditions of low-temperature heat treatment are characterized by high strength properties (HV 8.0–10.4 GPa;  $K_{IC}$  3.0–3.5 MPa·m<sup>1/2</sup>;  $\sigma_{bend}$  300–350 MPa, and the maximum operating temperature of 1300–1350°C); they can be used as high-strength structural elements of high-temperature equipment.

### Conclusions

The features of the change in the structure of magnesium aluminosilicate glass-ceramic materials during heat treatment have been analyzed. The

following successive processes take place: the formation of solid solutions of  $\beta$ -cordierite (900°C), spinel and  $\alpha$ -cordierite (1000°C); solid solutions based on  $\alpha$ -cordierite (1100°C); and the reaction of  $\alpha$ -cordierite and mullite (1100–1150°C).

The use of IR spectroscopy in combination with electron microscopy in studying the structure of magnesium-aluminosilicate glass-ceramic materials made it possible to establish the following features: the presence of cybotaxic groups at the initial stages of nucleation, the distortion of the cordierite structure, depending on their chemical composition and heat treatment temperature, and the formation of crystalline phases of  $\alpha$ -cordierite and mullite, depending on the ratios  $MgO:Al_2O_3:SiO_2=1:(1.7-2.0):(3.2-3.7)$  and  $MgO:Al_2O_3:SiO_2=1:3.3:5.7$ , respectively.

The formation of a reinforced ceramized structure in the investigated glass materials under conditions of low-temperature heat treatment determines their high strength properties (HV 8.0–10.4 GPa;  $K_{IC}$  3.0–3.5 MPa·m<sup>1/2</sup>;  $\sigma_{bend}$  300–350 MPa, and refractoriness 1300–1350°C). The obtained results can be used in the development of structural elements of high-temperature equipment, taking into account the aspects of energy saving.

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Received 25.05.2021

## ДОСЛІДЖЕННЯ СТРУКТУРИ ВИСОКОМІЦНИХ МАГНІЙАЛЮМОСИЛІКАТНИХ СКЛОКРИСТАЛІЧНИХ МАТЕРІАЛІВ ЗА ДАНИМИ ІЧ-СПЕКТРОСКОПІЇ

*О.В. Саввова, О.І. Фесенко, Г.К. Воронов, В.Д. Тимофеев, О.В. Бабіч*

Проаналізовано ефективність застосування ІЧ-спектроскопії при дослідженні структури магнійалюмосилікатних склокристалічних матеріалів. Встановлено, що формування структури дослідних склокристалічних матеріалів при термічній обробці пов'язано із викривлення структури кордієриту. Визначено наявність твердих розчинів, високого та низького кордієриту за системами смуг F<sub>2</sub>, E<sub>2</sub>, C<sub>2</sub> та D<sub>2</sub> у структурі дослідних матеріалів в залежності від температури їх термічної обробки. Визначено механізм фазоутворення в магнійалюмосилікатних склокристалічних матеріалах, який полягає у формуванні на початкових стадій зародкоутворення сиботаксичних груп майбутніх кристалів β-кордієриту та шпінелі та на етапі кристалізації кристалів α-кордієриту та муліту. Формування тонкодисперсної склокристалічної структури з вмістом переважно α-кордієриту або муліту в умовах низькотемпературної термічної обробки є визначальним для забезпечення високих термічних та механічних властивостей склокристалічних матеріалів. Це дозволяє застосовувати їх як конструкційні елементи приладів та обладнання при термічних та механічних навантаженнях.

**Ключові слова:** ІЧ-спектроскопія, високоміцний магнійалюмосилікатний склокристалічний матеріал, структура, кордієрит, муліт.

## INVESTIGATION OF THE STRUCTURE GLASS-CERAMIC MATERIALS ACCORDING TO DATA OF IR SPECTROSCOPY

*O.V. Savvova<sup>a,\*</sup>, O.I. Fesenko<sup>a</sup>, G.K. Voronov<sup>a</sup>, V.D. Tymofiev<sup>b</sup>, O.V. Babich<sup>c</sup>*

<sup>a</sup> O.M. Beketov National University of Urban Economy in Kharkiv, Kharkiv, Ukraine

<sup>b</sup> Military Institute of Armored Forces of National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine

<sup>c</sup> Research Institution «Ukrainian Research Institute of Environmental Problems», Kharkiv, Ukraine

\* e-mail: savvova\_oksana@ukr.net

The efficiency of the use of IR spectroscopy in studying the structure of magnesium-aluminosilicate glass-ceramic materials was analyzed. It was established that the formation of the structure of these glass-ceramic materials during the heat treatment is associated with a distortion of the cordierite structure. The presence of solid solutions, high and low cordierite in the structure of the materials under study was detected according to the systems of bands F<sub>2</sub>, E<sub>2</sub>, C<sub>2</sub> and D<sub>2</sub>, depending on the temperature of their heat treatment. The mechanism of phase formation in magnesium-aluminosilicate glass-ceramic materials has been determined, which consists in the formation of future crystals of β-cordierite and spinel at the initial stages of nucleation, and crystals of α-cordierite and mullite at the stage of crystallization. Formation of a finely dispersed glass-ceramic structure with a predominant content of α-cordierite or mullite under conditions of low-temperature heat treatment is a decisive factor in ensuring high thermal and mechanical properties of glass-ceramic materials. This allows them to be used as structural elements of devices and equipment under thermal and mechanical loads.

**Keywords:** IR spectroscopy; high strength magnesium-aluminosilicate glass-ceramic material; structure; cordierite; mullite.

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