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STUDY OF THE PHASE FORMATION OF TRANSPARENT MAGNESIUM ALUMINOSILICATE GLASS-CERAMIC MATERIALS

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Current trends in the development of materials for optics and laser technology were analyzed. The prospects of creating passively Q-switched Yb-Er glass lasers with eye-safe emission wavelengths based on glass-ceramic magnesium aluminosilicate materials for compact pulsed lasers were established. The main types of transparent glass-ceramic materials were analyzed and the main criteria for the synthesis of transparent nanostructured glass-ceramic materials with a crystalline phase content of approximately 70–80 vol.% were substantiated. Compositions of magnesium aluminosilicate glasses were synthesized and the differences of compositions with different types of optical transparency were determined, taking into account their thermal prehistory. The mechanism of phase formation and the differences of ΣMgO, Al_2O_3, MgO/Al_2O_3 and ΣRO_2 in their composition, which determine the character of crystallization, optical transparency and density under the conditions of heat treatment with a duration of 0.5 and 6 hours, were studied. The developed magnesium aluminosilicate glasses can be used as a basis for the creation of protective and functional high-strength nanostructured glass-ceramic materials based on spinel or cordierite with adjustable optical transparency for optics and laser technology.

Keywords: magnesium aluminosilicate glass-ceramic materials, phase formation, spinel, cordierite, optical transparency, density.

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Introduction

The rapid development of optics and photonics requires the creation of new glass materials with high light transmission and a complex of specified physical, chemical and operational properties. Advances in recent years have focused on the development and application of photonic glasses (e.g., laser, nonlinear optical, photochromic/photosensitive, and magnetooptical) and optical waveguides. The future of photonic glasses is expected to expand the scope of their application: environmental monitoring and medicine [1]. Growing requirements to ensure the reliable operation of ceramic materials for optics and laser technology determine the need to create alternative technological glass materials with high operational characteristics.

A comparative study of different types of materials allows us to conclude that spinels doped with cobalt show better Q-switching characteristics compared to other materials [2,3]. Unlike Co^{2+}-doped rare-earth garnets, they do not require intra-cavity radiation focusing (due to a much longer relaxation time; they have a higher damage threshold than Co^{2+}-doped chalcogenide crystals). However, growing single crystals is complicated by the need to use expensive equipment in high temperature conditions (T_m=about 2000^0C), and the need to observe the homogeneity of the distribution of the activator in the volume.

An alternative to single crystals is the use of transparent magnesium aluminate spinel ceramics with a high transmission coefficient. Such ceramics are produced by the method of 3D printing based on stereolithography using hot isostatic pressing [3]. However, the complexity of applying additive technologies for the production of ceramic materials is associated with the insufficient quality of the obtained products in accordance with the existing high requirements for their operating conditions and functional purpose, which does not allow it to be used in laser devices [4].

The solution to this problem is the creation of technological glass-ceramic materials as a basis for optically transparent protective materials for the development of passively Q-switched Yb–Er glass lasers with eye-safe emission wavelengths (1.5 μm) for compact pulsed lasers.

The use of transparent glass-ceramics based on cordierite and spinel crystals for the design of optical fibers, waveguides, optical and fiber amplifier devices is widely known [5]. High-strength glass-ceramics are obtained on the basis of aluminosilicate systems modified by crystallization catalysts, with the content of crystalline phases of gahnite, spodumene, cordierite, mullite provided with the help of ion exchange. They are used for the production of reinforced optical parts: mirrors of telescopes, screens for smartphones, cooking panels of electric and gas furnaces of Corning Inc., AGC Inc. (JP) and SCHOTT AG (DE), transparent armor elements [6–8] and protective transparent windows of high-temperature furnaces [9] (Table 1).

The difficulty in obtaining glass-ceramics with high mechanical properties, which is formed based on high-temperature crystalline phases, and at the same time with high transparency, is associated with the growth of crystals with a refractive index different from matrix glass. Changes in crystallization behavior have a more significant effect on crack resistance compared to fracture toughness, while changes in crystal size have a more pronounced effect on fracture toughness. In addition, ensuring high operational properties of transparent glass-ceramics is limited by the low content of the crystalline phase (from 3 to 70 vol.%). Hao et al. [5] obtained a volumetrically crystallized structure with a content of 87.5 vol.% of α-cordierite (indialite) crystals after heat treatment at 1030^{0}C for 6 hours. However, the Vickers hardness, which was only 8.1 GPa, is insufficient to obtain high-strength materials. At the same time, the considerable duration of the crystallization also makes

Table 1

Transparent glass-ceramic materials: compositions, properties and fields of application

Type of glass-ceramics, composition	Crystalline phase	Properties	Application	Ref.
Cordierite glass-ceramics (mol.%): 20 MgO; 20 Al_2O_3; 55 SiO_2; and 5 B_2O_3	$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	ρ=2.477 g/cm^3; $\alpha=1.435{\cdot}10^{-6}$ K^{-1}; HV=8.1 GPa	Transparent glass-ceramics	[5]
Gahnite-spinel glass-ceramics (mol. %): 35–60 SiO_2; >13 Al_2O_3; >8 ZnO; 0–8 MgO; 0–10 ZrO_2; 0–6 TiO_2; 0–10 Na_2O; 0–8 Li_2O; 0–10 HfO_2; 0–0.1 As_2O_5; and 0–0.3 SnO_2	$(Mg)_x(Zn_{1-x})Al_2O_4$ ZrO_2	E=98–113 GPa	Protective transparent screens	[6]
Spinel glass-ceramics (mol.%): 17.67 Al_2O_3; 55.52 SiO_2; 01.50 B_2O_3; 06.90 TiO_2; 16.66 MgO; 00.50 ZrO_2; and 01.25 Sb_2O_3	$MgO{\cdot}Al_2O_3$ $Al_2O_3{\cdot}SiO_2$ $4MgO{\cdot}5Al_2O_3{\cdot}2SiO_2$	HV=8.5±0.8 GPa, K_{1C}=0.6±1.1 MPa·m$^{1/2}$	Protective transparent armor elements	[7]
Lithium disilicate glass-ceramics (wt.%): R_2O–Σ(K_2O, Li_2O) 15.0–17.0; RO Σ(CaO, SrO, MgO, ZnO) 2.5–8.0; ZrO_2 0.0–12.0; CeO_2 0.0–0.5; R_2O_3 Σ(Al_2O_3, B_2O_3) 3.0–9.0; Sb_2O_3 0.0–1.5; P_2O_5 0.0–3.0; and SiO_2 60.0–67.0	$Li_2Si_2O_5$	KCU=5.6–6.0 kJ/m^2; HV=9.4–11.5 GPa; K_{1C}=3.25–12.0 MPa·m$^{1/2}$; $\sigma_{ст}$=810–850 GPa; υ=1.50–12.45 km/s; ρ=2.38–2.45 g/cm^3	Transparent armor elements for the protection of optical devices	[8]
Spodumene glass-ceramics (wt.%): 37.3–65.8 SiO_2; 10.0–31.6 Al_2O_3; 0.01–11.0 Li_2O; 0.01–10.47 Na_2O; 0.01–2.5 K_2O; 0.01–9.3 CaO; 0.01–3.0 MgO; 0.01–5.0 TiO_2; 0.01–8.0 ZrO_2; 0.01–4.0 ZnO; 0.01–1.0 SnO_2; 0.0–6.5 LiF; 0.0–15.0 CaF_2; 0.01–3.0 P_2O_5; 0.01–8.0 B_2O_3; 0.01–0.5 CeO_2; and 0.01–2.5 MnO_2	β-$LiAlSi_2O_6$	K_{1C}=2.6–3.5 MPa·m$^{1/2}$; HV=8.2–10.8 GPa; $\sigma_{ст}$=620–820 MPa; $\alpha=22.4–27.6{\cdot}10^{-7}$ K^{-1}; T_{soft}=1250^{0}C	Protective transparent windows of high-temperature furnaces	[9]

it difficult to obtain such materials.

The production of high-strength glass-ceramics based on spinel and mullite crystals in the $MgO-Al_2O_3-SiO_2$ (MAS) system using glass technology with subsequent heat treatment is a promising method for obtaining powdery, fine-grained, nanostructured material. However, spinel and mullite glass have, usually, an excessively high melting point of approximately 1600–1700^{0}C, which makes it difficult to manufacture homogeneous glass by this method. The study of the structure of magnesium aluminosilicate glasses under conditions of low-temperature heat treatment has not been systematically investigated. The question of the influence of these processes on crystallization remains debatable. The possibility of obtaining glass-ceramic material of high optical quality in this system determines the need for conducting fundamental research in this direction. Therefore, the development of high-strength transparent magnesium aluminosilicate glass-ceramics with a relatively low temperature of melting and heat treatment and a reduced duration of exposure while maintaining high performance properties for the operation and protection of optical devices is an urgent task.

Experimental

Complementary methods of physicochemical analysis were used for studying the processes of phase formation, structure and phase composition of materials: X-ray phase analysis (DRON-3M diffractometer), petrographic (NU-2E optical microscope), and gradient thermal analysis (gradient furnace). The microstructure of glasses was studied using REMMA-2000. Density was determined by hydrostatic weighing in toluene.

The selection of criteria that can be used to predict the formation of transparent glass-ceramic materials is an important stage in the research of the initial glass matrix, which will provide the necessary operational properties.

The combination of high operational properties of optically transparent glass-ceramic materials with light transmittance (greater than 80%) and high strength can be ensured by the formation of a sitallized nano- and submicron structure of the glass matrix during heat treatment as a result of the finely dispersed volume crystallization of glass at two-stage low-temperature (approximately 1000^{0}C) and short-term (less than 2 h) heat treatment mode due to the following factors:

– determined composition and content of crystalline (at least 80 vol.%) and glass phase;

– the particle size is smaller than the wavelength in the visible part of the spectrum;

– correspondence of the refractive indices of the crystalline and glass phases;

– low optical scattering and low atomic absorption in the visible region of the spectrum.

When developing a transparent glass matrix, the following synthesis criteria were defined:

– design of compositions of magnesium aluminosilicate glasses in the area of metastable phase separation of the MAS system with the possibility of its implementation by the spinodal mechanism and crystallization of nanosized spinel under conditions of low-temperature heat treatment;

– ensuring the formation of structurally formed $[AlO_4]^{6-}$ sybotaxic groups with the content of phase-forming oxides ΣMgO, Al_2O_3=22–45 wt.% and ratios of MgO/Al_2O_3=1.6–5.0;

– ensuring favorable conditions for nucleation during cooling and growth of crystals during heat treatment while providing the transparency coefficient $K_{tr}\geq 2.1$; crystallinity coefficient $K_{cr}>3.5$;

– ensuring the formation of a high-strength glass frame when Ψ_B and $\Psi_{Al}>1$; $f_{Si}>0.25$;

– obtaining the glass melt with a viscosity of $\approx 10^8$ Pa·s due to the introduction of Al_2O_3 and B_2O_3;

– use of the mixture of ZrO_2, TiO_2, ZnO, P_2O_5, CoO as a combined crystallization catalyst;

– use of CeO_2 as a crystallization catalyst and clarifier.

To provide the formation of a high-strength structure of glass-ceramic materials based on the glasses of the MAS system, it is important to ensure metastable phase separation, which occurs under conditions of increased viscosity in the glass transition interval. It is the high viscosity of the glass that determines the important contribution to the kinetics of the process: at a certain time, the glass cannot separate into two layers; the glassy phase that is released forms finely dispersed droplets, which leads to the formation of a developed droplet biframe structure in a short time. It should be noted that the glasses of MAS system show high viscosity. The viscosity of the MAS system glass melt increases with increasing the CeO_2 and ZrO_2 concentrations, while an increase in the CeO_2 content can lead to a decrease in the cordierite content. In general, the addition of oxides of rare earth elements to cordierite glass-ceramics of non-stoichiometric composition will allow reducing sintering to temperatures of 900–950^{0}C, improving the compaction process and reducing the energy of sintering activation [10]. Strontium and zinc oxides are used along with B_2O_3 to reduce viscosity at high temperatures and melting point, increase tensile, compressive and bending strength. The introduction of CeO_2 will contribute to the formation of a crystalline phase in the interval of lower temperatures, and ensure the transparency of glass-ceramic materials [8]. The introduction of barium oxide, which is a flux, in amount of above 3.0 mol.% into the composition of the frit contributes to its devitrification [11]. In order to form a nanostructure, P_2O_5 was introduced into the composition of glasses, which, together with zinc oxide, will allow expanding the regions of spinodal liquation in the system and will enable to form a high number of nuclei for sitallization of glass in the interval of low temperatures [9,12]. It is the application of the complex crystallization catalyst $P_2O_5/ZrO_2/TiO_2$ that makes it possible to obtain transparent glass-ceramics with transmittance >80% [13], which is ensured by the introduction of clarifiers and CeO_2. The introduction of cobalt oxide into the composition of magnesium aluminosilicate glasses will allow, through directional crystallization, to obtain optical glass-ceramics with spinel oxide nanocrystals, activated by Co^{2+} ions, which can be effectively used for passive Q-switching of Yb-Er lasers (1.5 μm), which is an extremely necessary stage of development of compact pulsed lasers of an eye-safe wavelengths [14].

Taking into account the specified criteria for glass matrix, the compositions with PSK marking were designed in the $MgO-ZnO-CaO-SrO-BaO-CoO-ZrO_2-TiO_2-Al_2O_3-B_2O_3-P_2O_5-SiO_2$ system. They are characterized by different contents of ΣMgO, $Al_2O_3=22-45$ wt.% and the ratio $MgO/Al_2O_3=1.6-5.0$ (Table 2) for the crystallization of spinel as a crystalline phase that provides high light transmission and mechanical strength.

Experimental glasses with PSK marking in the experimental system were melted in corundum crucibles at temperatures of 1550–1650^{0}C under condition of oxidizing atmosphere, and heat-treated at a temperature interval of 800–1200^{0}C.

The study of glass formation in experimental pseudo-ternary systems (Fig. 1), which was distinguished by the content of SiO_2 in the composition of the glasses, made it possible to establish that the experimental glasses after melting exhibited a transparent and microheterogeneous structure depending on the content of phase-forming, modifying components and crystallization catalysts (Table 2).

The study of the structural indicators of K_{tr} and K_{cr} allows us to establish that the developed glasses can be the basis for obtaining glass-ceramic materials by directional crystallization: they have a tendency to form sybotaxic groups in the melt, and the formation and growth of crystals during heat treatment. The possibility of forming a strengthened glass structure is evidenced by the values of calculated indicators Ψ_B and $\Psi_{Al}>1$ and $f_{Si}>0.25$ (Table 2).

Results and discussion

Studies of the crystallization ability of experimental glasses made it possible to determine the influence of the composition on the character of crystallization and changes in optical transparency. I Group glasses (PSK-1, PSK-2, PSK-3, and PSK-4), which belong to the high-silica area with a SiO_2 content greater than 50 wt.%, are characterized by the presence of a crystalline phase of mullite already after melting of 20–30 wt.%, which will contribute to the intensification of phase formation in the experimental glasses with the subsequent growth of crystals as the temperature increases. Such intensive crystallization will not only reduce the optical transparency of glass-ceramic materials, but also lead to a weakening of the structure and a decrease in the mechanical properties of materials. This is confirmed by a clear pattern of crystallization in experimental magnesium aluminosilicate glasses according to the traditional mechanism of phase formation in glasses of the MAS system, which was previously studied [15]. Solid solutions with the structure of high-temperature quartz of about 40 vol.% are released along with mullite in the I group glasses when they heated in a gradient furnace for 6 hours (Fig. 2,a), with a gradual increase in the finely dispersed crystalline

Table 2

Composition differences and structural indicators of experimental glasses

Components and indicators	Composition differences of glasses with PSK marking, wt.%										
	1	2	3	4	5	6	7	8	9	10	11
SiO_2	57	58	57	54	45	45	50	45	45	50	50
MgO/Al_2O_3	5	2.4	1.6	1.6	2.5	3.3	3.0	3.5	2.0	1.6	2.5
ΣMgO, Al_2O_3	24	27	32	32	35	39	40	45	45	40	35
ΣRO	10.3	6.3	4.5	3.0	6.0	2.1	3.0	3.5	3.0	2.5	4.1
ΣRO_2	6	6	3.8	6	7	5.9	4	4.5	3.5	2.0	4.4
P_2O_5	1.7	1.7	1.7	3.0	4.0	3	2	1	1.5	1.5	2
f_{Si}	0.33	0.33	0.32	0.25	0.30	0.25	0.27	0.25	0.26	0.27	0.27
K_{tr}	2.11	2.15	2.17	2.14	2.21	2.01	2.03	2.00	2.15	2.09	2.00
K_{cr}	19.7	10.23	12.13	5.99	10.17	5.47	11.02	10.61	13.92	8.22	5.50

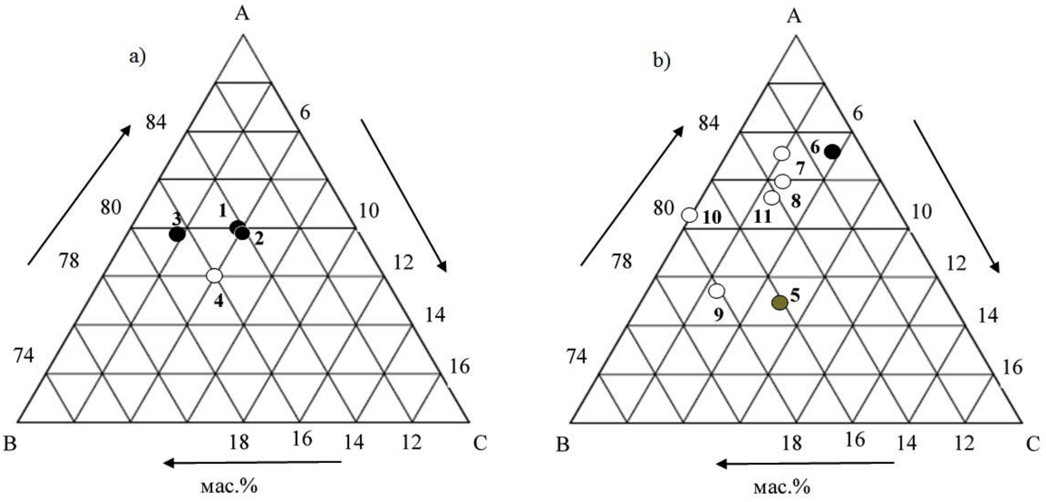
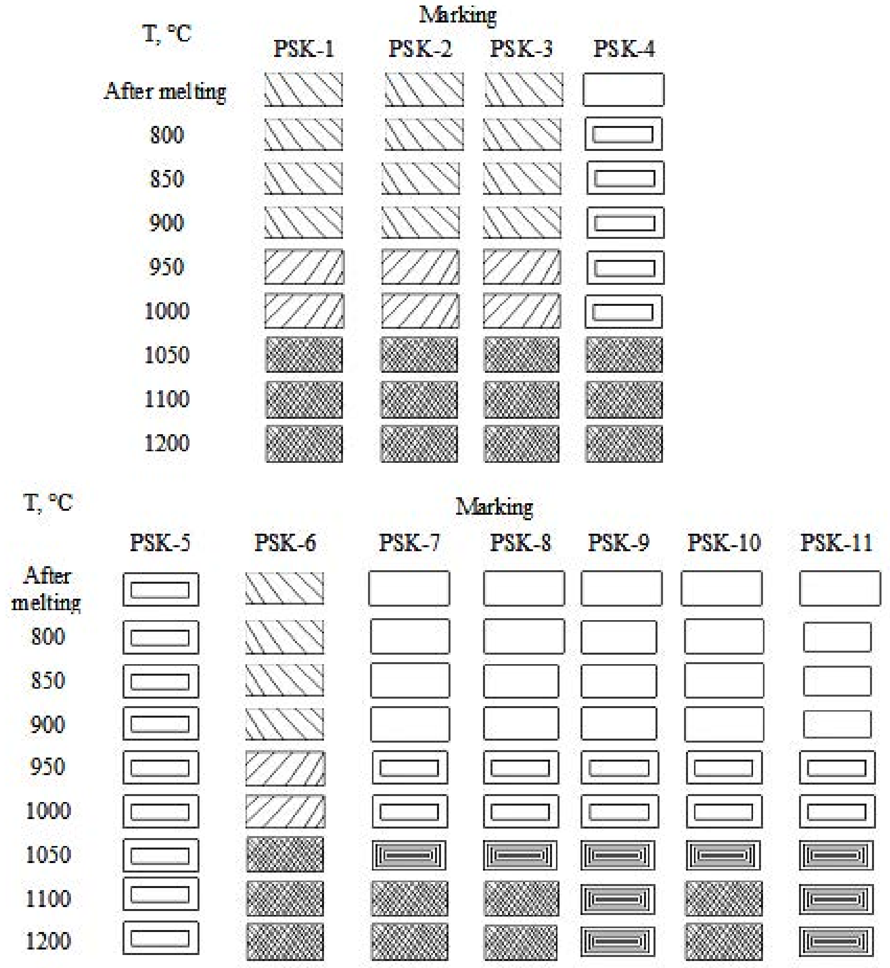


Fig. 1. Pseudo-ternary system A ($\Sigma SiO_2+Al_2O_3+B_2O_3+P_2O_5$)−B($\Sigma MgO+ZnO+BaO+SrO+CoO$)−C($\Sigma TiO_2+ZrO_2+CeO_2$): a − high-silica area; and b − low-silica area



T, °C	PSK-1	PSK-2	PSK-3	PSK-4
After melting	▧	▧	▧	□
800	▧	▧	▧	▭
850	▧	▧	▧	▭
900	▧	▧	▧	▭
950	▨	▨	▨	▭
1000	▨	▨	▨	▭
1050	▩	▩	▩	▩
1100	▩	▩	▩	▩
1200	▩	▩	▩	▩

T, °C	PSK-5	PSK-6	PSK-7	PSK-8	PSK-9	PSK-10	PSK-11
After melting	▭	▧	□	□	□	□	□
800	▭	▧	□	□	□	□	□
850	▭	▧	□	□	□	□	□
900	▭	▧	□	□	□	□	□
950	▭	▨	▭	▭	▭	▭	▭
1000	▭	▨	▭	▭	▭	▭	▭
1050	▭	▩	▣	▣	▣	▣	▣
1100	▭	▩	▩	▩	▣	▩	▣
1200	▭	▩	▩	▩	▣	▩	▣

Fig. 2. Crystallization ability of glasses according to gradient-thermal and petrographic analyses: □ absence of a crystalline phase; ▭ opalescence; ▧ volume crystallization of 30−40 vol.%; ▨ volume crystallization of 50−60 vol.%; ▩ volume crystallization of 70−80 vol.%; ▣ surface crystallization

phase up to 60 vol.% and 80 vol.% at temperatures of 950–1000°C and 1050–1200°C, respectively. Intense crystallization is associated with a significant content of alkaline earth metals, which reduce viscosity and expand the regions of phase separation to form additional nuclei of crystallization.

A decrease in the content of silicon, magnesium, and aluminum oxides significantly affects the crystallization of PSK-4 glass, which is transparent after melting and retains opalescence up to 1050°C. This allows us to conclude that the content of phase-forming oxides has a decisive influence on the crystallization ability. According to the data of petrographic and X-ray phase analyses of the I group glasses after thermal treatment during heating to a temperature of 1200°C for 6 hours, it was established that PSK-1 and PSK-2 glasses, which are characterized by ΣMgO, Al_2O_3=24–27 wt.% with a ratio of $\Sigma MgO/Al_2O_3$=2.4–5.0, contain α-cordierite (40–65 vol.%). The reduction of ΣMgO, Al_2O_3 to 32 wt.%, and the MgO/Al_2O_3 ratio to 1.6 in the composition of PSK-3 glasses promotes the crystallization of mullite (Table 3). An important factor is the ensuring the high-strength sitallized structure with a crystal growth limit of approximately 1 mm at the temperature of glass material formation.

A decrease in the content of silicon oxide to 45–50 wt.% and an increase in the content of magnesium and aluminum oxides in the II group glasses (PSK-5, PSK-6, PSK-7, PSK-8, PSK-9, PSK-10, and PSK-11) (Fig. 2,b) significantly affect the character of crystallization, namely change in intensity and size of the crystalline phase. The phase formation after melting for PSK-5 and PSK-6 glasses is associated with a significant content of crystallization catalysts in their composition: ΣRO_2=7.0 and 5.9 wt.%, respectively. However, a significant increase in the content of ΣMgO, Al_2O_3 up to 39 wt.% for PSK-6 glass under conditions of reduced viscosity due to a decrease in the content of silicon oxide to 45 wt.% results in its intensive crystallization as finely dispersed mullite up to 80 vol.% at temperatures of 1050–1200°C (Table 3).

Reduction of ΣRO_2 content to 2.0–4.5 wt.% for experimental glasses PSK-7, PSK-8, PSK-9, PSK-10, and PSK-11 affects the growth of the crystalline phase to a size greater than 0.4 μm, which contributes to opalescence (there is no opalescence for PSK-7 in Fig. 2) of the glass in the temperature range of 950–1000°C and crystallization of α-cordierite at a temperature of 1200°C (Table 3). In the temperature range of 1050–1200°C for glasses PSK-9 and PSK-11, surface crystallization of α-cordierite is observed, which is a consequence of long exposure in a gradient furnace for 6 hours (Fig. 2). This fact indicates the ability for nanoscale crystallization of the II group glasses, which can retain light transmission with reduced heat treatment terms.

The confirmation of the crystallization of the II group glasses at the initial stages is the change in the density of the glasses during heat treatment (Fig. 3). It is the increase in density, as an indicator of the appearance of the growth of the crystalline phase, that points to the crystallization in the structure of glass-ceramic materials. The density of the PSK series glass-ceramic materials under study, which are transparent after melting, increases in accordance with the appearance of crystalline phases in magnesium aluminosilicate glasses in the process of phase formation in the temperature range of 850–1100°C. After increasing the temperature to 1200°C, the final formation of the structure of glass-ceramic materials and an increase in density are observed in accordance with the type and content of the crystalline phase. In general, the density is an additive quantity and varies depending on the type and content of the crystalline

Table 3

Content of the crystalline phase and density of glass-ceramic materials after exposure in a gradient furnace for 6 hours

Marking	Crystalline phase content	ρ, kg/m^3
PSK-1	α-cordierite 65 vol.%, mullite 20 vol.%	2600
PSK-2	α-cordierite 40 vol.%, mullite 20 vol.%, spinel 10 vol.%, α-cristobalite 10 vol.%	2950
PSK-3	mullite 40 vol.%, cristobalite 20 vol.%, spinel 10 vol.%	3050
PSK-4	α-cristobalite 85 vol.%	1900
PSK-5	mullite 20 vol.%, spinel 10 vol.%	2400
PSK-6	mullite 80 vol.%	2800
PSK-7	α-cordierite 80 vol.%	2650
PSK-8	α-cordierite 20 vol.%	1800
PSK-9	α-cordierite 30 vol.%	1850
PSK-10	α-cordierite 70 vol.%	2600
PSK-11	α-cordierite 40 vol.%	1950

phase. The highest density of 2950–3050 kg/m^3 is inherent in glass-ceramic materials that contain crystalline phases of spinel and mullite. The presence of α-cordierite in the composition of glass-ceramic materials significantly reduces their density to 1800 kg/m^3 (at the content of 20 vol.%). The lowest values (about 1900 kg/m^3) are observed for glass-ceramic materials with an α-cristobalite content of 85 vol.%.

It is especially important to study the density at the initial stages of crystallization for optically transparent glasses, since the formation of a nano- and submicron structure cannot be investigated by using traditional X-ray phase and petrographic analysis methods. The study of changes in the density of experimental glass-ceramic materials made it possible to establish the phase formation processes at the stages of nucleation. This is confirmed by scanning electron microscopy data for the PSK-7 glass (Fig. 4).

Investigation of the structure of the PSK 7 experimental glass during heat treatment in the temperature range of 20–1200^{0}C for 0.5 h allows establishing the peculiarities of its crystallization in relation to its light transmission. The structure of glass at a temperature of 850^{0}C is heterogeneous: on the general background of the nanostructure, heterophase fluctuations with a size of 10 to 100 nm (Fig. 4) are observed, which are formed on the basis of sybotaxic groups. It is the given character of the thermal prehistory of the materials that plays an important role in the subsequent formation of a self-organized nanostructure. The formation of solid solutions is manifested in the fusion of spherical inhomogeneities in the ridge at a temperature of 900^{0}C (Fig. 4). At a temperature of 1000^{0}C, a dense packing of spinel crystals is observed, which is the basis for the formation of short-prismatic rhombic syngony crystals of high-temperature α-cordierite at a temperature of 1100^{0}C. There is an interesting combination of α-cordierite crystals and the formation of threads based on small cuboidal short-prismatic mullite primary crystals, which are found in the material in small quantities (Fig. 4). The interplanar distances of short-prismatic and acicular mullite are very close to each other, so it is impossible to determine the crystal form of mullite nuclei by X-ray phase analysis.

This ordering of the dissipative structure of the glass due to fluctuating inhomogeneities at the initial stages of nucleation will make it possible to form already at 1000^{0}C a significant amount of spinel crystals (≈70 vol.%), which has a dimension of ≤0.4 μm to ensure light transmission and high mechanical strength.

Conclusions

The relevance of creating new transparent glass materials with high light transmission and a complex of high physicochemical and operational properties for optics and photonics has been determined. The compositions, properties, and fields of application of transparent glass-ceramic materials were analyzed, and the prospective use of magnesium aluminosilicate glass-ceramic materials for the operation and protection of optical devices was established. It was established that the combination of high operational properties of optically transparent glass-ceramic materials with light transmittance of greater than 80% and high strength can be realized by forming a sitallized nano- and submicron structure. The choice of a magnesium aluminosilicate system with a defined ratio of phase-

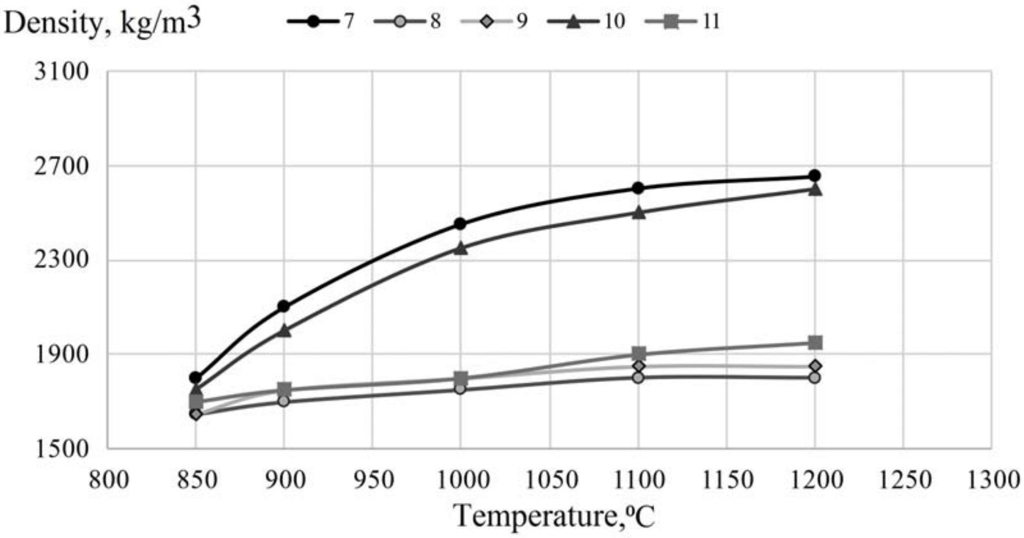


Fig. 3. Change in the density of glass-ceramic materials of the PSK series as a function of temperature

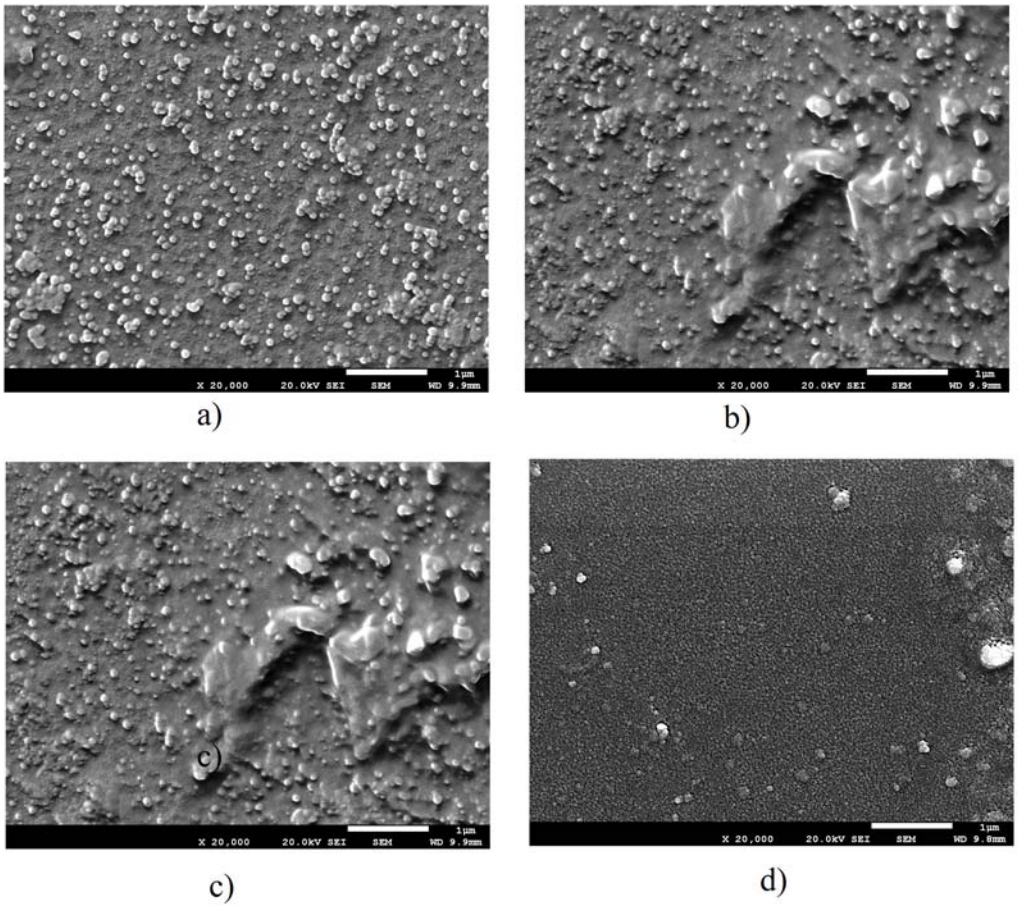


Fig. 4. Phase formation processes and structure of the PSK-7 glass during heat treatment: a) 850⁰C, nucleation and crystallization of quartz-like solid solutions; b) 900⁰C, formation of solid solutions with the structure of high-temperature quartz, spinel; c) 1000⁰C, crystallization of spinel and α-cristobalite; and d) 1100⁰C, formation of solid solutions based on α-cordierite and its decomposition into mullite and corundum

forming and glass-forming components and crystallization catalysts was justified, and the area of glass formation and the thermal prehistory of the experimental glasses were investigated.

The relationship between the crystallization ability and optical transparency of experimental glasses under the conditions of long-term heat treatment (for 6 h at T=20–1200⁰C) was established. It was determined that volumetrically crystallized opaque glasses with the content of finely dispersed crystalline phase with a size of ≈1 μm in the amount of 70–80 vol.% in the high-silica area with the content of ΣMgO, Al_2O_3=24–27 wt.% with a ratio of MgO/Al_2O_3=2.4–5.0 are characterized by the main crystalline phase of α-cordierite; while mullite is the main crystalline phase with ΣMgO, Al_2O_3=32 wt.% and MgO/Al_2O_3=1.6; and α-cordierite is the main crystalline phase is glasses in the low-silica area with ΣMgO, Al_2O_3=40 wt.% and MgO/Al_2O_3=1.6–3.0. The change in the density of experimental glasses during heat treatment was studied as an indicator of the crystallization process during the formation of a nanostructured material.

It was established that the formation of a transparent structure is realized for magnesium aluminosilicate glasses of the low-silica area through its self-organization under the conditions of high-speed (0.5 h) low-temperature (T=1000⁰C) heat treatment due to the formation of solid solutions based on spherical inhomogeneities, nuclei of crystallization (T=850⁰C), which merge into ridges (T=900⁰C) and form a dense packing of nanosized spinel crystals (T=1000⁰C).

The investigated magnesium aluminosilicate glass-ceramic materials containing spinel and cordierite can be used as a basis for the development of nanostructured materials with adjustable light transmission for protective and functional elements of optics and laser equipment.

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ДОСЛІДЖЕННЯ ФАЗОУТВОРЕННЯ ПРОЗОРИХ МАГНІЙАЛЮМОСИЛІКАТНИХ СКЛОКРИСТАЛІЧНИХ МАТЕРІАЛІВ

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Проаналізовано актуальні напрями розвитку матеріалів для оптики та лазерної техніки. Встановлено перспективність створення пасивних модуляторів добротності випромінювання Yb-Er лазерів для компактних імпульсних лазерів з безпечним для зору діапазоном довжин хвиль на основі склокристалічних магнійалюмосилікатних матеріалів. Проаналізовано основні види прозорих склокристалічних матеріалів та обгрунтовано основні критерії синтезу прозорих наноструктурованих скло- кристалічних матеріалів з вмістом кристалічної фази приблизно 70–80 об.%. Синтезовано склади магнійалюмоси-лікатних стекол та визначено відмінності складів з різним характером світлопроникності з урахуванням їх термічної передісторії. Досліджено механізм фазоутворення та визначено відмінності їх складу ΣMgO, Al_2O_3, MgO/Al_2O_3 та ΣRO_2, які визначають характер кристалізації світлопроникності та щільності в умовах термічного оброблення з тривалістю 0,5 та 6 годин. Розроблені магнійалюмосилікатні стекла можуть бути застосовані як основа при розробці захисних і функціональних високоміцних наноструктурованих склокристалічних матеріалів на основі шпінелі або кордієриту з регульованою світлопроникністю для оптики та лазерної техніки.

Ключові слова: магнійалюмосилікатні склокристалічні матеріали, кристалізаційна здатність, шпінель, кордієрит, світлопроникність, щільність.

STUDY OF THE PHASE FORMATION OF TRANSPARENT MAGNESIUM ALUMINOSILICATE GLASS-CERAMIC MATERIALS

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Current trends in the development of materials for optics and laser technology were analyzed. The prospects of creating passively Q-switched Yb-Er glass lasers with eye-safe emission wavelengths based on glass-ceramic magnesium aluminosilicate materials for compact pulsed lasers were established. The main types of transparent glass-ceramic materials were analyzed and the main criteria for the synthesis of transparent nanostructured glass-ceramic materials with a crystalline phase content of approximately 70–80 vol.% were substantiated. Compositions of magnesium aluminosilicate glasses were synthesized and the differences of compositions with different types of optical transparency were determined, taking into account their thermal prehistory. The mechanism of phase formation and the differences of ΣMgO, Al_2O_3, MgO/Al_2O_3 and ΣRO_2 in their composition, which determine the character of crystallization, optical transparency and density under the conditions of heat treatment with a duration of 0.5 and 6 hours, were studied. The developed magnesium aluminosilicate glasses can be used as a basis for the creation of protective and functional high-strength nanostructured glass-ceramic materials based on spinel or cordierite with adjustable optical transparency for optics and laser technology.

Keywords: magnesium aluminosilicate glass-ceramic materials; phase formation; spinel; cordierite; optical transparency; density.

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