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**ПЕРСПЕКТИВНІ ЛІТІЙАЛОМОСИЛКАТНІ СКЛОКРИСТАЛІЧНІ МАТЕРІАЛИ ДЛЯ**  
**ІМПУЛЬСНОЇ ДАЛЬНОМЕТРІЇ**

Встановлена актуальність створення імпульсних наносекундних лазерних приладів поліфункціонального призначення з довжиною хвилі генерації, що лежить в умовно безпечній для зору області спектру  $1,5\div 1,6$  мкм. Визначено перспективність використання режиму пасивної модуляції добротності при отриманні потужних наносекундних лазерних імпульсів з розбіжністю випромінювання, близькою до дифракційної. Проаналізовано матеріали для затворів, які функціонують у режимі пасивної модуляції добротності: твердотільні нелінійно-оптичні матеріали на основі монокристалів ітрієво-алюмінієвого гранату легованого катіонами неодиму, хрому, ванадію та інших Nd- або Yb-легованих кристалів в діапазоні довжин хвилі  $0,8 - 1,2$  мкм. Підтверджена перспективність використання оксидних монокристалів, що активовані іонами  $\text{Co}^{2+}$  у чотирьох координованих киснем позиціях для  $\text{MgAl}_2\text{O}_4$ ,  $\text{LiGa}_5\text{O}_8$ ,  $\text{LaMgAl}_{11}\text{O}_{19}$ . Визначена доцільність розробки прозорої склокераміки на основі алюмомагнієвої та літєвогалієвої шпінелі для імпульсної дальнометрії, зважаючи на її комерційну доступність, простоту технології виробництва, а також однорідність розподілу активатора у об'ємі. Визначена доцільність створення нового типу нелінійно-оптичних матеріалів на основі наноструктурованої термостійкої літійалюмосилкатної склокераміки з нанокристаллами шпінелі, які активовані іонами  $\text{Co}^{2+}$  в умовах низькотемпературної термічної обробки. Сформульовано мету та завдання роботи, які полягають у обґрунтуванні вибору системи та складів стекол для одержання склокристалічних матеріалів як пасивного лазерного затвору для потужних лазерів, які функціонують на довжині хвилі  $1,54$  мкм та відрізняються високою термостійкістю. Обґрунтовано вибір літійалюмосилкатної системи  $\text{R}_2\text{O} - \text{RO} - \text{RO}_2 - \text{P}_2\text{O}_5 - \text{R}_2\text{O}_3 - \text{SiO}_2$  на основі фазоутворюючих  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Li}_2\text{O}$ , модифікуючих  $\text{K}_2\text{O}$ ;  $\text{RO} - \text{MgO}$ ,  $\text{ZnO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{BaO}$  компонентів та комплексного каталізатору кристалізації  $\text{P}_2\text{O}_5$ ,  $\text{CeO}_2$ ,  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZrO}_2$  та  $\text{ZnO}$ , сформульовано структурні критерії до скломатриці. Спроектовано склади модельних стекол з урахуванням розрахованих показників  $f_{\text{Si}} > 0,22$ ,  $K_{\text{кр}} \geq 3,5$ ,  $K_{\text{пр}} \geq 2,1$  та встановлена вірогідність одержання на їх основі прозорих склокристалічних матеріалів із ситалізованою структурою для імпульсної дальнометрії.

**Ключові слова:** літійалюмосилкатні стекла; склокристалічні матеріали; наноструктура; шпінель; затвори; пасивна модуляція добротності

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**PROSPECTIVE LITHIUM ALUMINOSILICATE GLASS-CERAMIC MATERIALS FOR PULSE**  
**RANGEFINDERS**

The relevance of creating multi-functional nanosecond pulsed laser devices with a generation wavelength that lies in the conditionally eye-safe region of the spectrum of  $1.5\div 1.6$   $\mu\text{m}$  has been established. The prospects of using the mode of passive Q-switching when receiving powerful nanosecond laser pulses with a radiation divergence close to the diffraction one have been determined. Materials for shutters that function in the mode of passive Q-switching were analyzed: solid-state nonlinear optical materials based on single crystals of yttrium-aluminum garnet doped with cations of neodymium, chromium, vanadium and other Nd- or Yb-doped crystals in the wavelength range of  $0.8-1.2$   $\mu\text{m}$ . The promising use of oxide single crystals activated by  $\text{Co}^{2+}$  ions in four-coordinated oxygen positions for  $\text{MgAl}_2\text{O}_4$ ,  $\text{LiGa}_5\text{O}_8$ ,  $\text{LaMgAl}_{11}\text{O}_{19}$  has been confirmed. The feasibility of developing transparent glass-ceramics based on aluminomagnesium and lithium gallium spinel for pulsed ranging was determined, taking into account its commercial availability, the simplicity of the production technology, as well as the homogeneity of the distribution of the activator in the volume. The feasibility of creating a new type of nonlinear optical materials based on nanostructured heat-resistant lithium aluminosilicate glass ceramics with spinel nanocrystals activated by  $\text{Co}^{2+}$  ions under low-temperature heat treatment conditions, has been determined. The purpose and tasks of the work are formulated, which consist in justifying the choice of the system and compositions of glasses for obtaining glass-ceramic materials as a passive laser shutter for powerful lasers that operate at a wavelength of  $1.54$   $\mu\text{m}$  and are characterized by high heat resistance. The choice of the lithium aluminosilicate system  $\text{R}_2\text{O} - \text{RO} - \text{RO}_2 - \text{P}_2\text{O}_5 - \text{R}_2\text{O}_3 - \text{SiO}_2$  based on phase-forming  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Li}_2\text{O}$ , modifying  $\text{K}_2\text{O}$  is substantiated;  $\text{RO} - \text{MgO}$ ,  $\text{ZnO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{BaO}$  components and a complex crystallization catalyst of  $\text{P}_2\text{O}_5$ ,  $\text{CeO}_2$ ,  $\text{TiO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZrO}_2$  and  $\text{ZnO}$ . The structural criteria for the glass matrix were formulated. Compositions of model glasses were designed taking into account the calculated parameters  $f_{\text{Si}} > 0.22$ ,  $K_{\text{cr}} \geq 3.5$ ,  $K_{\text{pr}} \geq 2.1$ , and the probability of obtaining transparent glass-ceramic materials with a sitalized structure for pulse rangefinders was established on their basis.

**Keywords:** lithium aluminosilicate glasses; glass-ceramic materials; nanostructure; spinel; shutter; passive Q-switching

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**ПЕРСПЕКТИВНЫЕ ЛИТИЙАЛОМОСИЛКАТНЫЕ СТЕКЛОКРИСТАЛЛИЧЕСКИЕ**  
**МАТЕРИАЛЫ ДЛЯ ИМПУЛЬСНОЙ ДАЛЬНОМЕТРИИ**

Установлена актуальность создания импульсных наносекундных лазерных приборов полифункционального назначения с длиной генерации волны, лежащей в условно безопасной для зрения области спектра  $1,5\div 1,6$  мкм. Определена перспективность использования режима пассивной модуляции добротности при получении мощных наносекундных лазерных импульсов с расхождением излучения, близким к дифракционному. Проанализированы материалы для затворов, функционирующих в режиме пассивной модуляции добротности: твердотельные нелинейно-оптические материалы на основе монокристаллов итрієво-алюмінієвого граната легированного катіонами неодима, хрома, ванадія і других Nd- или Yb-легируемых кристаллов в диапазоне длин волн  $0,8 - 1,2$  мкм. Определена актуальность разработки прозрачной стеклокерамики на основе алюмомагнієвої і літєвогалієвої шпінелі для імпульсної дальнометрії, учитывая ее коммерческую доступность, простоту технологии производства, а также однородность распределения активатора в объеме. Определена целесообразность создания нового типа нелинейно-оптических материалов на основе термостойкой наноструктурированной литийалюмосилкатной стеклокерамики с нанокристаллами шпінелі, которые активированы ионами  $\text{Co}^{2+}$  в условиях низкотемпературной термической обработки. Обоснован выбор системы, модифицирующих компонентов и комплексного катализатора кристаллизации и сформулированы структурные критерии к скломатрице. Спроектированы составы модельных стекол с учетом рассчитанных показателей  $f_{\text{Si}} > 0,22$ ,  $K_{\text{кр}} \geq 3,5$ ,  $K_{\text{пр}} \geq 2,1$  и установлена вероятность получения на их основе прозрачных стеклокристаллических материалов с ситализованной структурой для импульсной дальнометрии.

**Ключевые слова:** литийалюмосилкатные стекла; стеклокристаллические материалы; наноструктура; шпінель; затвори; пассивная модуляция добротности

**Introduction.** Today, nanosecond pulsed laser devices are widely used in machine vision systems, virtual reality, geodesy, environmental monitoring systems, spacecraft landing systems, laser surgery, and distance measurement [1]. There is a particularly great need for the creation of radiation sources with a generation wavelength that lies in the conditionally eye-safe range of the spectrum (1.5–1.6  $\mu\text{m}$ ), which is extremely important in connection with the risk of interaction of radiation with people. This feature of lasers in the eye-safe spectrum region allows to work with radiation energies of lasers of nanosecond duration three orders of magnitude higher than for lasers with a radiation wavelength in the range of 1  $\mu\text{m}$ . An additional advantage of such lasers is the availability of photodetectors for a wavelength of 1.5–1.6  $\mu\text{m}$  with maximum sensitivity at room temperature, as well as the fact that this spectral range is in the window of atmospheric transparency.

Laser ranging is one of the first areas of practical application of lasers in the military field. Currently, laser rangefinders are used in military equipment (artillery, tank), in aviation (rangefinders, altimeters, target pointers), in the navy. To ensure high peak power, it is necessary to use lasers operating in Q-switching mode. Currently, rangefinders mainly use cumbersome and expensive active Q-switching of radiation, which have a weak effect on spatial characteristics and require additional power supply and control. An alternative and most promising method of obtaining powerful nanosecond laser pulses with a radiation divergence close to the diffraction one is the use of the passive Q-switching mode. This mode is carried out using passive shutters (PS) based on solid-state nonlinear optical materials - saturable absorbers, the transmittance of which depends nonlinearly on the radiation energy density. The use of PS miniature that does not require external control provides the Q-switching mode of lasers with a radiation divergence close to the diffraction one. In addition, the use of PS allows to minimize the dimensions and energy consumption of lasers that are developed for pulse rangefinders, which corresponds to the trends in the development of technology. All this determines the urgency of creating a new type of technological materials for passive Q-switchings. This will ensure the high functionality of military equipment and machinery, especially in the conditions of hostilities.

**Literature review.** Lasers based on Yb:Er phosphate glass, which is currently the most effective and available active medium for obtaining high energies of nanosecond duration, have become widely used in pulsed ranging in the eye-safe range [2]. In order to create compact and reliable lasers in the eye-safe spectrum region, it is necessary to ensure the simplicity of their implementation. The use of affordable, compact and reliable semiconductor laser pumping diodes with a generation wavelength in the range of 940–980 nm allows

efficient pumping of Yb<sup>3+</sup> ions into the 2F7/2 → 2F5/2 transition with subsequent non-radiative energy transfer to Er<sup>3+</sup> ions in Yb:Er glass.

The yttrium-aluminum garnet crystal doped with trivalent vanadium V<sup>3+</sup> in the tetrahedral position is a relatively new material for passive Q-switching (PQS). The V:YAG crystal works as an effective Q-switching for lasers operating in the 1.0 ~ 1.5  $\mu\text{m}$  region by the 3A2 → 3T2 transition of the V<sup>3+</sup> ion into the tetrahedral position of the garnet lattice. The concentration of V<sup>3+</sup> in the tetrahedral position is controlled by growth and annealing conditions [3]. One of the notable features of Cr<sup>4+</sup>:YAG is the high threshold of MW/cm<sup>2</sup> damage [4].

Single crystals based on Nd:YAG, Nd:LuAG and other Nd- or Yb-doped crystals in the wavelength range of 0.8–1.2  $\mu\text{m}$  are an effective material for shutters that function in the mode of passive Q-switching [5]. Efficient Q-switching of lasers operating at both 1.064 and 1.3 microns has been achieved with a range of active media such as Nd:YAG, Nd:YVO<sub>4</sub>, Nd:KGd(WO<sub>4</sub>)<sub>2</sub> under flash and pump laser diode [6].

Wide use of polycrystalline magnesium aluminate (MgAl<sub>2</sub>O<sub>4</sub>) in science and technology is explained by a unique combination of chemical, mechanical and optical properties [7]. To date, the effectiveness of its use as UV lenses for lithography, electrical insulation and for protective windows in the range of IR radiation, in the development of armor materials [8], Al- and Mg-ion batteries [9], and pigments for glazes in the ceramic industry has been confirmed [10].

Spinel crystals have attracted a lot of attention during the last decade due to the rapid development of the telecommunications industry. They are effectively used for manufacturing passive shutters of Q-switching lasers or decoupling systems of multi-cascade generators [11, 12]. Materials based on Co<sup>2+</sup> ions are the most effective and common among nonlinear absorbers in lasers in the eye-safe range. Tetracoordinated Co<sup>2+</sup> ions are widely used as an impurity material for the illuminating medium in lasers of the eye-safe spectrum.

In general, the creation of materials for nonlinear optical absorbers of laser radiation at a wavelength of about 1.5  $\mu\text{m}$  is promising based on oxide single crystals activated by Co<sup>2+</sup> ions in four-coordinated oxygen positions (Co<sup>2+</sup>: MgAl<sub>2</sub>O<sub>4</sub>, Co<sup>2+</sup>: LiGa<sub>5</sub>O<sub>8</sub>, Co<sup>2+</sup>: LaMgAl<sub>11</sub>O<sub>19</sub>). Their spectroscopic parameters satisfy the conditions for ensuring an effective PQS mode of laser operation, which is confirmed by works on obtaining a PQS mode based on them with high energies and short pulse durations.

But the synthesis of oxide single crystals is complicated by the need to use expensive equipment and equipment under conditions of high temperatures (melting temperature ≈ 2273 K), the need to observe the homogeneity of the distribution of the activator in the volume, and low optical quality. For crystals of aluminomagnesium spinel and lithium gallium spinel, which are activated by tetrahedrally coordinated divalent

cobalt ions, cobalt ions have an absorption band in the region of 1.3-1.6  $\mu\text{m}$ , the absorption cross section in which is significantly higher than the cross section of the stimulated emission of erbium ions in active elements based on phosphate glasses. Therefore, the use of such passive shutters is possible without additional focusing of extraction inside the laser resonator. The disadvantages of such materials are their low commercial availability, complex and expensive production technology, as well as the heterogeneity of the distribution of the activator in the volume.

Obtaining composite materials based on optical glass-ceramics with oxide nanocrystals activated by  $\text{Co}^{2+}$  ions will create a scientific and technological basis for the development of materials production technology for passive q-switching of the radiation of Yb-Er lasers (1.5  $\mu\text{m}$ ), which is an indispensable stage in the development of compact pulsed lasers of eye-safe range of wavelengths. It is the nanophase glass-ceramic materials that make it possible to provide a set of the necessary nonlinear optical, spectroscopic properties and operational characteristics for the effective use of these materials in lasers in the eye-safe spectral region.

Alternative glass-ceramic materials containing the spinel crystal phase  $\text{Co}^{2+}:\text{MgAl}_2\text{O}_4$  [12]  $\text{Co}^{2+}:\gamma\text{-Ga}_x\text{Al}_{2-x}\text{O}_3$  [13] are known. For transparent glass-ceramics based on  $\text{Co}^{2+}:\text{MgAl}_2\text{O}_4$  for elements of passive Q-switching in the Er:glass laser at 1.534  $\mu\text{m}$ , the fundamental properties of the samples important for the internal cavity operation of the laser were determined: thermo-optical coefficient  $dn/dT = (-3.8 \pm 1) \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ , thermal lensing factor  $L\text{-}1d(nL)/dT = 2.59 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ , thermal polarization coefficient  $\phi = (7.2 \pm 2.2) \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  and the damage threshold  $\sim 6.5 \text{ J/cm}^2$ , coefficient of linear thermal expansion  $\alpha = (3.9 \pm 0.6) \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  [12]. The disadvantage of the material is that it contains only one crystalline phase – normal spinel with  $\alpha = (50\text{-}70) \cdot 10^{-7} \text{ }^\circ\text{C}^{-1}$ , which makes it impossible to use it for the manufacture of passive Q-switching of powerful lasers, i.e. such material is characterized by low heat resistance. This problem can be solved by creating a new type of nonlinear optical materials based on nanostructured heat-resistant glass-ceramics with nanocrystals that are activated by  $\text{Co}^{2+}$  ions for lasers that emit in the eye-safe range.

**The purpose of the work.** The purpose of this work is to substantiate the choice of the system and composition of glasses for obtaining glass-ceramic materials as a passive laser shutter for powerful lasers that operate at a wavelength of 1.54  $\mu\text{m}$  and are characterized by high thermal resistance

To achieve this purpose, the following tasks were set:

- analysis of the current state of development of materials for laser rangefinding;
- rationale for choosing a system for obtaining optical glass-ceramic materials;

- design of glass compositions for obtaining glass-ceramic materials for a passive laser shutter;

- calculation of structural coefficients of model glasses, selection of the area of compositions for synthesis of glasses.

#### The experimental results and their discussion.

Most of the development of glass-ceramic materials for this purpose refers to the  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  (M-A-S) systems, which differ in the content of spinel with a coefficient of linear thermal expansion of  $(50\text{-}70) \cdot 10^{-7} \text{ }^\circ\text{C}^{-1}$ . This limits their use for the manufacture of passive Q-factor modulators of powerful lasers, since such material is not characterized by high thermal resistance. Also, for glasses of the M-A-S system, melting is carried out at temperatures of 1853-1923 K followed by annealing at 913 K, the nucleation stage takes place at 1023 K for 6 hours, and the crystallization stage at 1073-1323 K for 6 hours. Such multi-stage, high temperatures and duration complicate the technological process and increase the cost of materials.

The high demand for the production of transparent glass-ceramics with high heat resistance and saturated absorption determines the need to create new types of technological nanostructured glass-ceramics. The choice of the lithium aluminosilicate system (L-A-S) in the creation of glass-ceramic materials for passive laser shutters in the wavelength range of 1.2-1.6  $\mu\text{m}$  is determined not only by the low absorption saturation intensity at this wavelength, the low value of coefficient of linear thermal expansion, but also by the possibility of forming a nanostructure with spinel content under conditions of short-term (2 h) low-temperature heat treatment (at the first stage 953-1023 K, at the second stage 1023-1073 K) to ensure high physico-chemical properties. To solve this problem, it is necessary to develop a new material for passive laser shutters - transparent glass-ceramics based on the lithium aluminum silicate system, which contains crystalline phases of normal spinel, which is modified by  $\text{Co}^{2+}$  ions in tetrahedral coordination in a concentration from 0.02 to 0.2 wt.% and  $\beta$ -quartz solid solution. The crystalline phase of traditional spinel, which is modified with cobalt ions, provides saturated absorption in the wavelength range of 1.2-1.6  $\mu\text{m}$ , and the lithium aluminosilicate crystalline phase with a  $\beta$ -quartz structure - the coefficient of linear thermal expansion of the resulting material is close to zero. Broadband absorption in the range (for Co:AS) is due to the transition  $4A_2(4F) \rightarrow 4T_1(4F)$  of  $\text{Co}^{2+}$  ions having tetrahedral coordination in the corresponding nanocrystals [14-15].

Achieving high transparency in the visible part of the spectrum, intense saturated absorption in the wavelength range of 1.2-1.6  $\mu\text{m}$ , and thermal strength of lithium aluminosilicate glass-ceramic materials is expedient to implement by ensuring nano-scale fine-dispersed volumetric crystallization of the initial glass by the mechanism of phase separation with the formation of crystalline phases of cobalt aluminates and lithium aluminosilicates by directed low-temperature

crystallization of glass under the conditions of two-stage short-term heat treatment.

To solve this problem, the compositions of glasses in the L-A-S system in the area of crystallization of normal spinel and  $\beta$ -eucryptite or  $\alpha$ -spodumene with a specific content of phase-forming components and modifying additives and crystallization catalysts were chosen. In order to obtain glass-ceramic materials with an adjustable content of crystalline phases, the content of phase-forming components is chosen in a wide range, mass. %:  $\text{SiO}_2$  45-60,  $\text{Al}_2\text{O}_3$  20-36,  $\text{Li}_2\text{O}$  4.0-6.5.

A complex crystallization catalyst containing  $\Sigma$   $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{P}_2\text{O}_5$  and  $\text{CeO}_2$  with a content of 2.5 to 6.5 wt. % was chosen to ensure the formation of a self-organized dissipative structure of glasses after melting and heat treatment. The introduction of  $\text{P}_2\text{O}_5$  in the range of 2.0-3.0 wt. % into the composition of materials allows for the processes of nanostructuring of glass at the initial stages of nucleation, and, together with the presence of  $\text{ZnO}$  (up to 2.0 wt. %) and  $\text{CeO}_2$  (0.1-0.5 wt. %), will contribute to the formation of a thin crystalline interlocked structure by the mechanism of spinodal phase separation in the range of low temperatures. The introduction of  $\text{ZnO}$  also makes it possible to significantly reduce scattering. However, the content of  $\text{ZnO}$  should be at least 1.0 wt. % for the need to initialize nucleation and shift the nucleation interval to the range of lower temperatures to obtain a nanoscale structure.

The efficiency of intensive heterogeneous nucleation and reduction of the time of sinterization is ensured by the introduction of  $\text{TiO}_2$  and  $\text{ZrO}_2$  in the amount of 1.0 to 1.5 wt.% each and  $\text{SnO}_2$  from 0.1 to 2.5 wt.%. Addition of  $\text{ZrO}_2$  will also provide the correspondence of the refractive indices of the amorphous and crystalline phases in the structure, which will have a positive effect on the light transmission, chemical resistance, strength and heat resistance of the material. The sum of  $\text{TiO}_2 + \text{ZrO}_2 + \text{SnO}_2$  nucleating agents should be from 2.1 to 5.5 wt.%, the minimum content is necessary for fast enough nucleation, the upper limit of up to 5 wt.% follows from the requirements for devitrification resistance. Exceeding the  $\text{TiO}_2$  content above 2.5 wt. % is unfavorable for ensuring the optical transparency of the material, as the formation of the coloring complex  $\text{SnO}_2/\text{TiO}_2$  can be observed. Therefore, the content of  $\text{SnO}_2$  should be  $\geq 0.1$  wt.% to ensure a sufficient lighting effect. Physical depigmentation agent  $\text{Nd}_2\text{O}_3$  was introduced in the amount of 0.01 to 0.03 wt.% to reduce coloration based on coloring complexes  $\text{SnO}_2/\text{TiO}_2$ . Exceeding the content of the specified crystallization catalysts can negatively affect the melting behavior of the batch and affect the intensive growth of crystals during heat treatment, which will lead to a loss of transparency and strength of the glass-ceramic material. Important for the crystallization process is the presence of  $\text{MgO}$ ,  $\text{ZnO}$ ,  $\text{CaO}$ ,  $\text{SrO}$  and  $\text{BaO}$  divalent components, which can be effectively added in the amount of 1.5-5.0 wt. %. Alkaline earth metals  $\text{CaO}$ ,  $\text{SrO}$ , and  $\text{BaO}$  increase the resistance of glass to uncontrolled devitrification by Zr-containing crystals,

such as baddeleyite or zirconium silicate, which will negatively affect the transparency and ability to form glass-ceramic material in a short time during low-temperature heat treatment. It is the shortening of the crystallization time that allows to minimize the dispersion of the material and ensure the formation of a self-organized, high-strength sinterized structure. The introduction of  $\text{MgO}$  into the composition in the amount of 0.2 to 1.0 wt.% affects the reduction of the viscosity of the glass melt at high temperature. Importantly, the introduction of  $\text{BaO}$  will increase the refractive index of the glass, which is necessary to balance the refractive index of the residual glass and the crystalline phase. Too high content negatively affects the crystallization process during the formation of glass-ceramic material. In addition, a high content of alkaline earth metals can significantly reduce the heat resistance of products. Therefore, the total content of  $\text{CaO}$  and  $\text{SrO}$  alkaline earth oxides should be up to 1.5 wt.%, and the content of  $\text{BaO}$  is from 0.05 to 1.5 wt.% [15].

The technical difficulties of obtaining transparent sinterals are related to two factors: firstly, due to the high viscosity of the melt, the glass melting temperature is above 1873 K. Secondly, as a result of heat treatment, the residual glass phase is characterized by a positive, and the crystalline phase ( $\beta$ -quartz solid solutions) by a negative CLTE, which leads to cracking. Lowering the melting temperature is possible due to the introduction of impurities into the glass composition, which reduce the viscosity of the melt and, accordingly, the melting temperature and refining of the glass mass. At the same time, the type and size of crystals released during the heat treatment of glasses should ensure optical transparency  $\leq 40 \mu\text{m}$  and a low coefficient of linear expansion of sinteral in the temperature range of its operation  $(15-25) \cdot 10^{-7} 1/^\circ\text{C}$ . In order to reduce the melting temperature and ensure the transparency of the glass [16],  $\text{B}_2\text{O}_3$  was added to the composition of glasses in the amount of 3.0 to 5.0 wt.%. Stibium oxide in the amount of 1.0 wt.% was added to the composition of glasses to simultaneously reduce the viscosity of the melt and improve the refining conditions of the glass mass. For developed glass-ceramic materials with a degree of crystallinity of at least 50 vol. %, taking into account the high tendency of stibium oxide to glass formation, the structure of the residual glass phase will be formed with the participation of oxides of silicon, phosphorus, stibium and boron. Since the strength of the  $\text{Sb}-\text{O}$  bonds is significantly lower than the bond strength of other glass formers, the elastic properties of the residual glass phase decrease, and the formed nanocrystals are located in a more plastic matrix. This determines the significant stability of CLTE of sinterals in a wide range of temperatures and a decrease in the glass melting temperature. Increasing the content of  $\text{K}_2\text{O}$  alkaline oxide more than 2.0 wt. % can lead to an increase in the coefficient of linear thermal expansion of glass-ceramics and an increase in scattering, which is unacceptable when obtaining optically transparent thermally stable materials. Therefore, the  $\text{K}_2\text{O}$  content was 0.5-1.5 wt.%.

The simultaneous introduction of  $B_2O_3$ ,  $Al_2O_3$ ,  $SiO_2$  will make it possible to form a strong aluminoborosilicate frame of glass, and with the same time introduction of  $ZrO_2$ ,  $MgO$ , increase the impact toughness of glasses and crack resistance of glasses, which creates favorable conditions for their use under significant thermal loads in powerful lasers. To establish the area of initial glasses, the  $R_2O - RO - RO_2 - P_2O_5 - R_2O_3 - SiO_2$  system was chosen where,  $R_2O - Li_2O, K_2O; RO - MgO, ZnO, CaO,$

$SrO, BaO; RO_2 - TiO_2, ZrO_2, CeO_2, SnO_2; R_2O_3 - Al_2O_3, B_2O_3, Sb_2O_3, Nd_2O_3,$  and compositions of lithium aluminosilicate glasses with ShLSK marking were selected (Table 1).

When designing compositions of model glasses, the determining factor is ensuring the strength of the  $f_{Si}$  silica framework and the required degree of crystallinity when forming an optically transparent structure (Table 2).

Table 1. – Chemical content of oxides in the composition of glasses

Oxides	Glass marking									
	ShLSK-1	ShLSK-2	ShLSK-3	ShLSK-4	ShLSK-5	ShLSK-6	ShLSK-7	ShLSK-8	ShLSK-9	ShLSK-10
	Differences in chemical composition, wt. %									
$SiO_2$	45	48	49	50	52	53	55	56	58	60
$Al_2O_3$	36	34	35	28	22	26	25	27	26	20
$R_2O$	7.0	6.19	5.3	6.0	7.0	4.5	5.8	5.0	4.5	7.0
RO	2.0	2.5	1.6	3.0	5.0	5.5	3.0	2.2	2.0	2.0
$RO_2$	2.48	2.1	2.6	5.0	5.5	2.98	3.2	2.28	3.49	4.48
$P_2O_5$	2.5	3.0	2.0	3.0	2.49	3.0	3.0	2.5	2.0	2.5
$R_2O_3$	5.0	4.2	4.48	4.98	6.0	5.0	4.98	5.0	4.0	4.0
CoO	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.02	0.01	0.02

Table 2. – Calculated values of structural coefficients for model glass

Calculated coefficients	Glass marking									
	ShLSK-1	ShLSK-2	ShLSK-3	ShLSK-4	ShLSK-5	ShLSK-6	ShLSK-7	ShLSK-8	ShLSK-9	ShLSK-10
Coefficient of silicon-oxygen framework bonding, $f_{Si}$	0.331	0.331	0.322	0.253	0.309	0.245	0.277	0.256	0.261	0.273
Structural factor, $\Psi_{A/B}$	-	-	-	-2.04	-	-2.46	-12.19	-14.25	-	-1.61
Transparency coefficient, $K_{tr}$	2.11	2.15	2.17	2.14	2.20	2.01	2.03	2.00	2.15	2.09
Crystallinity coefficient, $K_{cr}$	19.74	10.23	12.15	6.01	9.26	5.42	11.02	10.61	13.92	8.22

All experimental glasses are structurally strong, as they are characterized by  $f_{Si} > 0.22$  and the  $\Psi_{A/B}$  ratio, whose numerical values for all compositions are greater than unity, indicating the predominant presence of  $[BO_4]$  and  $[AlO_4]$  tetrahedra in the glass structure. The value of the crystallinity coefficient  $K_{cr} > 3.5$  indicates that the total content of modifier oxides in the composition of the melt is sufficient for the formation of structurally formed sybotaxic groups, which are the nuclei of the crystalline phase, the value of the transparency coefficient  $K_{tr} > 2.1$  indicates favorable conditions for nucleation during cooling and growth of crystals during heat treatment. The presence of a complex crystallization catalyst of  $P_2O_5$ ,  $CeO_2$ ,  $TiO_2$ ,  $SnO_2$ ,  $ZrO_2$  and  $ZnO$  will allow the formation of nuclei by the phase separation mechanism and ensure nanostructuring during sinterization. The theoretical justification of the choice of the system and the value of the calculation criteria make it possible to choose the range of composition of model glasses for obtaining glass-ceramic materials, for shutters that function in the mode of passive Q-switching.

**Conclusions.** The choice of the lithium aluminosilicate system with the content of the  $MgO$ ,  $ZnO$ ,

$CaO$ ,  $SrO$ ,  $BaO$  modifying components, the  $P_2O_5$ ,  $CeO_2$ ,  $TiO_2$ ,  $SnO_2$ ,  $ZrO_2$  and  $ZnO$  complex catalyst of crystallization is substantiated for the production of glass-ceramic materials for passive laser shutters which operate in the mode of passive Q-switching. The influence of the chemical composition on the structure and properties of glass-ceramic materials based on them was analyzed. The structural criteria for the glass matrix were formulated and the compositions of model glasses were designed for the synthesis of heat resistance glass-ceramic materials, which are characterized by  $f_{Si} > 0.22$ ,  $K_{cr} \geq 3.5$ ,  $K_{tr} \geq 2.1$ .

It has been established that intense saturated absorption in the wavelength range of 1.2-1.6  $\mu m$  and heat resistance can be realized by ensuring nanoscale fine-dispersed volume crystallization of the initial glass by the phase separation mechanism with the formation of crystalline phases of aluminomagnesium spinel activated by  $Co^{2+}$  ions and lithium aluminosilicates by directed low-temperature crystallization of glass under conditions of two-stage short-term heat treatment. The theoretical justification of the choice of the system and composition of model glasses will allow the synthesis of glass-ceramic materials with a defined structure and properties, taking into account modern requirements for the development of new materials for pulse rangefinders.

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