Promising cobalt-containing magnesium aluminosilicate glass-ceramic materials for lasers on Yb-Er glass

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Abstract* – The aim of this work is to develop efficient saturated absorbers based on magnesium aluminosilicate glass-ceramic materials for lasers based on Yb-Er glass. The system was chosen and the mechanism of phase formation was studied. Transparent sitals based on spinel nanocrystals doped with Co^{2+} ions and modified with ZnO, P_2O_5 CeO_2, and B_2O_3 were obtained.

Keywords – magnesium aluminum silicate glass, spinel nanocrystals, Q-factor modulation, passive gates.

Introduction

The intensive use of pulsed nanosecond laser devices for measuring distances with high accuracy for environmental monitoring systems, geodesy, and military purposes determines the need to develop new effective materials for laser rangefinders [1]. Global Laser Rangefinder market was valued at USD 960 million in 2020 and it is expected to reach USD 1703 million by the end of 2027, growing at a CAGR of 8.5 % during 2021-2027 [2].

Especially great is the need to create radiation sources with a generation wavelength lying in the region of the spectrum (1.5–1.6 μm) that is conditionally safe for sight, which is extremely important in connection with the risk of radiation interaction with people. To achieve a pulse duration of tens of nanoseconds in safe vision lasers, the main method for obtaining such pulses with high peak power is used: the Q-switched (QS) mode. There are two ways to provide Q-switching: active Q-switching (AQS), which is provided by an externally controlled device, and passive Q-switching (PQS), which is provided by a saturable absorber (SA). Compared to the AQS methods, the PQS mode is a simple and compact method for obtaining a monopulse, which is explained by the absence of the need to use external control systems. The energies of pulses into lasers with PQS are, as a rule, lower than when using AQS methods [3]. The PQS mode is implemented using passive shutters based on solid-state nonlinear optical materials – saturable absorbers, the transmission of which depends nonlinearly on the energy density of the incident radiation. The use of miniature passive shutters (PS) that do not require external control provides the Q-switching regime for lasers with radiation divergence close to diffraction. In addition, the use of PS makes it possible to minimize the dimensions and power consumption of lasers developed for pulsed rangefinders, which corresponds to the trends in the development of technology.

Single crystals based on Nd:YAG, Nd:LuAG, Nd:YVO4 and other Nd- or Yb-doped crystals are an effective active medium material for those operating in the passive Q-switching mode [3]. Lasers based on Yb:Er phosphate glass, which is currently the most effective and currently available active medium for obtaining high energies of nanosecond duration, will receive significant distribution and further development in pulsed farometry of the range safe for sight. The disadvantage of Yb:Er glass is its low thermal conductivity, which limits the frequency of passage of laser pulses based on it. Er^{3+}-containing lasers-on-crystals operating in a spectrum that is safe for sight are largely deprived of this shortcoming [1]. They use PSs activated by Er^{3+} ($Ca_5(PO_4)F_3$), U^{2+} (CaF_2), Cr^{2+} (LiCaF [4], ZnSe) and Co^{2+} ions for passive Q-factor modulation. The most effective and widespread, among them, are materials based on Co^{2+} ions. Tetracoordinated Co2+ ions are widely used as an impurity material for an antireflection medium in lasers in eye-safe spectral regions. For Co^{2+}: ZnS, Co^{2+}:ZnSe, $Co^{2+}:MgAl_2O_4$, $Co^{2+}:LiGa_5O_8$, $Co^{2+}:LaMgAl_{11}O_{19}$ crystals, their spectroscopic parameters are sufficient to ensure the effective PQS mode of laser operation. The disadvantages of crystalline PS based on Co^{2+} ions are the inhomogeneity of the distribution of the activator over the volume of the material and low commercial availability due to the complex and expensive production technology.

Obtaining composite materials based on optical glass-ceramics with oxide nanocrystals activated by Co^{2+} ions will create a scientific and technological basis for the development of a technology for the production of materials for passive Q-switches of Yb-Er lasers (1.5 μm). It is nanophase glass-ceramic materials that make it possible to provide the set of necessary nonlinear optical, spectroscopic, and operational properties for the effective use of these materials in lasers in the sight-safe region of the spectrum.

Most spinel-containing optically transparent nanostructured glass-ceramic materials are developed on the basis of the $MgO–Al_2O_3–SiO_2$ system. To ensure the flow of the necessary phase formation processes at relatively high temperatures of cooking and heat treatment at (950 °C), crystallization catalysts – TiO_2 (5 wt. %) and ZrO_2 (3 wt. %) are introduced into their composition [6]. However, the high viscosity of such materials complicates the formation of products from them by traditional glass technology methods.

Nanophase glassceramics [7] are known for the manufacture of passive gates operating in the PQS mode, based on glasses mol. %: 20 MgO, 20 Al_2O_3, 60 SiO_2, and 10 TiO_2 doped with Ga_2O_3 (2.5 mol. %) and CoO (0.1 wt. %). The technology for obtaining this material provides for a number of successive processes associated with heat treatment of the material at different temperatures, namely: synthesis of glass-ceramics (matrix) – 1580 °C; annealing – 660 ºC; nucleation (nucleation of crystals) – 750 °C for 6 hours; crystallization (crystal growth) – at 800–950 °C for 6 hours. Such a multi-stage synthesis, its high temperatures and duration of heat treatment complicate the technological process and increase the cost of materials. The solution to this problem is the creation of nanostructured glass-ceramic materials based on cobalt-containing spinel with a reduced temperature and duration of heat treatment.

Experimental part

For this purpose, a magnesium aluminosilicate system was chosen containing a complex crystallization catalyst that contains TiO_2, ZrO_2, ZnO, P_2O_5 and CeO_2 to provide a nanoscale structure and B_2O_3 to reduce viscosity. The introduction of P_2O_5, ZnO, CeO_2 and TiO_2 into the composition of magnesium aluminosilicate glasses will accelerate the processes of the nucleus in their structure at low temperatures, and will contribute to the formation of a nanocrystalline interconnected structure already at a temperature of 900 °C for only 0.5 hours. Approximation of the refractive index of the glass phase of the phase due to the introduction of ZrO_2 will make it possible to obtain a crystallized structure with high optical and thermal characteristics. The introduction of CoO in an amount of 0.2 wt. % will ensure the absorption cross section from the ground state for Co^{2+} ions $\sigma GSA = (2.5 \pm 0.3)\ 10^{-19}$ cm^2, and the absorption cross section from the excited state $\sigma ESA = (0.4 \pm 0.2)\ 10^{-19}$ cm^2.

Ensuring a high coefficient of non-selective diffuse absorption (95–97%) in the visible and IR spectral regions for saturated absorbers (passive laser switches) based on magnesium aluminosilicate glass ceramics can be realized by providing finely dispersed bulk crystallization of the initial $Co^{2+}:MgAl_2O_4$ glass. This process proceeds by directed low-temperature crystallization of glass according to the healing mechanism of the embryo under conditions of two-stage high-speed heat treatment.

Important parameters for the formation of a material structure with nonlinear optical characteristics are:

- the content of the crystalline phase is not more than 50 vol. %;
- particle size is less 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.

The compositions of model glasses were synthesized in the temperature range 1550–1600 °C and the region of glass formation was investigated. The mechanism of magnesium aluminosilicate glass-ceramic materials during heat treatment, consisting in the flow of: the process of the nucleus (750–850 ºC) and the subsequent formation of solid solutions with the structure of high-temperature quartz (800–900 °C) and spinel (900–1000 °C) has been established. The study of phase transformations and features of crystallization of the developed magnesium aluminosilicate glass-ceramic materials under conditions of low-temperature short-term heat treatment makes it possible to establish the possibility of obtaining on their basis optical sitals based on spinel nanocrystals doped with Co^{2+} ions with a reduced molding temperature.

Conclusions

The choice of the initial system is substantiated and the initial glasses are synthesized. The features of the processes of structure and phase formation during the heat treatment of experimental glasses are determined. The developed nanostructured magnesium aluminosilicate glass-ceramic materials are promising for obtaining passive switches for lasers emitting at a wavelength of 1.54 μm.

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