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Formation of nanostructured state in $LaBGeO_5$ monolithic glass using pulsed magnetic fields

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Abstract. Using the methods of transmission electron microscopy, X-ray structure analysis and thermal differential analysis, it has been discovered that the pulsed magnetic field (PMF) intensifies homogeneous crystallization in $LaBGeO_5$-glass system, promotes homogenization of crystalline phase distribution inside the bulk of glass matrix. A possibility of obtaining the volume nanostructured state in $LaBGeO_5$-glass due to application of PMF has been suggested and experimentally grounded.

Keywords: glass nanocomposites, sensors, stillwellite, pulsed magnetic field.

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1. Introduction

Development of optoelectronics, photonics and communication technologies has greatly increased demand for novel advanced materials with non-linear optical or sensor (pyroelectric, ferroelectric, etc.) properties. In this relation, glass is of great interest as a class of the materials that combines extremely high optical performance and low-cost as compared with monocrystalline analogues.

In the past, glass was considered as a viscous liquid with short-range order, while crystalline matter was attributed to the presence both short– and long-range orders [1, 2]. Nowadays, the crystalline and amorphous states are no longer regarded as strictly polar substance of the condensed matter. For instance, intermediate nanoscale states were found in solid solutions of glass at initial stages of phase separation, which are responsible for unique combination of electrical, mechanical and optical properties [3]. Controlled formation of the glass functional structures at nanoscale is extremely perspective for a new generation of the functional materials, such as transparent ferroelectric glass ceramic, glass with piezo- and pyroelectric properties, gradient optical media for laser technologies, optoelectronics and photonics.

Ferroelectric $LaBGeO_5$-glass (LBG) along with unique combination of pyroelectric properties, like low ferroelectric losses (tg $\delta \sim 0.001$) at a significant level of pyroelectric activity ($\gamma \sim 5…10$ nC/cm^{2}K), high value of electrical resistance ($\rho_v > 10$ GOhm·cm at 300 K) [4, 5], high coercive force and ability to bulk polarization, has

the coefficient of thermal expansion (CTE) of $(6\times10^{-6})K^{-1}$ [6], which corresponds to the ceramic materials. Therefore, due to nanostructural organization, the composite materials based on $LaBGeO_5$-glass are promising for usage both as an active media for lasers and optoelectronic communication technologies (namely, for active elements of generating, amplifying and controlling systems) as well as a constructural material for high-temperature ceramic composites in the ***solid oxide fuel cell*** technology (SOFC).

Due to superficial nature of LBG-glass crystallization, it is very difficult to get a high dense, nanodimensional crystalline phase in a bulk, which is responsible for functional and physical-mechanical properties of the resulted materials.

Taking into account the significant thermodynamic instability of the glass structure and quantum nature of the nanosized crystalline cells formation process in the bulk of a glass matrix, one of the promising approaches is usage of an external structure-forming actions of electromagnetic nature, namely, pulsed magnetic fields (PMF).

It was shown for a wide range of non-magnetic materials that PMF initiates a long-term change of the structure and physical properties in condensed matter. Both melting temperature, activation energy and crystallization temperature changed after brief exposure by weak PMF of $10^5…10^6$ A/m [7, 8, 9]. However, the questions of the nanoscale structures formation in oxide glass using PMF are not enough highlighted in literature. The possibility of weak PMF to intensify the processes of structural transformation in oxide glass, in particular of $MgO\text{-}Al_2O_3\text{-}SiO_2$ composition [10], and bulk character of the electromagnetic field influence on diamagnetic materials allows to expect a positive PMF effect on nanostructures formation in LBG-glass.

This work is aimed at validation of the above mentioned statement and investigation of the relevant effects of weak PMF influence on structural transformation in the bulk of LBG glass system.

2. Experimental

Amorphous glass was obtained by fast cooling between metal plates, the mixture consisted of molten oxides of LaO_2 (25%) – $50B_2O_3$ (50%) – $25GeO_5$ (25%). The melt was obtained by induction heating of the co-mingled oxides up to a 1500 °C in a platinum crucible and soaking time of 20 min. After polishing, the transparent $LaBGeO_5$-glass plates (with the surface area close to 1 cm^2 and the average weight of 0.6 g) were subjected to the thermal treatment at 600 °C for 2 h aimed at removal of internal stresses. The obtained samples were treated at room temperature by exponentially growing weak magnetic field pulses (peak intensity (H) of 10^6 A/m) with the frequency (f) close to 1 Hz, while the untreated ones were used as reference onset. Then, the crystallization annealing of the samples was performed in two steps: (1) "step-by-step" increase of temperature for 6 h between 650 to 680 °C with the step of 5 °C; followed by (2) increase of the temperature up to 705 °C and soaking time 2 h.

In some cases, PMF treatment was carried out both at room temperature and at annealing stage as well. Samples were studied using X-ray analysis (XRD) with DRON-3 diffractometer, Electron Spin Resonance (ESR) with RE-1306 spectrometer, Differential Thermal Analysis (DTA) with "Metler" derivatograph, Optical (POLAM R-311 polarization microscope) and Transmission Electron Microscopy (TEM) with JEM 200A devices. Before registering the ESR spectra, the reference and PMF-treated samples were subjected to the thermal treatment at 530 °C for 2 h and then exposed by strong X-ray radiation for 45 min at room temperature.

3. Results and discussion

According to X-ray investigation, the $LaBGeO_5$ crystal has monoclinic structure[1)] and belongs to the simple monocentric compounds (acentric spatial groups of $P3_1$ or $P3_121$) [11]. The stillwellite structure consists of spiral positioned chains of BO_4 tetrahedrons, (B–O bonds are of 1.454…1.502 Å), which stretches along the helical axis of the third order (Fig. 1a). In the $LaBGeO_5$ structures, atoms of Ge are similar to Si atoms in $LaBSiO_5$ stillwellite and are arranged in distorted tetrahedrons (Ge–O bonds are of 1.719…1.789 Å), La atoms are arranged in 9-hedrons (polyhedrons) above and under the Ge-tetrahedrons (Fig. 1b) [12]. La-polyhedrons have two common edges with GeO_4- and BO_4-tetrahedrons; and common edges in 9-hedrons are the shortest ones.

Under thermal treatment at low-temperature (T ~ 650…680 °C), the amorphous borogermanate glass transforms into two different chemical phases with developed interface. However, the homogeneous bulk crystallization do not proceed [13], because none of them contains a nuclear of the stillwellite phase. Homogeneous crystallization (or the so-called "crystallization without catalyst") in such glass systems, according to Ya. Fedorovsky's studies [14], realizes by diffusion processes of the glass crystal structure reconstruction with oxygen-cationic tetrahedral and polyhedral functional groups presented in solid glass composition. These processes are of considerable activation energy, thus requiring certain kinetics stimulus. In general, the thermodynamic conditions for the realization of homogeneous nucleation in bulk are presented. However, much higher temperature is required than that of growth and development of the LBG phase on the defects or/and heterogeneous surface presented in the bulk glass after synthesis (the so-called heterogeneous nucleation). According to the XRD analysis data (Fig. 2a) heterogeneous selection of

[1] Composition LnBGeO5 (Ln – La, Pr) is characterized by polymorphism

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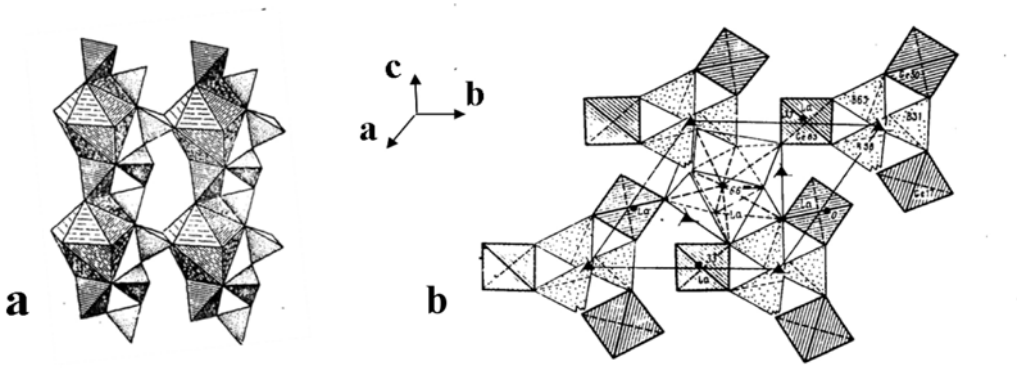

Fig. 1. Fragment of the $LaBGeO_5$ stillwellite structure. Translationally identical columns and B-chains of tetrahedrons (a). Motive of BO_4- and GeO_4-tetrahedrons in the projection on a plane, which is normal to the helical axis of the third order (b).

crystallites from the amorphous matrix into crystalline phase in the LBG-system takes already place at ca. 650…700 °C. Therefore, at the process stage when thermodynamic conditions correspond to the realization of the bulk nucleation process, the major glass structures are already crystalline and consisted of anisotropic crystallites of large size. Thus, formation of the well-distributed nanodispersed crystalline phase in a bulk of the LBG-glass under normal conditions is virtually impossible.

Differential thermal analysis showed significant differences in nature of relaxation processes in the reference and PMF treated at room temperature samples (Fig. 3).

There are two individual exothermic peaks (Fig. 3). Wide low-temperature peak is associated to the processes of amorphous matrix structural relaxation into the crystalline state transformation. The high-temperature peak is associated to the crystallization.

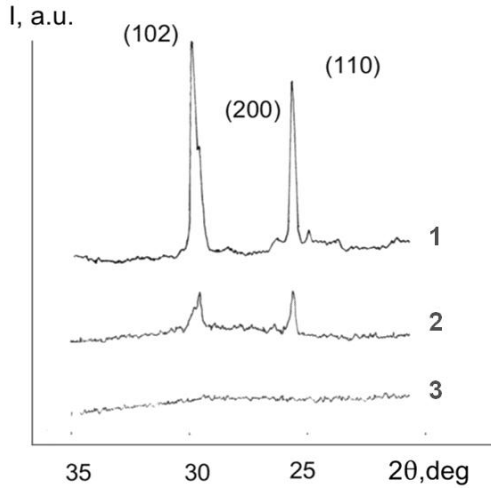

Fig. 2. XPD data of the $LaBGeO_5$ glass crystallization, where: *1* – 750 °C, *2* – 700 °C, *3* – 600 °C. Pure crystalline phase reflexes appear at $T \geq 700$ °C.

The glass verification temperature (T_g) of 670 °C is situated between two exothermic peaks. In case in Fig. 1b, a high-temperature peak is more narrow than in Fig. 2a, which testifies to the less term of crystallization of PMF-standards, as compared to the reference. Temperature of the PMF glass crystallization (close to 805 °C) is of 35 °C above crystallization temperature for the reference sample (of 770 °C). Therefore, crystallization of the PMF glass starts later, but runs faster than for the reference sample. Temperatures of the maximum of exothermal events for the reference and the PMF treated samples are, respectively, of 870 and 880 °C.

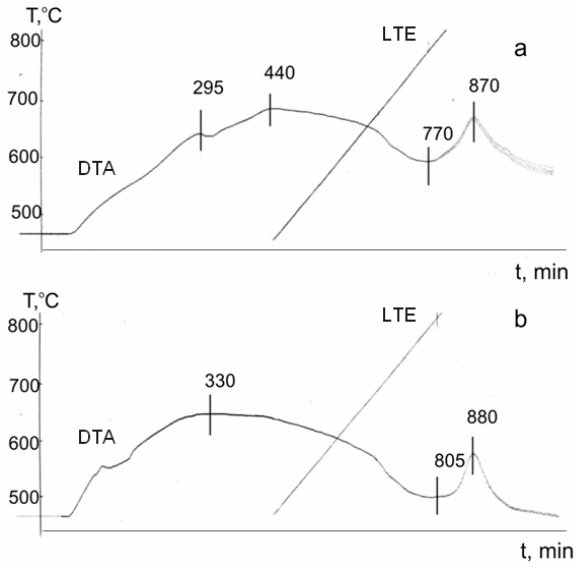

Fig. 3. DTA data for (a) reference and (b) PMF treated (f = 1 Hz) $LaBGeO_5$ glass systems (samples weight is of 0.51 g and 0.5 g, respectively; the dynamic mode; air atmosphere; heating rate 5 deg. × min^{-1}).

The main difference is observed for the relaxation peaks. It is narrower for the PMF sample with a

maximum shifted to a low temperature range down to 100 °C. This fact indicates that relaxation process in the PMF sample is accomplished earlier than that in the reference one. Therefore, PMF irradiation accelerates the preparatory stage of an amorphous matrix for crystallization.

The dilatometric data indicates a significant influence of PMF pre-treatment on glass transformation at all the subsequent stages of structural evolution. It has to be noted that when the relaxation processes are rapid, the crystallization of the irradiated materials starts later than those in the reference sample.

X-ray analysis reveals that the content of LBG-phase in the PMF treated samples is superior of 30% as compared to the reference one.

Slight changes in the samples transparency is identified after their X-ray irradiation. ESR profiles present a single line for both the reference and PMF treated samples (Fig. 4). The peak intensity, at the same line width of 48.5 Gauss and the g-factor values of $g_{\perp}$ = [1.9907±0.0003] and $g_{\parallel}$ = [2.020±0.0003] and taking into account the samples weight, for the PMF treated sample is higher than that for the reference one. These parameters, considering the error of measurements, are typical for E'-centers, which represent broken interatomic bonds [15]. The high peak intensity of the PMF sample (Fig. 4) indicates diffusion of oxygen within Ge-octahedron, and redistribution of oxygen atoms resulted in reduction of the corresponding concentration gradients. Therefore, the PMF pre-treatment ($T \approx 27$ °C, $f = 1$ Hz) followed by annealing at 500 °C leads to glass homogenization at the atomic level. Further temperature increase (up to 650…680 °C) reveals the difference between reference and PMF-treated samples already at a microscopic level.

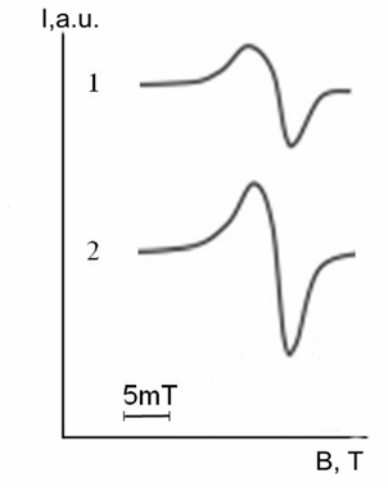

Fig. 4. ESR spectra of the (1) reference (172 mg) and (2) PMF-treated (196 mg) samples annealed at 500 °C for 2 h. Etalon is Cr^{3+} in Al_2O_3.

Optical microscopy reveals a better dispersion and homogeneous distribution of the nuclear in a bulk of the irradiated PMF samples as compared to the reference one (Fig. 5a). Therefore, PMF pre-treatment decreases the crystallite size and increases the tightness and density of their distribution in the glass surface layers. Further temperature increase (> 700 °C) leads to an increase in the grain size in content of the crystalline phase and appearance of texture in the directions (200) and (110) [16].

4. Formation of nanostructured state in the LBG-glass

Accomplished investigations prove that the effectiveness of PMF treatment increases with additional thermal treatment along with annealing at temperature of phase separation of the glass matrix, i.e., at 650…680 °C.

Formation of the bulk nanodimensional crystalline structures in glass with crystallite size close to 30 nm was detected by TEM analysis for the PMF-treated sample, while the crystallite size of the reference sample still being in a microscopic range. Pre-treatment conditions was as follows: PMF treatment ($f = 1$ Hz) at 27 °C for 1 h, followed by annealing at 600 °C, 2 h (without PMF); then by PMF treatment ($f = 1$ Hz) using step-by-step heating from 650 to 680 °C for 6 h (*i.e.*, with the step of 5 °C) and annealing at 705 °C, 2 h (Fig. 5b). Thus, one can conclude that effects of PMF pre-treatment both at the stage of phase separation and at the beginning of glass crystallization are responsible for the changes in crystallization process character from heterogeneous (surface) towards the homogeneous one (bulk).

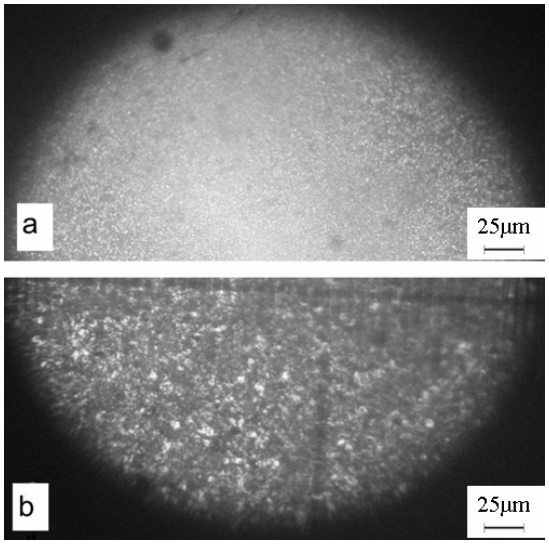

Fig. 5. Polarization optical microscopy (×400) of the crystalline phase dispersion at the glass surface. Crystallization at 705 °C, 2 h: (a) PMF pre-treated sample by using the frequency close to 1 Hz; and (b) reference sample.

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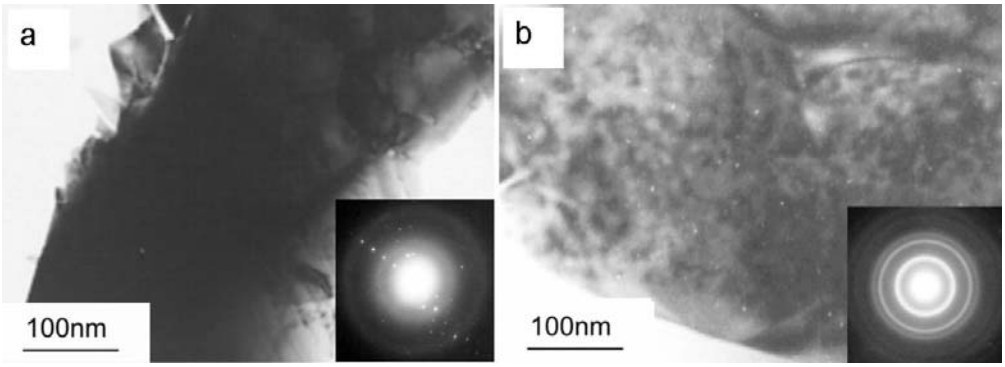

Fig. 6. TEM data. Crystal structure of glass formed by the following annealing conditions: a) T = 600 °C, 2 h at step-by-step heating from 650 up to 680 °C, for 6 h with the step of 5 °C and annealing at 705 °C, 2 h; b) PMF treatment (f = 1 Hz) at 27 °C, 1 h, followed by annealing at 600 °C, 2 h; then by PMF treatment (f = 1 Hz) at step-by-step heating from 650 up to 680 °C, 6 h with the step of 5 °C and annealing at 705 °C, 2 h.

5. Interpretation of results

All the above mentioned findings suggest that PMF treatment under certain thermodynamic conditions (such as heat treatment, X-irradiation) leads to a homogenization of the material structure from subatomic (Fig. 4) to microscopic levels (Fig. 5) [17]. In terms of thermodynamics, it means a transition of the solid-phase disperse system to a state with a lower free energy (in this case, the lowest free energy corresponds to the crystalline state) and is in agreement with well-known PMF effects in condensed matter.

From the point of view that glass is a supercooled liquid [18, 19], the delay of crystallization (according to DTA data) via homogenisation of the structural elements distribution (according to ESR data) and its further acceleration (according to DTA data) could be a consequence of an artificial increase of a "supercooling" level, *i.e.*, an artificial increase of the amorphous glass matrix resistance to crystallization. The authors suggest that course of the processes occurring in the $LaBGeO_5$ upon PMF exposure follows abovementioned principles. According to DTA data (the relaxation exothermic peak), the magnetic-induced homogenization of the glass matrix occurs at relatively low (300…500 °C) temperatures [20]. Taking into account that formation of the crystalline structure in the LBG-glass occurs due to association of the oxygen-cationic tetrahedral and polyhedral functional groups presented in the glass solid solutions (such as Ge-, B-tetrahedron, and La-polyhedron) [21-23], the role of PMF treatment becomes to be evident in shortage of oxygen ions. Namely, PMF treatment (i) aligns the existing concentration gradients of the oxygen vacancies by destruction of defective complexes[2)]; (ii) blocks association of functional groups with a specific atomic order; and (iii) constrains formation of nuclei of critical sizes on the surface defects below crystallization temperature range. Therefore, PMF treatment increases potential interaction of the partially ordered glass elements, thus reducing the efficiency of the processes of heterogeneous nucleation.

At the temperature when a majority of partially ordered functional elements located in a bulk glass are getting enough energy to overcome an activation barrier of nucleation, a rapid transformation of the glass to the glass-crystalline state occurs. According to the optical and electron microscopy data, phase differentiation displays mainly a bulk behavior (Fig. 6). According to the DTA data, increase of the temperature of activation of the crystallization process leads to the formation of a more dispersed nuclei as compared with the reference sample, which is similar to the case of "supercooled" solid solution crystallization.

6. Conclusions

It has been shown that PMF pre-treatment can significantly affect the kinetics of the structure formation in the $LaBGeO_5$ glass. Namely, under certain conditions PMF pre-treatment can alter the character of crystallization from the surface to bulk matter and increase the degree of homogeneity of the materials at micro- and submicron scale levels. The proposed fundamentally new approach is of practical importance due to its high potential. Namely, physical modification of the glass with surface crystallization using electromagnetic irradiation can be used for controlled synthesis of new bulk nanostructured glass materials with a unique complex of electrophysical properties for modern communication technologies and technology of nonlinear optics.

[2)] According to [20-23] weak magnetic field removes the ban on electronic transitions with spin inversion, which contribute to reducing the chemical bonds in the defect complexes, whereas, structural alterations occur due to thermal and elastic energy of the crystal lattice.

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