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Near-infrared luminescent barium gallium-germanate glasses and glass-ceramics doped with bismuth

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ABSTRACT

A series of barium gallium-germanate glasses (84-x) GeO_2–14BaO–2Ga_2O_3–x Bi_2O_3 (x = 0; 0,1; 1; 3; 5 mol%) was synthesized by crucible technology. It was revealed that the appearance of a $BaGe_4O_9$ crystalline phase took place after additional thermal treatment of the glass samples. The structural and optical properties of the glasses and glass-ceramics were studied. It was shown that the spectral shapes and the peak positions of the absorption, luminescence and excitation bands strongly depend on the type of materials. In particular, the absorption band peaked at 480 and 660 nm is characteristic for the glass samples whereas in the absorption spectrum of the glass-ceramic two bands at 480 nm and 560 nm were observed. Moreover, with the appearance of a crystalline phase, the luminescence peak shifts towards shorter wavelengths, while its intensity increases. The possible states of Bi ions in the $BaGe_4O_9$ crystalline phase were calculated using a molecular cluster model. The obtained results indicate that an incorporated in the crystalline phase Bi^+ ion could be considered as a possible near IR luminescence source.

1. Introduction

Optically activated materials in a spectral region of 1150–1500 nm are of great importance for a development of new fiber lasers and optical amplifiers, which could find many potential applications in different fields of modern technology, such as medicine, astrophysics, or optical communication systems of the next generation [1–5]. Recently, it was shown that the optical glasses doped with bismuth can have wideband luminescent bands in the wavelength region from 1000 to 1700 nm or even > 2000 nm [6–12].

The first bismuth laser for a spectral region of 1150–1215 nm using a fiber with aluminosilicate core glass was created in 2005. Thereafter, bismuth-doped fiber lasers for long-wavelength regions 1300–1550 nm [13–14] and 1600–1800 nm [15] were demonstrated. It should be noted that bismuth-doped fibers were low-concentrated that does not allow to produce clad-pumping. It is a limit to use intensively lasers based on these fibers in practical applications. One of the possible ways to overcome it is to study and understand an exact structure of the bismuth-related active center (BAC) responsible for lasing.

Nowadays, there is a number of proposed models of the BAC (Bi^{3+}, Bi^{2+}, Bi^+ bismuth clusters etc.) in bismuth-doped aluminophosphate, aluminosilicate, borate, chalcogenide, silicate, germanate glasses and different types of crystals [16–27]. The contradictory of the BAC nature occurs because of the presence of multiple valence states of bismuth atoms, strong effect of local environment in glass etc. Moreover, low concentration of bismuth leads to the difficulty to determine of a Bi valence state by conventional methods such as X-ray photoelectron spectroscopy, electron paramagnetic resonance etc. Taking into consideration the above-mentioned, the new experimental results are required to clear understanding of structure of BAC.

This paper reports a study of formation of optically active centers in bismuth-doped barium gallium-germanate glasses and glass-ceramics obtained by heat treatment of the glasses. The calculation of equilibrium configurations of the bismuth-related centers in a molecular cluster was performed and discussed.

2. Experimental

All samples of BaGaGe:Bi glasses were synthesized by the melting of solid batch materials according to the crucible technology. The $BaCO_3$, Ga_2O_3, GeO_2, and Bi_2O_3 chemical compounds were selected as raw materials. All the compounds were of a chemical grade of high purity. A series of batches was prepared having composition of (84-x) GeO_2–14BaO–2Ga_2O_3–x Bi_2O_3, where x = 0; 0.1; 1; 3; 5 mol%. The accuracy of the weight determination of each chemical reagent was ~1%. The batches were homogenized in a planetary mortar mixer

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machine. The samples were synthesized in quartz crucibles on air. The synthesis temperature was equal to 1400 ± 20 °C while synthesis time was 2 h. The glass melts were poured onto a massive steel mold and pressed with a steel plate to prevent spontaneous crystallization.

The temperature of crystallization was determined utilizing a differential scanning calorimeter Netzsch DSC 404 F1 Pegasus. All the measurements were done with a rate of heating of 10 K/min on air.

The glass-ceramic samples were obtained after original amorphous samples were annealed in a resistive furnace in the atmosphere of air. The heating rate of the samples up to the temperature set point was also 10 K/min. The annealing of the samples was carried out at the temperature which was close to the temperature of crystallization (660 ± 2 °C). The duration of the process was equal to 1 h. After that the samples slowly cooled down inside the furnace.

For optical measurements samples of 1 mm thickness were cut and polished to optical quality. The transmission spectra of the samples prepared were measured using a double beam spectrophotometer Perkin Elmer Lambda 950 in the 350–1000 nm range with 1 nm resolution. The luminescence spectra as well as the excitation spectra were recorded utilizing a spectrofluorimeter FLSP920 Edinburgh Instruments (the resolution of the excitation and emission spectra was 10 nm). A 200-W Xe lamp was exploited as an excitation source.

The content and parameters of crystalline phase in the thermally treated samples were controlled using X-ray diffractometer Empyrean PANanalytical. The registration was carried out utilizing the filtered radiation from a copper anode and a linear scanning detector. The analysis was performed using analytical software HighScore Plus and the PDF-2 databases. The lattice constant refinement was realized via full diffraction profile analysis.

3. Results

3.1. XRD analysis, glass structure

The differential scanning calorimetry (DSC) curves of the studied glasses are presented in Fig. 1. One can observe the glass transition temperature (T_g), and the maximum crystallization temperature (T_c). It is seen that the glass transition temperature as well as the maximum crystallization temperature shift towards lower temperatures when Bi_2O_3 content changes from 1 to 5 mol%. The crystallization and the glass transition temperatures of the undoped sample and of the sample with 0.1 mol% of Bi_2O_3 are close.

The XRD patterns of the series of the ceramic samples which were devitrified at 640 °C, and containing 1, 3, and 5 mol% of bismuth oxide are shown on Fig. 2a. For the sake of comparison the XRD pattern of the original (prior devitrification) glass sample is also presented. It contains the characteristic halo instead of a set of sharp peeks. The diffraction peeks of the all investigated samples correspond to $BaGe_4O_9$ crystalline phase.

The structure of $BaGe[Ge_3O_9]$ depicted in Fig. 2b consists of GeO_4 tetrahedra which are connected to each other through GeO_6 octahedra and barium atoms [28]. The GeO_4 tetrahedra form six member rings Ge_3O_9. Therefore, in the $BaGe[Ge_3O_9]$ structure there exist germanium atoms having a coordination number (CN) of 4 and 6. The length of the chemical bond in Ge_3O_9 (CN of Ge is 4) varies in the 1.62 ± 0.04–1.89 ± 0.05 Å range. In GeO_6 (CN of Ge is 6) the length of the short chemical bonds varies in the 1.72 ± 0.06–1.86 ± 0.06 Å range while for the long chemical bonds it varies in the 1.86 ± 0.06–2.02 ± 0.04 Å range. The germanium atoms of GeO_4 and GeO_6 connected to each other by bridging oxygen atoms. The average distance between germanium atoms d (Ge–Ge) is equal to 3.15 Å. Up to 10 atoms of oxygen are coordinated around a barium atom. Barium ions are located in the channels which are formed by three Ge_3O_9 rings. The value of d (Ba–O) ranges between the 2.66 ± 0.03 and 3.28 ± 0.09 Å.

The lattice constants refinement was carried out via full diffraction profile analysis. The results of the calculations are presented in Table 1. As one can see from the table, the introduction of Ga_2O_3 playing the role of glass former as well as Bi_2O_3 facilitating BAC formation into the composition of germanosilicate glass does not lead to any significant change of the lattice parameters in comparison with the ideal structure of $BaGe[Ge_3O_9]$. When Bi_2O_3 is introduced into barium germanate modified by Ga_2O_3 in an amount of 1–3 mol% the change relative to $BaGe[Ge_3O_9]$ of the lattice constants *a* and *c*, as well as the crystal cell volume *V* did not excided 0.4%. The increase of the Bi_2O_3 content led to decrease of the crystal cell volume *V*, as well as the average size of the crystallites, and to increase of the lattice microdistortions. Acceptable convergence of the results of the full diffraction profile analysis (the expected R-factor (R_{exp}) is 1.19, the weighted profile R-factor (R_{wp}) is 4.28, the goodness of fit (GoF) is 13.02) takes place when a partial replacement of Ba → Bi, Ge → Ga is made with the simultaneous formation of oxygen vacancies. The general chemical formula of the crystalline phase of the ceramic samples according to XRD analysis:

for the composition with 1 mol% of Bi_2O_3 — $(Ba_{0.64}Bi_{0.24})$

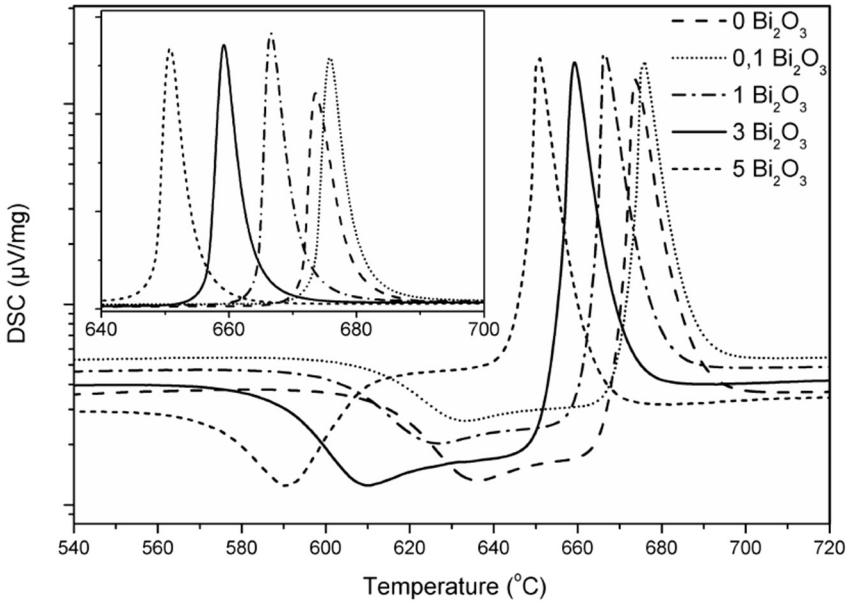

Fig. 1. DSC curves of the investigated samples. Inset – a set of peaks corresponding to the glass crystallization temperatures.