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NANOPHOTONICS AND BIOPHOTONICS

Spectral–Luminescent Investigations of Glasses and Glass-Ceramic Materials in Bi_2O_3–GeO_2–Fe_2O_3 System

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Abstract—Glasses of $2Bi_2O_3$–$3GeO_2$–xFe_2O_3 composition, where $x = 0$–1.5, are obtained under oxidizing and reducing conditions. Glass-ceramic materials are produced by the thermal treatment of the glasses, the properties of which, as well as those of the original glasses, are studied by the methods of X-ray phase analysis and optical and luminescent spectroscopy. It is found that the Fe^{3+}/Fe^{2+} ion ratio in the samples changes depending on the synthesis conditions of the original glasses and crystallization process.

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INTRODUCTION

Bismuth germanate glasses are used as materials for IR windows and as an active medium in Raman fiber amplifiers [1]. The addition of high concentrations of ions of transition elements to glasses significantly changes their mechanical, electrical, magnetic, optical, and luminescent properties. Because these ions (Cr, Mn, and Fe) can be present in a glass in several charge states simultaneously, their ratio also affects the properties of the glass [2, 3]. The aim of our investigation is to obtain new functional materials alloyed by iron ions in different concentrations and to determine how iron ions affect the mechanical and spectral–luminescent properties of synthesized glasses and glass-ceramic materials.

EXPERIMENT

Glasses of the $2Bi_2O_3$–$3GeO_2$–xFe_2O_3 composition (where $x = 0.005$, 0.05, 0.5, 1, and 1.5) were produced by melting the original blend at 1100°C for 30 min and subsequently casting the melt on a steel substrate. Some of the glasses were synthesized in air, while others were synthesized in a CO atmosphere.

For further study, 1-mm-thick plates were cut from ingots. The densities of the samples were determined by hydrostatic weighing, while their microhardness was measured by the Vickers–Rockwell method from the indentation diagonal of a diamond pyramid. The refractive index was measured by Lodochnikov's method. Vitrification temperatures were determined by the dilatometric method (using the expansion curves of the samples). The electrical characteristics were measured using an E7–12 L, C, R digital resistive bridge in the temperature range of 25–450°C. The contacts were applied with silver paste baking.

To obtain glass-ceramic materials (GCMs), the original glasses were thermally treated in two stages, i.e., at 415°C for 5 h, then at 450°C for 4 h. These regimes were chosen to check the effect of the heat-treatment conditions on glass crystallization.

The absorption spectra were obtained in the range of 350–1700 nm at 300 K using a Shimadzu UV-3 101 PC spectrometer. Luminescence was measured at room temperature in the visible and near-IR ranges (up to 1200 nm) using an INS-250 instrument (from ARC). The spectra were excited by white light-emitting diodes at wavelengths determined by a CC-15 light filter placed in the excitation channel. To reduce the probability of luminescence by a scattering object, an OC-11 filter was used that cut off the scattered light of excitation. The experiment conditions were as follows: the time of signal accumulation was 500 ms and the slit was 50 μm = 0.5 nm.

DISCUSSION

The area of glass formation in the $2Bi_2O_3$–$3GeO_2$–xFe_2O_3 system (up to $x = 5$) is presented in Fig. 1. Under our conditions, we failed to obtain glasses at concentrations of Fe_2O_3 of 40 mol % ($x = 2$) and higher. The values of the density, microhardness, vitrification temperature, and refractive index, as well as the temperature dependence of the dielectric permittivity of glasses at different concentrations of iron ions, are listed in the table. It can be seen from the table that iron ions influence all of the above-mentioned properties, except for the refractive index. Thus, the values of density and microhardness of glasses rise significantly with increasing concentration of ferric oxide. It is likely that this is related to the strengthening of glass network due to modifying properties of ferric oxide. Characteristic temperatures lower with increasing

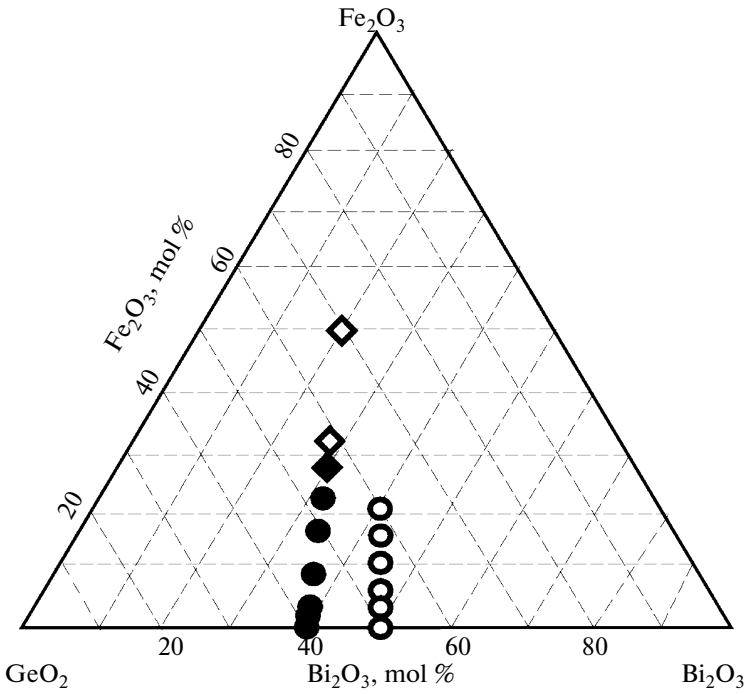

Fig. 1. Glass formation area in Bi_2O_3–GeO_2–Fe_2O_3 system: (filled circles) glasses, (filled diamonds) partly crystallized glasses, (open diamonds) crystallized melt, and (open circles) glasses obtained in [3].

content of ferric oxide, whereas values of the dielectric permittivity increase, which is especially noticeable at high temperatures.

In the optical absorption spectra of iron-containing glasses, the absorption edge is shifted to long-wavelength range (Fig. 2). According to [4], the absorption shoulder at 500 nm in undoped glass can belong to Bi-centers. In [5], the absorption band in this range was assigned to a dimer Bi^{2+} (1) – Bi^{3+} (Bi^{2+} and Bi^{3+} ions are separated by the anionic vacancy).

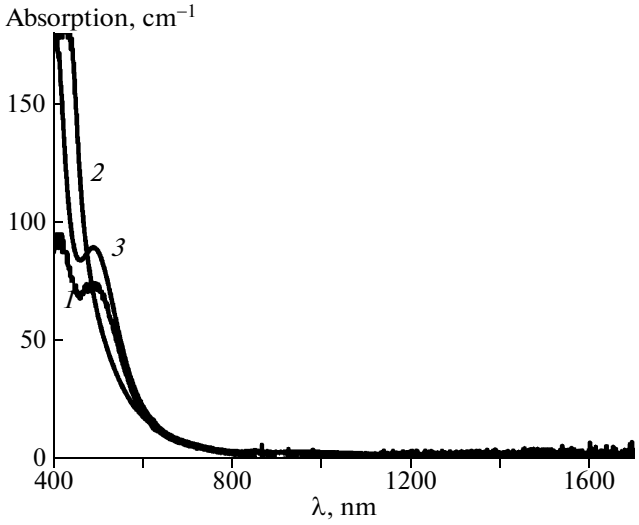

Fig. 2. Absorption spectra of origin glasses: (*1*) $2Bi_2O_3$–$3GeO_2$, (*2*) $2Bi_2O_3$–$3GeO_2$–$0.005Fe_2O_3$, and (*3*) $2Bi_2O_3$–$3GeO_2$–$0.05Fe_2O_3$.

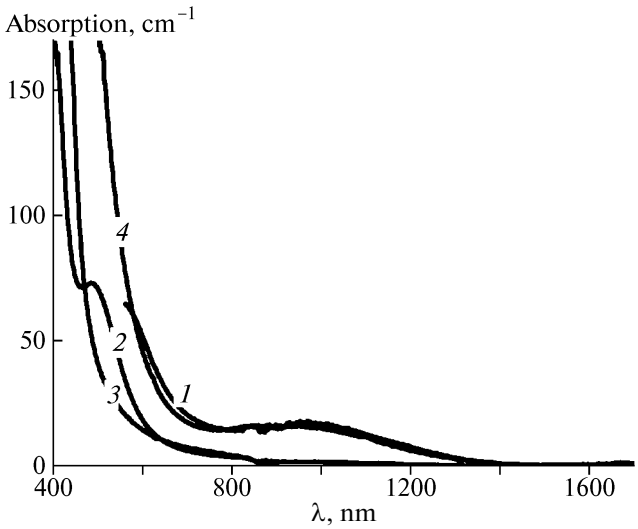

Fig. 3. Absorption spectra of (*1*) $2Bi_2O_3$–$3GeO_2$–$0.05Fe_2O_3$ glass synthesized in CO atmosphere and GCMs produced by heat treatment at 415°C: (*2*) $2Bi_2O_3$–$3GeO_2$, (*3*) $2Bi_2O_3$–$3GeO_2$–$0.005Fe_2O_3$, and (*4*) $2Bi_2O_3$–$3GeO_2$–$0.05Fe_2O_3$.

Properties of new glasses

Glass composition	T_g, °C, ±3	Density, g/cm^3, ±0.05	Microhardness, kg/mm^2, ±10	Refractive index, ±0.05	Dielectric permittivity, ±2	
					at 25°C	at 450°C
$2Bi_2O_3$–$3GeO_2$	440	6.05	350	2.02	25	30
$2Bi_2O_3$–$3GeO_2$–$0.005Fe_2O_3$	415	6.25	500	2.02	28	32
$2Bi_2O_3$–$3GeO_2$–$0.05Fe_2O_3$	410	6.30	540	2.02	29	37
$2Bi_2O_3$–$3GeO_2$–$0.5Fe_2O_3$	395	6.45	670	–	32	46

The addition of 0.1 mol % of ferric oxide to the glass composition leads to the vanishing of absorption at 500 nm. It is likely that this is related to the fact that Fe^{3+} ions that incorporate into the glass network impede the formation of bismuthic dimers, which absorb in this range. An increase in the content of ferric oxide of up to $0.05Fe_2O_3$ results in the formation in the glass of associates of iron ions of the cluster type [6], which do not affect the formation of Bi centers. Therefore, the absorption shoulder at 500 nm for the $2Bi_2O_3$–$3GeO_2$–$0.05Fe_2O_3$ glass can be explained by the absorption of Bi centers or color centers. The investigation of their nature was beyond the scope of our work.

A broad absorption band in the range of 1000 nm appears in the GCM spectrum with an increase in the iron concentration up to $0.05Fe_2O_3$ (Fig. 3), which can be attributed to the presence of Fe^{2+} ions. A similar band was also observed in the spectrum of glass synthesized in the CO reducing atmosphere. The presence of Fe^{2+} ions in the GCM samples synthesized in air can result from the appearance of the oxidation–reduction equilibrium of Fe^{3+} ions with bismuth ions, which are present in the formed crystal phase, e.g., $Bi^{3+} + 2Fe^{3+} = Bi^{5+} + 2Fe^{2+}$ [7]. In this case, a change in the heat treatment conditions does not significantly effect the spectral properties of GCMs, whereas an increase in the total concentration of iron ions leads to the appearance of Fe^{2+} ions. The same effect was observed in [8] for xFe_2O_3–$(100 - x)[1Bi_2O_3$–$1GeO_2]$ glasses at concentrations of Fe_2O_3 higher than 5 mol %.

The luminescence spectra exhibit weak bands caused by the luminescence of Fe^{3+} ions (Fig. 4). Thus, we found that, in the obtained glasses and GCMs, iron ions are in the form of Fe^{3+} and Fe^{2+} and their ratio depends on both the conditions of obtaining the initial glasses (oxidizing or reducing atmosphere) and the formation of the crystal phase.

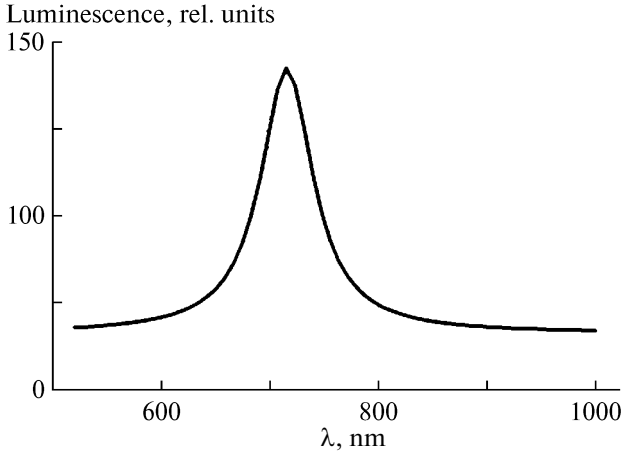

Fig. 4. Luminescence spectrum of glass-ceramic $2Bi_2O_3$–$3GeO_2$–$0.005Fe_2O_3$ obtained by successive heat treatment at 415 and 450°C.

CONCLUSIONS

Charge states of iron ions in glasses and glass-ceramic materials of the $2Bi_2O_3$–$3GeO_2$–xFe_2O_3 composition have been determined by spectral–luminescent methods in the range of up to $x = 0.05$. It was shown that the Fe^{3+}/Fe^{2+} ion ratio depends on the total concentration of iron ions in the glass, as well as on the synthesis regime of the glass and its crystallization.

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