Structural and optical properties of the bismuth-containing quartz-like glasses

M. A. Girsova¹, S. V. Firstov², T.V. Antropova¹

¹Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, nab. Makarova 2, 199034 Saint-Petersburg, Russia
²Fiber Optics Research Center of the Russian Academy of Sciences, 38 Vavilov Street, 119333 Moscow, Russia

E-mail: girsovamarina@rambler.ru

Abstract. Bismuth-containing quartz-like glasses (BCQGs) were synthesized by an impregnation of the silica porous glasses (PGs) with Bi(NO₃)₃ aqueous solution. Then the samples were sintered at the temperatures T from 700 °C to ≥ 1500 °C up to closing the pores. Characterization of BCQGs was carried out using the UV-VIS-NIR spectroscopy and IR spectroscopy. The absorption and luminescence properties of the BCQGs are discussed. It is shown that the growth of absorption in the short-wave region is characteristic for BCQGs. IR spectra confirmed the presence [BiO₃] and [BiO₆] units and α – Bi₂O₃ phase in BCQGs. The spectral dependences of the luminescence and excitation of the luminescence of the synthesized glass depending on their thermal prehistory were investigated. For the first time, 3-dimensional luminescence spectra have been obtained for BCQG.

1. Introduction

Bismuth-doped glasses are new active optical materials having a broad luminescence spectrum in the spectral range 1000-1700 nm. IR luminescence lifetime of such glasses is amounted to 0.1-1 ms [1, 2]. Bismuth-activated glasses can be used for development multifunctional 3D sources [3, 4], fibers doped with bismuth that are basis for superluminescent light source, tunable high-power lasers, and broadband optical amplifiers for spectral region of 1300–1530 nm [5-7]. Among them the bismuth-containing quartz-like glasses produced on porous glass matrices are of particular interest because of the resource-saving technology [4, 8-10].

2. Experimental

Bismuth-doped glasses (BCQGs) were fabricated by an impregnation of the silica porous glasses (PGs) with Bi(NO₃)₃ aqueous solution. Initially, PG samples (in the form of the rectangular plane-parallel plates in the size (1.5±0.03) x (10–15) x (15–25) mm³) were placed in Bi(NO₃)₃ aqueous solution. Then obtained composite material was sintered at 700-900 °C under air atmosphere for 10-30 min, heating rate 1-4 °C/min only or additionally heat-treated at T ≥ 1500 °C. In detail synthesis technique of BCQGs was described in [9, 10]. The glasses under study have following compositions (as analyzed, wt. %): 0.30 Na₂O, 3.14 B₂O₃, 0.11 Al₂O₃, 96.45 SiO₂ (PGs); ≤ 0.2 Na₂O, (2.7–3.2) B₂O₃, (92.7–96.1) SiO₂, (0.9–1.6) Bi₂O₃, ≤0.10 Al₂O₃ (BCQGs).

Transmission spectra of synthesized glasses were measured by SF-2000 UV / VIS spectrophotometer in the wavelength range of 190–1100 nm with a step of 0.115 nm. IR transmission
spectra in the range of 4000 to 400 cm\(^{-1}\) at the spectral resolution of 4 cm\(^{-1}\) were recorded with SPECORD M-80 spectrophotometer. For measurements of IR spectra the glasses were powdered and mixed with KBr in order to obtain thin pellets by vacuum pressing. Luminescence spectra of the BCQGs were collected by FLSP920 optical spectrofluorometer. All measurements were conducted at room temperature.

3. Results and discussion

According to the transmission spectra (Fig. 1) and optical loss spectra [10] of the glasses under study the strong absorption in UV spectral region is characteristic of them. There are seven peaks at below 240, 471, 522, 713 nm (Fig. 1a, curve 1); 204, 497, 568 nm (Fig. 1a, curve 2) which assigned to the glass matrix. The UV-VIS transmission spectra of bismuth-containing glasses are shown in Fig. 1b. It was found that bismuth-containing glasses have two bands at <280 nm and around 400 nm. Presence of UV absorption of Bismuth-doped glasses (here, <280 nm) could be associated with different states of bismuth oxidation: Bi\(^{3+}\) [11], Bi\(^{2+}\) [2], colloidal bismuth [12]. Emission properties of BCQGs confirmed that UV absorption band is associated to Bi\(^{3+}\) ions. The band at 405-408 nm corresponds to absorbance band of Bi\(^0\) nanoparticles (NPs) [9]. In our case an origin of this band was still unknown.

![Figure 1. Transmission spectra of the glasses: (a) 1 – silica porous glass without bismuth, 2 – quartz-like glasses without bismuth (T ≥ 870 °C); (b) 1 – bismuth-containing porous glass (T ≤ 700 °C), 2 – bismuth-containing quartz-like glass (T ≥ 870 °C).](image)

IR transmission spectra of glasses under study are shown in Fig. 2. It was found that all types of glasses have eight fundamental absorption bands at 3684–3676, 3496–3472, 3432–3416, 2932–2908, 2824–2808, 1664–1644, 1400–1380, 1108–1084 cm\(^{-1}\). Using published data [13-21] the obtained IR bands have been identified. Broad bands placed at 3684–3676, 3496–3472, 3432–3416, 1664–1644 cm\(^{-1}\) are assigned to stretching vibrations of hydroxyl and water groups. Two bands at 2932–2908 and 2824–2808 cm\(^{-1}\) are associated with hydrogen bonds. The band at 1400–1380 cm\(^{-1}\) is connected with asymmetrical stretching vibrations of B-O and B-O\(^{−}\) bond in trigonal BO\(_3\) units and is characteristic of =B-O-B= linkage with one of the boron in tetrahedral coordination. Asymmetrical vibrations of [SiO\(_4\)] tetrahedral in a polymerized network with dominated Si–O–Si linkages and presence of tri-, tetra-, pentaborate and diborate groups belonging to BO\(_x\) groups are responsible for band at 1108–1084 cm\(^{-1}\). Apart from above-mentioned bands, it was observed the additional bands in IR transmission spectra of bismuth-activated glasses. The spectra analysis showed that BO\(_3\) and BO\(_6\) units formed in glasses. The band at 944-924 cm\(^{-1}\) (Fig. 2b, curves 2, 3) is caused by the increasing of the degree of cross-linking by Bi-O-Si linkages. It was revealed that band at 940 nm appeared after annealing T>870 °C. The band at 676–652 cm\(^{-1}\) (Fig. 2b, curves 1, 3) may be assigned to Bi-O bending vibrations in BiO\(_6\) units and indicates the presence of \(\alpha-\text{Bi}_2\text{O}_3\) phase also. The peaks around 576–
564 cm\(^{-1}\) (Figs 2b, curve 2) are ascribed to doubly degenerate stretching vibrations of Bi–O bonds in BiO\(_3\) and BiO\(_6\) units, Bi-O-Bi and Bi-O bending vibrations in BiO\(_6\) units.

The luminescence spectra of the glasses are given in Fig. 3. The obtained luminescence spectrum of initial matrix without bismuth consists of one band in the UV region (close to 315 nm) (Fig. 3, curve 1). It was revealed that heat treatment process of BCQGs at T < 870 °C initiated blue-green luminescence with the maximum at 450 nm (excitation at 250 nm), which is originated from Bi\(^{3+}\) ions.

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**Figure 2.** IR transmission spectra of the glasses: (a) 1 – silica porous glass without bismuth, 2 – quartz-like glasses without bismuth (T \(\geq\) 870 °C); (b) 1 – bismuth-containing porous glass (T \(\leq\) 700 °C), 2 – bismuth-containing quartz-like glass (T \(\geq\) 870 °C), 3 – bismuth-containing quartz-like glass (T \(\geq\) 1500 °C).

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**Figure 3.** Luminescence spectra of the studied glasses with the different thermal prehistory: (1) quartz-like glass without bismuth (T \(\geq\) 870 °C; excited at 280 nm); (2) bismuth-containing porous glass (T \(\leq\) 700 °C; excited at 280 nm); (3, 4) the bismuth-containing quartz-like glass, heat-treated at T \(\geq\) 870 °C (3 – excited at 500 nm, 4 – excited at 300 nm); (5, 6) the bismuth-containing quartz-like glass, additionally heat-treated at T \(\geq\) 1500 °C (5 – excited at 500 nm and 6 – excited at 420 nm).
in the glass (Fig. 3, curve 2). It is determined that heat treatment of BCQGs at $T \geq 870 \degree C$ leads to decrease in the intensity of blue-green luminescence (Fig. 3, curve 4). The observed changes are caused by reduction of the $\text{Bi}^{3+}$ to $\text{Bi}^{2+}$. $\text{Bi}^{2+}$ ions are responsible for red luminescence with the maxima at 610 and 750 nm at excitation at 480 nm. These emission bands can be observed after annealing process at temperature higher than 870 °C (Fig. 3, curve 3). Re-annealing of BCQGs at high temperatures ($T \geq 1500 \degree C$) leads to an increase in red luminescence intensity owing to the growth of divalent bismuth (Fig. 3, curve 5). Moreover two bands of infrared luminescence with maxima about 830 nm and 1410 nm can be seen also (Fig. 3, curve 6).

![Figure 4](image)

**Figure 4.** IR luminescence intensity distribution vs the luminescence and excitation wavelengths in the bismuth-containing quartz-like glass heat-treated at $T \geq 1500 \degree C$.

Fig. 4 shows the distribution of the intensity of IR luminescence depending on the wavelengths of excitation and luminescence. In this diagram four bright peaks A, A1, B, and B1 are distinctly seen. Earlier the similar bands in silicate glass were obtained in [22]. These bands are inherent to IR active bismuth centres formed in silica-based glass.

![Figure 5](image)

**Figure 5.** Excitation spectra of blue luminescence in the bismuth-containing quartz-like glass heat-treated at: 1 – $T \geq 870 \degree C$ ($\lambda_{em} = 450$ nm); 2 – $T \geq 1500 \degree C$ ($\lambda_{em} = 450$ nm).
Fig. 5 demonstrates excitation spectra of BCQG annealed at $\geq 870$ °C (1) and $>1500$ °C (2). We have observed the transformation of the excitation spectra of blue luminescence at the increasing of treatment temperature. Main change is an appearance of additional excitation band at 220 nm at higher temperature. Recently this band was also observed in the absorption spectrum of the fibre preforms from pure silica glass doped with bismuth ions and was attributed to Bi$^{3+}$ [23].

Thus, the appearance of the red and infrared luminescence is accompanied by structural changes (increasing of the degree of cross-linking by Bi-O-Si linkages) in the glass network.

**Conclusion**

In conclusion, fabrication technique for new bismuth-containing quartz-like glasses has been developed. Series of BCSG on the base of silica porous glass matrices have synthesized. Their structural, optical and luminescent properties have been investigated.

It has been shown that synthesized glasses can emit blue-green, red and also infrared luminescence owing to presence of different bismuth active centres. Formation of red and IR active centers is accompanied by glass network modification at annealing process.

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