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Synthesis and Study of Bismuth-Containing High-Silica Glass by the IR Spectroscopy Method[1]

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Abstract—Bismuth-containing high-silica glasses (BCHSGs) based on the matrices of high-silica nanoporous glasses have been synthesized. The structure of BCHSG plates has been investigated by means of the IR spectroscopy method in the frequency range 4000–400 cm^{-1}. The bands corresponding to vibrations of the Bi–O bonds in structural units $[BiO_3]$ and $[BiO_6]$ were found on the spectral transmission curves of the synthesized BCHSGs. Besides, peaks corresponding to the presence of the α-Bi_2O_3 phase in the glass were revealed. It has been established that, depending on the BCHSG thermal treatment and the bismuth concentration in glass, changes of the glass structure and formation of Bi–O–Si bonds take place.

Keywords: bismuth-containing high-silica glass, IR spectroscopy

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INTRODUCTION

Glasses doped with bismuth are characterized by luminescence in a broad spectral range from 450–750 [1–8] to 1000–1700 nm [3–5, 8–11]. Different methods of glass fabrication are known: for instance, powder-in-tube technology [5, 11, 12]; modified chemical vapor deposition (MCVD) [5, 13, 14]; method of growing single crystals of solid solutions [15, 16]; method of oxide melt quench hardening (charge melting) [17, 18]; and fabricating bismuth-containing composites based on porous silicate glass [3, 4, 6–8, 19, 20]. One should mention that the latter method is power- and resource-saving in comparison to traditional ones.

Glasses doped with bismuth are used to create new tunable broadband radiation sources [3, 4, 20–23], fiber optical waveguides, lasers and amplifiers [11, 13, 24–26], amplifiers for the second telecommunication transparency window (1.2–1.35 μm) [24, 27], fibers with the transmission band width from 1.3 to 1.6 μm [3], and 3D active micro- and nanosized photonic integrated circuits [4], etc.

In view of the intensive development of the advanced optical and information technologies, it is a matter of urgency to create materials with nanostructured elements, which are known to provide their unique physical properties. For example, bismuth-containing high-silica glasses (BCHSGs) are characterized by the unique luminescent properties in a broad spectral range from blue-green to red luminescence and, further, to near infrared luminescence [6–8, 19].

The results obtained from studying the spectral-luminescent properties of synthesized BCHSGs demonstrated that, depending on the synthesis conditions, one observes the appearance of thermally induced bismuth centers and changes in the glass structure [6–8, 19]. The presence of bismuth in different valence states in BCHSGs is indicated by the data of X-ray power diffraction (XRPD) and the results of studies of the glass spectral-optical properties (spectra of absorption, luminescence, and luminescence excitation). Additional information on the structure of BCHSGs can be obtained by the results of IR spectroscopy, which was the subject of the present work.

METHODOLOGY

The synthesis of BCHSGs, in particular, bismuth-containing porous glasses (BCPGs) and quartz-like glasses (BCQGs) in the form of plane-parallel plates of a thickness of 1.5 mm, was carried out in accordance with the procedure described in general in [6, 8, 19]. In the present work, BCHSGs were fabricated by the impregnation of plates of high-silica nanoporous glasses (HSNPGs) at room temperature for 0.5–72 h in a 0.5 M aqueous solution of bismuth nitrate prepared based on a 2 M solution of HNO_3 followed by thermal treatment at T from 700 to ≥870°C. According to the chemical analysis data, the synthesized BCPGs and BCQGs contain (as analyzed, wt %) (0.12–0.21) Na_2O, (2.90–3.43) B_2O_3, (95.13–95.61)

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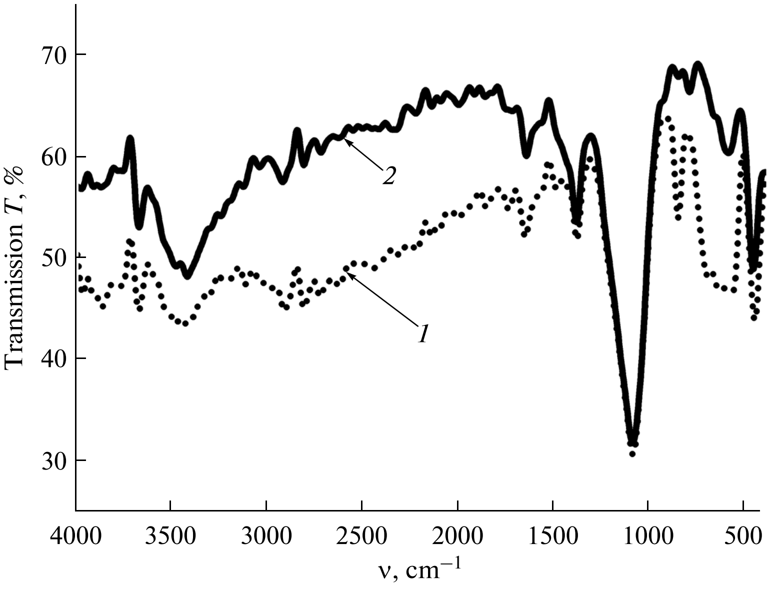

Fig. 1. IR transmission spectra of glasses not containing bismuth: (*1*) porous glass, (*2*) quartz-like glass (T = 870°C) [19].

SiO_2, (0.97–1.60) Bi_2O_3, and ≤0.10 Al_2O_3. In the course of IR studies, HSNPG and quart-like glass (QG) samples not containing bismuth were used as standards [8].

IR transmission spectra of the glass samples were fabricated at room temperature in the range 4000–400 cm^{-1} using a SPECORD M-80 spectrophotometer (Carl Zeiss JENA). The samples were measured in the form of tablets pressed from mixtures of glass powders with KBr. The experimental spectra were processed using the program Origin Lab 8.6 32Bit. The plot smoothening was performed by the FFT Filter method, unlike [6], in which the Savitzky–Golay method was used. To identify structural elements, the data in the literature [28–41] were used.

EXPERIMENTAL

The transmission spectral dependences for HSNPG and QG not containing bismuth and of BCHSGs in the IR range (Figs. 1–3) demonstrate 16 fundamental bands: 3688–3672, 3492–3472, 3432–3412, 2940–2912, 2820–2808, 2736–2720, 2340–2308, 2152–2140, 2104–2080, 2016–2000, 1872–1860, 1664–1644, 1396–1384, 1108–1084, 872–852, and 468–456 cm^{-1}. The bands observed at 3688–3672, 3492–3472, 3432–3412, 2736–2720, 2340–2308, 2152–2140, 2104–2080, 2016–2000, and 1664–1644 cm^{-1} are caused by the stretching vibrations of hydroxyl groups and water, asymmetric stretching ν_{as} for OH, and symmetric stretching vibration ν_s for H–O–H-groups [28–32]. The band at 3432–3412 cm^{-1} is assigned to vibrations of the structure Si–O–Si and the stretching Si–OH [33]. The bands at 2940–2912, 2820–2808, and 2736–2720 cm^{-1} correspond to hydrogen bonds [28]. The weak band at 1872–1860 cm^{-1} is caused by the symmetric bending and stretching of Si–O bonds [34]. Asymmetric stretching vibrations of B–O bonds in the structural units [BO_3] are observed at 1396–1384 cm^{-1} [30, 35]. The band at 1108–1084 cm^{-1} corresponds to the degenerate asymmetric stretching vibration of ν_{as} groups [BO_3] [31] and the asymmetric vibrations of the tetrahedron [SiO_4] in the polymerised network with the dominant bridge bonds Si–O–Si [36]. Asymmetric vibrations ν_{as} of the tetrahedron [SiO_4] and stretching vibrations of the B–O bonds in the structural units [BO_4] are assigned with the band 872–852 cm^{-1} [31, 35]. The glass spectra (Figs. 1–3) contain the band at 468–456 cm^{-1} corresponding to the bending vibrations of the Si–O bonds [37].

The broad and strong band observed in the range 1496–1484 cm^{-1} (Fig. 1, curve *1*; Fig. 3, curve *1*) is caused by the asymmetric vibrations of B—O bonds in the trigonal structural units [BO_3] [35]. The weak band observed at 808–792 cm^{-1} (Fig. 1, curve *2*; Fig. 2, curves *2*, *5*; Fig. 3) corresponds to the symmetric vibrations of the SiO_4 and AlO_4 groups in tetrahedral positions [37, 38]. The strong band at 716–704 cm^{-1} (Fig. 1, curve *1*; Fig. 2, curve *3*) is due to bending vibrations of B–O–B bonds in [BO_3] groups [30, 39]. The intensive absorption in the range 604–568 cm^{-1} confirms the presence of structural units [BO_3] and [BO_4] in (Figs. 1–3) [31, 37] and may indicate the presence of [AlO_6] octahedra.

The band at 940–936 cm^{-1} appears for BCQG (Fig. 3, curve *2*), which is associated with the cross-linking of the glass structure by Bi–O–Si bridges [36].

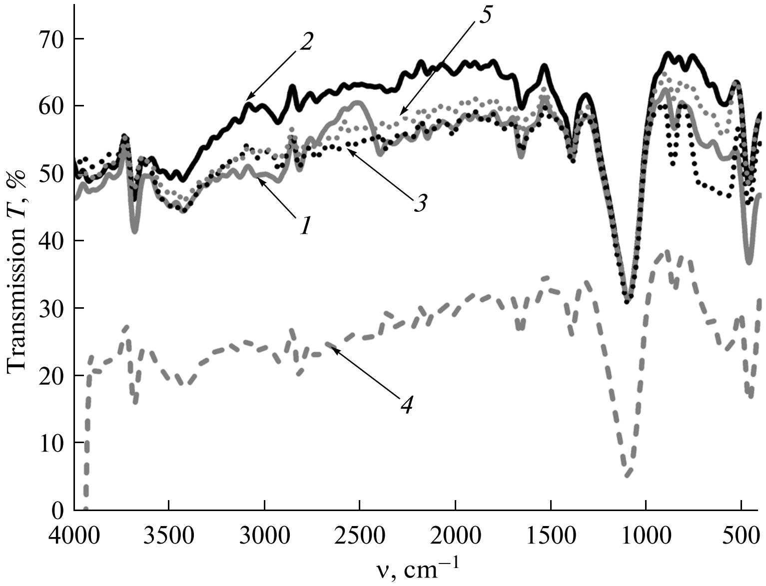

Fig. 2. IR transmission spectra of bismuth-containing porous glasses. Impregnation time: (*1*) 0.5, (*2*) 7, (*3*) 24, (*4*) 48, (*5*) 72 h.

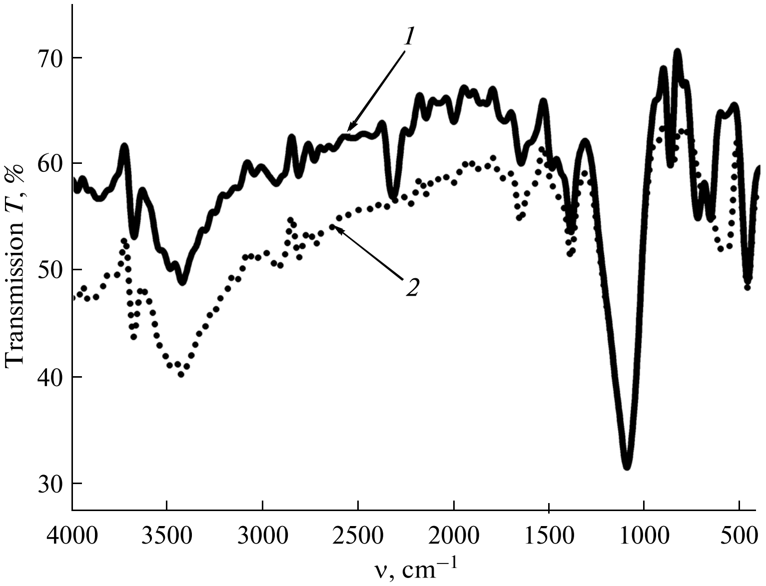

Fig. 3. IR transmission spectra of bismuth-containing high-silica glasses (*1*) BCPG (impregnation for 48 h, $T \leq 700°C$), (*2*) BCQG (impregnation for 48 h, $T \geq 870°C$).

Earlier, this band was observed for the samples impregnated for 72 h and thermally treated at $T \geq 870°C$ and $T \geq 1500°C$ [19]. In Fig. 3 (curve *1*), one reveals the band at 728–724 cm^{-1}, corresponding to vibrations of the γ ($Bi_{(3)}$–O) bonds and the symmetric stretching vibrations in the [BiO_3] groups [40, 41]. The band in the range 688–660 cm^{-1} (Fig. 2, curves *1*, *2*, *4*, *5*; Fig. 3, curve *1*) is caused by the vibrations of the γ ($Bi_{(3)}$–O) and Bi–O bonds of different lengths in distorted [BiO_6] structural units [40, 41]. Besides, this band indicates the presence of phase α-Bi_2O_3 in BCPG (impregnation for 48 h, $T \leq 700°C$) [40].

CONCLUSIONS

Bismuth-containing high-silica glasses have been synthesized based on matrices of high-silica nanoporous glasses. The synthesized glass structure was investigated by means of the method of IR spectroscopy.

Vibrations of Bi–O bonds in [BiO_3] and [BiO_6] structural units were identified in the synthesized samples. Besides, the bands corresponding to the presence of the α-Bi_2O_3 phase were found. It has been established that cross Bi–O–Si bonds are formed in the structure of bismuth-containing high-silica glass thermally treated at temperatures of ≥870°C.

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