

The local structure of bismuth borate glasses doped with europium ions evidenced by FT-IR spectroscopy

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Abstract Glasses of the $x\text{Eu}_2\text{O}_3 \cdot (100 - x)[4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3]$ system, with $0 \leq x \leq 40$ mol% were studied by FT-IR spectroscopy and density measurements. FT-IR spectroscopy and density data suggest that the europium ions play the network modifier role in the studied glasses. These data show that the glass structure consists on the BiO_3 , BiO_6 , BO_3 and BO_4 units, and the conversion among these units mainly depends on the Eu_2O_3 content.

1 Introduction

Rare earth glasses have attracted much attention, because they have large practical and potential applications in many fields, such as glass lasers, optical fiber amplifiers, phosphors, electro-luminescent devices, memory devices and flat-panel displays, etc. [1–8]. Among them, considerable interest was accorded to glasses containing europium ions [6, 7]. Europium ions have potential application in memory devices and phosphors [6, 7] and activators to detect local environments [9–12]. Most of the rare earth ions incorporated in oxide glass matrices present a single valence state, namely the 3+ one [13, 14] while, europium ions were reported to be present in both their 2+ and 3+ valence states [15, 16].

Glasses based on heavy-metal oxides such as Bi_2O_3 have received increased attention due to their manifold

possible application in the field of glass ceramics, layers for optical and optoelectronic devices, thermal and mechanical sensors, reflecting windows, etc. [17–19]. It was also reported that glasses containing Bi_2O_3 are investigated for possible use in scintillation detectors for high-energy physics and the large polarizability of bismuth makes them suitable for possible non-linear optical uses and environmental guide-lines [18, 19]. Bi_2O_3 is not traditionally known to form glass, but in the presence of conventional glass-forming cations such as P^{5+} , Si^{4+} , B^{3+} it may have this property. This is possible because Bi^{3+} ions are highly polarizable and the asymmetry of their oxygen coordination polyhedra can inhibit the crystallization of melts in which they are incorporated. The bismuthate glass networks may consist of both BiO_6 octahedral and BiO_3 pyramidal units [17, 20].

B_2O_3 is one of the most common glass former oxides and is present in almost all commercially important glasses. It is often used as a dielectric and insulating material and borate glasses are also of academic interest because of the occurrence of boron anomaly [21]. The structure of vitreous B_2O_3 is composed essentially of BO_3 triangles forming three-member (boroxol) rings connected by B–O–B linkages [22]. Moreover, the addition of a modifier oxide causes a progressive change of some BO_3 triangles to BO_4 tetrahedra and results in the formation of various cyclic units like diborate, triborate, tetraborate or pentaborate groups [19, 23]. At higher concentrations of the modifier, the formation of BO_3 units with non-bridging oxygen atoms (NBOs) are reported (pyroborate or ortoborate) [19, 24].

We considered the $4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ glass matrix to be a very interesting host for the europium ions. The purpose of the present work was to investigate by density and FT-IR spectroscopy the bismuth-borate glasses containing Eu_2O_3 in order to establish the structural changes induced by

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europium oxide addition and to obtain information concerning structural properties of these glasses.

2 Experimental

Glasses of the $x\text{Eu}_2\text{O}_3 \cdot (100 - x)[4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3]$ system were prepared using reagent grade purity Bi_2O_3 , H_3BO_3 and Eu_2O_3 in suitable proportion. The mechanically homogenized mixtures were melted in sintered corundum crucibles at 1,100 °C, in an electric furnace. The samples were put into the electric furnace direct at this temperature. After 15 min, the molten material was quenched at room temperature by pouring onto a stainless-steel plate. The samples were analyzed by means of X-ray diffraction using a Bruker D8 ADVANCE X-ray Diffractometer. The pattern obtained did not reveal any crystalline phase in the samples up to 40 mol%.

The density of samples was measured using Archimedes' method with demonized water as immersion liquid. Mass was measured using a digital balance sensitive to 0.0001 g. The molar volume was calculated from density and molar mass.

The FT-IR absorption spectra of the glasses in the 400–1,500 cm^{-1} spectral range were obtained with a JASCO FT-IR 6200 spectrometer. The IR absorption measurements were done using the KBr pellet technique. In order to obtain good quality spectra the samples were crushed in an agate mortar to obtain particles of micrometer size. This procedure was applied every time to fragments of bulk glass to avoid structural modifications due to ambient moisture.

3 Results and discussion

3.1 Density data

Density responds to variations in glass composition sensitively in technological practice. Density of glass, in general, is explained in terms of a competition between the masses and size of the various structural groups present in glass. Accordingly, the density is related to how tightly the ions and ionic groups are packed together in the structure. The composition dependence of the density, ρ , of the present glass samples is shown in Fig. 1. The progressive adding of Eu_2O_3 to the $4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ glass matrix shows a non-linear decrease in density (Fig. 1). The relationship between density and composition of an oxide glass system can be expressed in terms of an apparent volume V_m occupied by 1 g atom of oxygen. The molar volume, V_m , of all the prepared glasses, defined as the mean molecular weight (M) of its constituents divided by its experimental

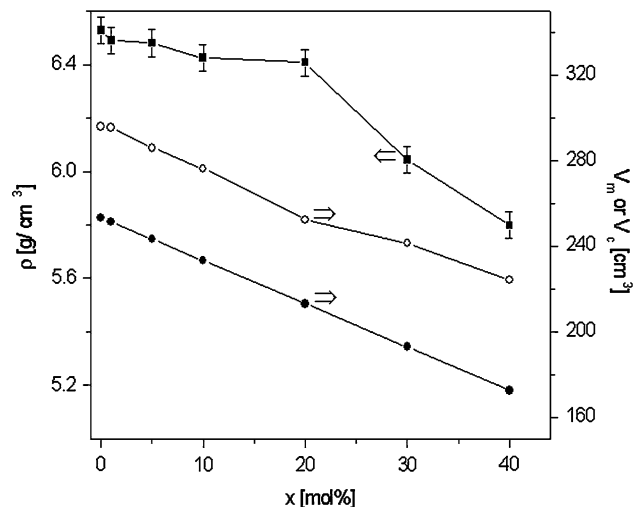


Fig. 1 Composition dependence of crystalline (●) and glassy molar volume (○) and density (■) of $x\text{Eu}_2\text{O}_3 \cdot (100-x)[4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3]$ system

density as given by the equation, $V_m = M/\rho$ and the sum of the molar volumes, V_c , of the components of the glasses in their crystalline states were calculated and are also shown in Fig. 1. It can be observed that the molar volume of the glasses is always greater than their hypothetical mixed crystalline phase, indicating the presence of excess structural volume in the glasses. Increasing the europium oxide content the difference between V_m and V_c decreases up to 20 mol% Eu_2O_3 , while for higher content of Eu_2O_3 the difference between V_m and V_c increases. These results show that the better packing of coordination polyhedra in the structural network of bismuth-borate glasses is obtained for the sample containing 20 mol% Eu_2O_3 .

3.2 FT-IR data

In order to understand the effect of addition of Eu_2O_3 in $4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ glass matrix, we consider the mid infrared region (400–1,600 cm^{-1}) where the vibration modes of bismuth-borate glasses are active. It is known that Bi_2O_3 can form in glass networks deformed BiO_6 units, both BiO_6 and BiO_3 units, and only BiO_3 pyramidal units [19]. The BiO_3 unit belongs to the pyramidal point group C_{3v} and have four fundamental vibration: a totally symmetric stretching vibration at 840 cm^{-1} , a doubly degenerate stretching vibration at 540–620 cm^{-1} , a totally symmetric bending vibration at 470 cm^{-1} and a doubly degenerate bending vibration at 350 cm^{-1} [25]. The vibrations of strongly distorted BiO_6 octahedral give, in the IR spectra, the following absorption bands centered at 860, 575–600, 470–520 and 430 cm^{-1} [25]. Therefore, it is proposed that the 840 and 860 cm^{-1} absorption bands can be used to identify the BiO_3 and BiO_6 units [19, 25]. On the other

hand, the vibration modes of the borate glasses occur in three IR spectral regions [24, 26–28]: the first region 600–800 cm^{-1} is due to bending vibrations of various borate segments, the second region 800–1,150 cm^{-1} can be attributed to the B–O stretching vibrations of BO_4 units and the third region 1,150–1,550 cm^{-1} is due to the B–O and B–O $^-$ stretching vibrations of BO_3 and BO_2O^- units.

The experimental IR spectra of $x\text{Eu}_2\text{O}_3 \cdot (100 - x)[4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3]$ glass system with various contents of europium oxide ($0 \leq x \leq 40$ mol%) were presented in Fig. 2. Since the majority of the bands are large and asymmetric, presenting also some shoulders, a deconvolution of the experimental spectra was necessary. This fact was made with the Spectra Manager program using a Gaussian type function that allowed us a better identification of all the bands which appear in these spectra and their assignments. Thus, by determining the number of all independent components, it is possible to carry out a quantitative analysis of the spectra and to find the concentration distribution of these components across the investigated mixtures. The proportion of particular struc-

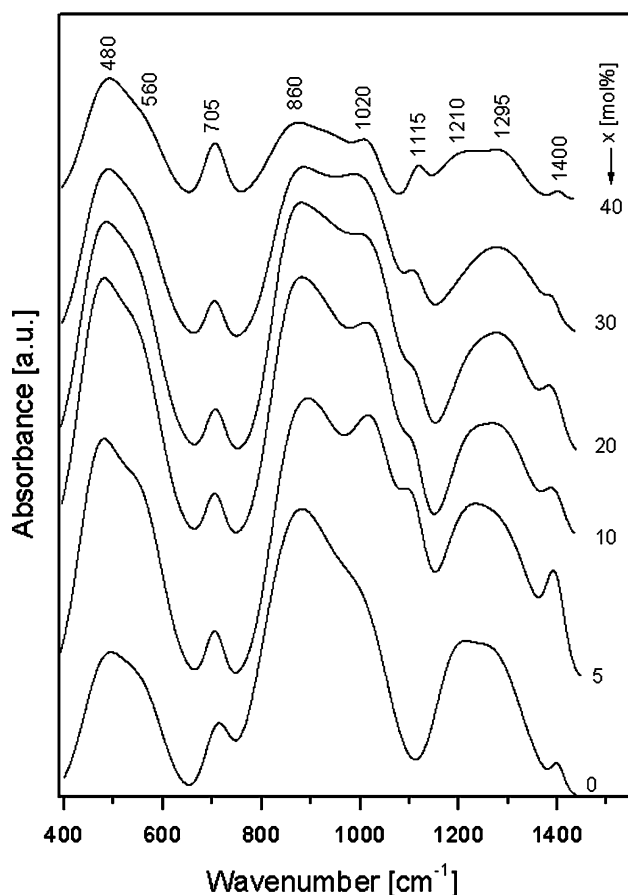


Fig. 2 Infrared absorption spectra of $x\text{Eu}_2\text{O}_3 \cdot (100 - x)[4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3]$ glasses

tures corresponding to different vibration modes was calculated from areas of the fitted Gaussian bands divided to the total area of all bands. The four parameter of each band (peak frequency, half-width at half-height and relative areas) were allowed to float during the iterations. As an example Fig. 3 shows the deconvolution, in Gaussian bands, of the spectrum for binary $4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ glasses (Fig. 3a) and for these glasses containing 5 mol% Eu_2O_3 (Fig. 3b). The deconvolution process makes it possible to calculate the relative area of each component band [29, 30]. Each component band is related to some type of vibration in specific structural groups. The concentration of the structural group is proportional to the relative area of its component band. The deconvolution parameters, the band centers C and the relative area A as well as the bands assignments for the studied glasses are given in Table 1. The result of peak deconvolution, indicates a number of 8–9 peaks in the spectral region from 390 at 1,450 cm^{-1} . The deconvolution IR spectrum of binary $4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ glasses (Fig. 3a) shows the presence of the following bands centered at: ~ 478 , ~ 558 , ~ 710 , ~ 840 , ~ 916 , 1,017, $\sim 1,183$,

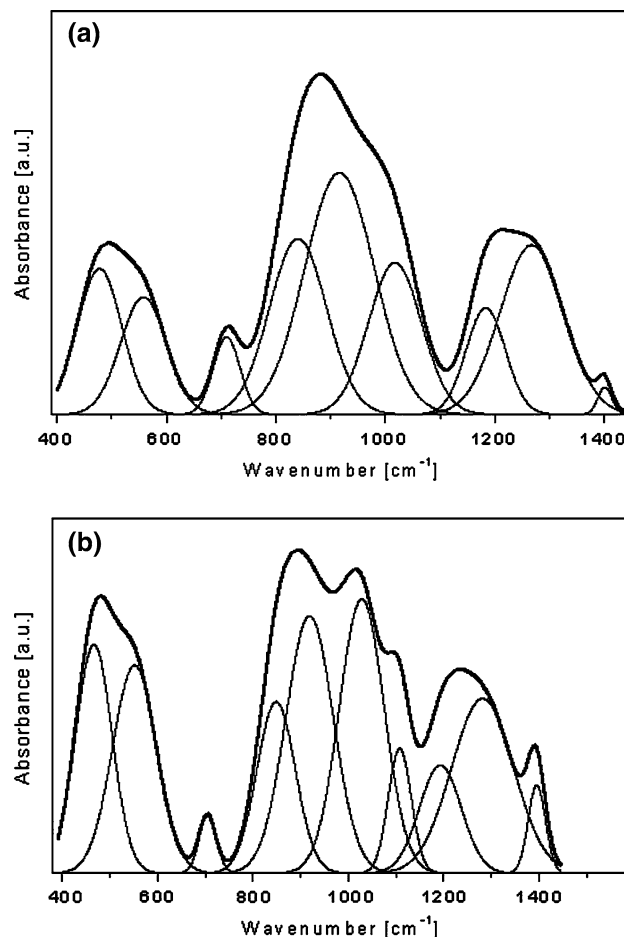


Fig. 3 Deconvoluted FT-IR spectra of $x\text{Eu}_2\text{O}_3 \cdot (100 - x)[4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3]$ glasses using a Gaussian-type function for $x = 0$ mol% (a) and $x = 5$ mol% (b)

Table 1 Deconvolution parameters (the band centers C and the relative area A) and the bands assignments for the $x\text{Eu}_2\text{O}_3 \cdot (100 - x)[4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3]$ glasses

$x = 0$		$x = 5$		$x = 10$		$x = 20$		$x = 30$		$x = 40$		Assignments
C	A	C	A	C	A	C	A	C	A	C	A	
478	4.41	466	6.79	464	6.86	463	5.51	471	4.45	481	3.95	Bi–O bend in BiO_3 units
558	3.65	551	7.47	546	8.07	542	7.70	548	4.99	561	2.36	Bi–O bend in BiO_6 units
710	1.40	705	0.81	704	0.74	706	0.74	705	0.62	705	0.60	B–O–B bend
840	6.84	848	5.37	849	5.02	850	4.56	852	3.49	860	2.73	Bi–O _{sym} stretch in BiO_3 units Bi–O vibration in distorted BiO_6 units
916	11.43	918	10.96	921	9.86	921	9.33	925	6.30	954	2.15	B–O stretch in BO_4 units from di-borate groups
1,017	5.47	1,028	10.01	1,030	7.19	1,026	7.72	1,020	5.18	1,019	0.75	B–O stretch in BO_4 units from tri-, tetra- and penta-borate groups
–	–	1,107	2.33	1,109	0.91	1,113	0.73	1,113	0.63	1,116	0.33	B–O _{sym} stretch in BO_4 units from varied types of borate groups
1,183	2.83	1,192	3.68	1,207	1.29	1,211	1.95	1,210	1.87	1,208	1.95	B–O _{asym} stretch in BO_3 units from pyro- and ortho-borate groups
1,267	7.32	1,281	7.81	1,281	6.69	1,293	5.42	1,296	4.73	1,295	1.17	B–O stretch in BO_3 units from boroxol rings
1,400	0.26	1,395	1.24	1,394	0.59	1,390	0.57	1,390	0.19	1,400	0.18	B–O [–] stretch in BO_3 units from varied types of borate groups

~1,267 and ~1,400 cm^{-1} . The band from ~478 was ascribed to the Bi–O bending vibration in BiO_3 pyramidal units while the band from ~558 cm^{-1} was assigned to the Bi–O bending vibration in BiO_6 units [25, 31, 32]. At ~710 cm^{-1} appears a band due to the bending vibrations of B–O–B linkage in the borate network [26–28]. The band at ~840 cm^{-1} was assigned to the Bi–O symmetrical stretching vibration in BiO_3 units [25]. Absorption from ~916 cm^{-1} can be due to the B–O stretching vibrations in BO_4 units from di-borate groups [26–28] while the band from ~1,017 cm^{-1} was assigned to the B–O stretching vibrations in BO_4 units from tri-, tetra- and penta-borate groups [26–28]. The band from ~1,183 cm^{-1} was ascribed to B–O[–] asymmetric stretching vibrations in BO_3 units from pyro- and ortho-borate [24], these groups containing a large number of NBOs. The band from ~1,267 cm^{-1} was attributed to B–O stretching vibration in boroxol rings while the band from ~1,400 cm^{-1} were assigned to B–O[–] stretching vibrations in BO_3 units from varied types of borate groups [26–28]. The addition of Eu_2O_3 in the $4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ glass matrix, gives some change in the FT-IR spectra of these glasses (Fig. 3b). At ~1,107 cm^{-1} appears a new band, which can be due to the symmetrical stretching vibration of B–O bonds in BO_4 units from varied types of borate groups [26–28]. The intensity of the bands from ~478 and 558 cm^{-1} increases with the increasing of the Eu_2O_3 content up to 10 mol% Eu_2O_3 after that decreases while the intensity of the band from ~710 cm^{-1} decreases in the whole concentration range. It is also remarked that the center of the band from 840 cm^{-1} shift to higher wavenumber, around 860 cm^{-1} , as Eu_2O_3 content

increases to 40 mol%, and its intensity decrease. This band (860 cm^{-1}) can be due to vibration of strongly distorted BiO_6 octahedral units [25, 31]. This suggests the conversion of the BiO_3 into BiO_6 units with the increasing of europium ions content. Thus, the presence of europium ions seems to influence the surrounding of the Bi^{3+} cations favoring the formation of BiO_6 units. To quantify the europium ions effect to the changes in the relative population of triangular and tetrahedral borate units we have calculated the fraction of four-coordination boron atoms, N_4 , which was estimated as follows [29]:

$$N_4 = \frac{A_4}{A_3 + A_4}$$

where A_4 and A_3 denoted the areas of BO_4 units (the areas of component bands from 916–954, 1,017–1,030, 1,107–1,116 cm^{-1}) and BO_3 units (the areas of component bands from 1,183–1,211, 1,267–1,296, 1,390–1,400 cm^{-1}), respectively. Fraction of four-coordination boron atoms, N_4 , is plotted in Fig. 4 vs. Eu_2O_3 content. The amount of BO_4 increased as the content of Eu_2O_3 increased. The maximum amount of BO_4 was observed at 20 mol% Eu_2O_3 . A further addition of Eu_2O_3 over 20 mol% led to a decrease in the amount of BO_4 . This is due to the structural changes from BO_3 to BO_4 as the content of the glass modifier Eu_2O_3 increased, i.e., the BO_3 units in the bismuth–borate glasses prefer a coordination change to BO_4 rather than producing NBOs. This $\text{BO}_3 \rightarrow \text{BO}_4$ conversion will increase the stability of the glasses. The reverse structural change from the BO_4 units to the non-bridging

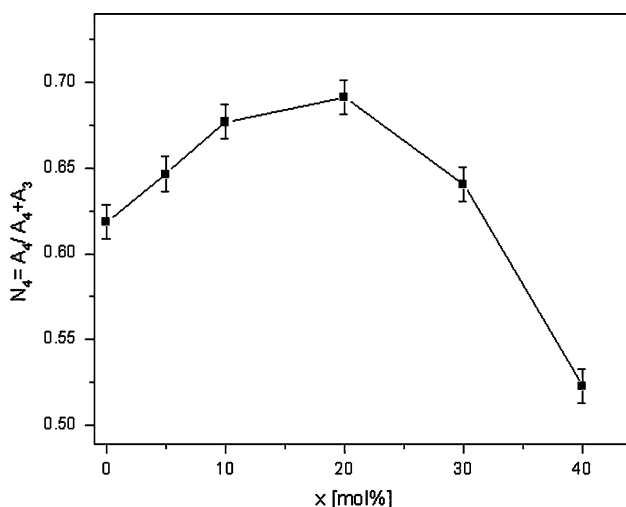


Fig. 4 Fraction of four-coordination boron atoms N_4 versus Eu_2O_3 content for the $x\text{Eu}_2\text{O}_3 \cdot (100 - x) [4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3]$ glasses

oxygen containing BO_3 units occurred when more than 20 mol% of Eu_2O_3 is added, which reduced the stability of the glasses. The fourfold boron atoms are favored in the investigated system as compared with the threefold ones.

The structural changes observed by increasing the Eu_2O_3 content in $4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ glass matrix evidenced by the FT-IR investigation suggest that the europium ions play a network modifier role in these glasses.

4 Conclusions

Glasses of the $x\text{Eu}_2\text{O}_3 \cdot (100-x)[4\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3]$ system were obtained within a large concentration range, i.e., $0 \leq x \leq 40$ mol%. The compositional variation of the glassy molar volume (V_m) and the corresponding crystalline molar volume (V_c) indicate that Eu_2O_3 plays the role of modifier and both Bi_2O_3 and B_2O_3 play the role of network formers. The FT-IR studies show that the glass structure consist of BiO_3 , BiO_6 , BO_3 and BO_4 units, but their proportion depends on the europium ions content in these glasses. Density and FT-IR spectroscopy measurements show that the better packing of coordination polyhedra in these glasses is obtained for sample containing 20 mol% Eu_2O_3 .

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