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FTIR spectroscopic study of Gd_2O_3-Bi_2O_3-B_2O_3 glasses♣

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FTIR spectroscopy measurements were performed on the $xGd_2O_3 \cdot (100-x)[2Bi_2O_3 \cdot B_2O_3]$ system with $0 \le x \le 25$ mol% in order to point out the effect of Gd_2O_3 addition in the bismuth-borate glass matrix on the local order of this system. FTIR spectroscopy data suggest that the gadolinium ions play the network modifier role in the studied glasses. These data show that the glass structure consists on the BiO_6, BO_3 and BO_4 structural units, and the conversion among these units mainly depends on the Gd_2O_3 content.

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1. Introduction

Bismuthate glasses have important properties such as high non-linear refractive index, high density, high polarizability, high transmission in visible and near infrared region as well as optical non-linearity effect which make them useful for a wide range of technical applications [1-6]. Bi_2O_3 is not traditionally known to form glass, but in the presence of conventional glass-forming cations such as B^{3+}, P^{5+}, Si^{4+} it may have this property. The bismuthate glass networks may consist of both BiO_6 octahedral and BiO_3 pyramidal units [7- 9]. On the other hand, B_2O_3 is one of the most common glass former oxides, is present in almost all commercially important glasses and borate glasses are also of academic interest because of the occurrence of boron anomaly. 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 [10]. It was reported that addition of a network modifier in borate glasses causes a progressive change of some the triangular BO_3 structural units to BO_4 tetrahedra with a coordination number of 4, which are incorporated in more complex cyclic groups such as di-, tri-, tetra- or penta-borate groups [9, 11]. At higher concentrations of the modifier, the formations of BO_3 units with non-bridging oxygen atoms (NBOs) are reported (pyro- or orto-borate) [9, 12].

The aim of the present work is to investigate by FTIR spectroscopy measurements the bismuth-borate glasses doped with Gd_2O_3 in order to establish the structural changes induced by gadolinium oxide addition and to obtain information regarding the local structure of these glasses.

2. Experimental

Glasses of the $xGd_2O_3 \cdot (100-x)[2Bi_2O_3 \cdot B_2O_3]$ system were prepared using reagent grade purity Bi_2O_3, H_3BO_3 and Gd_2O_3 in suitable proportion. The mechanically homogenized mixtures were melted in sintered corundum crucibles at 1100 °C, in an electric furnace. The samples were put into the electric furnace direct at this temperature. After 15 minutes, 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 25 mol%.

The FT-IR absorption spectra of the glasses in the 400 - 1500 cm^{-1} spectral range were obtained with a JASCO FTIR 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

In order to understand the structural changes induced by addition of Gd_2O_3 in $2Bi_2O_3 \cdot B_2O_3$ glass matrix we consider the mid infrared region (400-1500 cm^{-1}) where the vibration modes of bismuth-borate glasses are active. Fig. 1 shows the experimental FTIR spectra of $xGd_2O_3 \cdot (100-x)[2Bi_2O_3 \cdot B_2O_3]$ glass system with various contents of gadolinium oxide ($0 \le x \le 25$ mol%).

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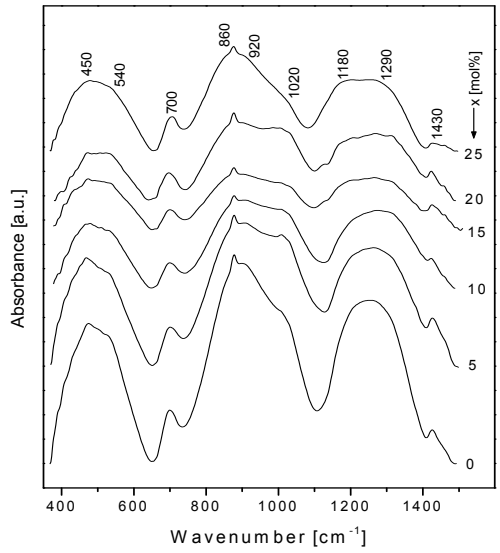

Fig. 1. FTIR spectra of $xGd_2O_3 \cdot (100-x)[2Bi_2O_3 \cdot B_2O_3]$ glasses.

Because the majority of the bands are large and asymmetric, presenting also some shoulders, the 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. The proportion of particular structures corresponding to different vibration modes was calculated from areas of the fitted Gaussian bands divided to the total area of all bands. As an example Fig. 2 shows the deconvolution, in Gaussian bands, of the spectrum for binary $2Bi_2O_3 \cdot B_2O_3$ glasses (Fig. 2a) and for these glasses containing 20 mol% Gd_2O_3 (Fig. 2b). The deconvolution process makes it possible to calculate the relative area of each component band [13, 14]. 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 deconvolution IR spectrum of glass matrix (Fig. 2a) show absorptions bands centered at ~ 447, ~ 535, ~ 700, ~ 860, ~ 932, ~ 1030, ~ 1192, ~ 1298 and ~ 1437 cm^{-1}.

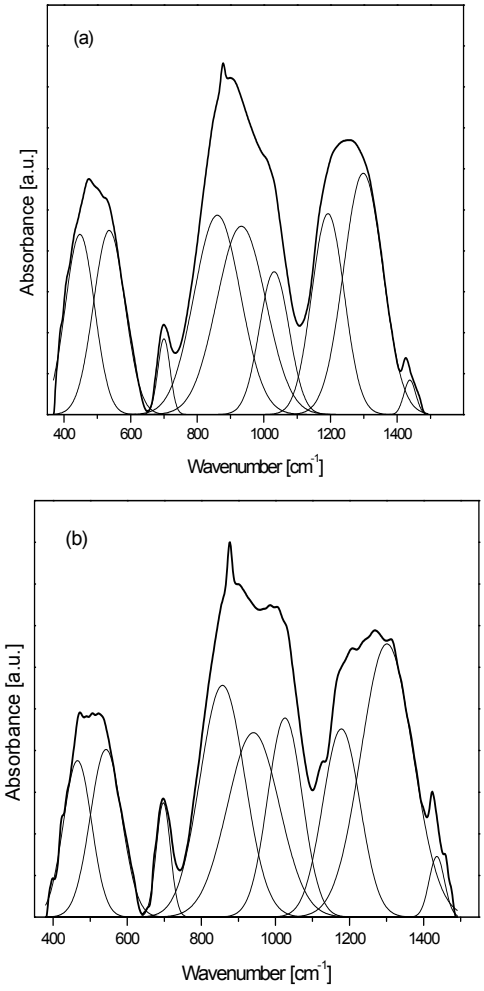

Fig. 2. Deconvoluted FTIR spectra of $xGd_2O_3 \cdot (100-x)[2Bi_2O_3 \cdot B_2O_3]$ glasses using a Gaussian – type function for x = 0 mol% (a) and x = 20 mol% (b).

Table 1. Deconvolution parameters (the band centers C and the relative area A) and the bands assignments for the $xGd_2O_3 \cdot (100-x)[2Bi_2O_3 \cdot B_2O_3]$ glasses.

x = 0		x = 5		x = 10		x = 15		x = 20		x = 25		Assignments
C	A	C	A	C	A	C	A	C	A	C	A	
447	12.1	446	9.7	457	5.8	447	4.3	465	3.6	450	6.1	
535	13.2	536	9.6	543	5.2	532	4.8	542	4.3	541	7.2	Bi-O bend in BiO_6 units
700	2.1	704	1.6	701	1.1	701	0.8	697	1.3	703	1.5	B-O-B bend
860	21.2	854	16	861	6.8	855	3.4	857	8.4	856	12.3	Bi-O vibration in BiO_6 units
932	21.1	909	8.8	904	9.2	906	8	940	7.8	929	8.6	B-O stretch in BO_4 units from di-borate groups
1030	9.7	1022	17	1025	8.5	1026	3.7	1025	5.6	1013	2.6	B-O stretch in BO_4 units from tri-, tetra- and penta-borate groups
1192	14.9	1191	8.6	1192	3.9	1176	4.4	1177	5.7	1180	9.6	$B–O^-_{asym}$ stretch in BO_3 units from pyro- and ortho-borate groups
1298	21.6	1300	19.5	1299	14.6	1298	8.7	1300	11.5	1296	8	B-O stretch in BO_3 units from varied types of borate groups
1437	0.9	1439	1.4	1431	0.4	1439	1	1435	0.8	1447	0.4	$B-O^-$ stretch in BO_3 units from varied types of borate groups

At low wavenumber the bands from ~ 447 and ~ 535 cm^{-1} can be related to the Bi-O bending vibration in BiO_6 units [15, 16]. The intensity of these bands increases up to 20 mol% Gd_2O_3 and after that decreases. The existence of a band at about ~ 700 cm^{-1} (bending vibrations of B-O-B linkage in the borate network [17-19]) was suggested to point out that at least some super structural borate units are retailed in the structure of this bismuth-borate glass [6]. Absorption from ~ 860 cm^{-1} can be due to vibration of strongly distorted BiO_6 octahedral units [15, 16]. Its intensity decreases with the increase of Gd_2O_3 content till x = 15 mol%. For higher content of gadolinium ions the intensity of this band increases. It was shown that Bi_2O_3 appears in the glass networks as deformed BiO_6 units [9, 16], both BiO_6 and BiO_3 polyhedra [15] or only as BiO_3 pyramidal units [8]. The most important condition for the existence of BiO_3 polyhedra is the presence of a band at 830 cm^{-1} in the FTIR spectra [15, 16]. The absence of this band in the FTIR spectra of the studied glasses proofs that Bi^{3+} cations are incorporated in the structure of glasses as only BiO_6 octahedral units. Thus, the presence of gadolinium ions seems to influence the surrounding of the Bi^{3+} cations favoring the formation of BiO_6 units. Absorption in the 850-1150 cm^{-1} range can be attributed to the B-O stretching vibration of BO_4 units [12]. Thus, the band at ~ 932 cm^{-1} can be due to the B-O stretching vibrations in BO_4 units from di-borate groups [17-19] while the band from ~ 1030 cm^{-1} was assigned to the B – O stretching vibrations in BO_4 units from tri-, tetra- and penta-borate groups [17-19]. The high frequency absorption profile (1150-1550 cm^{-1}) originates from the stretching vibration and asymmetric stretching vibrations of B-O and B-O^- bonds in borate triangular units, which are of the BO_3 and BO_2O^- type [20]. Thus, the band from ~ 1192 cm^{-1} was ascribed to B – O^- asymmetric stretching vibrations in BO_3 units from pyro- and ortho-borate [12], these groups containing a large number of NBOs. The band from ~ 1298 cm^{-1} was attributed to B-O stretching vibration in varied types of borate groups while the band from ~ 1437 cm^{-1} were assigned to B – O^- stretching vibrations in BO_3 units from varied types of borate groups [17-19]. To quantify the gadolinium ions effect to the changes in the relative population of BO_4 and BO_3 units we have calculated the fraction of four-coordination boron atoms, N_4, which was estimated as follows [14]:

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

where A_4 and A_3 denoted the areas of BO_4 units (the areas of component bands from 904-940, 1013-1030 cm^{-1}) and BO_3 units (the areas of component bands from 1176-1192, 1296-1300, 1431-1447 cm^{-1}), respectively. Fraction of four-coordination boron atoms, N_4, is plotted in Fig. 3 versus Gd_2O_3 content.

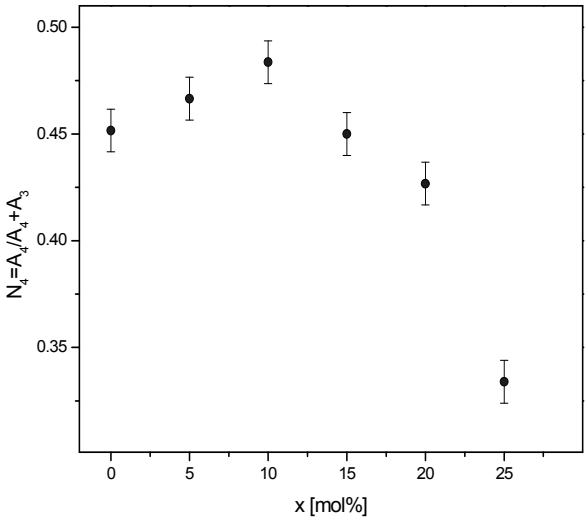

Fig. 3. Fraction of four-coordination boron atoms N_4 versus Gd_2O_3 content for the $xGd_2O_3 \cdot (100- x)[2Bi_2O_3 \cdot B_2O_3]$ glasses.

The amount of BO_4 increases as the content of Gd_2O_3 increasing up to 10 mol% Gd_2O_3. A further addition of Gd_2O_3 over 10 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 Gd_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 $BO_3 \rightarrow BO_4$ conversion will increase the stability of the glasses. The reverse structural change from the BO_4 units to the NBOs containing BO_3 units occurred when more than 10 mol% of Gd_2O_3 is added, which reduced the stability of the glasses. The threefold boron atoms are favored in the investigated system as compared with the fourfold ones.

4. Conclusions

Glasses of the $xGd_2O_3 \cdot (100-x)[2Bi_2O_3 \cdot B_2O_3]$ system were obtained within a large concentration range, i.e. $0 \leq x \leq 25$ mol %. The FTIR studies show that the glass structure consist of BiO_6, BO_3 and BO_4 units, but their proportion depends on the gadolinium ions content in these glasses. The structural changes observed by varying the Gd_2O_3 content in these glasses and evidenced by FTIR investigation suggests that the gadolinium ions play a network modifier role in these glasses and both Bi_2O_3 and B_2O_3 play the role of network formers.

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