Study of some physical properties of bismuth doped borate glass

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ABSTRACT

Glass samples of the formula (70-x) B_2O_3 -xBi_2O_3-15Zn-15Na_2O have been prepared by the melting quenching technique. The structural and optical characterisations of the glassy system were carried out by XRD, density, molar volume and FTIR technique. The powder X- ray diffraction of the prepared glass confirms the amorphous nature. FTIR analysis indicates dependence of the number of structural units of BO_3 and BO_4 on Bi_2O_3 concentration. It is assumed that Bi_2O_3 enters the structure in the form of BiO_6. Bi_2O_3 in different structural units like tri, tetra, penta and octahedral groups are confirmed in the glass matrix. The change of density, molar volume and N_4 ratio with Bi_2O_3 content confirm the transformation of structural units of BO_3 into BO_4 by Bi_2O_3 addition.

Keywords: *Borate glass, X-ray, FTIR, Density, Molar volume, N_4 ratio, BO_3 and BO_4 structural units.*

1. INTRODUCTION

In modern technology, glass material exhibits enhanced interest. Among oxide glasses, borate glass is one of important glass former and has been incorporated in many kinds of glass systems to achieve special chemical and physical properties. In borate glass, B_2O_3 is the fundamental glass former because of its higher field strength, lower cation size, small heat of fusion and trivalent nature of B. In boron oxide, B^{3+} ions are triangularly coordinated by oxygen and corner bonded in a random configuration [1]. Borate glasses with heavy metal ions such as Bi, Pb, Zn etc. shows good nonlinear optical properties[2]. At the same time borate glass provides a good shielding against IR radiations[3].

ZnO, Bi_2O_3 are two metal oxides, which do not form glasses [4] by themselves but do so readily in combination with other glass formers. Bi_2O_3 shows high refractive index, and exhibits high optical basicity, large polarizability and large optical susceptibility values [5-7] which make them ideal candidates for applications in infrared optics, ultra fast optical switches, and photonic devices. Moreover, bismuth oxide containing glasses shows extremely high radioactive resistance because of their high density and atomic number[8].

In the present work, an attempt has been made for the preparation and characterization of bismuth borate glasses with the addition of zinc and sodium oxide as modifiers. The structural features of the glasses has been investigated by density, molar volume, x-ray diffraction and Fourier Transformation Infrared spectroscopy (FTIR). The composition of the investigated glass samples have the form (70-x) B_2O_3 -xBi_2O_3-15Zn-15Na_2O (x = 0, 5, 10, 15, 20, 25) table 1.

Table 1 compositions of glasses (in mol %) prepared in the present work

X	Glass system
0	70 B_2O_3 0Bi_2O_3 15ZnO 15Na_2O
5	65 B_2O_3 5Bi_2O_3 15ZnO 15Na_2O
10	60 B_2O_3 10Bi_2O_3 15ZnO 15Na_2O
15	55 B_2O_3 15Bi_2O_3 15ZnO 15Na_2O
20	50 B_2O_3 20Bi_2O_3 15ZnO 15Na_2O
25	45 B_2O_3 25Bi_2O_3 15ZnO 15Na_2O

2. EXPERIMENTAL DETAILS

The glass system having the general formula (70-x)% B_2O_3-15) % ZnO-15%Na_2O-x%Bi_2O_3 were prepared by conventional melt quenching method. The required quantities of given chemical composition were taken and mixed powders were melted in ceramic crucibles at 1150°C. The melts were kept at 1150°C for half an hour. The melt were shaken in order to get homogenized samples. The melt was poured into preheated copper rectangular moulds. Furthermore, the mould was kept at 400°C for four hours to remove the internal stresses from the glasses before leaving it to cool down slowly to room temperature.

X-ray diffraction patterns of the prepared glass samples are shown in Fig. 1. The amorphous nature of the samples is confirmed by X-ray diffraction (XRD) study using a Philips X-ray diffractometer using monochromatized CuKα1 radiation of wavelength $1.54056A^0$ from a fixed source operated at 40KV and 40mA at the scanning rate of 2^o/min and 2θ varied from 5^o to 70^o.

The density of glass samples at room temperature was measured by the standard Archimedes method [9] using a sensitive 4- digit microbalance(AnD, HR200). The density, ρ, was determined from the relation.

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b$$

where W_a is the weight in air, W_b is the weight in carbonteterachloride (CCL_4) with ρ_b= 1.592 g/cm^3. The corresponding molar volume V_m was calculated using the relation, $V_m = M_T/\rho$, where M_T is the molecular weight.

The infrared transmission spectra of the multi-component glass system are measured at room temperature in the range 400- 4000 cm^{-1} by a Fourier Transform computerized infrared spectrometer type (Thermo Nicolet 200 spectrometer). The prepared glasses are mixed in the form of fine powder with KBr in the ratio 1:100 mg (glass powder ; KBr), respectively. The weighted mixtures are then subjected to a pressure 12 TON/cm^2 to produce homogeneous pellets. The infrared transmission measurements are measured immediately after preparing the pellets.

3. RESULTS AND DISCUSSION

X-ray diffraction pattern of the samples in consideration is shown in Fig 1. The figure exhibits no discrete sharp peaks which confirmed the amorphous nature of glass samples.

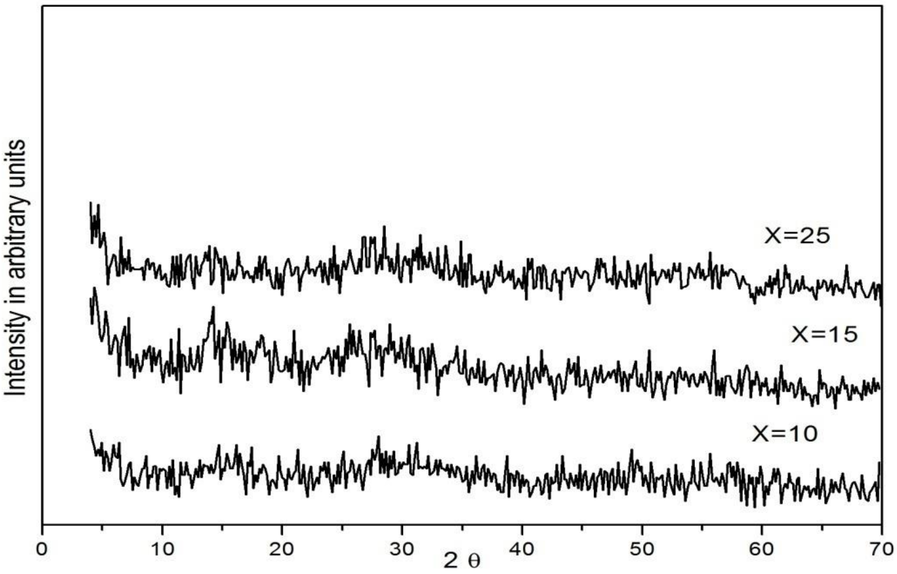
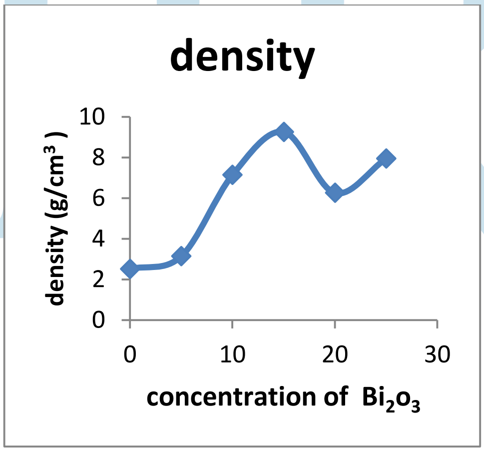


Fig. 1. x-ray diffraction patterns of some glass samples.

The density measurement is considered to be an important tool to detect the structural unit changes in the glass. The density and molar volume of the prepared glass samples are tabulated in table2 and shown in Fig.2 and fig.3, respectively. The obtained data reveal non- linear behaviour with x. It is seen that the density of the glass samples increases with increasing Bi_2O_3 content from x = 0 to x = 15, while molar volume shows opposite trend. This is might be due to higher molecular weight of Bi_2O_3 with respect to that of B_2O_3. However, the abrupt decrease in density and increase in molar volume when Bi_2O_3 reaches to 15% and after that the density increases when Bi_2O_3 reaches to 20% while molar volume decreases, can be attributed most likely due to the change in N_4 ratio. N_4 is defined as the ratio of ($\frac{\text{concentration of}\,[BO_4]\,\text{units}}{\text{cocentration of}\,[BO_4+BO_3]\,\text{units}}$). It is well established that BO_4 structural units are open structures, the increase of which leads to reduction in the density (increase of molar volume). On the other hand BO_3 structural units is closely packed units, the increase of which leads to increase of density (reduction in molar volume V_m). In such a case one should expect that the dependence of N_4 on Bi_2O_3 should follow the pattern of V_m and exhibit opposite trend to that of density ρ. This is clearly observed from the obtained data. For sake of conformation one should measure FTIR spectra.

Table2 density and molar volume Bi_2O_3 concentration

X	Density	VM
0	2.513029	45.63019
5	3.138283	41.99112
10	7.136941	20.86328
15	9.260971	15.40875
20	6.256948	21.82054
25	7.940948	16.41492



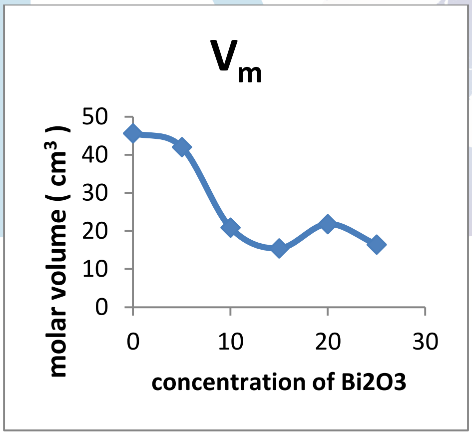


Fig.2 density of the glass samples

Fig.3 Molar volume versus Bi_2O_3 concentrations

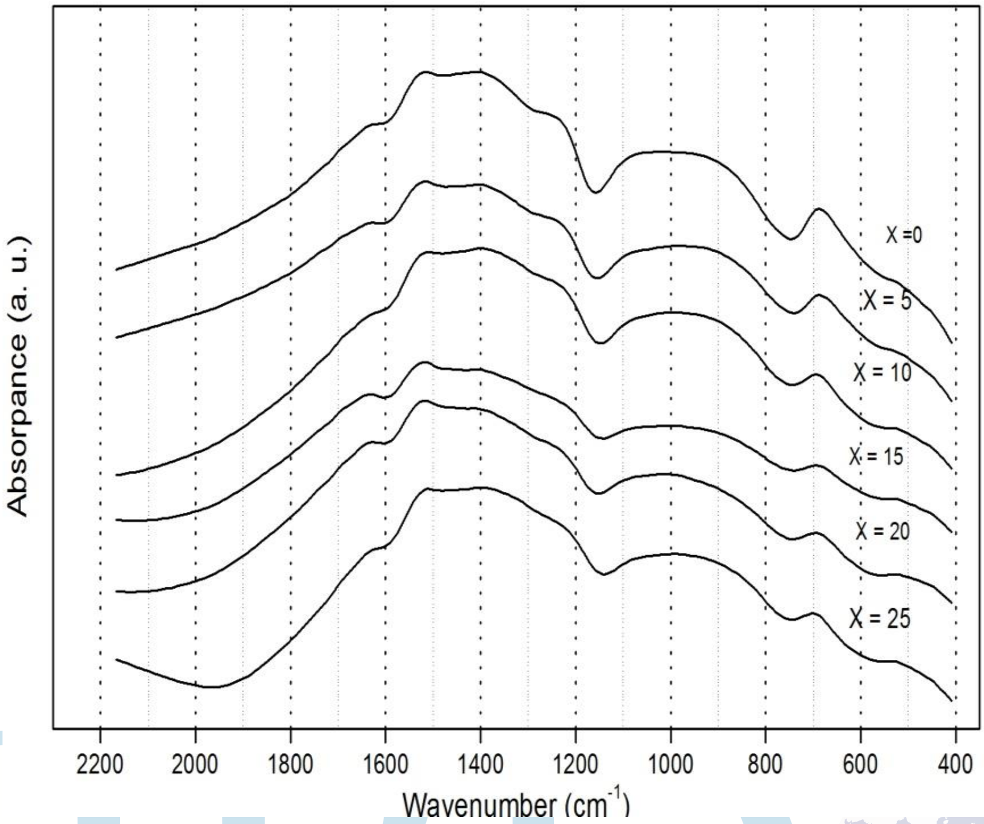


Fig 4: Infrared spectra of the investigated (70-x) B_2O_3 -xBi_2O_3-15Zn-15Na_2O glasses. Numbers at the plots represent Bi_2O_3 content in mol%.

FTIR absorption spectra of (70-x) B_2O_3 -xBi_2O_3-15Zn-15Na_2O glasses are shown in Fig. 4. The spectra were deconvoluted and N_4 ratio was estimated. The observed peaks in the glass samples are given in table 3 along with their assignment in table 4.

The main active vibrational modes of the borate network are usually observed in three regions namely:- (1200-1700 cm^{-1}, 800-1200 cm^{-1}and 600-800 cm^{-1} [10]. The glass system reveals several absorption bands extending from the beginning of the measurements at 400 up to 4000 cm^{-1}. The main observed absorption bands are about 650, 850, 1000, 1200, 1400, 1500, 1700 cm^{-1}. The broad absorption bands extending in the near infrared region 2500-4000 cm^{-1} are due to hydroxyl (OH) group. The presence of the hydroxyl groups or water molecules could be attributed to the KBr technique and may also arise due to the presence of water in H_3BO_3.

Table 3 Deconvolution parameters of the infrared spectra of (70-x) B_2O_3 -xBi_2O_3-15ZnO-15Na_2O glasses. C is the component band center (cm^{-1}) and A is the relative area (%) of the component band.

0 Bi_2O_3	C	675.6	861.6	997.8	1095	1228	1390	1525	1660
	A	14.59	23.9	34.08	8.4	8.0	110.8	3.5	42.1
5 Bi_2O_3	C	673	868	1010	1097	1226	1387	1524	1666
	A	9.93	25.1	24	5.1	6.67	83.9	3.4	37.5
10 Bi_2O_3	C	682	892	1028	1097	1220	1393	1522	1687
	A	9.4	44.6	18.6	4.6	6.8	140.8	3.9	31.1
15 Bi_2O_3	C	682	921	1046	741	1411	1527	1656	1755
	A	2.3	22.2	4.97	20.8	154.0	3.3	3.3	11.9
20 Bi_2O_3	C	679	928	1105	1042	1223	1397	1522	1675
	A	5.4	51.0	3.0	7.4	7.3	110.7	3.0	45.3
25 Bi_2O_3	C	686	943	1054	844	1285	1520	1751	1664
	A	4.6	36.5	7.8	24.8	93	79	18	4.5

Table 4 assignments of absorption bands in the infrared spectra of the glass samples (70-x) B_2O_3 -xBi_2O_3-15ZnO-15Na_2O

Wavenumber	IR band assignments (cm^{-1})
400-600	Bi–O–Bi + Bi–O in BiO_6 octahedral [11–13]
600-700	Bending vibration of B–O–B in BO_3 triangles [14,15,16]
800-1000	Stretching vibration of B-O bonds in BO_4 units in various structural from tri, tetra and penta borate groups [14,15,16]
1200-1500	B–O stretching vibrations of trigonal BO_3 units only [14,15,16]

It is well established that pure B_2O_3 glass consists mainly of boroxol ring $B_3O_{9/2}$ with a three co-ordinated BO_3 unit. Addition of Bi_2O_3 will change the borate structure by creating BO_4 units at the expense of BO_3 structural units[19]. Stone et al. [18] and Cheng et al. [19] studied the binary glass system Bi_2O_3–B_2O_3. The infrared spectra show that by increasing the Bi_2O_3 content a broad absorption band arises in the region 850–950 cm^{-1}. Bands in this region are not observed in the infrared spectra of vitreous B_2O_3. They [18, 19] attributed infrared absorption between 900 and 950 cm^{-1} to stretching vibrations of BO_4 units that are connected by the bismuth cations. The crystalline phase of the 70Bi_2O_3 - 30B_2O_3 (mol%) glass consists of 3Bi_2O_3 - 5B_2O_3, which contains super-structural units in the form of isolated dipentaborate groups ($B_5O^{7-}_{11}$) [18,19]. The dipentaborate groups are formed due to acquisition of BO_4 tetrahedron resulting in a highly cross linked network. Absorption of infrared radiation below 610 cm^{-1} is most likely attributed either to cationic vibrations in the network [14] or to various modes of Bi–O vibration in BiO_6 [11–13].

Absorption bands around 840 cm^{-1} are related to stretching vibrations of Bi–O in BiO_3 units [20,12,21]. BiO_3 units could not be detected in xB_2O_3-(100-x)Bi_2O_3 glasses, where $40 \leq x \leq 70$ mol% [22]. This is most likely due to the masking of boron oxide bonds.

Vibrations of borate units appear as absorption peaks in the infrared spectra between 700 and 1550 cm^{-1} [14,15,16]. Assignment of the vibration modes is summarized in Table 4. Due to the absence of absorption bands at 840 cm^{-1} in the infrared spectra (Figs. 4), BiO_6 units will be expected to influence the borate network of the studied glasses. Therefore, bands around 600 cm^{-1} are due to doubly degenerate bending vibrations of BiO_6. The peak positions that lie between 800 and 1000 cm^{-1} are attributed to the B-O bond stretching of the tetrahedral BO_4 units and the bands around 700 cm^{-1} are due to the bending B-O-B linkages in the borate BO_3 networks [23, 24]. The bands in the range 1250-1680 cm^{-1} in the glass samples are due to the asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units.

The observed broad peak is the result of overlapping of individual bands with each other. Each individual band has its characteristic parameters such as its center (C), which is related to some type of vibrations of a specific structural group, and its relative area (A), which is proportional to the concentration of this structural group. A deconvolution process, as described elsewhere [25], should be performed to get such parameters. To follow the change in borate matrix due to additions of Bi_2O_3, the deconvolution should be carried out. The deconvoluted bands for the investigated glasses are given in Table 3.

Fig.5 shows the deconvoluted spectrum of the sample having 15 mol% Bi_2O_3 as an example. The deconvoluted peaks of the base glass spectrum agree well with that reported by Cheng et al.[21] and did not indicate the presence of the band at 840 cm^{-1} which is characteristic of BiO_3 units [26]. Table 4 summarizes the major observed absorption bands in the investigated glasses and their vibrational types, respectively.

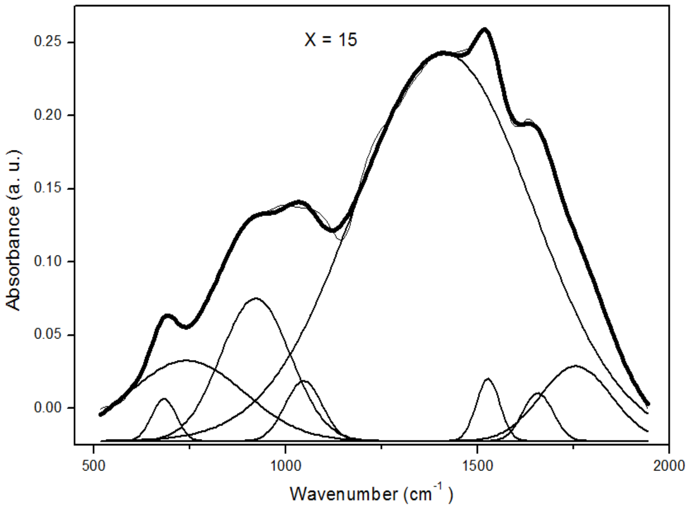


Fig.5 . Deconvolution of the infrared spectrum of the glass (70-x) B_2O_3 -xBi_2O_3-15ZnO-15 Na_2O

The parameters C and A of component bands (Table 3) can be used to calculate the ratio N_4 of borate matrix. The relative area of the band corresponds to BO_3 and BO_4 [25]. Then, by assigning the component bands structural units (Table 4), the calculated values of the ratio N_4 are listed in table 5. Fig.6 shows a common decrease of N_4 with increasing Bi_2O_3 content in glass systems, and suddenly increases when Bi_2O_3 concentration reaches to 15% and return to decrease. It shows the same trend as the molar volume changes, while it has an opposite trend with respect to density. It can be due to strong interaction between BO_4 and BO_3 groups and a value of about 0.32 for N_4 of the base glass composition reveals that the B_2O_3 matrix is progressively modified by Bi_2O_3 concentration.

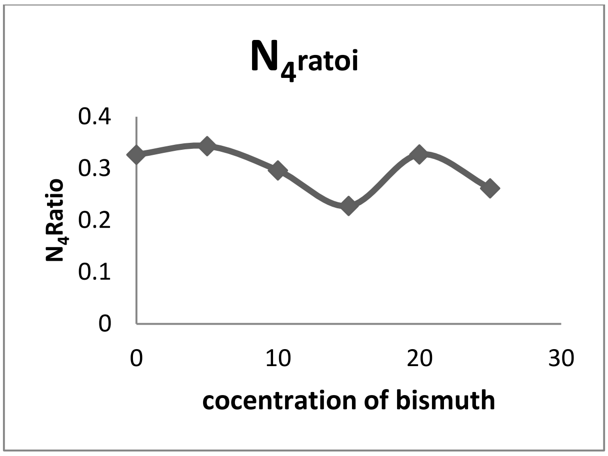


Fig. 6. N_4 ratio versus Bi_2O_3 concentration

Table 5. N_4 ratio with Bi_2O_3 concentration

X	N4=E/(E+J)
0	0.326493956
5	0.343150614
10	0.296204922
15	0.227357282
20	0.326982837
25	0.261560909

CONCLUSIONS

Glassy system of composition (70-x) B_2O_3 -xBi_2O_3-15Zn-15Na_2O has been prepared by conventional quenching melting method. The system was characterised by XRD, density ρ and molar volume V_m , and FTIR. XRD results indicate the amorphous nature of the prepared samples. The density shows non-linear dependence of Bi_2O_3 content, however, it follows opposite trend to that of molar volume V_m. The obtained FTIR spectra were deconvoluted and the resultant peaks were assigned. The deconvoluted data allow to estimate N_4. The latter follow the pattern of V_m and oppose that of ρ. This allows to assume the consistence of obtained results.

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