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Optical and spectroscopic studies of $ZnO–Bi_2O_3–B_2O_3$ glasses

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The effect of zinc oxide on the structural, physical and optical properties of bismuth borate glasses system has been investigated by means of infrared and optical absorption spectroscopic techniques. The samples were prepared by normal melt-quench technique. The formation of tetrahedral coordination of Zn (i.e. ZnO_4) is not observed in glasses under study. The fundamental absorption edge for all the glass samples has been identified using the theory proposed by Davis and Mott. The optical band gap is found to increase with increase in ZnO content. The theoretical optical basicity has been reported as a function of Bi_2O_3. The density and molar volume of the present glass system are found to depend on ZnO substitution.

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Keywords: Borate glasses, FTIR, UV absorption, Optical properties, Molar volume

1. Introduction

The glasses containing heavy metal oxide e.g. Bi_2O_3 have attracted attention in recent years because of their wide range of applications in the field of glass ceramics, thermal and mechanical sensors, reflecting windows etc. [1-2]. The large polarizability and small field strength of Bi^{3+} ions in oxide glasses makes them suitable for optical devices such as ultra fast all-optical switches, optical isolator, Optical Kerr Shutter (OKS) and environment guidelines [3]. As Bi^{3+} ions have small field strength, due to which Bi_2O_3 can not work as a network former; however, in the presence of classical glass former e.g. B_2O_3 the glass formation is possible and it may result in the formation of glass network of $[BiO_n]$ (n= 3,6) pyramids [4]. The structural role played by Bi_2O_3 in these glasses is complicated and not well understood because of the $[BiO_n]$ polyhedra are highly distorted due to lone pair electrons [5].

Infrared spectroscopy is a unique and powerful technique for characterization of the structure of local arrangements in the glasses [6-7]. In oxide glasses, B_2O_3 is a basic glass former because of its higher bond-strength, lower cation size and smaller heat of fusion and tri-valency of boron. In B_2O_3 glasses, the units are triangles, which are corner bonded in a random configuration [8]. The main structural units of borate glasses are BO_3 triangles forming six member (boroxol) rings connected by B-O-B linkage [9]. The addition of metal oxide modifies the boroxol ring in to complex borate groups results in the formation of various cyclic units like diborate or tetraborate groups [10]. Many investigations have also been reported on the structural, physical and optical properties of various heavy metal oxide doped borate glasses [11-12]. However the addition of transition metal oxide in these glass matrix cause changes in the structure and influence the semiconducting behavior of the glass system when the metal oxide is acting as a modifier [3, 5]. ZnO is a wide band gap semiconductor and has received increasing research interest. It is an important multifunctional material due to its specific chemical, surface and micro structural properties. It is used in various applications such as gas sensors, varistors, saw devices transparent electrodes, catalysts etc [13]. ZnO can enter in the glass network either in the form of glass former or as a modifier or both.

The aim of the present work is to study the effect of transition metal oxide (ZnO) on the structural, physical and optical properties of bismuth borate glasses using FTIR and optical absorption spectroscopy techniques. The interest for the present investigation also arises due to the presence of two network forming oxides, the classical B_2O_3 and unconventional Bi_2O_3. Both Boron and Bismuth are known to have more than one stable coordination i.e. boron triangles and tetrahedra and bismuth pyramidal and octahedral units. Moreover, the bismuth is able to form independent interconnected network of the borate groups [14].

2. Experimental details

Zinc doped bismuth borate glasses were prepared from reagent grade powder of ZnO, Bi_2O_3 and H_3BO_3, which are thoroughly mixed in appropriate proportions. The batch materials were dry mixed and melted in silica crucibles placed in an electrically heated muffle furnace at 1523K for about two hours, until a bubble free liquid was formed. The molten glass was equilibrated at the melting temperature until a clear and homogeneous melt was obtained. The glass melt was poured and subsequently pressed on a cooled carbon die held at room temperature.

The as obtained samples were then polished and cut in to definite shape. The vibration spectra of the glass system were obtained at room temperature using FTIR spectrometer in the range 500-3000 cm^{-1}. The measurements were performed directly on glass pallets mentioned above. The density (*d)* of the glasses was determined at room temperature using Archimede's Principle with Xylene as an inert immersion liquid. The molar volume (V_M) of each glass sample was calculated using the formula [15]

$$V_M = \sum \frac{x_i M_i}{d} \tag{1}$$

where x_i is the molar fraction and M_i is the molecular weight of the *i*th component. The optical absorption spectra were recorded at room temperature in the wave length range 340-900 nm using Perkin-Elmer (Lambda 20) UV-VIS spectrometer.

3. Results and discussion

3.1 FTIR Transmission spectra

The infrared spectra of *x* ZnO (30- *x*) Bi_2O_3 -70 B_2O_3 glass system; *x* = 0, 5, 10, 15 & 20 mol % are displayed in Fig. 1. According to Krogh-Moe model, the structure of borate glass consists of BO_3 triangles with certain fraction of six membered (boroxol) rings [8]. In B_2O_3 glasses boron [B^{3+}] ions are triangularly coordinated by oxygen to form glasses easily. The BO_3 triangles are corner bonded in a random network [9]. The introduction of transition metal ions in these glasses helps the boron to form tetraborate groups and progressive substitution of boroxal rings by triborate and tetraborate groups [11]. The boroxal ring shows its characteristic frequency at 806 cm^{-1} and the presence or absence of this band decides the existence or absence of boroxal rings in the structure. In the present set of glasses no band was observed at or around 806 cm^{-1} indicating that no boroxol rings are present in these glasses.

The peaks of the IR spectra of the glasses under study are listed in Table 1. The bands observed in the region 1660-1672 and 2366- 2371, in all the glass samples are attributed to the hydroxyl or water group [16]. The present set of glasses show very strong transmission bands in the region 1268-1279, 1187-1213, 996-1005, 651-668 and 583-586 cm^{-1}. However, there are also some other weak bands observed in the IR spectra of these glasses. In borate glasses it has been reported that the bands observed in the region 1200-1600 cm^{-1} are due to the asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units [17]. Whereas, the bands observed in the range 800-1200 cm^{-1} are assigned due to B-O bond stretching of the tetrahedral BO_4 units [18]. The band observed around 700 cm^{-1} is the bond bending mode of B-O-B vibrations [19]. In the present glass system, the intermerging bonds observed in the region 1268-1321 and 1187-1213 cm^{-1} are assigned to the asymmetric stretching of B-O bond in the trigonal and tetragonal units respectively [17-18].

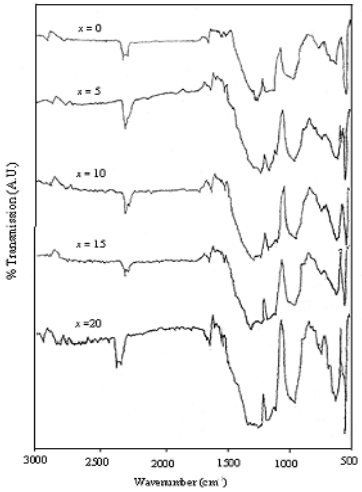

Fig.1. IR transmission spectra for ZnO-Bi_2O_3-B_2O_3 glasses

It has been reported that Bi_2O_3 appears in the bismuth borate glass networks either as [BiO_3] or as [BiO_6] or both [20-22]. The existence of [BiO_3] polyhedra must show its characteristic band at 830 cm^{-1} in the IR spectra [21]. However, the Fig. 1 shows no such band at or around 830 cm^{-1} indicating the absence of [BiO_3] units. Therefore it may be inferred that only [BiO_6] octahedral form the bismuthate structure in these glasses. However, the same could not be confirmed as the characteristic frequency of [BiO_6] group at 480 cm^{-1}, falls outside the range of the present measurements. While the infrared bands at 830 and 480 cm^{-1} are due to symmetric stretching bending vibrations of Bi-O bond, the bands that arise in the spectral range 530-620 cm^{-1} are due to the characteristics of doubly degenerated stretching vibrations of [BiO_3] and [BiO_6] polyhedra [23]. Therefore in the present glass system the band at 584 cm^{-1} is due to the stretching mode of Bi-O bond in the doubly degenerated [BiO_3] and [BiO_6] units [23].

Table 1. FTIR analysis of ZnO - Bi_2O_3- B_2O_3 glasses.

Peak positions (cm^{-})	Assignments
583-586	Stretching vibration of Bi-O bond in the doubly degenerated [BiO_3] and [BiO_6] units [22]
651- 668	Bending vibrations of O-B-O linkage.
773-788	Bending mode of =B-O-B≡ bonds [23]
996-1005	B-O bond stretching of the tetrahedral BO_4 units [24]
1187- 1213	Asymmetric stretching vibration of B-O bond in the tetragonal units [17]
1268-1279, 1295-1321, 1295-1321, 1560-1573	Asymmetric stretching vibration of B-O bond in the trigonal units [16]
1660-1672, 2366-2371	Absorption due to hydroxol group [15]

The strong IR bands observed in the spectral range 650-670 cm^{-1} are assigned to the plane bending mode of O-B-O linkage. Whereas, the band around 780 cm^{-1} is the bending mode of =B-O-B≡ bonds in which oxygen bridges between one tetrahedral and one trigonal boron atom [24]. The band around 1000 cm^{-1} originates from B-O bond stretching of the tetrahedral BO_4 units and is due to the vibration of some boron atoms attached to the non-bridging oxygen in the form of BO_4 vibrations [25]. Due to the presence of two network formers in the present glass system i.e. B_2O_3 and Bi_2O_3, some overlapping of Bi-O and B-O vibrations is expected [1]. Moreover, the presence of Bi in the neighborhood of BO_3 and BO_4 units would shift the various bands and that is perhaps the reason that many broad bands include some finer details in them observed in the present transmission spectra (Fig. 1). In the IR spectra of the present glass system it was found that the incorporation of ZnO does not show much effect on the structure of the glasses under study. It has been reported that the appearance of band at 840 cm^{-1} is the characteristic frequency of Zn-O tetrahedral bending vibrations [26]. The absence of this frequency band in the IR spectra of the glasses under study indicates that ZnO does not form tetrahedral [ZnO_4] units. The addition of ZnO in the present glass system produces a very small change in the IR bands that do not account for the major structural changes. Therefore, these results indicate that in the present glass network, ZnO enters as a glass former**.** In many glass systems in which ZnO is a major constituent the possibility of formation of ZnO_4 may be more [26]. S. Bale et al. have reported the formation of ZnO_4 units with increase in zinc oxide content [5].

3.2 Density and Molar Volume

The determined values of density (*d*) and molar volume (V_M) of the glass samples are presented in Table 2. It is found that (Fig. 2), the density decreases with increasing ZnO content. This is due to the fact that zinc oxide has relatively lower molar mass as compared to Bi_2O_3, therefore it is an expected result. The variation of molar volume with ZnO (mol %), also follows the similar trend (Fig. 2).

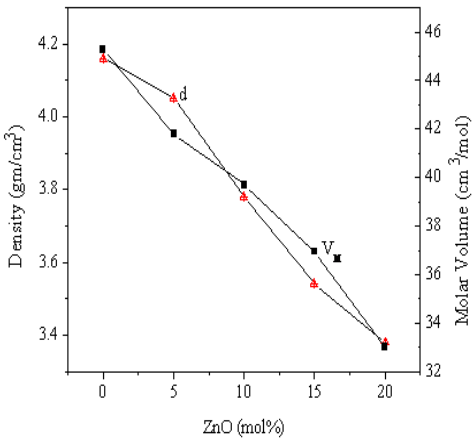

Fig. 2. Variation of density and the molar volume with ZnO (mol %).

3.3 Theoretical Optical Basicity

In the present glass system the theoretical optical basicity of the glasses has been calculated using the relation [27].

$$\Lambda_{th} = X(ZnO)\Lambda(ZnO) + X(Bi_2O_3)\Lambda(Bi_2O_3) + X(B_2O_3)\Lambda(B_2O_3) \quad (2)$$

where X(ZnO), X(Bi_2O_3) and X(B_2O_3) are the equivalent fraction of different oxides and Λ(ZnO), Λ(Bi_2O_3) and Λ(B_2O_3) are the optical basicity values assigned to the constituent oxides. The values of Λ(ZnO) = 0.82, Λ(Bi_2O_3) =1.19 and Λ(B_2O_3) = 0.425 have been taken from the literature [28]. The optical basicity represents the basicity of the glass in terms of electron density carried by oxygen. The calculated value of theoretical basicity ($\Lambda_{th)\ of}$ the glasses under study are listed in Table 2. It is found that the optical basicity decreases with increase in ZnO (or decrease in Bi_2O_3) content and can be explained by using the relation [29]

$$\Lambda_{th} = 1.67\left[1 - \frac{1}{\alpha_0^{2-}}\right] \quad (3)$$

where α_0^{2-} is the oxide ion polarazibilty. From this equation it can be observed that with increase in polarazibilty, basicity also increases. It is reported that Bi^{3+} ions possesses a lone pair of valance shell are highly polarizable due to their large ionic radii and small cation unit field strength. Further it is observed (Table 2) that the optical band gap in the glasses under study decreases with increase in optical basicity. Therefore with increase in the ZnO content the number of bridging oxygens increases, which cause increase in optical band gap and decrease in optical basicity. These observations are analogous with the reported results [5, 30].

3.4 UV-VIS measurements

The optical absorption spectra for all the samples recorded at room temperature, are shown in Fig. 3. The absorption coefficient *α(ν)* near the edge of each curve was determined from the relation [31]

$$\alpha(\nu) = \left(\frac{1}{t}\right) In\left(\frac{I_i}{I_t}\right) \quad (4)$$

where *t* is the thickness of the each sample, *ln* (I_i/I_t) is the absorbance factor, I_i and I_t are the intensities of incident and transmitted beams respectively. The absorption edge as observed in UV region (Fig. 3) can be divided into two regions depending on the value of the absorption coefficient (α(ν)) for many glassy and amorphous non metallic materials.

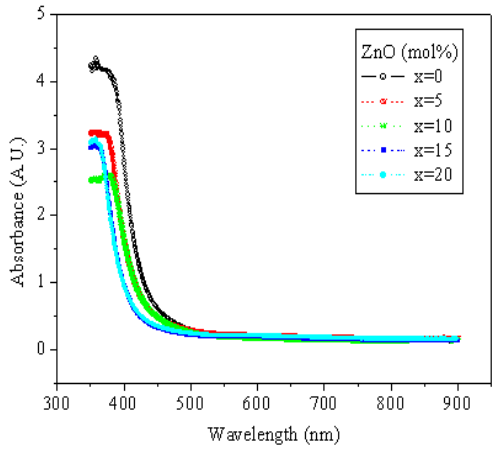

Fig. 3. Optical absorption as a function of wavelength for ZnO-Bi_2O_3-B_2O_3 glasses.

The first region usually known as Urbach tail [32], which is characterized with $\alpha\ (\nu) < 10^4$ cm^{-1} and depends exponentially on the photon energy as

$$\alpha(\nu) = C\, e^{\left(\frac{h\nu}{\Delta E}\right)} \qquad (5)$$

where C is constant and 'ΔE' is the width of band tail energy. At higher value of $\alpha\ (\nu)$ ($\geq 10^4$ cm^{-1}) optical absorption follows the general relation given by Davis and Mott [33]

$$\alpha h\nu = B(h\nu - E_g)^r \qquad (6)$$

where r is the index and can takes different values i.e. 2, 3, 1/2 and 1/3 depending on mechanism of inter band transitions, B is a constant called band tailing parameter, $h\nu$ is the incident photon energy and E_g is the optical band gap energy.

In various glassy systems Eq. (6) depicts a straight line for $r = 2$ which is related to the indirect allowed transitions [34-36]. The values of optical band gap energy (E_g) are determined from the linear region of the curve after extrapolating to meet $h\nu$ axis at $(\alpha h\nu)^{1/2} = 0$ and are presented in Table 2. It is found that for $r = 2$, the equation (6) gives the best fit of the data as shown in Fig 4 and this corresponds to the indirect allowed transition. The same absorbance data was used in Eq. (6) for $r = 3$ also, to calculate the value of optical band gap (Table 2). For $r = 3$, the curve fitting of Fig. 5 shows some deviation from linear fit for the given data.

The optical band gap for the two transitions lies between 2.64-2.81 eV and 2.60-2.73 eV for $r = 2$ and $r = 3$ respectively. On the basis of these results it is interpreted that the glass system under study behaves as indirect band gap semiconductors.

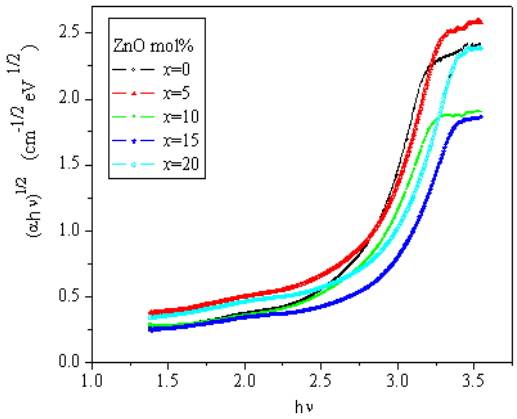

Fig. 4. Tauc's plot for studied glasses for r = 2.

The values of band tailing parameter *(B)* were obtained from linear portion of Fig. 4 & 5 (listed in Table 2). The values of 'B' obtained from Fig. 4 lies between 4.53-3.74 (cm eV)$^{-1/2}$ for $r = 2$ and 2.26-2.15 (cm$^{-1/3}$ eV$^{-2/3}$) for $r = 3$ (from Fig. 5). These observations are in well agreement with reported results [5, 30].

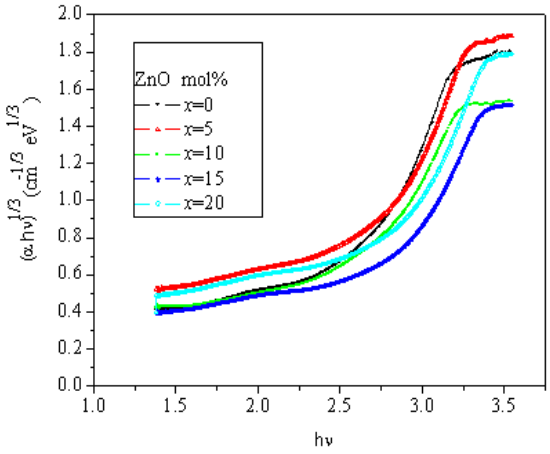

Fig. 5. Tauc's plot for studied glasses for r = 3.

It is observed that on addition of ZnO content, the position of the fundamental absorption edge and cutoff wave length shifted towards lower wavelength. The values of cutoff wavelengths are listed in Table 2. The shifting of cutoff wavelength towards lower wavelength can be attributed to an increase in number of bridging oxygen (BO) atoms [37], where it was suggested that the shift of the UV absorption edge corresponds to transition to the BOs which bind an excited electron less tightly than a non-bridging oxygen and leading to a increases in the value of E_g.

Table 2. Physical parameter of x ZnO (30- x) Bi_2O_3 -70 B_2O_3 glasses

Parameter	$x = 0$	$x = 5$	$x = 10$	$x = 15$	$x = 20$
Average molecular weight (gm/mol)	188.50	169.28	150.05	130.82	111.59
Density (gm/mol)	4.16	4.05	3.78	3.54	3.38
Molar volume (cm^3/mol)	45.26	41.79	39.69	36.95	33.01
Optical basicity	0.654	0.635	0.617	0.598	0.580
Cut-off wavelength	395	386	380	366	357
Optical band gap (eV) r =2	2.64	2.69	2.71	2.77	2.81
r =3	2.60	2.64	2.67	2.69	2.73
B (r = 2) / B (r = 3)	4.53 / 2.26	4.28 / 2.41	3.10 / 1.85	2.95 / 1.77	3.74 / 2.15
Urbach Energy ΔE (eV)	0.21	0.21	0.25	0.23	0.28

The Urbach energy was used to characterize the degree of disorderness in amorphous and crystalline solids. The materials which have large value of *ΔE* would have great tendency to convert weak bonds in to defects. The width of the band tails (*ΔE)* associated with valance and conduction bands was believed to be originated from electron transition between localized states, where the density of these localized states is exponentially dependent on energy [38]. Also it was suggested that this energy '*ΔE*' arises from the random potential fluctuations in the material into the band gap and normally shows exponential behavior. [39]. It has been reported that the experimental tail observed in various materials with different structures have the same physical origin and this can be attributed to the phonon-assisted indirect electronic transition [40-41]. The values of Urbach energy (*ΔE)* are calculated from the reciprocal of the slope of $ln\alpha$ versus $h\nu$ curve (Fig. 6). The values of *ΔE* for the present glass system lie between 0.21-0.28 eV.

The variation of band gap energy with ZnO (mol %) shows that there is slight increase in band gap energy on addition of ZnO concentration (Fig. 7). This can be explained in term of the minor structural changes that may be taking place in the glass system. As explained in IR spectra, the present glass system consists of randomly connected BO_3 and BO_4 structural units.

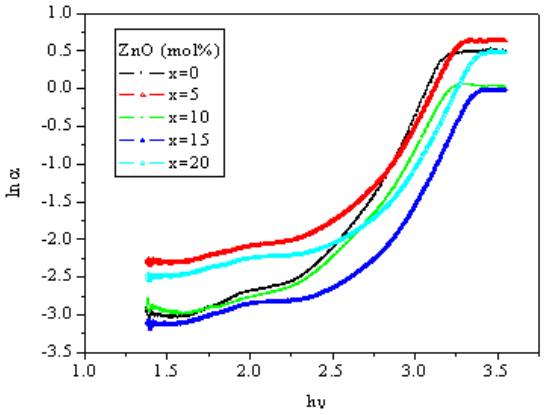

Fig. 6. Urbach plot for studied glasses.

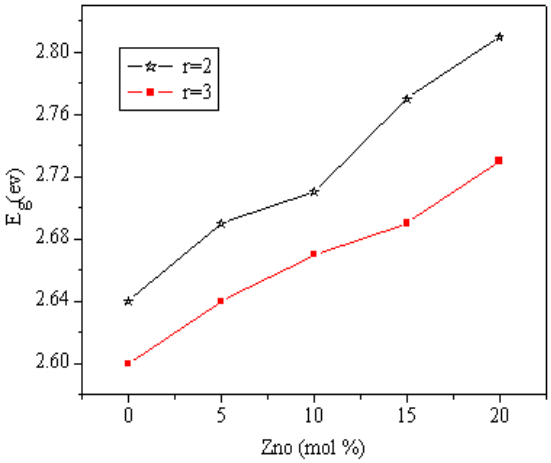

Fig. 7. Variation of band gap energy with ZnO (mol %) for r = 2 & r = 3.

On addition of ZnO, no major structural changes take place inspite of slight increase in intensity of these structural units. These results suggest that ZnO enters in the present glass system in the form of network former.

It is well established that borate glasses without any modifier are found to have fairly large band gap energy (E_g) and the formation of non-bridging oxygen is blocked. The increase in ZnO is related to the progressive decrease in the concentration of non-bridging oxygen, which in turn gives rise to a possible increase in bridging oxygen. As bridging oxygens are more excited than the NBOs, therefore with addition of ZnO concentration E_g increases slightly. Similar observations were reported by other authors [2].

4. Conclusions

The physical, structural and optical properties of the glass system with composition *x* ZnO (30-*x*)

Bi_2O_3 -70B_2O_3, have been studied and it is found that the structure of zinc doped bismuth borate glasses consists

of randomly connected BO_3 and BO_4 groups. No boroxol ring formation was observed in the structure of these glasses. The structure of present glass system is independent of change in composition. Very small change in the IR bands may occur that do not account for the major structural changes. The density and molar volume of all the glass samples decreases almost linearly with ZnO content. This is due to the relatively lower molar mass of the zinc oxide as compared to Bi_2O_3. The theoretical optical basicity of the present glass system is also found to decrease with increase in ZnO content. The values of different optical parameters i.e., cutoff wavelength, optical band gap, Urbach energy and band tailing parameters have been reported. It is observed that optical band gap increases slightly with increase in ZnO content and is due to increase in BOs. From the theoretical fitting of the experimental absorption coefficients for all the glass samples, it is concluded that the present glass system behaves as an indirect band gap semiconductor.

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