Physical, Optical and FT-IR studies of Bismuth-Boro-tellurite Glasses containing BaO as modifier

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Abstract. The addition of glass modifier changes the properties of host glass network. The role of Ba^{2+} as glass modifier has been investigated using physical, UV-Visible and FT-IR studies on $xBaO-(30-x)TeO_2-35Bi_2O_3-35B_2O_3$ (where x =5,10,15,20 and 25 mole%) glasses. X-ray diffractograms of crushed glass samples were recorded at room temperature. The absence of sharp peaks in X-ray diffractograms confirms the amorphous nature of the glass samples. Density (ρ) of glass samples were estimated using Archimedes principle. Physical properties such as molar volume (V_M), oxygen packing density (OPD), optical basicity etc. were determined. The optical absorption spectra were recorded in the wave length range of 200–1000 nm at room temperature. From the optical absorption spectra indirect allowed optical band gap, Urbach energy, refractive index (n), dielectric constant (ε), reflection loss (R), molar refractivity (R_m) and metallization criteria values were evaluated. The refractive index values were decreasing while optical band gap values were increasing with increasing concentration of BaO. IR spectra were recorded in the spectral range 400 - 4000 cm^{-1}.

1. Introduction

Borate glasses containing heavy metal oxides (HMO) such as Bismuth oxide, tellurium oxide and Barium oxide have been attracting researchers to synthesis and to study structural and physical properties due to their low melting temperature, widespread glass formation range, high density, high physical and chemical stability, and nonlinear optical properties. Generally heavy metal oxides do not form glasses on their own compare to the conventional glass forming oxides due to their low field strength. In HMO containing glasses, bismuth oxide glasses have shown wide range of applications in the area of glass ceramics, reflecting windows, γ-ray absorbers, thermal and mechanical sensors, optoelectronic devices and scintillation detectors [1, 2]. High polarizable Bi^{3+} ions and asymmetry of their oxygen coordination polyhedra can assist the non-crystallization of melts [3]. On the other hand covalently bonded B_2O_3 is a very good glass former with interesting physical and chemical properties. Basically B_2O_3 glasses are insulating in nature and the B^{3+} ion in borate crystals and glasses usually coordinates with either three or four oxygen atoms forming $[BO_3]$ or $[BO_4]$ structural units. Borate glass is well-known and best choice as optical material for its high transparency, low melting point and high thermal stability [4]. A.M. Abdelghany et.al [5] have prepared and characterized the borate glasses containing SrO substituting both CaO and NaO for their bioactivity or bone bonding ability. They have confirmed the formation of nodular texture of calcium phosphate (hydroxyapatite) and transform to micro-grains with increase of SrO. Tellurite glasses have paid extensive attention as

promising candidates for optical fibers, ultra-fast optical switching devices and high non-linear optical devices because of their low-phonon energy, high refractive index, high polarisability of the non-bonding electron lone pair of Te^{4+} ions and low crystallization ability [6-8]. However, it must be noted that pure TeO_2 does not possesses its own glassy network, under normal melting conditions. Hence addition of network modifiers or glass forming oxides is needed to form tellurite-based glasses [9]. Structural and physical properties of glasses can be altered by the addition of a network modifier such as alkali or alkaline earth oxides and sometimes both alkali and alkaline earth oxide combinations. These network modifier oxides generate non-bridging oxygens (NBO) in the glass network by breaking the bridging oxygen bonding.

2. Experimental

Bismuth-Boro-tellurate glasses containing BaO as network modifier were prepared with the composition $xBaO-(30-x)TeO_2-35Bi_2O_3-35B_2O_3$ (with the glass codes as, x=5; BTBiB1, x=10;BTBiB2, x=15; BTBiB3; x=20; BTBiB4 and x=25;BTBiB5) by melt quenching technique. Analytic reagent grade chemicals of highest purity BaO, TeO2, Bi_2O_3 and B_2O_3 were used as starting materials which are thoroughly mixed in an agate mortar for 20 min. The batch materials were taken in porcelain crucibles and placed in an electrically heated muffle furnace kept around 1200 to1280 K for about one hour, until a bubble free, clear and homogeneous melt was obtained. The homogeneous melt was then quickly poured onto a stainless steel plate and pressed with another stainless steel plate, both were maintained at 500 K. The obtained glass samples were kept at 500K for 5h to relieve the thermal strains in the glass. Density measurements were carried out at room temperature using the Archimedes method with xylene as the immersion liquid. The X-ray diffractograms were recorded at room temperature using the Philips X-ray diffractometer with copper K_α tube target and nickel filter operated at 40 kV, 30 mA. The optical absorption spectra of all the glass samples were recorded at room temperature on a UV–VIS spectrophotometer (model JASCO V 570) in the wavelength range 200–1000 nm. The FTIR spectra were recorded at room temperature by using a Perkin Elmer Frontier FTIR in the wave number range (400–4000 cm^{-1}).

3. Results and discussion

3.1 X-ray diffraction
XRD patterns of $xBaO-(30-x)TeO_2-35Bi_2O_3-35B_2O_3$ glasses are shown in figure 1The absence of characteristic peaks indicated that all the glass samples are amorphous in nature.

3.2. Physical properties
The Densities of all of the glass samples were estimated using the formula

$$\rho = \left(\frac{w_{air}}{w_{air} - w_{xylene}} \times 0.865 \right) \qquad (1)$$

where W_{air} and W_{xylene} are the weights of the glass sample in air and xylene, respectively, and 0.865 g/cm^3 is the density of the xylene at room temperature. The molar volume of the glass composition was calculated using the formula

$$V_m = \frac{\sum x_i M_i}{\rho} \qquad (2)$$

where x_i is the molar fraction, M_i is the molecular weight of the ith component of the glass and ρ is the density of the glass. The Molar volume relates directly to the spatial distribution of the oxygen in the glass network. The Density and molar volume values are given in table 1. From the table 1it was found

that the density increases from 5.73 to 6.12 g/cm3 with the increase of BaO content. This could be due to the higher density of BaO (ρ = 5.72 g/cm^3) than that of TeO_2 (ρ = 5.67 g/cm^3). Figure 2 shows the variation of Density (ρ) and Molar volume (V_m) as a function of BaO content. From the figure 2 it was found that the density and molar volume shows opposite behavior [10, 11].

Oxygen packing densities (OPD) of glass samples were calculated using the expression given below and the values obtained were tabulated in table 1.

$$\text{OPD} = \frac{\rho}{M} \times O_n \qquad (3)$$

Here O_n is total number of oxygen atoms per chemical formula. From the table 1 it was observed that the OPD values were found to decrease from 59.28 to56.86 mol/l. This decrease in OPD values may be attributed to the increase in molecular weight of the glass.
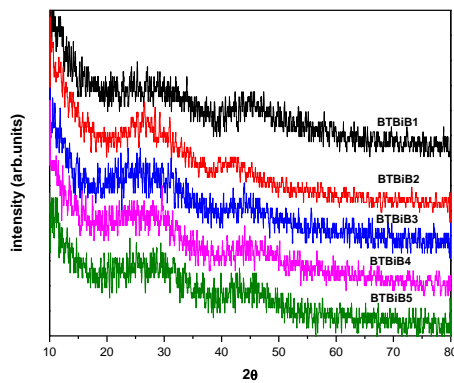

Figure 1. XRD patterns of xBaO-(30-x)TeO$_2$-35B$_2$O$_3$-35Bi$_2$O$_3$ glasses
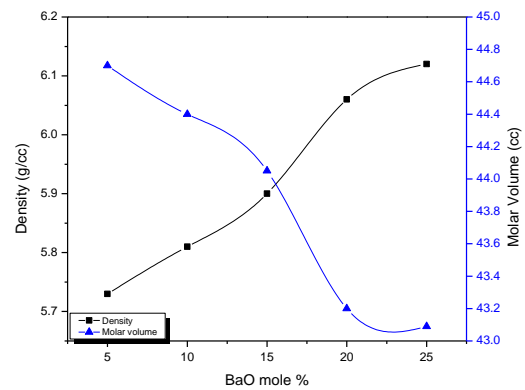

Figure 2. Variation of density and molar volume with BaO content

3.3. Optical Band Gap and Urbach Energy

The optical absorption spectra of the glass samples are shown in figure 3. The power law region is clearly observed in absorption spectra and fundamental absorption edges are not sharp. This is the characteristic feature of amorphous glass samples. From table 1, it was observed that that the fundamental absorption edge shifts to higher wavelength side with an increase of BaO content. Absorption coefficient near the edge of each curve was determined by using the relation

$$\alpha(\upsilon) = (1/t)\log(I_0/I) \qquad (4)$$

where log (I_0/I) is the absorbance, I_0 and I are the intensities of incident and transmitted light respectively. According to Davis and Mott[12], the absorption co-efficient as a function of photon energy is given by the relation

$$\alpha(\upsilon) = B(h\upsilon - E_{opt})^n / h\upsilon \qquad (5)$$

where E_{opt} is the optical band gap energy, B is the constant related to the extension of the Urbach tail and 'n' take the values of 2, 1/2, 3, and 3/2 depending on the nature of electronic transitions responsible for absorption. For amorphous materials, indirect transitions are valid according to Tauc's relation [13]. The values of E_{opt} were obtained by extrapolating to $(\alpha h\upsilon)^{1/2}=0$ for indirect transitions. [$(\alpha h\upsilon)^{1/2}$ Vs hυ are plotted in (figure 4)], to find optical band gap energies. E_{opt} values were found to increase with an increase of BaO content. In glass and amorphous materials there exist band tailing in

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the forbidden energy band gap. The extent of this band tailing is a measure of the disorder in the material and can be estimated by using the Urbach equation [14, 15] given by,

$$\alpha(\upsilon) = C \exp(h\upsilon / \Delta E) \tag{6}$$

where, C is a constant and ΔE is the width of band tail also known as Urbach energy. The lack of crystalline long range order or the presence of defects in the amorphous materials is associated with a tailing of density of states [16]. Urbach energies (ΔE) are calculated by taking the reciprocals of slopes of linear portion in lower photon energy regions of these curves and are shown in figure 5 Urbach energy (ΔE) provides a measure of disorder in the amorphous and crystalline solids. Smaller is the value of Urbach energy, greater is the structural stability of the glass system. In the present glass system Urbach energies are in the range of 0.19eV to 0.27eV. The smaller values of Urbach energies show high stability of the prepared glasses. Refractive index of the $xBaO-(30-x)TeO_2-35Bi_2O_3$ - $35B_2O_3$ glasses is decreasing with increase of BaO content. The polarizability of barium ion is larger than the other cations [17]. High refractive index is attributed to the higher polarization of BaO. According to the Herzfeld theory [18] of metallization the valence electrons, which before have been quasi-elastically bound to their atoms, are now set free via mutual polarization in the condensed state and the solid material becomes a metallic conductor. In this regard the following criterion appears to be a necessary condition to predict the metallic or non-metallic nature of solids i.e $R_m /V_m > 1$ (for metals) and $R_m/V_m < 1$ (for nonmetals). The present reported values of R_m /V_m are in the range of 0.3624 to 0.3745. As BaO concentration is increasing in glass network an increased tendency to metallization was noticed. The smaller value of M (metallization) of these glasses indicated that the width of both conduction band and valence band increases resulting in narrow band gap.
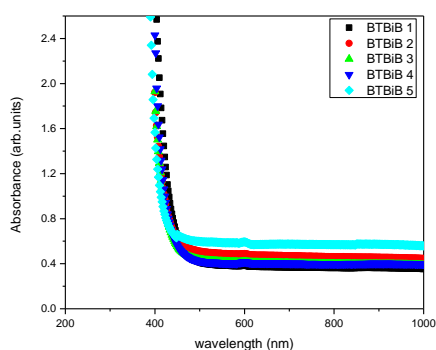

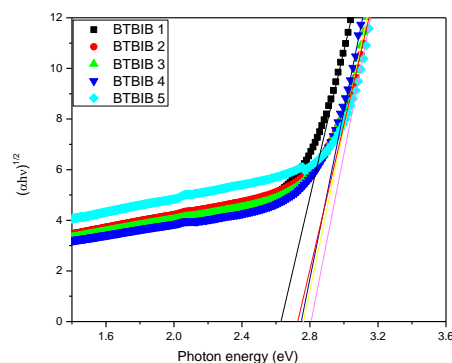**Figure 3.** Optical absorbance spectra of $xBaO-(30-x)TeO_2-35Bi_2O_3-35B_2O_3$

Figure 4. Plot of $(\alpha h\upsilon)^{1/2}$ as a function hυ of for the present glasses

3.4. Optical Basicity

In the development of the Lewis acid-base principles Duffy and Ingram have made great contribution by introducing the "optical basicity" concept. This concept is very useful for quantitative evaluation of the acid-basic properties of glasses, alloys, slags, molten salts, etc. The degree of polarization plays an important role to transfer electron density from oxygen to surrounding cations. High polarizable cations such as P^{5+}, Si^{4+}, B^{3+} ions decreases the donor nature of oxygen by influencing the electron cloud of oxygen. According to the Duffy [19], the theoretical optical basicity (Λ_{th}), for the present glasses is calculated using the following formula

$$\Lambda_{th} = X_{BaO}\Lambda_{BaO} + X_{TeO}{}^2\Lambda_{Teo}{}^2 + X_{Bi2O3}\Lambda_{Bi2O3} + X_{B2O3}\Lambda_{B2O3} \tag{7}$$

Where X_{BaO}, X_{TeO2}, X_{Bi2O3} and X_{B2O3} are the contents of individual oxides in mole%. Λ_{BaO}, Λ_{Teo2}, Λ_{Bi2O3} and Λ_{B2O3} are the theoretical optical basicity values corsponding to the each oxides have been taken from the literature . The theoretical optical basicity Λ_{th} values calculated using above equation for the brium bismuth boro-tellurate glasses are presented in table 1. It is found that the theoretical optical basicity decreases slightly with increasing BaO content.
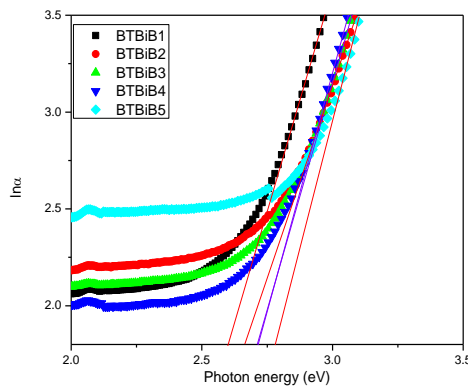

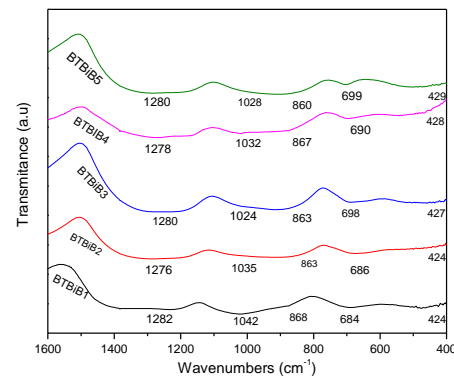**Figure 5**. Urbach energy plot of xBaO-(30-x)TeO$_2$-35Bi$_2$O$_3$-35B$_2$O$_3$glasses

Figure 6. FTIR spectra of xBaO-(30-x)TeO$_2$-35Bi$_2$O$_3$-35B$_2$O$_3$glasses

Table 1. Physical and optical parameters of xBaO-(30-x)TeO$_2$-35Bi$_2$O$_3$ -35B$_2$O$_3$ glass system.

Physical & optical Parameters	Glass codes				
	BTBiB-1	**BTBiB-2**	**BTBiB-3**	**BTBiB-4**	**BTBiB-5**
Density (ρ) (g/cc)	5.73	5.81	5.90	6.06	6.12
Molar volume (V_m) (cc/mol)	44.70	44.40	44.05	43.20	43.09
Oxygen packing density (mol/l)	59.28	58.56	57.89	57.87	56.86
Cut-off wavelength (nm)	441	442	445	451	458
Indirect optical band gap (eV)	2.63	2.72	2.75	2.75	2.81
Urbach energy E (eV)	0.20	0.27	0.20	0.19	0.20
Refractive index (n)	2.51	2.48	2.47	2.47	2.45
Dielectric constant (ε)	6.28	6.13	6.08	6.09	6.01
Reflection loss (R)	0.1844	0.1803	0.1790	0.1792	0.1769
Molar refractivity (R_m) (cm$^{-3)}$	28.50	28.01	27.70	27.19	26.95
Metallization (M)	0.3624	0.3690	0.3711	0.3707	0.3745
Theoretical optical basicity (Λ_{th})	0.1602	0.1587	0.1571	0.1556	0.1540

3.5 IR spectra

The infrared transmittance spectra of the glasses with composition xBaO-(30-x)TeO$_2$-35Bi$_2$O$_3$ -35B$_2$O$_3$ are shown in figure 6 From the figure it was observed that the absorption bands were found around 428 cm^{-1}, 690 cm^{-1}, 863 cm^{-1}, 1030 cm^{-1},and 1280 cm^{-1} for all the glass samples. The small and feeble absorption band found around 428 cm^{-1} is assigned to the Bi-O bond in BiO$_6$ polyhedra [10]. The prominent band found around 690 cm^{-1} is due to TeO$_3$ (tp) trigonal pyramidal units [20]. Another prominent band observed around 863 cm^{-1} is attributed to the vibration of tri, penta and diborate groups of BO$_4$ tetrahedra [21]. A shallow broad absorption band found around 1030 cm^{-1} is attributed to B-O stretching vibrations of tetra hedral BO$_4$ units [22]. Another shallow broad absorption band

observed in the region 1280 cm^{-1} is attributed to the asymmetric stretching vibrations of B-O in trigonal BO$_3$ units [22].

4. Conclusions

The density values increases from 5.73 to 6.12 g/cm3 with the increase of BaO content. The density and molar volume shows opposite behavior. Refractive index of the present glasses is decreasing with increase of BaO content. High refractive index values are due to the higher polarization of BaO. From the infrared transmittance spectra of the glasses, it is observed that the absorption bands around 428 cm^{-1} is assigned to the Bi-O bond in BiO$_6$ polyhedra, 690 cm^{-1} is ^{1} is due to TeO$_3$ (tp), 863 cm^{-1} is attributed to the vibration of tri, penta and diborate groups of BO$_4$ tetrahedra, 1030 cm^{-1} is attributed to B-O stretching vibrations of tetra hedral BO$_4$ units and 1280 cm^{-1} band is due to asymmetric stretching vibrations of B-O in trigonal BO$_3$ units.

Acknowledgements

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