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Synthesis and Characterization of Lithium Borate Glasses Containing Bismuth

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Abstract: *A lithium bismuth borate glass system is prepared by the conventional melt quenching technique. The Powder X-Ray diffraction analysis of the prepared samples confirms the amorphous nature of the samples. The density and molar volume studies report the change of structure with the increase of bismuth content. The FTIR analysis of the samples revealed that the network structure of the prepared samples is mainly based on the* BO_3 *and* BO_4 *units. From the UV-Vis spectra it has been observed that the bandgap decreases with an increase in* Bi_2O_3 *content. The refractive index also decreases with an increase in wavelength. Optical basicity increases with an increase in* Bi_2O_3 *content.*

Keywords: *Borate Glass, X Ray Diffraction, FTIR Spectroscopy, UV/Visible Spectroscopy*

1. INTRODUCTION

Borate is one of the most important glass former and has been incorporated in many kinds of glass systems to achieve chemical and physical properties. In borate glasses, 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 which, B^{3+} ions are triangularly coordinated by oxygen and corner bonded in a random configuration [1]. Borate glasses containing Li^+ ions are considered to be the potential candidates for electrolytes of thin film batteries as they exhibit isotropic ion conductivity and stability at high voltage [2]. High valence cations such as Bi^{3+} are commonly used as intermediate species [3]. It is well reported in the literature that Bi_2O_3 can act as a glass former when it has BiO_4 structural unit. On the other hand, it can also act as glass modifier when bismuth connected with octahedrally. The structure of glasses with composition $x\ B_2O_3 – (1-x)\ M_2O$, (M= Li, Na, K, Rb, Cs) consists of B – O network, built up from planner three- coordinated and tetrahedral four coordinated B atoms [4]. Pure vitreous B_2O_3 contains only three coordinated boron atoms $[BO_3]^{3-}$ and if an alkali oxide (M_2O) is added some of these units transform into four coordinated tetrahedral (BO_4) [5]. The addition of alkali metals or alkaline earth metals leading to create non-bridging oxygen’s. The creation of oxygen (NBO) changes the chemical and physical properties of glasses such as thermal expansion coefficient (TEC), electrical conductivity etc. Basically, modification in glass matrix due to addition of modifier, depending on their connectivity changed these properties.

In this work, an attempt has been made for the preparation and characterization of bismuth-borate glasses with the addition of lithium oxide as modifier. The structural investigation of the glasses has been studied with the help of molar volume measurements and Fourier Transform-Infrared spectroscopy (FTIR). The optical band gap of prepared glasses is calculated using UV-Visible data.

Table 1. *Nominal Composition*

Sample	Bi_2O_3 (%)	Li_2O (%)	B_2O_3 (%)
Bi_1	1.5	18.5	80
Bi_2	3	17	80
Bi_3	4.5	15.5	80
Bi_4	6	14	80
Bi_5	7.5	12.5	80

2. EXPERIMENTAL DETAILS

The glasses having the general chemical formula 80% B_2O_3-(20-x) % Li_2O- x% Bi_2O_3 were prepared by melt quenching techniques. The required stoichiometric quantity of Li_2CO_3, B_2O_3 and Bi_2O_3 were taken and mixed powders were melted in silica crucibles at 1150 C. The melts were kept at 1150 C for 2 hours to get homogenized melt by stirring time to time. The melt was poured into preheated graphite rectangular moulds. Furthermore, the mould was kept at 400 C for 12 hours to remove the thermal stresses from the glasses. In order to check the glassy nature of the samples, X-ray diffraction (XRD) measurements were done using XPERT PRO Pan Analytical XRD diffractometer. The patterns obtained from copper target using an in built Ni filter were taken at a scanning rate of 2^0 min^{-1} and 2θ varied from 10^0-60^0 with Cu K_α (λ= 1.5418 A^0) radiation. The densities of as prepared glasses were measured in Benzene media using Archimedes principle. The accuracy of the balance was ±0.001g. The molar volume of the glasses were calculated using following equations:

$$V_m = \frac{M}{d}$$

where M is the molar mass of the glasses and d is their density.

FT-IR were recorded in 400-400 cm^{-1} using Perkin Elmer spectrometer. The FTIR samples were prepared taking glass powder and KBr. After mixing the pellets were made using pressure.

3. RESULTS AND DISCUSSIONS

The patterns confirm the amorphous nature of the glass samples. The XRD patterns with different weight percent of Bi_2O_3 are shown in Fig. 1.

3.1. Physical Parameters

Table 2. *Density & Molar Volume*

Sample.	Bi_1	Bi_2	Bi_3	Bi_4	Bi_5
Bi_2O_3%	1.5	3	4.5	6	7.5
Density	2.37	2.57	2.66	2.72	3.17
Mol. Vol.	32.2	28.4	27.9	27.8	24.3

The density measurement is considered to be a very important tool to detect the structural changes in the glass network. The density is supposed to change abruptly when the structure of the glass is slightly changed. The density is additive property and structural insensitive. However, it also depends on the coordination number, non-bridging oxygens and presence of the cross-linking in structural units. Basically, all these above mentioned parameters influence the packing of the local structural units and ultimately change the volume of the bulk glass samples. The density of present samples appears to increase gradually from 2.37 to 3.17gm cm^{-3} with the increase of Bi_2O_3 content which further increases at the expense of lithium oxide. This increase in the density can be due to replacement of low density lithium (0.53 g/cm^3) by high density bismuth element (9.78 g/cm^3) [6]. Also non-bridging oxygen decreases in the glass network on increasing the Bi_2O_3 content, which tend to consolidate their structure, maintaining homogeneity of the glasses and thus increasing density [7]. Molar volume indicates the spatial distribution of the oxygen in the glass network. The gradual decrease in the molar volume can be attributed to closing up of glass structure.

3.2. XRD

The powder X- ray diffraction analysis of the samples in consideration is shown in Fig. 1. This figure exhibits no detectable peaks which confirmed the proper preparation of glass samples. This confirms their amorphous nature as well as long range structural disorder of glasses.

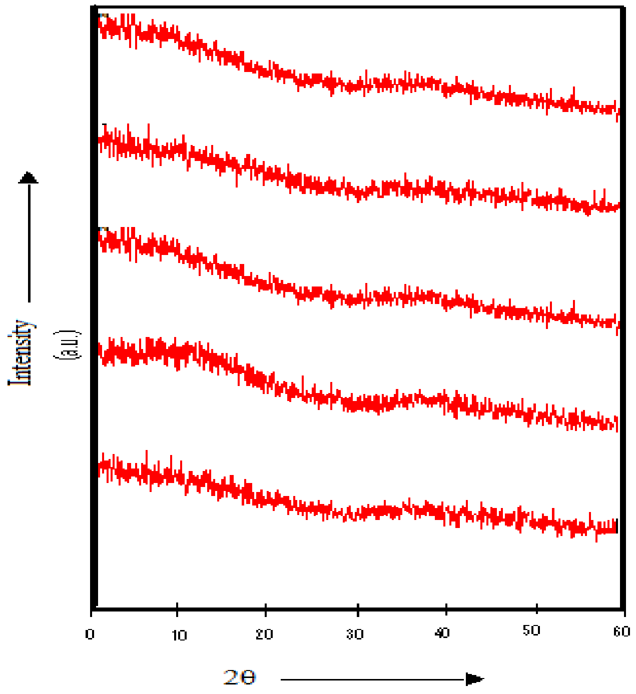

Figure 1. *XRD spectrum of glass sample*

3.3. Fourier Transforms Infrared Analysis

For structural analysis of oxide glasses the following information is required [8]:

(i) Type of the bridging bonds of oxygen which link the coordination polyhedra of framework and the composition of chemical inhomogeneities in the structure of glass

(ii) The coordination number of the compound with respect to oxygen, especially of network formers

(iii) The change in oxygen bonds of the framework, induced by the cation modifiers which combine with the oxygen bonds.

Boron has the smallest mass as compared to the other network forming elements, and thus the main vibrational modes associated with the glass network appear well above 500 cm^{-1} (in the mid–infrared region) [10]. Fig. 2 shows IR spectra of as prepared glasses. A weak band appears around 415 cm^{-1} showing the presence of Li-O bond in all the glass samples [11]. Another band appears around 450 cm^{-1} which can be assigned to vibration of Li^{+} [12]. The band observed around 500 cm^{-1} can be attributed to B-O-B bonds bending vibrations. The band around 700 cm^{-1} can be attributed to some deformation modes of the glass network structure [13-14]. Another band near 770 cm^{-1} can be associated with the B-O-B bending vibrations of BO_3 and BO_4 structural units [15].The band at 925 cm^{-1} is observed. This band is associated with diborate [16]. The band appearing at 1025 cm^{-1} may characterize vibrations of diborate bridging to pentaborate groups, and to the asymmetric and stretching vibrations of BO_4 groups [15]. The band that arises around 1100 cm^{-1} can be due to stretching of the BO_4 structural units [15-17].

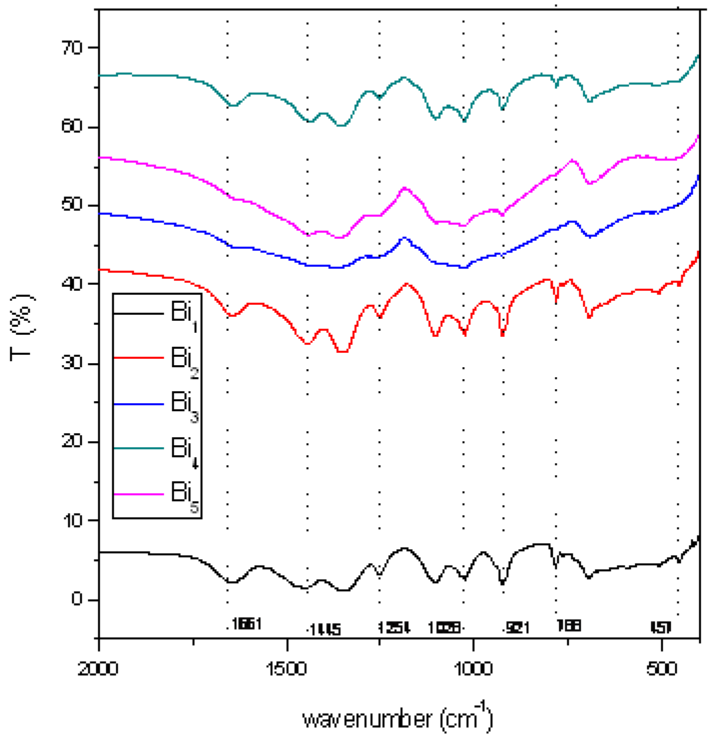

Figure 2. *IR spectra of glasses*

Another band which appeared at 1252 cm^{-1} can be assigned to B-O stretching vibrations mainly the linkages between oxygen and different groups as well as B-O bridging between boroxol rings and trigonal BO_3 [15-16]. At 1356 cm^{-1}, a band emerges and it is due to asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units and various borate groups [18-19]. Another band is observed around 1430 cm^{-1} can be due to stretching vibrations of borate triangles with NBO. B-O bond stretching vibrations of borate units in which boron atoms are coordinated with three oxygen atoms leads to formation of a band around 1600 cm^{-1} . The bands that appeared after that are attributed to presence of water groups and O-H bond vibrations [20]. As Bi_2O_3 concentrations increases the band shift towards lower wave numbers. It is clearly manifestation that the addition of higher atomic number cations shifts bands towards lower number due to strong bonding.

3.4. UV-Vis Spectroscopy

According to Tauc, the variation of absorption coefficient with photon energy shows three regions in many amorphous materials. The first region corresponds to “Tauc region” which is for high absorption. The second region known as Urbach region is exponential region due to randomness and structural disorientations of the system. The third region is the weak absorption tail produced from defects and impurities in UV-Spectra [21]. The fundamental optical band gap of the glasses has been computed based on their UV-Vis absorption spectra, for understanding their optically induced transitions. There are two types of optical transition which can occur at the fundamental absorption edge of crystalline and non-crystalline materials. In direct and indirect transitions, electromagnetic waves interact with the electrons in the valence band, which are raised across the fundamental band gap to the conduction band. For photon energies hυ just above the fundamental edge, the absorption α follows the standard relation,

$$\alpha = A\frac{(h\nu - E_g)^{1/2}}{h\nu} \tag{1}$$

Where A is a constant and E_g is defined as the energy band gap. The value of E_g for indirect transition is obtained by extrapolation of $(\alpha h\upsilon)^{1/2}$ versus hυ plot to $\alpha^{1/2} = 0$ [22]. Figs. 3 and 4 show the plots for direct band gap and indirect band gap for the prepared samples and their values are listed in Table 3.

Table 3. *Band gap Energy & Cut off wavelength*

Sample.	**Bi_1**	**Bi_2**	**Bi_3**	**Bi_4**	**Bi_5**
Bi_2O_3%	1.5	3	4.5	6	7.5
Direct bandgap (eV)	3.549	3.367	3.076	2.999	2.974
Indirect bandgap (eV)	3.246	3.105	2.908	2.865	2.817
Cut-off wavelength (nm)	429	427	423	414	401

It is noticed that E_{opt} decreases with increasing Bi_2O_3 content. Decrease in band gap is also reported to be due to the formation of BO_4 instead of BO_3 units which is also supported by FTIR spectra. There must be some change in bonds which is reflected by lowering of band gap values. Moreover, alkali metals oxide has higher ionic and metallic bond characteristics than Bi_2O_3. Therefore, it is also related to the progressive decrease in the metallic bond characteristics [23]. The noticed change may also arise from the photon- lattice interaction [24]. The decrease in band gap is also due to decrease of NBO and also the formation of bridging oxygen that changes the absorption characteristics [25]. This also is in accord with our results for density i.e. the formation of BO_4 units at the expense of BO_3 units with the increase of Bi_2O_3 content.

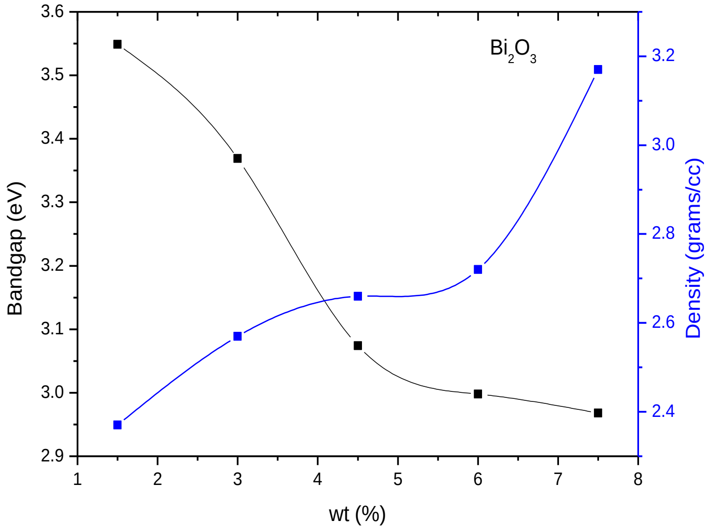

Figure 3. *Band gap and density versus Aluminium content*

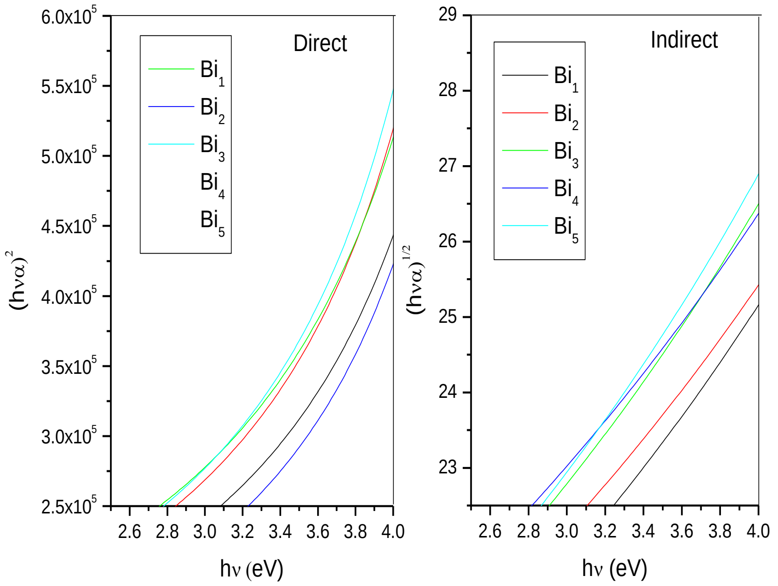

Figure 4. *Direct and indirect energy band gaps of Bismuth based lithium borate glasses*

3.5. Determination of Refractive Indexes

According to the theory of reflectivity of light the refractive index, *n* [26], as a function of the transmission measurements is determined by the quadratic equation:

$$n = \left[1 + (1 - T^2)^{1/2}\right]/T \qquad (2)$$

It is clear from the figure that the refractive index decreases with an increase in the wavelength of the incident photon. The variation of refractive index can be explained as:

- It varies directly in accordance with the density.
- Co-ordination number also affects the refractive index. A strong modifier creates more NBOs which in turn increase the average co-ordination number of glasses.
- Increase in NBOs lead to creation of more ionic bonds at the cost of covalent bond. This further gives larger polarizability, hence increasing the refractive index values.

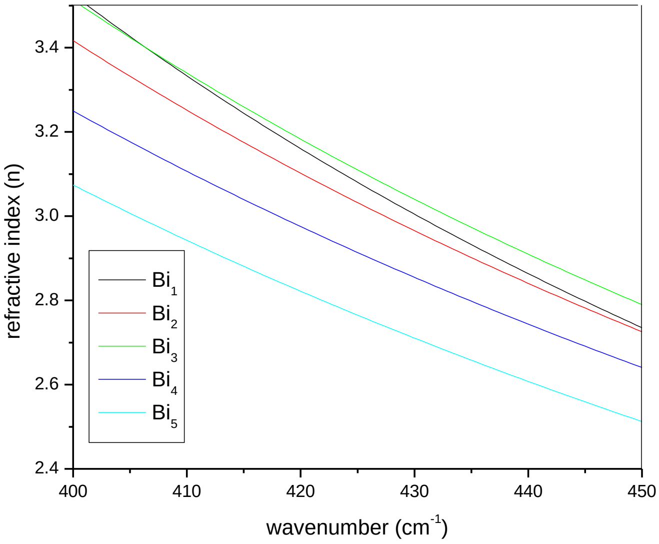

Figure 5. *Variation of refractive index with wavelength at different Bi_2O_3 content*

3.6. Theoretical Optical Basicity (Λth)

Duffy and Ingram [27-28] calculated the theoretical optical basicity of multiple component glass system on the basis of the following equation:

$\Lambda_{th}=X_1\Lambda_1+X_2\Lambda_2+\ldots\ldots\ldots+X_n\Lambda_n$

Where X_1, X_2,….X_n are equivalent fractions based on the amount of oxygen each oxide contributes to the overall glass stochiometry and Λ_1, Λ_2,…. Λ_n are the basicities assigned to the individual oxides. The above equation expresses the average bulk basicity from all oxide species such as bridging and non-bridging and in the present form it could not estimate the coordination number changes of the cations.

Table 4. *Optical basicity versus Bi_2O_3 content*

Sample	X (Bi_2O_3 %)	Λ(Bi_2O_3)	Λ(Li_2O)	Λ(B_2O_3)	Λ_{th}
Bi_1	1.5	1.19	1.00	0.42	0.525
Bi_2	3.0	1.19	1.00	0.42	0.546
Bi_3	4.5	1.19	1.00	0.42	0.549
Bi_4	6.0	1.19	1.00	0.42	0.551
Bi_5	7.5	1.19	1.00	0.42	0.554

4. DISCUSSION

Density and molar volume are determined by structure and bonding within a glass and are therefore strongly affected by changes in glass composition. The relatively sharper FTIR peaks of glass samples can be due to strong vibrational frequency of the various groups present in the glass, from the table it can be seen that the band gap decreases. This is due to the breakage of bond and non-bonding oxygen appeared in the glass. Shift of energy gap to lower energies can be due to the formation of NBO. The change in optical band gap is attributed to the structural changes due to occupancy of different cites by cations. The refractive index of the glass samples increases with increase in the wavelength. The values of theoretical optical basicity increase with increase in the Bi_2O_3 content.

5. CONCLUSIONS

The series of Bismuth containing lithium borate glasses have been prepared by melt quenching technique. The sharp peaks which are characteristic of crystal structure are absent and presence of broad humps confirms amorphous nature of glasses. Unlike in crystals the probability of finding atoms is neither regularly spaced non-uniform in glasses. Because of variations in the inter atomic distances, the peaks get broader. The molar volumes from density data provide further insight into glass structure. The addition of Bi_2O_3 to network increases the density and hence reduces molar volume, implying the shrinkage of network. This change is observed due to the decrease in NBOs. The decrease in band gap is due to decrease in NBOs and also the formation of bridging oxygen that changes the absorption characteristics. This is again in accord with the density i.e. formation of BO_4 units at the expense of BO_3 units. The cutoff wavelength shifts towards lower side with an increase in Bi_2O_3 content. Increasing values of optical basicity is attributed to the increase in NBOs in the glass systems.

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