Study of ZnO modified Lithium Borate Bismuth glasses

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Abstract. Quaternary glasses with composition (40-x) Li2O:30B2O3:30Bi2O3: x ZnO have been prepared with x varying from 0 to 6 mol%. The structural investigation of these glasses has been carried out by infrared (IR) absorption spectra. Addition of ZnO in the glass is favorable for the creation of BiO6 units on account of the substitution of B-O bond by Bi-O bond. Changes in density and molar volume in glasses have been studied. Molar volume reduces which is ascribed to the decrease in boron-boron spacing, d＜B-B＞. Increment in cut off wave length and decrement in optical band gap energy is observed in Optical absorption spectra with increase in ZnO on a count of rise in Non-Bridging Oxygens Electronic polarizability and optical basicity was also studied.

Keywords. Bismuthate glass; IR spectra, Tauc’s plot; Optical band gap

1 Introduction

Transition metal ions have been the center of attraction since many years due of their possible applications in electro-optic devices, uses in the fields of optical communications, X- and γ-ray absorbers. Borate glasses with alkaline earth oxides containing modifiers like ZnO, TeO2, Bi2O3, and BaO as glass modifiers are optimistic candidates in these fields. [1–7]. IR and UV–visible spectroscopy measurements are some of the profound methods used for the depiction of local order of structure building units in glasses together with the coordination and valence states of transition metal ions. These collective spectral investigations have been useful to examine the valence states of transition metal ions in alkali borate [8,9] Heavy metal oxide glasses have some benefits against semiconductor containing glasses and organic materials. This is due to their fast response times, small two-photon absorption and negligible linear loss. Mechanically durability and suitability for waveguide fabrication systems are the special features of these glasses. Applications of glasses and glass ceramics doped with zinc oxide have grabbed attention mainly in the field of barrier ribs in plasma display panels, dielectric layers, varistors and transparent dielectrics. [10, 11]

ZnO is a semiconductor with a broad band gap. It has gained more research interest in past years. Some current developments lead to more studies for the applications like electronic and optical devices. Additionally, ZnO may be transformed to multipurpose material which can end up in broad applications. It
can be attained through proper doping method such as transparent-conducting electrodes by doping with fluorine and aluminum, piezoelectric layers [12].

In this paper the author mainly emphasizes on preparation and characterization of physical, structural and optical properties of prepared glasses.

2. Experimental

![Figure 1. Optically polished glasses.](image)

Synthesis of all the glass samples having composition (40-x) Li2O:30B2O3:30Bi2O3: xZnO with x = 0, 2, 4 and 6 mol% has been done in platinum crucible by melt quenching technique. Analytical reagent grade chemicals Li2CO3 (E Merck), B2O3 (E Merck), Bi2O3 (E Merck) and ZnO (E Merck) were used for synthesis. Figure 1 shows optically polished glasses.

Powders of different oxides and carbonates have been weighed in required quantities. The weighed powders of desired chemicals have been mixed meticulously under acetone in an agate mortar for one hour. Then it was introduced in the synthesis furnace. The mixture gets decarbonized at around 650°C. The temperature of the furnace has been gradually increased up to around 850°C and melt was soaked for one hour to ensure homogeneity. The melt was shaken frequently to obtain clear glass samples without bubbles. Then the quenching of melt was done on a hot aluminum mold to obtain rectangular glass samples. Quenched glass samples are immediately transferred to the annealing furnace to relieve internal stresses. The annealed samples have been then used for further characterization. Transparent rectangular glasses of thickness 1 to 2 mm are used for optical characterization shown in figure 1.

DTA was done to investigate thermal behavior of glass samples. Glass transition temperature (Tg) was determined using heating rate of 10°C/min. Density of glasses was measured. Infrared measurements were done on FTIR Spectrometer using KBr pellet technique. UV-VIS spectrophotometer was used to record the absorption spectra in spectral region 300 to 1200 nm.
3. Results and discussion

Figure 2 shows the effect of ZnO mol% on Tg and the size of the oxygen packing density (OPD). The temperature change of Tg depends on the chemical bonding strength in the glass structure. It can be seen from figure 2 that the magnitude of Tg and oxygen packing increases with the increment in ZnO content. This reflects the tight packaging of the glass structure with the rise in ZnO concentration. It requires a lot of internal energy for the chain mobility in compact macromolecular structure that is essential for the transformation of glass. Therefore, ZnO addition requires the formation of a more macromolecular series in the glass system results in increase in Tg [13,14] This can also be ascribed to the creation of Zn-O bonds which are stronger as compared to Li-O bonds.

Figure 3 reveals the changes in density and molar volume with ZnO concentration. It is seen from the figure that the density rises with increase in ZnO concentration which is ascribed to the heavier mass of ZnO as compared to Li2O. Oxygen packing density rises with ZnO content. It makes the structure compact which as a result decreases molar volume and hence density increases. Table 1 gives Boron-Boron distance for the glasses. Table 1 revels that Boron-Boron distance declines with ZnO content it further supports the increase in density [15]

Table 1. Dependence of Boron-Boron distance on mol% of ZnO.

| mol% ZnO | Boron-Boron distance (nm) |
|----------|---------------------------|
| 0        | 34.59                     |
| 2        | 34.53                     |
| 4        | 34.42                     |
| 6        | 34.41                     |
Figure 4. IR absorption spectra.

Table 2. Assignments of the IR bands.

| mol % ZnO | Li⁺ ion , Bi³⁺ motion of [BiO₆] | Bending vibrations of B-O-B bonds in borate network | BO₃ triangular unit vibrations | BO₄ units | Stretching vibrations from different groups having Non-Bridging Oxygens | B-O bond Asymmetric stretching vibrations in BO₃ units | BO₃ and BO₄ groups and NBO in the form of tetraborate and diborate groups. [9] |
|-----------|---------------------------------|--------------------------------------------------|-----------------------------|----------|-----------------------------|-----------------------------------------------|-----------------------------------------------------|
| 0         | 506                             | 721                                              | 864                         | 1123     | 1329                         | 1427                                          |
| 2         | 498                             | 724                                              | 869                         | 1147     | 1312                         | 1424                                          |
| 4         | 502                             | 723                                              | 872                         | 1154     | 1310                         | 1424                                          |
| 6         | 503                             | 723                                              | 872                         | 1158     | 1308                         | 1424                                          |

FTIR Spectra for the glasses are displayed in Figure 4. Table 2 summarizes the IR bands and their vibrations. IR bands are observed at 506, 721, 864, 1123, 1329 and 1427 cm⁻¹. The band at 1427 cm⁻¹ arises due to BO₃ and BO₄ units and non-bridging oxygen in tetraborate and diborate groups [16] to anti-
symmetrical stretching vibrations of Non-Bridging Oxygens of B-O-B units [17,18,19] Shifting of this band is not observed. A band around 1329 cm\(^{-1}\) may be ascribed to asymmetric stretching vibrations of the B-O bonds in borate triangles. A peak is observed at 1123 cm\(^{-1}\) can be attributed (BO4 units Stretching vibrations from different groups having Non-Bridging Oxygens) to stretching vibrations of tetragonal BO\(_3\) units from different borate groups comprising Non-Bridging Oxygens [20].

Band corresponding to 862 can be assigned to vibrations of BO\(_3\) triangular unit. Band observed at 720 can be attributed to Bending vibrations of B-O-B linkages in borate network. A band seen at 506 cm\(^{-1}\) may be associated with the vibrations of Bi\(^{3+}\) in BiO\(_6\) octahedral units [15].

Consequently, it may be concluded that the structure of glasses is built up of three main structural units BiO\(_6\), BO\(_3\) and BO\(_4\).

![Figure 5](image1.png)

**Figure 5.** Transmittance spectra in the UV–Vis region for the glasses.

![Figure 6](image2.png)

**Figure 6.** Plots of (hv) vs. \((\alpha hv)^{1/2}\) for the glasses.

Figure 5 and 6 shows optical transmission spectra and Tauc’s plots for the glasses.

**Table 3.** Optical parameters for the glasses.

| mol % ZnO | \(\lambda_{\text{cutoff}}\) (nm) | \(E_{\text{opt}}\) (eV) | \(a_{\text{opt}}\) \(\left(\frac{E_{\text{opt}}}{A}\right)\) | Theoretical optical basicity \((\Lambda_{\text{Bi}})\) |
|----------|-----------------|----------------|-----------------|-----------------|
| 0        | 474             | 2.02           | 3.658           | 0.840           |
| 2        | 478             | 1.91           | 3.721           | 0.847           |
| 4        | 485             | 1.69           | 3.822           | 0.853           |
| 6        | 498             | 1.66           | 3.867           | 0.859           |
Table 3 displays the variation of cut off wavelength ($\lambda_{\text{cutoff}}$), optical band gap ($E_{\text{opt}}$), electronic polarizability $\alpha_{\text{opt}}$, and optical basicity ($\Lambda_{\text{th}}$) of the glass samples. Table 3 depicts the reduction in optical band gap and rise in cutoff wavelength with increment in ZnO content. It may be because of the structural changes which are happening due to the substitution of ZnO in place of Li$_2$O and increase in Non-Bridging Oxygens. Oxide ion polarizability $\alpha_{\text{oz}}$ rises with increment in ZnO content. The values of optical basicity rise with rise in ZnO content, which may be ascribed to the high polarizability of zinc ions.

4 Conclusions
In this series, the effect of ZnO concentration on various properties of the glasses has been investigated. The increase in glass transition temperature is attributed to the dense structure of glass with the addition of ZnO. This is also further supported by increase in oxygen packing density. The density increases due to the heavier ZnO replacing Li$_2$O. Molar volume decreases which is attributed to the decrease in $d_{\text{B-B}}$. Addition of ZnO in the glass expedites the creation of BiO$_6$ octahedral units owing to substitution of B-O bond by Bi-O bond. Optical band gap reduces and cut off wavelength rises with ZnO content on account of increase in Non-Bridging Oxygens which is also evidenced by IR. Electronic polarizability and optical basicity rises due to rise in Non-Bridging Oxygens.

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