Structural investigation and optical properties of xMnO$_2$ -25Li$_2$O-5Na$_2$O-15Bi$_2$O$_3$-(55-x)B$_2$O$_3$ glasses

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Abstract: This paper deals with the new mixed system of glass compositions Lithium sodium bismuth borate glasses doped with transition metal oxide. The technique used to prepare a sample is by melt quenching. The XRD profile pattern confirmed the amorphous phase of the present glass system. The network structure is based on BO$_3$, BO$_4$ units and BiO$_6$ octahedral units. No boroxyl rings observed in the glass structure. The addition of MnO$_2$ in small amount does not account for major structural changes. Optical band gap lies in the range 1.89 to 0.96 eV. Density, molar volume, oxygen packing density, Tg, direct optical band gap and refractive index show anomalous behavior.

Key words: Lithium Sodium Bismuth Borate glasses, Optical band gap, Transition metal oxide doping.

1 Introduction

The glasses containing heavy metal oxides like Bi$_2$O$_3$ have attracted attention in recent years. Such glasses can be used as sensors, photonic devices etc.[1-3]. They are chemically durable and thermally stable [4], show high value of refractive index, optical basicity, polarizability, and optical susceptibility [5-7]. However, due to the high polarizability of Bi$^{3+}$ ions, Bi$_2$O$_3$ is not a good glass former [8].

B$_2$O$_3$ is the most common basic glass former and an important commercial glass. Borate glasses exhibit boron anomaly [9]. The main structural units are connected by B-O-B linkages forming boroxyl rings and BO$_3$ triangles. The structural changes occur by the addition of modifier oxide which changes the triangular BO$_3$ units in to BO$_4$ tetrahedral units and various cyclic units that exist in different structural borate groups [10-12]. The insulating nature of borate glasses changes to semiconducting type by the addition of MnO$_2$ and Fe$_2$O$_3$ transition metal oxides [13]. It is very interesting to study manganese ions doped in glasses because of the existence of variable valence states among different glass network[14-17]. The addition of transition metals to glasses show interesting optical, photo conducting properties [18,19].

In the present paper, physical, optical, and structural analysis of MnO$_2$ doped lithium sodium bismuth borate glasses have been investigated.
2. Experimental

The glass samples of composition \( x\text{MnO}_2 + 25\text{Li}_2\text{O} + 5\text{Na}_2\text{O} + 15\text{Bi}_2\text{O}_3 + (55-x)\text{B}_2\text{O}_3 \) (\( x=0,2,4,6 \)) were prepared by melt quenching technique. The AR grade \( \text{Bi}_2\text{O}_3, \text{H}_3\text{BO}_3, \text{Li}_2\text{CO}_3, \text{Na}_2\text{CO}_3 \) and \( \text{MnO}_2 \) were homogeneously ground for 2 h and melted at 1100 C in a high temperature SiC furnace. At this temperature, the melt was kept for 30 min in furnace and in the mean time to get homogeneity the melt was continuously stirred. The melt was rapidly quenched on a stainless steel mould. The glass samples so formed were annealed at 300 C for 3 h so as to release the thermal stress in the glasses.

2.1 Glass Characterization

The XRD profiles of prepared glass samples were obtained by using PANalytical X’Pert Pro powder x-ray diffractometer operated at 45 kV and 30 mA using Cu-K\( \alpha \) radiation. The glass transition temperature was determined using Differential Scanning Calorimeter (Model METTLER-TOLEDO DSC1) at a heating rate of 10 C/min. By using Thermo Nicolet 6700 FTIR spectrometer, the IR spectra were recorded in the region 400-4000 cm\(^{-1}\). Analytic Jena SPECORD S-600 Spectrophotometer was employed to record the UV-Visible spectra in the region 390–1050 nm. Following the standard Archimedes principle at room temperature, the density measurements were done using xylene (density 0.86 gm/cc) as an immersion liquid.

3. Results and Discussion

3.1 XRD

Figure 1 shows the broad hump, at all glass compositions, their by confirming the amorphous nature of the prepared glasses.

![XRD of prepared glass samples](image.png)

Figure 1. XRD of prepared glass samples.

3.2. Physical properties

Glass density was calculated using,

\[
\rho = \frac{W_a \times 0.86}{W_a - W_b}
\]  (1)
where, \( W_a \) is the sample weight in air, \( W_b \) is the sample weight in the Xylene. Similarly, the molar volume was calculated using,
\[
V_m = \frac{M}{\rho}
\] 
(2)
where, \( M \) is a sample molecular weight. After obtaining the density and molecular weight values, the value of oxygen packing density (OPD) was calculated using
\[
OPD = C \times 1000 \frac{\rho}{M}
\] 
(3)
where, \( C \) is the number of oxygen per formula unit.

| Code of samples | Density (g/cc) | Molar volume (cc/mol) | \( T_g \) (C) | OPD (g.atm/L) |
|-----------------|----------------|-----------------------|----------------|---------------|
| 0MLNBiB         | 4.044          | 33.57                 | 447            | 71.48         |
| 2MLNBiB         | 4.406          | 30.93                 | 411            | 76.95         |
| 4MLNBiB         | 4.054          | 33.75                 | 406            | 69.95         |
| 6MLNBiB         | 4.258          | 32.24                 | 413            | 63.28         |

Table 1. The values of density, molar volume, OPD, glass transition temperature of glasses.

Figure 2. Compositional variations of density and molar volume with \( \text{MnO}_2 \)

Density is a very important parameter to know the glass co-ordination, cross linkage, structure of glasses, geometrical configuration and compactness. From the value of density the molar volume and OPD have been calculated and tabulated in Table 1. As doping of \( \text{MnO}_2 \) increased, density first increased up to \( x=2\% \), further decreased and reached minimum at \( x = 4\% \) and again increased showing anomalous behavior, while molar volume variation with doping shows opposite behavior. Compositional variation of density and molar volume by the addition of \( \text{MnO}_2 \) is as shown in figure 2.
3.3 DSC Characterization

The DSC of present glasses is shown in figure 3. Initially the Tg decreased up to x = 4% and there after it increased with the increase of MnO$_2$ content. The initial decrease in Tg gives information regarding the increase in the number of non bridging oxygen (NBOs) up to x = 4%. This indicates that the stability of glasses decreases up to x = 4% and further increase of MnO$_2$ content increases the Tg. In this result, OPD increased up to x=2% and then decreased indicating that the glass structure become loosely packed. Tg and OPD both have shown anomalous behaviour. The anomaly in the variation of Tg and OPD with MnO$_2$ are as shown in figure 4.

![Figure 3. DSC of glasses](image1)

![Figure 4. Compositional variation of Tg and OPD with MnO$_2$ content.](image2)
### 3.4 UV Spectral analysis

From the near absorption edge of photon energies, the absorption coefficient $\alpha (\nu)$ can be determined using [20,21].

$$\alpha (\nu) = \frac{2.303 \times A}{d}$$  \hspace{1cm} (4)

where 'A' represents the absorbance and 'd' is the sample thickness. In an optical transition there are two types: they are direct transition and indirect transition. These transitions occur in crystalline and non-crystalline materials at the fundamental absorption edge which gives information regarding band structure and energy gap. The absorption co-efficient, $\alpha (\nu)$ for the direct and indirect transitions was calculated using the formula given by Davis and Mott [22]. To find the direct transitions the formula used is

$$\alpha (\nu) = \frac{B (h\nu - E_{opt})^n}{h\nu}$$  \hspace{1cm} (5)

for allowed transition $n = 1/2$, where B is a constant and $E_{opt}$ is direct optical band gap.

By plotting $(\alpha h\nu)^2$ vs $h\nu$, direct optical band gap energy can be obtained for direct transitions by extrapolating to $(\alpha h\nu)^2 = 0$. The direct optical band gap energy decreased up to $x=2\%$ further increased and thereafter decreased. This shows that direct optical band gap energy values also vary anomalously with doping.

![Figure 5. $(\alpha h\nu)^2$ vs $h\nu$ of glasses (direct transition).](image)

Thus, the obtained lower values of direct optical band gap imply the semiconducting nature of the present glasses due to doping of manganese oxide. This decrease in $E_{opt}$ can be understood in terms of structural changes due to doping of the glasses and the decrease in the direct optical band gap gives the idea of increasing the NBOs in the prepared glass matrix. The plot between $(\alpha h\nu)^2$ and $h\nu$ are shown in figure 5.
Table 2. The values of direct band gap energy and refractive index (n) of glasses.

| Code of samples | Direct optical band gap (eV) | n   |
|-----------------|-----------------------------|-----|
| 0MLNBiB         | 1.89                        | 2.35|
| 2MLNBiB         | 0.96                        | 2.84|
| 4MLNBiB         | 1.07                        | 2.76|
| 6MLNBiB         | 1.02                        | 2.80|

Dimitrov and Sakka proposed the following formula to determine the refractive index value can be obtained by using \( E_{opt} \) [23,24].

\[
\frac{n^2 - 1}{n^2 + 1} = 1 - \left( \frac{E_{opt}}{20} \right)^{1/2}
\]  

The non linear variation values of refractive index and optical band gap energy are tabulated in Table 2. The refractive index also shows anomalous behaviour. The compositional variation of direct band gap and refractive index with MnO\(_2\) content is shown in figure 6.

Figure 6. Compositional variation of direct band gap and refractive index with MnO\(_2\) content.
3.5 FTIR Analysis

In borate network, the vibrational modes are mainly classified into three active IR regions [25,26]. The band of first group lies in the range 1200–1600 cm\(^{-1}\) that indicate the B–O bond asymmetric stretching relaxation of the trigonal BO\(_3\) units. The band of second group lies in the range 800–1200 cm\(^{-1}\) and that shows stretching of the B–O bond of tetrahedral BO\(_4\) units. The band of third group of IR bands exist around 700 cm\(^{-1}\) and indicate that B–O–B bending links are formed in the borate network. The absence of a band at 806 cm\(^{-1}\) confirms the absence of boroxyl ring formation in the present glasses. In the literature, it has been reported that Bi\(_2\)O\(_3\) appears in the bismuth borate glass network either as BiO\(_3\) or as BiO\(_6\) or both [27-29]. Generally, the existence of the BiO\(_3\) shows characteristic band at 830 cm\(^{-1}\) [29]. This is not the case here. Only BiO\(_6\) octahedral units are present in the bismuthate structure in these glasses. The absorption bands around 508 cm\(^{-1}\) to 527 cm\(^{-1}\) are specific to the Bi–O bonds vibrations in octahedral units of BiO\(_6\) [30-32]. The FTIR spectra of all prepared glasses are shown in figure 7. The FTIR assignment of peak bands is shown in Table 3. The bands in the range 685 to 715 cm\(^{-1}\) signifies B-O-B bending vibrations. The band around 957 cm\(^{-1}\) to 1023 cm\(^{-1}\) indicates stretching vibrations of B-O bond in BO\(_4\) tetrahedral units. The band around 1385 cm\(^{-1}\) to 1430 cm\(^{-1}\) specifies the B-O stretching vibrations in BO\(_3\) trigonal units. All the peaks observed at lower wave number are very weak and a well defined broad peak can be observed for higher wave number. For 4MLNBiB glass, the peaks are well defined and broad peak is observed at higher wave number, with some structural changes at this composition. The glass matrix remains unchanged at lower concentration of MnO\(_2\).
### Table 3 IR absorption band assignments of glasses.

| Sample code and Peak position | IR assignment                           |
|------------------------------|-----------------------------------------|
| 0MLNBiB 508                  | Bi-O bonds in BiO$_6$ octahedral units  |
| 2MLNBiB 715                  | B-O-B bending vibrations                |
| 4MLNBiB 685                  | B-O stretching vibrations in BO$_4$     |
| 6MLNBiB 990                  | B-O stretching vibrations in BO$_3$     |
| 6MLNBiB 990                  | B-O stretching vibrations in BO$_3$     |
| 1385 1391                    |                                        |

### 4. Conclusion

Present glasses have been prepared by melt quenching technique. XRD confirms their amorphous nature. The OPD and Tg are show anomalous behaviour. The prepared glass network structure is based on BO$_3$, BO$_4$ and BiO$_6$ octahedral units. A small changes shown in the absorption bands indicate no major structural changes due to the addition of MnO$_2$. The direct optical band gap lies in the range 1.89-0.96 eV. The lower values imply semiconducting nature due to doping of manganese oxide. These results are very well supported by the corresponding variations in density and molar volume both of which suggest that NBOs are formed on transition metal ion doping. Density, molar volume, direct optical band gap and refractive index show anomalous behavior.

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