INTRODUCTION

Glasses are receiving considerable attention due to their unique properties like hardness, good strength, transparency and excellent corrosion resistance. $\text{B}_2\text{O}_3$ is one of the best glass formers and due to boron anomaly borate glasses are good source of research (Griscom et al., 1978). The boron atom in borate crystals and glasses is usually coordinated with either three or four oxygen atoms forming $[\text{BO}_3]$ or $[\text{BO}_4]$ structural units. These two fundamental units can be arbitrarily combined to form either the so-called super-structure or different $\text{B}_2\text{O}_3$ structural groups like boroxyl ring, pentaborate, tetraborate, diborate groups etc. The number of the structural units depends on both the nature and the total concentration of the added modifiers (Yano et al., 2003; Shelby, 1997; Stone, 2000; Stehle, 1998). X-ray diffraction (XRD), density, infra-red spectroscopy and thermal analysis studies have been extensively employed over the years to investigate the structure of glasses (Pan and Ghosh, 2000; Jiri et al., 2009; Adrian, 2010; Pal, 1996). Essam, Shaahan (2011) reported that glass transition temperature ($T_g$) is represents the strength or rigidity of the glass structure. Shelby (1979) studied the $T_g$ is related to cross - link density and the tightness of packing in the network and the coordination of the network formers. Shapaan and Ebrabim (2010) have investigated the thermal and structural properties of $\text{B}_2\text{O}_3$ - $\text{Bi}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$ oxide glasses and they reported that $T_g$ values of the glasses decrease with increasing $\text{Bi}_2\text{O}_3$ content. This is due to the increasing of non - bridging oxygen atoms. In this investigation we report on detailed analysis of physical and structural properties of ternary $\text{B}_2\text{O}_3$ –$\text{MnO}_2$ –$\text{Na}_2\text{O}$ glass system. To best of our knowledge, there is no report on above said ternary glasses. The x-ray diffraction is used to study the glassy nature of the samples. Fourier transform infrared (IR) transmission spectra have been measured for obtaining the structural information of these glasses. The thermal behaviour of the prepared glass were studied by differential thermal analysis (DTA) and correlated with their structure. SEM is used to study the morphology of the glass samples. The present studies attempt to correlate the changes in density as the result of structural changes in the borate network.

EXPERIMENTAL PROCEDURE

Sample Preparation

$60\text{B}_2\text{O}_3–(40–x)\text{MnO}_2–x\text{Na}_2\text{O}$ glass system with $x = 0, 5, 10, 15$ and $20$ mol. % composition were prepared. The Analytical reagent grade powders of boron trioxide ($\text{B}_2\text{O}_3$), manganese oxide ($\text{MnO}_2$) and sodium carbonate ($\text{Na}_2\text{CO}_3$) were mixed in the appropriate composition. The powders were mixed thoroughly and then melted in a silica crucible for 3 hours in muffle furnace at $1000 \degree\text{C}$. The melt was poured into a brass mould to form samples of dimensions $10\textrm{mm} \times 1\textrm{mm} \times 1\textrm{mm}$ thickness. Glass samples were annealed at $475 \degree\text{C}$ for 2 hours to avoid the mechanical strain developed during the quench process. Then the furnace was switched off and glass was allowed to cool gradually to room temperature. The nominal compositions and density of the prepared glasses is given in Table 1.

Characterization

The amorphous nature of the sample is confirmed by X-ray diffraction technique using Philips (Philips PW 1050/51) X-ray
Table 1. Nominal compositions (mol. %) and density of glasses

<table>
<thead>
<tr>
<th>Samples</th>
<th>Nominal Composition</th>
<th>Density (ρ) (x10^3 kg/m³)</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>60B₂O₃ 40MnO₂ 0Na₂O</td>
<td>4.152</td>
<td>Amorphous</td>
</tr>
<tr>
<td>BMN 5</td>
<td>60B₂O₃ 35MnO₂ 5Na₂O</td>
<td>3.959</td>
<td></td>
</tr>
<tr>
<td>BMN 10</td>
<td>60B₂O₃ 30MnO₂ 10Na₂O</td>
<td>3.776</td>
<td></td>
</tr>
<tr>
<td>BMN 15</td>
<td>60B₂O₃ 25MnO₂ 15Na₂O</td>
<td>3.456</td>
<td></td>
</tr>
<tr>
<td>BMN 20</td>
<td>60B₂O₃ 20MnO₂ 20Na₂O</td>
<td>3.169</td>
<td></td>
</tr>
</tbody>
</table>

The density is a powerful tool for exploring the changes in the structure of glasses. The density is affected by the structural softening/compactness, change in geometrical configuration, coordination number, cross-link density and dimension of interstitial spaces of the glass. The density of glass has been shown in Table 1, the density values were found to decrease from 4152 (kg/m³) to 3169 (kg/m³) with increase of Na₂O concentration at expense of MnO₂. Due to the addition of Na₂O into BM glass, caused the density to decrease and this indicated that the network modifier (Na₂O) altered the structure of the glass by creating the NBOs in the network, so the structure turns to be more randomly oriented. Soliman et al.,(2010) have reported that the concentration of MnO is around 1.0 mol.%, manganese ions mostly exist in Mn²⁺ state, occupy network forming positions with MnO₄ structural units and increase the rigidity of the glass network. When MnO is in higher concentrations, these ions seems to exists mostly in the Mn³⁺ state and occupy modifying position.

RESULTS AND DISCUSSION

Density

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XRD and SEM studies

The XRD pattern and SEM micrograph of the BM and BMN20 glasses are shown in Figs. 1 & 2. XRD patterns of the as - prepared samples show no sharp Bragg’s peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature within the resolution limit of XRD instrument. From the SEM picture, it is observed that different sized grain particles are distributed and the size of the particles is to vary in each micrograph. The particles are extremely angular and spherical in nature. Some sphere like agglomerates were found spreading in the glass surface, due to the deposition of amorphous apatite.

FTIR Study

Fig. 3 represents the IR transmission spectra of as prepared glass samples. It show broad transmittance band which confirm the amorphous character of the samples studied and in agreement with x-ray measurement. The obtained band
position and their corresponding assignments are presented in Table 2.

Table 2. Position and assignments of the observed infrared transmittance bands of BMN glass system

<table>
<thead>
<tr>
<th>Peak position cm⁻¹</th>
<th>Assignments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>~700</td>
<td>Bending vibration of B-O-B linkage</td>
<td>Lakshmi Kumari et al., 2011.</td>
</tr>
<tr>
<td>1006-1066</td>
<td>B-O stretching vibration of the tetrahedral BO₄</td>
<td>Gopi Sharma et al., 2006.</td>
</tr>
<tr>
<td>~1384</td>
<td>B-O stretching vibration of the trigonal BO₃ unit</td>
<td>Sumalatha et al., 2011.</td>
</tr>
</tbody>
</table>

The vibrational modes of the borate glass network show the presence of three infrared spectral regions. The first group of bands in the region 1200-1600 cm⁻¹, is due to the asymmetric stretching vibration of the B-O bond of the triangle BO₃ unit containing non-bridging oxygen ions. The second group lies between 800 and 1200 cm⁻¹ and is due to the B-O bonds stretching of the tetrahedral BO₄ units. The third group is around 700 cm⁻¹ and is due to bridging B-O-B linkages in the borate network. In BM glass, a broad band at 1066 cm⁻¹ is due to B-O bond stretching of BO₄ groups (Gopi Sharma et al., 2006). The addition of Na₂O into BM glass matrix, the intensity of this band is shifting towards the lower wave number. The band around at ~ 1384 cm⁻¹ is due to the asymmetric vibration of trigonal BO₃ units (Sumalatha et al., 2011) in meta-, pyro- and ortho-borate units. The band centred at ~702 cm⁻¹ is assigned to the B-O-B bending vibration of BO₃ groups (Lakshmi Kumari et al., 2011). The band at 425 cm⁻¹ which is present in all samples is due to the vibration of metal cations in bi-valent state Mn²⁺ (Manisha Pal et al., 2011). The IR spectra also showed non-existence of band at 806 cm⁻¹, which reveals the absence of boroxol rings in the glasses and hence it consist of only BO₃ and BO₄ groups (Edukondalu et al., 2013). The region 2400-3000 cm⁻¹ is due hydroxyl groups (Kamitsos et al., 1990; Stoch and Sroda, 1999; Kamitsos et al., 1987).

Above results shows that the incorporation of MnO₂ and Na₂O has shifted the position and changed the intensity of the bands. This is due to change in coordination of borate network either due to formation of BO₃ or BO₄ units. It has been observed that for B₂O₃-MnO₂-Na₂O glass system the intensity of band in 800-1200 cm⁻¹ region decreases with an increase in the sodium oxide concentration. The added Na₂O gives rise to the formation of non-bridging oxygen.

**Thermal Analysis**

(a) Thermo Gravimetric analysis of BM and BMN20 Glasses

Thermal study of the glasses were performed because any change in the coordination number of network forming atoms, or the formation of non bridging oxygen, is known to be reflected in the T_g. The variation of the TG and DTA with mol. % content of Na₂O concentration is shown in Fig. 4. The total weight loss in TGA is 10 %. The weight loss of the first step corresponds to the water released in the sample 3% and other steps correspond to the decomposition of more percentage of B₂O₃ and followed by MnO₂ and Na₂O are 2.4 and 0.7 percentage decomposition.

![Fig. 4. TG/DTA analysis curves for 60B₂O₃ - 40MnO₂ (a) and 60B₂O₃ - 20MnO₂ - 20Na₂O (b) glass samples](image)

(b) Differential Thermal Analysis of BM and BMN20 Glasses

The glass transition temperature for BM and BMN20 is 230 ºC and 226 ºC respectively. The T_g is decreased by the introduction of Na₂O in to the BM glasses. Furthermore, the...
Conclusions

Conclusions drawn from the study of 60B<sub>2</sub>O<sub>3</sub> – (40 – x)MnO<sub>2</sub> – xNa<sub>2</sub>O glasses.

I. The density was decreased with increasing Na<sub>2</sub>O content consequently the decrease in dimensionality of borate network structure.

II. Both the x-ray diffraction and SEM studies confirm the amorphous nature of the as-prepared glasses.

III. The infrared studies indicate the presence of BO<sub>3</sub> and BO<sub>4</sub> units in the structure of the studied glasses, but their position and intensity depend on the concentration of Na<sub>2</sub>O added.

IV. The glass transition temperature (T<sub>g</sub>) of the glass samples is found to decrease with increasing Na<sub>2</sub>O content. The additions of alkali oxide Na<sub>2</sub>O in the glasses lose their stability significantly.

REFERENCES


