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RESEARCH ARTICLE

# STRUCTURAL AND THERMAL PROPERTIES OF $B_2O_3$–$MnO_2$–$Na_2O$ OXIDE GLASSES

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**ABSTRACT**

Glasses with composition $60B_2O_3$–(40–x)$MnO_2$–x$Na_2O$ (where x = 0, 5, 10, 15 and 20 mol. %) have been prepared using the melt quench technique. The structural analysis of glasses is carried out by X-ray diffraction, density, IR spectroscopy and thermal analysis measurements. The XRD profiles confirmed their glassy nature and FTIR spectra indicate that inclusion of modifier oxide produces $BO_3$ and $BO_4$ structural units by breaking the boroxol $B_3O_6$ ring. The glass transition temperature ($T_g$), crystallization temperature ($T_c$) and melting temperature ($T_m$) of the glasses decreases with increases of $Na_2O$ content in the system. Scanning electron microscopy study was also carried out with a view to throwing more light on their morphology aspects.



## INTRODUCTION

Glasses are receiving considerable attention due to their unique properties like hardness, good strength, transparency and excellent corrosion resistance. $B_2O_3$ 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 [$BO_3$] or [$BO_4$] structural units. These two fundamental units can be arbitrarily combined to form either the so-called super-structure or different $B_xO_y$ 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, Shaaban (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 $B_2O_3$ - $Bi_2O_3$ - $Fe_2O_3$ oxide glasses and they reported that $T_g$ values of the glasses decrease with increasing $Bi_2O_3$ 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 $B_2O_3$ –$MnO_2$ –$Na_2O$ 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.

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## EXPERIMENTAL PROCEDURE

### Sample Preparation

$60B_2O_3$–(40–x)$MnO_2$–x$Na_2O$ glass system with x = 0, 5, 10, 15 and 20 mol. % composition were prepared. The Analytical reagent grade powders of boron trioxide ($B_2O_3$), manganese oxide ($MnO_2$) and sodium carbonate ($Na_2CO_3$) 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 ºC. The melt was poured into a brass mould to form samples of dimensions 10mm diameters and 6mm thickness. Glass samples were annealed at 475 ºC 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**

| Samples | Nominal Composition | | | Density (ρ) ($x10^{-3}kg/m^3$) | XRD |
|---|---|---|---|---|---|
| | $B_2O_3$ | $MnO_2$ | $Na_2O$ | | |
| BM | 60 | 40 | 0 | 4.152 | Amorphous |
| BMN 5 | 60 | 35 | 5 | 3.959 | |
| BMN 10 | 60 | 30 | 10 | 3.776 | |
| BMN 15 | 60 | 25 | 15 | 3.456 | |
| BMN 20 | 60 | 20 | 20 | 3.169 | |

powder diffractometer with CuKα radiation. The scanning electron microscopy (SEM) investigations were performed on glass samples at room temperature using an JEOL auto fine coater Model JES-1600 for morphological studies. The infrared spectra of the prepared glasses were obtained by KBr pellet technique in the wavenumber range 4000 - 400 $cm^{-1}$ using a Perkin Elmer FTIR spectrometer model RX-1. Thermal studies were carried out in a STA - 1500 simultaneous thermal analyser instrument. Densities of the glasses were measured by the Archimedes method using deionised water as an immersion liquid. The accuracy of the determined densities of the different glasses is ±0.001g/$m^3$.

## RESULTS AND DISCUSSION

### Density

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/$m^3$) to 3169 (kg/$m^3$) with increase of $Na_2O$ concentration at expense of $MnO_2$. Due to the addition of $Na_2O$ into BM glass, caused the density to decrease and this indicated that the network modifier ($Na_2O$) 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 $Mn^{2+}$ state, occupy network forming positions with $MnO_4$ structural units and increase the rigidity of the glass network. When MnO is in higher concentrations, these ions seems to exists mostly in the $Mn^{3+}$ state and occupy modifying position.

### 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.

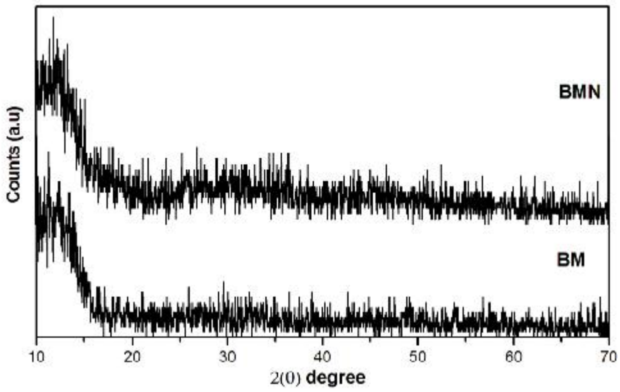
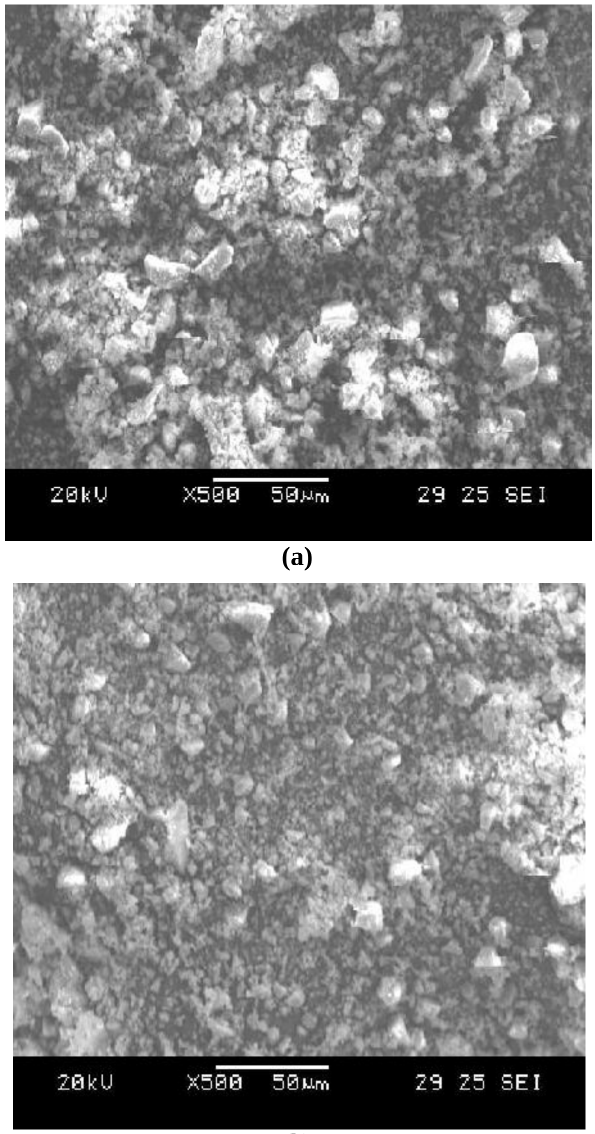



**Fig. 1. XRD pattern of BM and BMN**




**(a)**

**(b)**

**Fig. 2. SEM image of $60B_2O_3$-$40MnO_2$ (a) and $60B_2O_3$-$20MnO_2$-$20Na_2O$ (b)**

### 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**

| Peak position $cm^{-1}$ | Assignments | References |
|---|---|---|
| ~425 | Vibration of metal cations $Mn^{2+}$ | Manisha Pal, Baishakhi Roy and Mrinal Pal 2011. |
| ~700 | Bending vibration of B-O-B linkage | Lakshmi Kumari *et al.*, 2011. |
| 1006-1066 | B-O stretching vibration of the tetrahedral $BO_4$ | Gopi Sharma *et al*., 2006. |
| ~1384 | B-O stretching vibration of the trigonal $BO_3$ unit | Sumalatha *et al*., 2011. |

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 $BO_3$ unit containing non-bridging oxygen ions. The second group lies between 800and 1200 $cm^{-1}$ and is due to the B-O bonds stretching of the tetrahedral $BO_4$ 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 $BO_4$ groups (Gopi Sharmaa *et al*., 2006). The addition of $Na_2O$ 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 $BO_3$ 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 $BO_3$ 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 $Mn^{2+}$ (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 $BO_3$ and $BO_4$ 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).

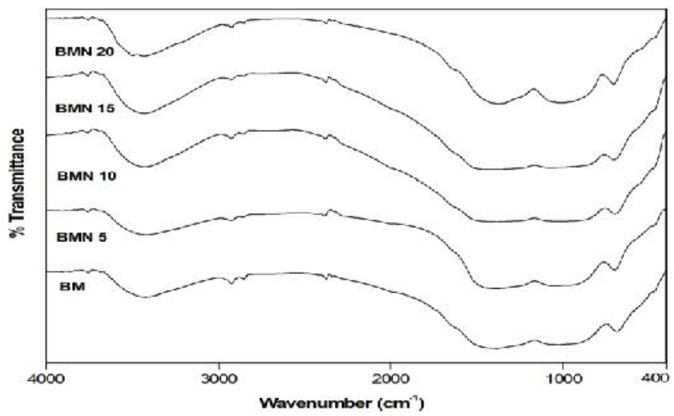


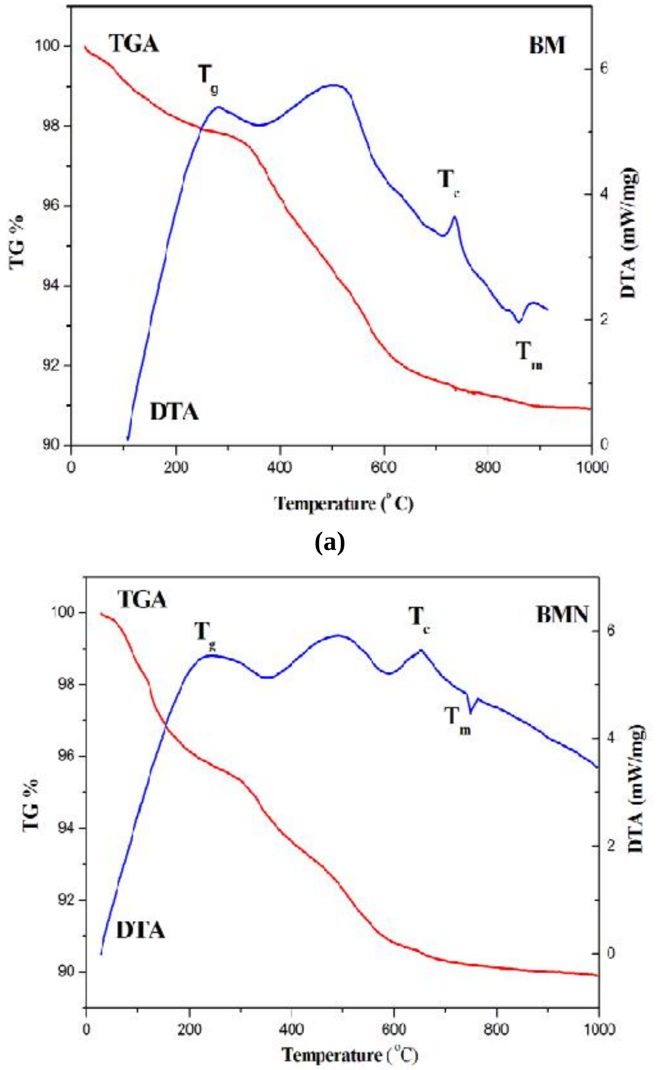

**Fig. 3. FT-IR spectra of $B_2O_3$-$MnO_2$-$Na_2O$ with various concentrations**

Above results shows that the incorporation of $MnO_2$ and $Na_2O$ 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 $BO_3$ or $BO_4$ units. It has been observed that for $B_2O_3$-$MnO_2$-$Na_2O$ glass system the intensity of band in 800-1200 $cm^{-1}$ region decreases with an increase in the sodium oxide concentration. The added $Na_2O$ 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 $Na_2O$ 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 $B_2O_3$ and followed by $MnO_2$ and $Na_2O$ are 2.4 and 0.7 percentage decomposition.




(b)

**Fig. 4.TG/DTA analysis curves for $60B_2O_3$ - $40MnO_2$ (a) and $60B_2O_3$ - $20MnO_2$ - $20Na_2O$ (b) glass samples**

### (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 $Na_2O$ in to the BM glasses. Furthermore, the exothermic peaks denoting the emergence of the crystallization can be detected in DTA plots. It indicated that the crystalline temperature ($T_c$) is decreased from 783 ºC (BM glass) to 687 ºC (BMN20 glass) and melting temperature for BM glass is 929 ºC and 732 ºC for BMN glass. The introduction of $Na_2O$ in BM glass decreasing the formation of $BO_4$ units and consequently decreases the connectivity of the network structure as supported by density results (Soliman *et al*., 2009).

**Conclusion**

Conclusions drawn from the study of $60B_2O_3 – (40 – x)MnO_2 – xNa_2O$ glasses.

I. The density was decrease with increasing $Na_2O$ 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 $BO_3$ and $BO_4$ units in the structure of the studied glasses, but their position and intensity depend on the concentration of $Na_2O$ added.
IV. The glass transition temperature ($T_g$) of the glass samples is found to decrease with increasing $Na_2O$ content. The additions of alkali oxide $Na_2O$ in the glasses lose their stability significantly.

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