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RESEARCH ARTICLE

CHARACTERIZATION OF ZINC BASED MANGANESE BISMUTHATE GLASSES USING SPECTROSCOPIC METHODS

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ABSTRACT

Glass samples belonging to the general chemical formula $60Bi_2O_3$–$(40\text{-}x)MnO_2$–$xZnO$ with x=5, 10, 15, 20, and 25 mol % are prepared by melt quench method. Characterization of the system was carried out using FT-IR, XRD, SEM and thermal analysis. The structural changes with composition of the glasses have been studied by FT-IR spectroscopy with special reference to structural units of bismuth. Analysis of FT-IR spectra indicate that ZnO is preferentially incorporated into the bismuthate network. Amorphous nature of the system was confirmed by XRD and SEM is used to study the morphology of glass samples. TGA is used to measure the weight loss as the temperature of the sample is increased. DTA is used to identify the glass transition temperature, crystallization temperature and melting temperature.

INTRODUCTION

Recently, glasses containing bismuth oxide have received increased interest due to their manifold possible applications (Bale, *et al.,* 2008). These glasses were found to be efficient gamma ray absorbers and also considered for use in scintillation detectors for high energy physics (Bishay and Maghrabi, 1969). The large polarizability and small field strength of Bi^{3+} in oxide glasses makes them suitable for optical devices such as ultra-fast optical switches, optical isolators, Optical Kerr Shutter (OKS) and environmental guidelines. Despite of the fact that Bi_2O_3 is not a classical glass former, in the presence of conventional glass formers (such as B_2O_3, SiO_2, etc.) it may build a glass network of $[BiO_n]$ (n = 3, 6) pyramids (Dumbaugh, 1986). The study of oxide glasses doped with Transition Metal Ions (TMI) has received considerable attention in nowadays due to their attractive combination of physical and chemical properties. Continued effort for the development of new glassy materials either by doping or by adding TMI, and the study of their novel properties is highly relevant due to their potential applications in various technological fields (Pal, *et al.,* 1998; Aleksandrov, *et al.,* 2007). Glasses doped with transition metal ions like Cu^{2+} and Mn^{2+} have attracted considerable interest because of their memory and photo conducting properties (Chinna Babu, *et al.,* 2005). The influence of manganese ions on optical, magnetic and electrical properties of various inorganic glass systems has been under extensive investigation in recent years (Murali, *et al.,* 2005; Machado, *et al.,* 2004). A considerable number of studies on the structural role of manganese ions in a variety of glass systems viz., Bi_2O_3, phosphate, etc. (Ardelean, *et al.,*2005; Ardelean, *et al.,* 2002) have been reported. During few decades, ZnO and the materials based on it are drawing more attention due to their interesting optical, electrical and magnetic properties in combination with its non toxicity, non-hygroscopic nature and low cost. Its direct wide band gap, intrinsic emitting property and a large exciton binding energy makes it a potential candidate for development of optoelectronic devices (Yamasaki, *et al.,* 2004; Alivov, *et al.,* 2004), UV emitting lasers (Saito, *et al.,* 2002), solar energy converters (Ferber and Luther, 2001) and gas sensors (Zhu, *et al.,* 2005). ZnO is a wide band gap semiconductor and has received increasing research interest. Furthermore, it can be made a versatile material with broad applications through a proper doping process such as transparent-conducting electrodes (doped with group IIIB, fluorine, and aluminum), piezoelectric as well as ferroelectric layers (Fujihara, *et al.,* 2000). The present work is focussed to study the structural changes taking place in unconventional Bi_2O_3-MnO_2-ZnO glass system. For this, a systematic study of FTIR, XRD, SEM and TG/DTA of ternary Bi_2O_3-MnO_2-ZnO are performed.

Experimental details

The glass samples having the general chemical formula $60Bi_2O_3$–$(40\text{-}x)MnO_2$–$xZnO$ with x=5, 10, 15, 20 and 25 mol % were prepared by rapid melt quench method using the starting materials as Bi_2O_3, MnO_2 and ZnO of reagent purity grade. The required amount (approximately 20g) in mol% of different chemicals in powder form were weighed using single pan balance having an accuracy of ±0.001g and mixed in a mortar. The mixtures corresponding to the desired compositions were melted in porcelain crucible in a muffle

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furnace. Melting is carried out under controlled conditions at a temperature from 900 to 1070ºC for all the compositions. The molten sample is cast into a copper mould having dimensions of 10mm diameter and 6mm thickness. Then the glass samples are annealed for two hours to avoid the mechanical strain developed during the quenching process. The samples prepared are chemically stable and non-hygroscopic. The samples are polished and the surfaces are made perfectly plane and smoothened by diamond disc and diamond powder. The nominal composition of BMZ glass samples are given in Table 1.

Table 1. Nominal composition of BMZ glass samples

Specimen	Nominal composition (mol %)		
	Bi_2O_3	MnO_2	ZnO
BMZ 1	60	35	05
BMZ 2	60	30	10
BMZ 3	60	25	15
BMZ 4	60	20	20
BMZ 5	60	15	25

The infrared spectra of the glasses were recorded at room temperature using KBr disc technique. Surface studies were carried out to check the amorphous nature of the samples using scanning electron microscope. The amorphous state of the glass samples is confirmed by X-ray diffraction method. Thermal analysis (TG/DTA) techniques yield specific physical properties and verifying some important transformations in materials of the glasses as a function of temperature.

RESULTS AND DISCUSSION

(i) FT-IR SPECTRA ANALYSIS

Infrared spectroscopy has proved to be an important tool for the investigation of structure and dynamics of disorder materials. IR spectra of materials may help to get the idea of the nature of vibration in a disorder system (Becker, 2003). The FT–IR spectra of BMZ glasses are presented in Fig.1 The FT-IR spectra of BMZ glasses exhibit broad bands as a consequence of the network disorder generally exists in glass matrices accompanied by band overlapping, originating from the presence of different structural polyhedra with characteristic vibrational modes occurring in the same wavenumber region. The data have been discussed on the basis of the method given by Tarte (1962) and Condrate (1986) by comparing the data obtained for the studied glasses with those of related crystalline compounds. In general, the FT–IR spectra of Bi_2O_3 present the absorption bands at: ~ 425 cm^{-1}, ~ 465 cm^{-1}, ~ 510 cm^{-1}, ~ 540 $cm^{-1}$and ~ 595 cm^{-1}characteristic to the vibrations of Bi-O bonds in BiO_6 octahedral units and the bands are identified at: ~ 540 cm^{-1}, ~ 620 cm^{-1} and ~ 840 cm^{-1} characteristic to the vibrations of Bi-O bonds in BiO_3 pyramidal units (Dimitrov, *et al.,*1994; Iordanova, 1996). The characteristic bands for MnO_2 are identified at ~ 400 cm^{-1} and ~ 615 cm^{-1} (Bentley, *et al.,*1986). The band in the range 400–600 cm^{-1} indicates the presence of Zn–O tetrahedral bending vibrations in the present glass system (Del Longo,*et al.,*1998; Motke, 2002).

In the present BMZ glasses, the IR spectra exhibits the vibrational bands at 420-439 cm^{-1}, ~729 cm^{-1}, 920-956 cm^{-1}, 1602-1635 cm^{-1} and 3427-3443 cm^{-1}. The band centered at 420-439 cm^{-1} is characteristic to stretching vibrations of Bi–O bonds in BiO_6 octahedral units (Fuxi, 1991; Dimitrov, *et al.,* 1994). Also this band can be attributed to the presence of Zn–O tetrahedral bending vibrations of ZnO_4 units (Bale, *et al.,* 2008; Doweidar and Yasser B. Saddeek, 2009).

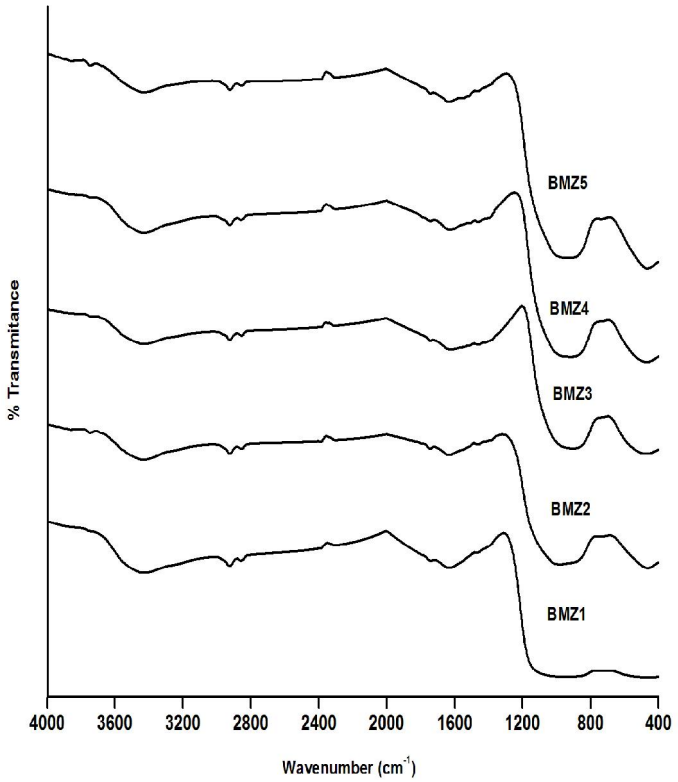
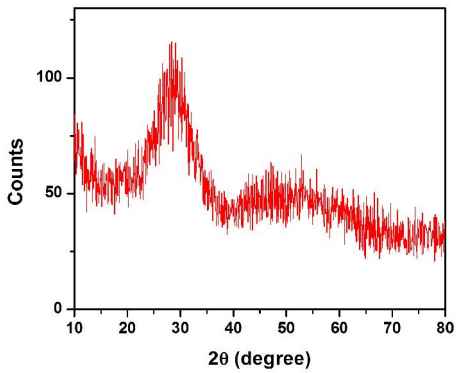


Fig. 1. FT-IR spectra of BMZ glasses with different concentrations

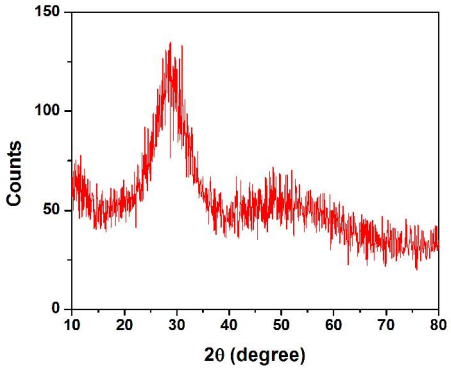
The band from ~729 cm^{-1} is assigned to the symmetric stretching vibrations of Bi–O bonds in BiO_3 units (Bishay and Maghrabi, 1969). It has been reported that the band in the IR spectra around 855 cm^{-1} represents the convolution of the absorbance bands reported for different bismuthate glasses at 840 cm^{-1} and 860 cm^{-1}, assigned to the total symmetric stretching vibrations of the [BiO_3] and [BiO_6] polyhedra, respectively (Miyaji, *et al.,*1990; Bale and Rahman, 2008). In the present study this band is observed at 920 and 956 cm^{-1}. Therefore it was found that Bi^{3+} cations are incorporated in the glass network as [BiO_3] pyramidal and [BiO_6] octahedral units. The weak band observed at 1602-1635 cm^{-1} is due to OH bending mode of vibration (Chowdari and Rong, 1996). The bands recorded around 3427-3443 cm^{-1} can be attributed to OH stretching vibrations (Bray, 1967).

(ii) XRD ANALYSIS

Fig. 2(a) and Fig. 2(b) show the X-ray Diffraction pattern (XRD) of BMZ1 and BMZ5 glass samples respectively. The XRD shows no continuous or discrete sharp peak but exhibit broad halo around $2\theta \approx 30^{\circ}$ (Aksan, *et al.,* 2000), which reflects the characteristics of amorphous glass structure. The appearance of broad profile around $2\theta \approx 30^{\circ}$, also suggests that some short range order in the bismuthate glasses are preserved. The absence of long-range atomic arrangement is a clear indication of glassy nature of the glass sample.



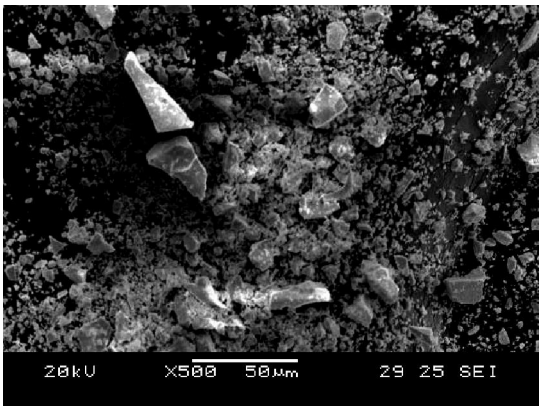
(a)



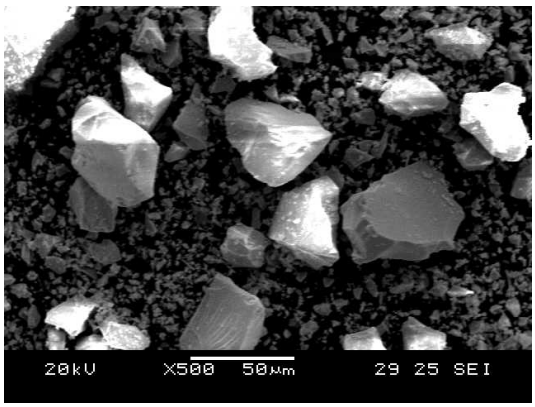
(b)

Fig. 2. XRD pattern of (a) BMZ1 glass and (b) BMZ5 glass

(iii) SEM ANALYSIS



(a)



(b)

Fig. 3. Scanning electron micrographs of (a) BMZ1 and (b) BMZ5 glasses

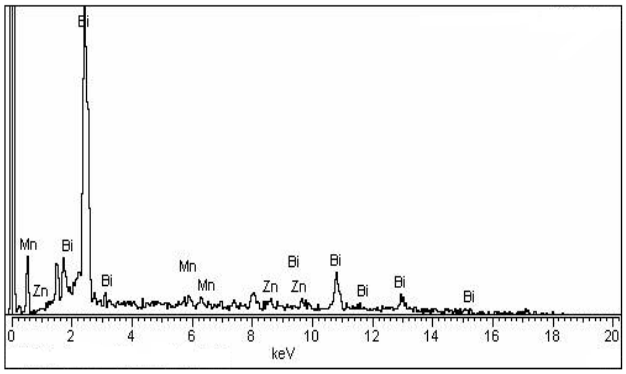


Fig. 4. Energy dispersive spectrum of BMZ1 glass

The microstructure of the pulverized glass samples were examined using Scanning Electron Microscope (SEM). The SEM photographs of the BMZ1 and BMZ5 samples are given in Figs. 3(a) and 3(b) respectively. It consists of densely packed grains free from holes. Some sphere-like agglomerates are found to be spreading due to deposition of amorphous apatite which clearly indicates the glassy nature of the samples (Regisha and Santha, 2011). In addition, the EDS analysis of the BMZ1 sample is given in Fig. 4. The EDS analysis shows that bismuth, manganese and zinc are present in BMZ1 glass sample.

(iv) THERMAL BEHAVIOR OF GLASS

(a) Thermo gravimetric analysis of BMZ5 glass

The thermal stability of the glass samples was investigated by Thermo Gravimetric Analysis (TGA) measurements. Thermal gravimetric analysis was used to measure the weight loss as a function of temperature. TG curve of BMZ5 glass sample is shown in Fig. 5. It is observed from the curve of TG that the total weight loss in BMZ5 glass is 3.0%. The weight loss in the first step corresponds to water released in the sample BMZ5 and the other steps correspond to the decomposition of the glass sample.

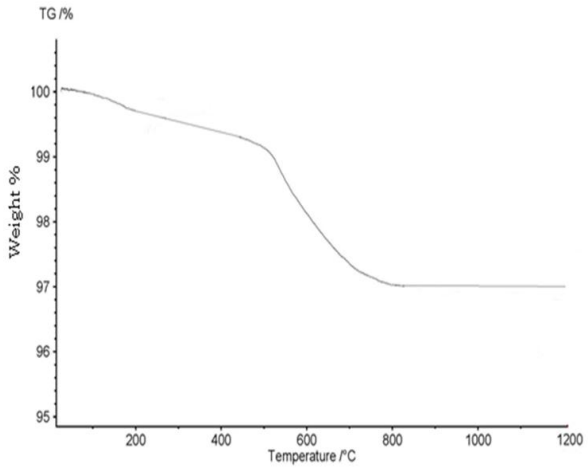


Fig. 5. Thermo gravimetric analysis curve for BMZ5 glass

(b) Differential thermal analysis of BMZ5 glass.

Differential thermal analysis is used to characterize the glass and to determine the thermo dynamical parameters. Fig.6

shows the differential thermal analysis curve for BMZ5 glass. The DTA curve for the glass BMZ5 show a small endothermic hump corresponding to the glass transition temperature (T_g) at 375˚C. This is followed by an exothermic peak corresponding to crystallization temperature (T_c) at 697˚C and other endothermic events corresponding to the melting temperature (T_m) at 895˚C. It has been reported that T_g is strictly related to the density of cross-linking, the tightness of the network formers, the coordination number of the network-forming atoms, etc. (Dutta and Ghosh, 2007).

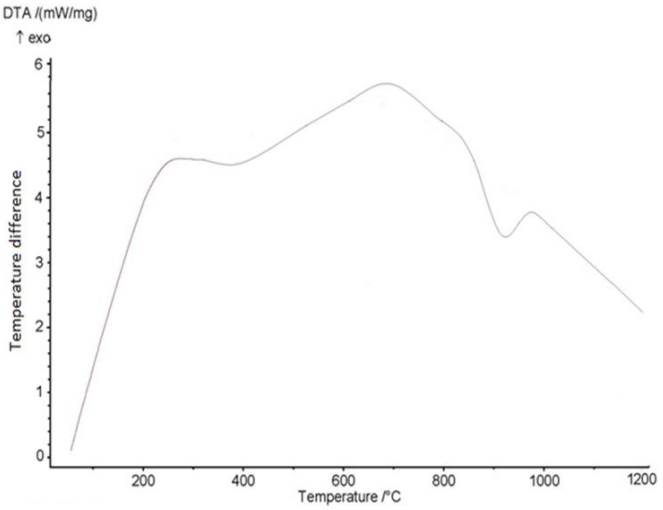


Fig. 6. Differential thermal analysis curve for BMZ5 glass

The exothermic peak is probably due to a reaction involving the crystallization process and it is observed by El-Ghannam, *et al.* (2001). The endothermic peak may be attributed to the melting of the glass sample. The thermal stability of glass is an important property both fundamentally and technologically and the structure of the glass determines its thermal stability. The close packed structure results in thermally stable glasses and loose packed structure yields unstable glasses (Hirashima, *et al.,* 1988). From the Table 2, two parameters have been commonly employed to evaluate thermal stability index of glasses. (i). Glass stability factor $S = (T_c - T_g)$. (ii). Hruby's parameter K_{g1}, defined as $K_{g1} = (T_c - T_g)/(T_m - T_c)$ (Thulasiramudu and Buddhudu, 2007). Generally, the larger temperature interval of glass stability factor (S) will indicate the higher Glass Forming Ability (GFA), which means that the width of the super cooled liquid region can exist in a wide temperature range without crystallization and has a high resistance to the nucleation and growth of crystallization phases, leading to good GFA (Soliman, 2008). Hruby's parameter gives information on the stability of the glass against devitrification. Table 2 reveals the obtained glass stability factors and Hruby's parameter of BMZ5 glass.

Table 2. DTA Analysis for the BMZ5 glass sample

Glass transition temperature, T_g (˚C)	375
Crystallization temperature, T_c (˚C)	697
Melting temperature, T_m (˚C)	895
Glass stability factor, $S = T_c - T_g$ (˚C)	322
Hruby's parameter, $K_{g1} = (T_c - T_g)/(T_m - T_c)$	1.62

Conclusion

The glass system Bi_2O_3–(60-x)MnO_2–xZnO with x=5, 10, 15, 20 and 25 mol % have been synthesized successfully by rapid melt quenching method. From the present investigation the following conclusions are drawn.

- The FT-IR absorption spectra have evidenced that a part of bismuth ions are incorporated in the glass network in both BiO_3 and BiO_6 units and zinc ions are incorporated in ZnO_4 units.
- XRD and SEM confirm the amorphous nature of the samples and EDS analysis confirms the presence of bismuth, manganese and zinc in the glass samples.
- The thermal stability of the prepared glass samples are studied by TG analysis and the weight losses in the glass samples have been measured as the temperature of the sample is increased.
- The DTA analysis exhibits the exothermic and endothermic signals corresponding to the glass transition, crystallization and melting temperature of the glasses.

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