STRUCTURAL AND THERMAL PROPERTIES OF ZnO MODIFIED BISMUTH BORATE GLASSES

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Abstract

Borate glasses containing the network modifier oxide ZnO was prepared by melt quenching technique. The structural characterization of these glass samples has been investigated by using X-ray powder diffraction technique (XRD). The morphology of these samples has been determined by using SEM. The transition temperature and crystallization temperature of these glasses were determined by TGA-DTA method. Thermal stability (ΔT) of the glass samples with the different compositions was identified. The FTIR spectroscopy was also used to study the bonding structure of these glasses in the range from 400 to 4000 cm^{-1}. It was found that the Bi^{3+} cations were incorporated in the glass structure as BiO_3 and BiO_6 units and also boron ions were incorporated as BO_3 and BO_4 units.

Keywords melt quenching method, XRD, SEM, DTA, FTIR

Introduction

Glasses are amorphous materials and they have the random periodic arrangement of atoms or ions or molecules [Khanna, A., et al., 2003]. Glasses have been synthesized the main properties such as rapidly freezing or super cooling their melts without crystallization [Pal, M., et al., 2011]. The structures and various properties of glasses depend on the quenching rates and compositions [Pal, M., et al., 2011]. Glasses are accepting significant consideration because of their interesting properties like hardness, good strength, transparency and excellent corrosion resistance [Oprea, I. I., et al., 2004]. There are various glasses in material research, a boric oxide B_2O_3 perform as the popular and brilliant glass formers, flux materials and has get great attention from the person which are study the material science because of its interesting electrical, optical and luminescent properties for various technical applications [Singh, L., et al., 2014].

Nowadays, Bi_2O_3, TeO_2 and PbO are heavy metal oxide glasses, theses oxides have been analysed widely in many applications [Bajaj, A., et al., 2009]. These glasses have several ranges of applications due to their high refractive index, infrared transmission, non-linear properties) low melting temperature and high dielectric constant [Ali, A. A., 2008].

There are two types of glass former in the glass system [Ali, A. A., 2008]. They are conditional glass former and conventional glass former [Ali, A. A., 2008]. B_2O_3 acts as a typical glass former or conventional glass former and Bi_2O_3 performs as a conditional glass former that is perform as well as modifier [Dong, M. G., et al., 2017]. Nevertheless, both network-forming and network modifying positions can applied in Bi_2O_3 depending on its concentration in the glass composition as well as ZnO [Doweidar, H., 2009]. In recent year, many applications such as optical and electronic devices, thermal and mechanical sensors, reflecting windows, radiation-shielding purposes, etc. apply Bi_2O_3 consist of glasses because of its interesting properties [ElBatal, F. H., et al., 2006]. The nature and concentration of constituent oxides are main part of the glass system because of these facts are strongly depended on the glass structure and properties [Radhakrishnan, A. A., 2014].

In this research work, the sample preparation was expressed about the network modifier type of zinc oxide bismuth borate glasses with the different compositions. The structural

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characterization of these glasses had been measured by using X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM), the thermal properties of these glasses had been determined by using Differential Thermal Analysis (DTA) and the bonding structure of these glasses was also analyzed by Fourier Transform Infrared Spectroscopy (FTIR).

Material and Methods

Sample Preparation

The flowchart of the sample preparation was shown in Figure 1. Borate glasses having the formula x ZnO + y Bi_2O_3 + (1 - x - y) B_2O_3 (where x = 0.1, 0.2, 0.3 and y = 0.1) were prepared by using the melt-quenching technique. The regent grade of the starting materials ZnO, Bi_2O_3 and H_3BO_3 had been mixed thoroughly in a porcelain pestle-mortar for an hour. After being pulverized, it was heated at 300 °C for two hours to convert from boric acid (H_3BO_3) to boric oxide (B_2O_3). Then, it was melted at 1100 °C for two hours again. The formation of zinc oxide bismuth borate glass (ZBB) molten samples was obtained. The melted homogeneous glass samples were then quenched by pouring it onto the copper plate and cooled down to room temperature. Finally, the brightly yellow of ZBB samples without bubbles were obtained.

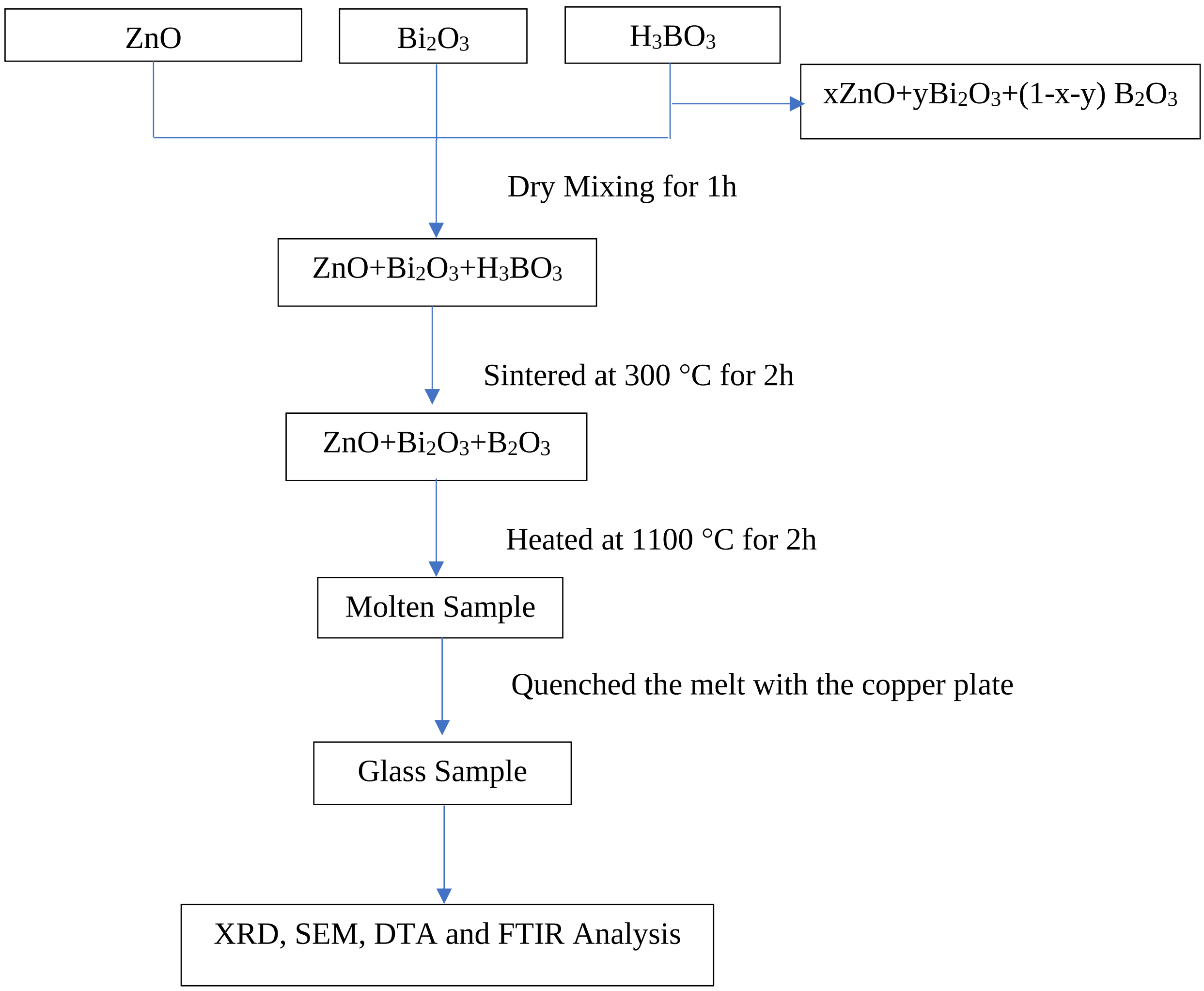


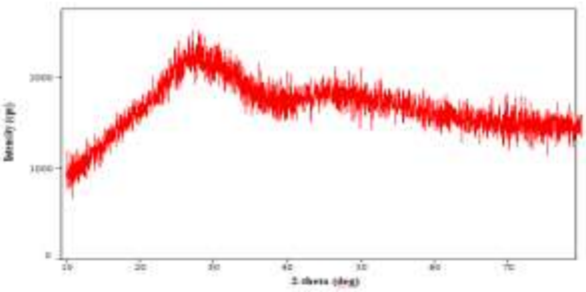
Figure 1 The Flow Diagram Showing the Process of the Sample Preparation

Results and Discussion

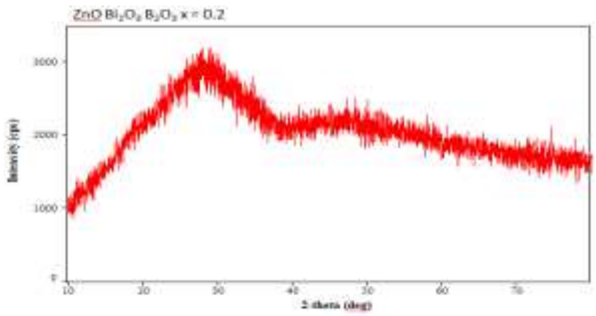
The study of glass structure and thermal properties are important because the properties exhibited by the glasses are both composition and structure sensitive. Network modifier type of zinc oxide based on bismuth borate glasses with the composition of ZnO contents x = 0.1, 0.2, 0.3 have been investigated for structural and thermal characterization. Therefore, the XRD, SEM, DTA and FTIR measurements have been employed for the structural and thermal characterization of these glasses.

XRD Analysis

Bismuth borate glass samples could be prepared in the system where in the ZnO varies corresponding to difference x values, x = 0.1, 0.2 and 0.3. The XRD patterns have a broad hump peak at about 20-30 degree, as in generally observed in several oxide glasses with an amorphous structure. The X-ray diffraction pattern of these prepared three glass samples show only few broad diffuse scatterings at angles characteristic of short-range structured disorder, confirming the amorphous nature of the samples in the composition range studies. The formation of homogeneous glass samples was confirmed by XRD is illustrated. The XRD patterns of the various samples with the composition x are shown in Figure 2(a), (b) and (c).



(a)



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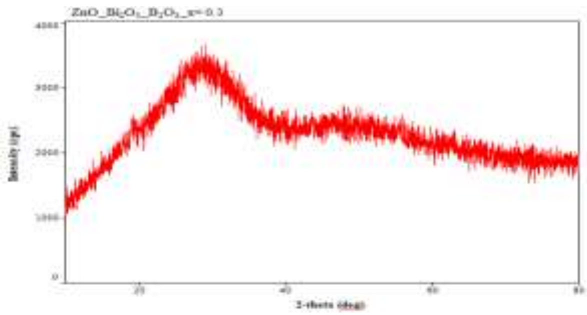
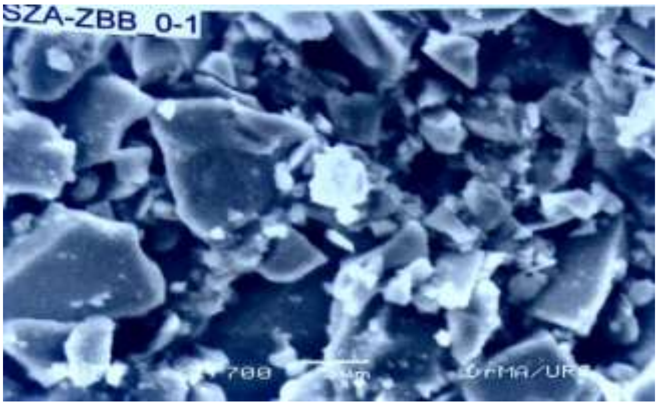


(c)

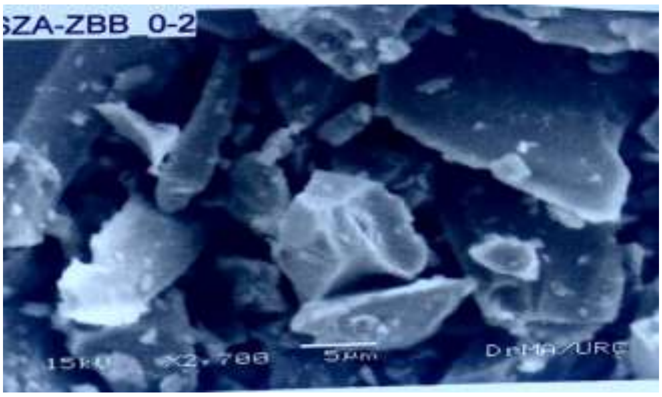
Figure 2 XRD Pattern of x ZnO + y Bi_2O_3 + (1 - x - y) B_2O_3 Glasses for (a) x = 0.1 and y = 0.1 (b) x = 0.2 and y = 0.1 (c) x = 0.3 and y = 0.1

SEM Analysis

SEM method was used to analyze the morphologies of the zinc bismuth borate glasses with different compositions. Figure 3(a), (b) and (c) illustrate the presence of non-spherical and irregularly shaped particles with sharp edges in all compositions. According to the results, all glasses with different compositions were extremely fine and contained grain sizes of 0.96 µm, 0.92 µm and 0.61 µm which tended to compact producing aggregates.



(a)



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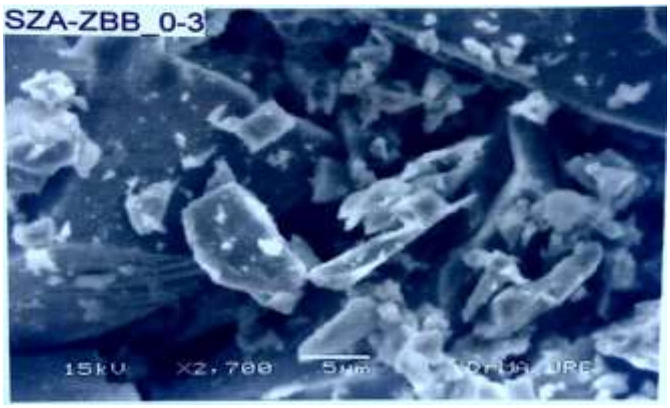
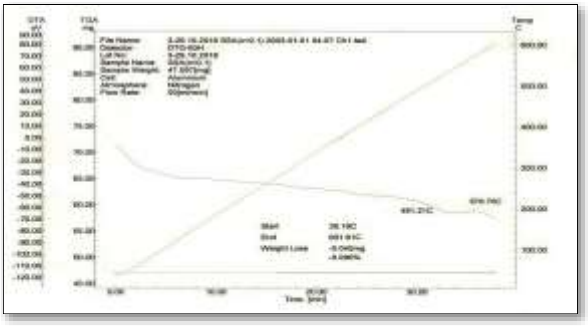


(c)

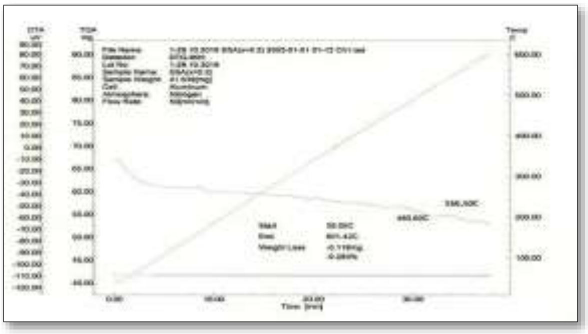
Figure 3 SEM images for ZBB glasses (a) x = 0.1 (b) x = 0.2 and (c) x = 0.3

DTA Analysis

The differential thermal analysis (DTA) studies of modifier oxide ZnO bismuth borate glasses with different composition were shown in Figure 4(a), (b) and (c). From these results, it was found that the transition temperature Tg decreased from 481 ˚C to 476 ˚C as the content of ZnO increased. Similarly, the crystallization temperature Tc also decreased from 571 ˚C to 554 ˚C as the content of ZnO increased. In the result of DTA analysis, the increasing value of ZnO oxide modifier content, the values of glass transition temperature Tg and crystalline temperature Tc were decreased. It is believed that Tg depending on the strength of chemical bonds in the structure. The increase of non-bridging oxygen suggests the breaking of chemical bonds, which successively decrease the Tg and Tc. The thermal stability ΔT was calculated by the equation ΔT = Tc - Tg. The values of the thermal stability of the glasses were obtained 90 ˚C, 87 ˚C and 78 ˚C with different compositions (ZnO = 0.1, 0.2 and 0.3).



(a)



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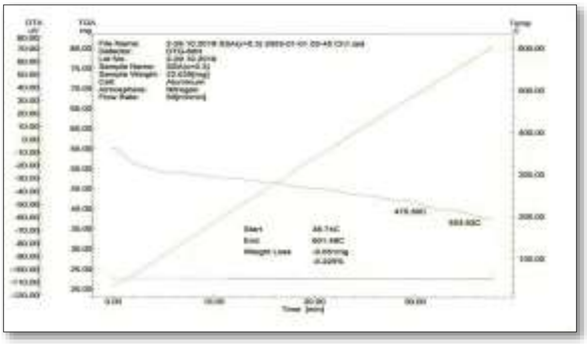


(c)

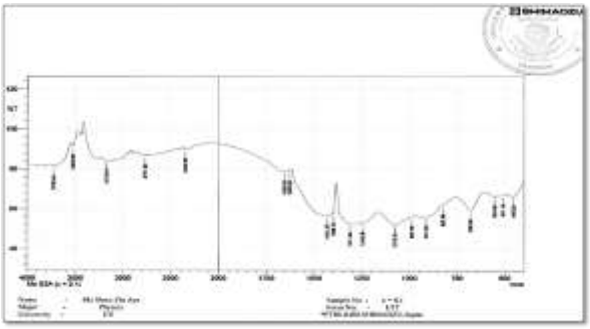
Figure 4 DTA Result of x ZnO + y Bi_2O_3 + (1 - x - y) B_2O_3 Glasses for (a) x = 0.1 and y = 0.1 (b) x = 0.2 and y = 0.1 (c) x = 0.3 and y = 0.1

FT-IR analysis

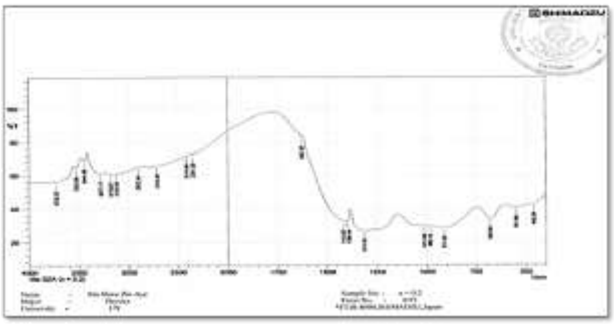
The characteristic absorption band studies of zinc oxide bismuth borate glasses with different composition were shown in Table 1 and Figure 5(a), (b) and (c).

Table 1. The FT-IR Absorption Bands of ZnO - Bi_2O_3 - B_2O_3 Glass with x = 0.1, 0.2, 0.3

Wavelength(cm^{-1})			**FTIR Assignment**
x = 0.1	**x = 0.2**	**x = 0.3**	
455	462	459	Zn-O bond vibrations in tetrahedral ZnO_4 units.
511	551	584	Stretching vibrations of Bi-O bonds in strongly distorted BiO_6 octahedral units, B-O-B bond bending vibration.
680	680	692	Symmetric stretching vibrations of Bi-O bonds in pyramidal BiO_3 units, O_3B-O-BO_3 bending vibrations.
825	914	831	Symmetric stretching vibrations of Bi-O bonds in pyramidal BiO_3 units, stretching vibrations of B-O bonds in BO_4 units from diborate groups.
987	1012	1190	Stretching vibrations of B-O bonds in BO_4 units from tri-, tetra-, and penta-borate groups.
1246	1315	1315	Stretching vibrations of B-O bonds in BO_3 units from meta- and ortho-borate groups.
1398	1413	1626	Asymmetric stretching vibrations of B-O bonds in BO_3 units.



(a)



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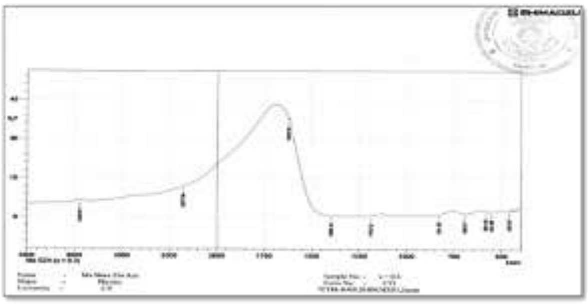

(c)

Figure 5 FT-IR Spectrum of x ZnO + y Bi_2O_3 + (1 - x - y) B_2O_3 Glasses for (a) x = 0.1 and y = 0.1 (b) x = 0.2 and y = 0.1 (c) x = 0.3 and y = 0.1

Conclusions

In this present work, the glass system x ZnO + y Bi_2O_3 + (1 - x - y) B_2O_3 with different compositions (x = 0.1, 0.2 and 0.3) were prepared by melt quenching method. From XRD results, all patterns of the zinc bismuth borate glasses show no sharp Bragg's peak, but only few broad diffuse humps which confirm that all samples have the amorphous nature.

From SEM result, all samples had irregular shape and grain sizes were smaller with the increasing of ZnO modifier content.

The DTA studies showed that the glass transition temperature Tg decreased with the increasing of the glass modifier content ZnO. ZnO, play the role of a network modifier and non-bridging oxygen increases with the increasing of modifier content. It is shown that the increasing of connectivity due to the increasing of non-bridging oxygen (BO_3 to BO_4) causes the thermal expansion to decrease and viscosity to increase. Therefore, the thermal stabilities also decrease with the increasing of ZnO compositions.

From FT-IR results, Zn-O bond converted to ZnO_4 structure in zinc bismuth borate glasses and Bi^{3+} cations were incorporated in the glass structure as BiO_3 and BiO_6 units and also boron ions were incorporated as BO_3 and BO_4 units. According to the results, the structure link of these glasses was improved with the increasing of the modifier content.

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