

Synthesis and Characterization of ZnO-Na₂O-Bi₂O₃-B₂O₃ Glass System

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Abstract - Glasses are characterized by very large possibilities of compositions. There are in fact some hundreds of thousands possible compositions of glasses. The aim of the present study is to prepare quaternary glass systems with the compositions $x\text{ZnO}-(30-x)\text{Na}_2\text{O}-36\text{Bi}_2\text{O}_3-34\text{B}_2\text{O}_3$ (the values of x ranging from 5 to 25 in mol% in steps of 5) by using melt quenching technique. We call the glasses of different compositions obtained with five different names G_1 , G_2 , G_3 , G_4 and G_5 . The glasses are prepared and the obtained glasses appearance and other physical properties are discussed. X-ray diffraction, Fourier Transform Infrared Spectroscopy and Scanning Electron Microscope have been used for the Characterization and study of density of glasses prepared.

Key Words: Glass, melt quenching technique, X-ray diffraction, Fourier Transform Infrared Spectroscopy, Scanning Electron Microscope and Density.

1. INTRODUCTION

Even though a large number of investigations have been reported on bismuth containing binary and ternary glasses, very few attempts have been made to study bismuth containing quaternary glass systems.

Glass forming ability is almost a universal property of condensable matter. A large number of techniques have been developed in the last few decades to form glasses out of a variety of materials. The choice of a particular method of preparation of an amorphous material depends on the material or composition of the materials.

The preparation techniques of amorphous materials can be broadly classified into quenching techniques, atomic deposition techniques and other techniques. The other techniques include inter diffusion, sintering and crystalline solid disorder (other than melting). Quenching techniques include both melt-quenching and vapor quenching techniques. The conventional melt-quenching technique has been employed in the present work. Quenching is a process of cooling a melt at a sufficient rate to bypass crystallization so that the disorder of the liquid is retained in the (glassy) solid state.

Glasses, unlike crystalline counter parts, have widely different physical and chemical properties, which are composition dependent. There are a few experimental techniques exclusively used for obtaining structural information of glasses, S.R. Elliot [1], A. Paul et al [8], and

C.N.R. Rao et al [9]. X-ray diffraction, Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopic analysis provides information about the properties of the amorphous substances.

Density of glass is explained generally in terms of masses and sizes, how tightly the ions and ionic groups are packed together in the substructure. Density is an intrinsic property capable of throwing light on short-range structure. Density value is needed in many experimental techniques such as neutron and X-ray scattering. The density of the current glass prepared is found by using Archimedes method.

2. MATERIALS AND METHODS

2.1 Materials:

The chemicals used here for preparation of glass were Zinc oxide (ZnO, 99% purity, Fisher Scientific), Sodium carbonate (Na₂CO₃ 95% purity, Loba Chemie Pvt. Ltd.), di-Born Trioxide (Boric Oxide) (B₂O₃ 99% purity, Loba Chemie Pvt. Ltd.) and Bismuth oxide (Bi₂O₃ 99% purity, Fisher Scientific). Properties of chemicals used given in table-1

2.2 Sample preparation:

The glasses were prepared by melt quenching technique. In the present investigation, the following quaternary glass samples were prepared: $x\text{ZnO}-(30-x)\text{Na}_2\text{O}-36\text{Bi}_2\text{O}_3-34\text{B}_2\text{O}_3$

The formulations of various $x\text{ZnO}-(30-x)\text{Na}_2\text{O}-36\text{Bi}_2\text{O}_3-34\text{B}_2\text{O}_3$ glass system given in table-2.

Thus using the compositions specified in the table, glasses of the following chemical formulae were obtained.

- 1) 5ZnO-25Na₂O-36Bi₂O₃-34B₂O₃
- 2) 10ZnO-20Na₂O-36Bi₂O₃-34B₂O₃
- 3) 15ZnO-15Na₂O-36Bi₂O₃-34B₂O₃
- 4) 20ZnO-10Na₂O-36Bi₂O₃-34B₂O₃
- 5) 25ZnO-5Na₂O-36Bi₂O₃-34B₂O₃

Table -1: Properties of chemicals used:

PROPERTY	CHEMICALS			
	ZnO	Na ₂ CO ₃	Bi ₂ O ₃	B ₂ O ₃
Molecular wt. (g/mole)	81.39	105.98	465.96	69.62
Density, (g/cc)	5.606	2.54	8.8	2.46
Melting point, (°C)	1975 decompose	851	817	450
Boiling point (°C)	2360	1600	1890	1860
Appearance	White solid	White solid	yellow powder	white, glassy solid
Solubility in water	0.16 mg/100 ml	22gm/100 ml	insoluble	2.2 g/100 ml
Solubility	--	Insoluble in alcohol and ethane	soluble in acids	partially soluble in methanol

Table -2: The formulations of various xZnO-(30-x)Na₂O-36Bi₂O₃-34B₂O₃ glass system

Formulation	ZnO, %mol	Na ₂ CO ₃ , %mol	Bi ₂ O ₃ , %mol	B ₂ O ₃ , %mol
G1	5	25	36	34
G2	10	20	36	34
G3	15	15	36	34
G4	20	10	36	34
G5	25	5	36	34

The Chemicals (in mole %) for various compositions were weighed to get 5 grams. Each of these compositions was ground in a mortar with a pestle to obtain homogeneous mixture. The batch was melted in a porcelain crucible in an electric furnace at a temperature 1273K for about half an hour to obtain a homogenous melt. The homogeneous melt was rapidly quenched onto a stainless steel mould kept at 473K and pressed with another steel plate maintained at a temperature of 373K. The obtained glasses were annealed

for 24 hours at the same temperature to remove mechanical stress.

2.3 Experimental Setup:



Fig-1: The preparation of ZnO-Na₂O-Bi₂O₃-B₂O₃ glass system.

2.4 Characterization of prepared glass system:

Glass samples were crushed into fine powder in porcelain bowl and then used for characterization. All glass samples characterization was carried out by using X-ray diffractometer, Fourier Transform Infrared Spectrometer, Scanning Electron Microscope of SHIMADZU Company, Japan.

The glass samples were crushed into fine powder porcelain bowl and used for XRD, SEM, and FTIR analysis.

X-Ray Diffraction studies were performed on the glass samples powder to determine the amorphous nature (non-crystallinity) of glass samples. Cu-K α radiation of wavelength (λ) 1.54048 Å powered at voltage 40 kV and current 30 mA is employed to carry out the characterization. The Fourier transform infrared spectroscopic measurements have been carried out to determine the functional group present in the glass samples prepared. KBr pellet technique has been used on a FTIR-8400 S. All IR spectra of the glasses were recorded at room temperature in the wave number range of 400–4000 cm⁻¹; Scanning Electron Microscopy (SEM) is one of the most commonly used techniques for characterizing glass systems; SEM analysis was done using S-3700 N, Scanning Electron Microscope (SEM). Scanning electron microscopy was carried out in order to characterize surface morphology and porosity of glasses. For this glass samples were mounted on aluminium mount, using double side adhesive tape and sputtered by gold vacuum and were at an accelerating voltage of 15 kV before observations.

3. RESULTS AND DISCUSSION

The Glass samples of different size and shape were transparent and yellow in color.

3.1 X-Ray Diffraction (XRD):

The X-ray diffractogram showed that XRD patterns of the glasses did not reveal any discrete or sharp peaks

corresponding to the amorphous nature, D.L. Griscom et al [10], B.D. Cullity et al [11]. The amorphous nature of all the samples was confirmed by the absence of Bragg's peak in X-ray diffraction pattern. The X-ray diffractograms of 5ZnO-25Na₂O-36Bi₂O₃-34B₂O₃ and 15ZnO-15Na₂O-36Bi₂O₃-34B₂O₃ glass samples are presented in Fig-2.

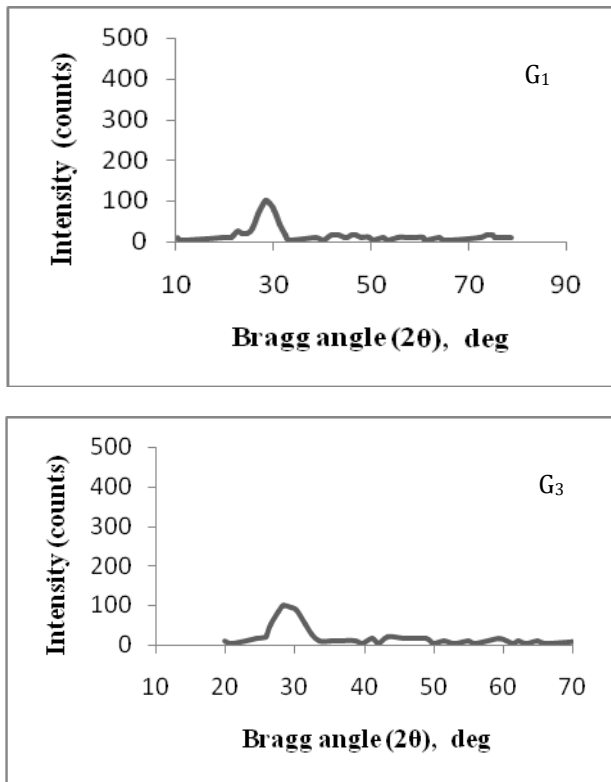


Fig-2: X-ray diffractograms of the glass G₁ and G₃

3.2 Fourier Transform Infrared Spectroscopic Analysis (FTIR):

The samples G₁, G₂, G₃, G₄, and G₅ were subjected to FTIR spectroscopic analysis. The FTIR spectra obtained is shown in the figures. The characteristic peaks of the xZnO-(30-x)Na₂O-36Bi₂O₃-34B₂O₃ glasses were compared with peaks obtained from Bi₂O₃-Li₂O-B₂O₃ and Na₂O-ZnO-B₂O₃ glasses. From the data obtained it was observed that characteristic peaks appears with identical or with minor differences.

The IR analysis of the borate network shows three distinct frequency regions: 1200-1500 cm⁻¹ (B-O stretching of trigonal BO₃ units), 850-1200 cm⁻¹ (B-O stretching of tetrahedral BO₄⁻ units), and 600-800 cm⁻¹ (bending vibrations of various borate segments). The far IR spectra of sodium borate glasses contain only two component bands at about 239 and 475 cm⁻¹ these bands are assigned to the vibrations of sodium cations at their localized sites, E. Kamitsos et al [2], G. Exarhos et al [4]. The band at around 460 cm⁻¹ is attributed to the vibrations of the Bi-O bond in the BiO₆ octahedral unit, L. Baia et al [5], Y. Cheg, H. Xiao et al [6]. The peak about 700 cm⁻¹ is assigned to the pentaborate units, E. Kamitsos et al [2]. The peak at around 1479-1429

cm⁻¹ is attributed to anti-symmetrical stretching vibrations three NBOs of the B-O-B groups. The band at around at 1400-1065 cm⁻¹ is due to linkages like B-O-Zn in the network, suggesting that the entry of Zn⁺² ions into the network, V C Veeranna Gowda And R V Anavekar [7].

The bond around 822 - 900 cm⁻¹ is attributed to the stretching vibrations of tetrahedral BO₄⁻ units. The band around 1090 cm⁻¹ is assigned to vibrations of pentaborate groups, E. Kamitsos et al [3]. The band around 1244-1217 cm⁻¹ is assigned to the stretching vibrations of the B-O band of (BO₃)³⁻ units involving mainly the linkage oxygen connecting different groups. The band around 1344 - 1251 cm⁻¹ is assigned to the stretching vibrations of the B-O of trigonal (BO₃)³⁻ units in metaborates, pyroborates, and orthoborates. The peak at about 1489 cm⁻¹ is assigned to anti-symmetrical stretching vibrations with three NBOs of the B-O-B groups. The FTIR transmission spectra of five glasses (G₁ and G₂) are presented in Fig-3.

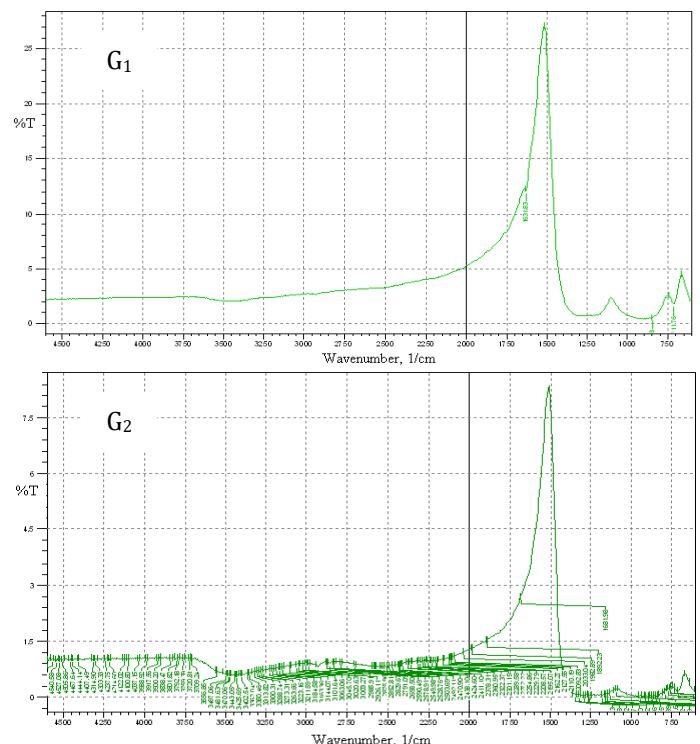


Fig-3: FTIR transmission spectra of glasses G₁ and G₂

3.3 Scanning Electron Microscope (SEM):

It was observed that in Fig-4, SEM micrographs of 5ZnO-25Na₂O-36Bi₂O₃-34B₂O₃ glass system at different magnification (A=250 X, B=500 X, C=1k X, and D=4.2k X) and based on SEM micrographs of G₁, G₂, G₃, and G₄ glasses at 2kX magnification shown in Fig-4. Particularly, microstructures of G₃ and G₄ glasses evidently indicate almost no porosity and high densification was achieved, Chuang-Chung Chiang et al [12].

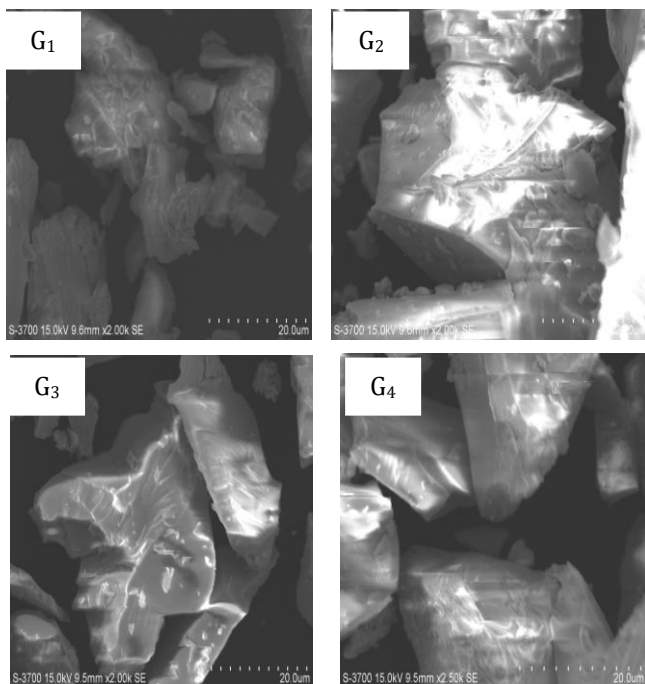


Fig-4: SEM micrographs of G₁, G₂, G₃, and G₄ glasses

3.4 DENSITY:

In this method, the weight of the glass sample was measured both in air (W_{air}) and when immersed in xylene (W_{xylene}). The density was calculated using the equation

$$\rho = W_{air} \times 0.86 / (W_{air} - W_{xylene})$$

Where 0.86 g/cm³ is the density of xylene at room temperature (25 °C). The density values were calculated precise to ± 0.01 gm/cm³.

Density measurements of the present glasses having the composition $xZnO-(30-x)Na_2O-36Bi_2O_3-34B_2O_3$ where $5 \leq x \leq 25$ were measured by the Archimedes. Fig-5 present the density data in the constant Bi_2O_3 and B_2O_3 glasses as a function of ZnO content, from the figure it is clear that the change in density with ZnO composition has shown inflections with increasing ZnO concentration.

As the relation was shown an inverted S-shape, it was found that the density is dependent on composition. The increase in density of the glasses under the present study may be attributed to formation of ZnO_4 tetrahedral and formation of borate groups containing non-bridging oxygen (NBO).

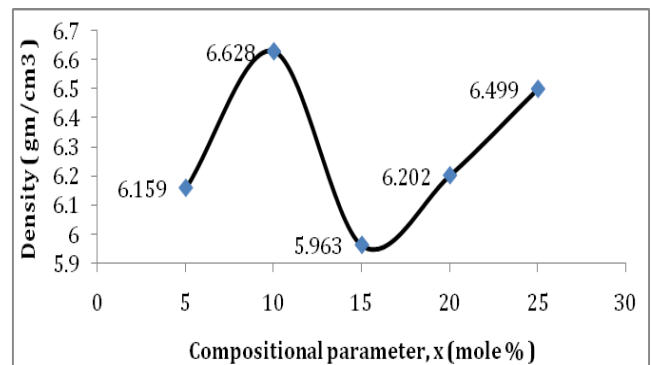


Fig-5: Variation of Density with compositional parameter of $xZnO-(30-x)Na_2O-36Bi_2O_3-34B_2O_3$ glass system

4. CONCLUSION

The XRD, SEM analyses that were carried out on the quenched samples confirmed their amorphous and glassy nature respectively and the density for the present glass system has shown strong positive deviation due to the increase in the oxide packing density with ZnO content.

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