

Ultrasonic and Structural Studies of Lead Sodium Borate Glasses Doped with ZnO

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Abstract: Glasses with various proportions of $[50\text{B}_2\text{O}_3\text{20Na}_2\text{O}] - (30-x)\text{PbO} - x\text{ZnO}$ ($x=0, 5, 10, 15, 20, \text{ and } 25 \text{ mol\%}$), have been prepared by the melt quenching technique. Elastic properties, X-ray and FT-IR spectroscopic studies have been employed to study the role of ZnO on the structure of the investigated glass systems. Elastic properties and Debye temperature have been investigated using sound wave velocity measurements at 4MHz at room temperature. The amorphous nature of these samples was verified by XRD and SEM is used to study the morphology of these glass samples. X-ray diffraction studies on all the glass samples were recorded at room temperature. Peak-free X-ray spectra confirmed the amorphous nature of the glasses. FTIR spectra of these glasses revealed that the borate network is affected by the increase in the concentration of ZnO content and the mixed alkali oxides. FTIR studies confirmed the presence of both $[\text{BO}_3]$ and $[\text{BO}_4]$ units, indicating that the glass network is made up of these two units placed in different structural groups. The non-linear variation of peak positions of B-O-B bending and stretching of $[\text{BO}_3]$ and $[\text{BO}_4]$ units. The structural explanation has been carried out by studying the ultrasonic velocities (longitudinal velocity U_l and Shear velocity U_s) and density of these glass samples.

Keywords: Ultrasonic velocity, Density, SEM, FTIR, XRD

1. Introduction

Glasses having high transparency, high chemical durability and excellent thermal, optical and electrical properties are the key materials in microelectronics, optics and optical fibre technology. [1]. Addition of some non-conventional glass former materials such as lead oxide (PbO) into the glass matrix may lead to a drastic change in the properties such as high density, high thermal and chemical durability, high non-linear optical susceptibility, high refractive index and excellent infrared transmission. These enable the use of the glasses in various applications such as optics and optoelectronics etc [2]. PbO is not a glass-forming oxide by itself, but when incorporated in considerable quantities into the other glass-forming oxide systems such as borate oxides.[3]

The structural role of PbO in oxide glasses is unique since lead oxide is known to behave both as a modifier and as network former depending on its content added in to the glass.[4]

Meanwhile, these glasses and their crystalline counterparts are considered to be good candidates for the optically induced elasto optic[5]. These glasses containing transition metal ions have attracted attention because of their potential applications in electrochemical, electronic, and electro-optic devices. A host of borate rich glasses containing alkaline earth oxides along with ZnO, PbO, TeO₂, Bi₂O₃, MgO, CaO, SrO, and BaO as glass modifiers are optimistic materials for their probable applications in the fields of optical communications (optical fibres), laser hosts, optical filters, X- and γ -ray absorbers, photonic devices, and so forth. Infrared spectroscopy (IR) is an important tool for understanding the structure and dynamics of amorphous materials. It is also used to assign the observed absorption peaks to the proper vibration of the atoms in geometric grouping .

ZnO applications in the field of glass-ceramics, thermal and mechanical sensors, reflecting windows or may be used as layers for optical and opto-electronic devices etc. Zinc oxide is a wide band gap metal oxide that is commonly used in various applications such as photo catalyst, photovoltaic, gas sensor and display devices, laser diodes and light emitting diodes (LEDs) [6]. ZnO-PbO -B₂O₃ glasses also show shielding against gamma radiation. Radiation resistance makes ZnO a suitable candidate for space applications . The zinc oxide based glasses are good candidates for ultrasonic materials [7]. The purpose of this work is to examine the effect of ZnO on structural properties of B₂O₃-Na₂O-PbO-ZnO glasses with the help of X-ray diffraction(XRD), density, Fourier transform infra-red spectroscopy(FTIR) and ultrasonic velocity measurement.

2. Experimental

The glass samples having the general chemical formula $(30-x)\text{PbO} - [20\text{Na}_2\text{O} - 50\text{B}_2\text{O}_3] - x\text{ZnO}$ ($x=0, 5, 10, 15, 20 \text{ and } 25 \text{ mol\%}$), have been prepared by the melt quenching technique. Required quantities of analar grade ZnO, PbO, Na₂O and B₂O₃ were mixed together by grinding the mixture repeatedly to obtain a fine powder. The mixture was melted in a porcelain crucible in an electrically heated furnace under ordinary atmospheric conditions at a temperature of about 1200K for 2 hours to homogenize the melt. The obtained glass samples from the melt quenching into preheated Copper mould were heat treated at a temperature of about 20K below their calorimetric glass transition temperature for 2 hours to remove any internal stresses. The obtained glasses were lapped and two opposite sides were polished to be suitable for use in the ultrasonic velocity measurements. The glass compositions are given in Table 1.

Table 1: Composition of the glass samples

S.No	Glass specimen	Composition in Mol% B ₂ O ₃ -Na ₂ O-PbO-ZnO
1	BNPZ 1	50-20-25-5
2	BNPZ 2	50-20-20-10
3	BNPZ 3	50-20-15-15
4	BNPZ 4	50-20-10-20
5	BNPZ 5	50-20-5-25

The infrared absorption spectra of the glasses in the wave number range 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹ were measured at room temperature by an infrared spectrophotometer. XRD were recorded in X-ray diffractometer. The ultrasonic wave velocities (longitudinal (U_l) and shear (U_s)) at room temperature were obtained using the pulse-echo interferometer method. In this method, x-cut and y-cut transducers operated at a fundamental frequency of 4MHz and a digital ultrasonic flaw detector were used.

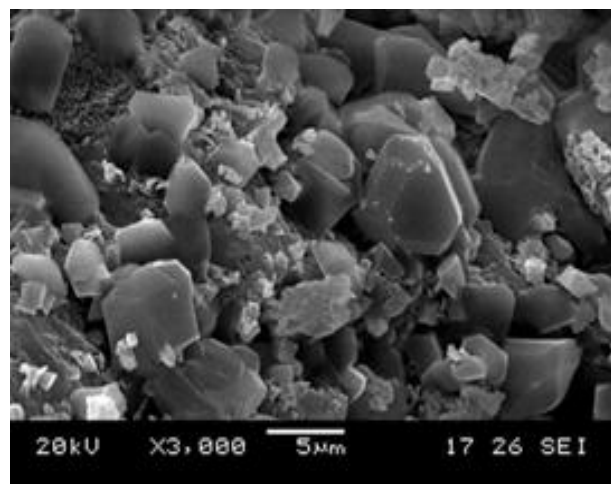


Figure 1: SEM analysis of BNPZ3 glass sample

Results and Discussions

3.1 Scanning electron microscope

The glass homogeneity was characterized by scanning electron microscope. Figure .1 shows the SEM image of **BNPZ3** glass sample. It is observed that the sample exhibits surfaces without microstructure and different sized grain particles. The image clearly indicates that there is no crystalline phase existing in the overall surface of the samples. This further confirms the amorphous nature of the glass samples.

3.2 XRD analysis

XRD spectrum of **BNPZ3** glass sample is shown in Fig.2 The XRD spectrum show a broad halo, which reflects the characteristic of amorphous or glass structure, obtained at around $2\theta=30^\circ$ [8]. The absence of sharp, strongly diffracted beams in the x-ray diffraction patterns from glass indicated that there were no well defined planes in the structure on or around which the constituent atoms were regularly arranged.

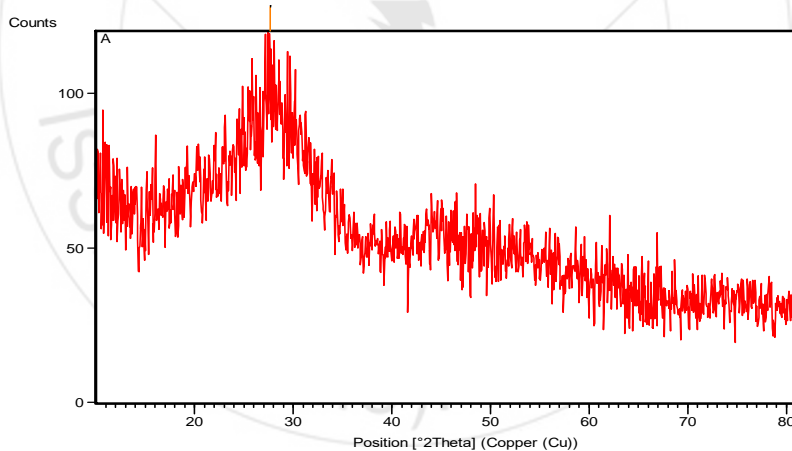


Figure 2: XRD spectrum of BNPZ3 glass sample

3.3 FT-IR Analysis

Infrared spectroscopic studies were used to get essential information about the arrangement of the structural units in the glass samples. It is assumed that the vibrations of a characteristic group of atoms in the glass network are independent of vibration of the other neighbouring groups in the glass [9].

Fig.3 shows the FTIR spectra of the glass samples, the spectra were obtained between 4000-400 cm⁻¹. The overall spectra consist of distinctive absorption peaks centred in the mid region extending from 450-1650 cm⁻¹. The FT-IR spectra showed four distinct frequency regions. In the band at 754 is due to B-O-B bending vibrations of BO₃ and BO₄ groups. Intensity of this band has increased with an addition

of zinc oxide.[10] The new band at 1150 has been assigned to B-O bond stretching of BO₄ group vibration with an increase in the percentage of ZnO, this band shifts towards the higher wave number from 1150 to 1165. The weak band at 665 is due to PbO bond vibration. The band at 1600 is due to asymmetric stretching of the B-O bond of BO₃ unit[11]. The band from 2310 to 3000 is due to hydrogen bonding on OH group.[12] The decrease in intensity of bands at 1600 with the contents of zinc and corresponding increase in intensity of band at 1150 reveal the conversion of trigonal BO₃ to tetrahedral BO₄ groups.

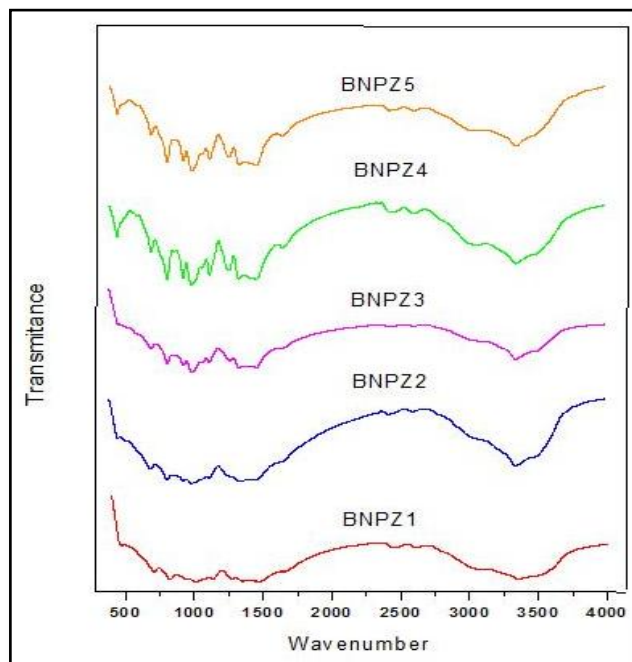


Figure 3: FT-IR Spectra of prepared glass samples

The structural changes involved with the addition of ZnO were analyzed and was known that zinc ions were produced in the triangular and tetrahedral borate units

3.4 Density and Ultrasonic Velocity

The elastic constants of the glass specimen were calculated at room temperature using the measured density (ρ), longitudinal velocity (U_l) and shear velocity (U_s) at room temperature.

The density of the glass samples were measured using Archimedes's Principle. Ultrasonic longitudinal and shear velocities of the specimen were determined by using the conventional pulse-echo method at room temperature by making use of 2.25 MHz X-cut and Y-cut transducers.

Density is a useful physical parameter used to investigate the degree of structure compactness, modification of the geometrical configurations of the glass network, change in coordination and variation of the dimension of the interstitial holes.

The experimental values of density (ρ), longitudinal ultrasonic velocity (U_l) and shear ultrasonic velocity (U_s) of the different glass specimen with respect to the change in the mol% of ZnO are listed in Table 2.

Table 2: Ultrasonic velocities and density

Name of the sample	Density $\rho/(\times 10^3 \text{ kg. m}^{-3})$	Ultrasonic Velocity $U/(\text{m.s}^{-1})$	
		Longitudinal Velocity (U_l)	Shear Velocity (U_s)
BNPZ1	3.2751	4133	2197
BNPZ2	3.4528	4414	2203
BNPZ3	3.5201	4483	2207
BNPZ4	3.7722	4500	2212
BNPZ5	3.8371	4643	2241

For BNPZ glasses, the density shows a continuous increase with increase in mol% of ZnO. The structure of the glass depends on the nature of the ions entering in the network and hence the density of glass [13]. It is seen from the Table 2 that both longitudinal velocity (U_l) and shear velocity (U_s) increase almost linearly with the concentration of ZnO, but the rate of increase of U_l is greater than that of U_s . The increase in ultrasonic velocity has been attributed to an increase in density because of the transformation of coordination of Boron ions. These increasing modes indicate that ZnO tries to form a ring structure in the form of a regular ZnO_4 tetrahedral coordination [14].

Conclusion

Zinc doped sodium borate glass in the form of $[50\text{B}_2\text{O}_3 \cdot 20\text{Na}_2\text{O}] - (30-x)\text{PbO} - x\text{ZnO}$ were prepared and structural properties have been studied. The following conclusions were arrived. XRD patterns have confirmed the amorphous nature of these prepared glass samples. Morphological analysis of SEM shows the amorphous nature of the prepared glass samples. The FT-IR spectral analysis confirms the presence of absorption bands due to characteristic groups of BO_3 and BO_4 units. The increase in ultrasonic velocity has been attributed to an increase in density because of the transformation of coordination of boron ions. These increasing modes indicate that ZnO tries to form a ring structure in the form of a regular ZnO_4 tetrahedral coordination.

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