

Effect of Zno on Physical, Structural and Mechanical Properties of $B_2O_3 - Na_2O - ZnO$ Glasses

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Abstract: A series of transparent glasses with the composition $70B_2O_3-(30-x)Na_2O-xZnO$ ($x= 5, 10, 15, 20$ and 25 mol\%) were prepared and characterized using X-ray diffraction (XRD), differential thermal analysis (DTA), Fourier transform infrared (FTIR) and ultrasonic studies. XRD analysis confirmed the glassy nature of the prepared samples. The compositional dependence of the glass transition (T_g), crystallization (T_c) and melting (T_m) temperatures were determined by DTA investigations. The values of T_g , T_c , T_m , thermal stability and Hruby's parameter show a fall upto 5 mol% and then shoots up for higher concentration of ZnO content. FTIR spectra revealed that the glass network consists of BO_3 , BO_4 and ZnO_4 structural units. Ultrasonic (longitudinal and shear) velocities and density have been measured at room temperature using the pulse echo overlap and relative measurement methods respectively. The density increases and molar volume decreases while both velocities decrease at 5 mol% of ZnO and then increase with further addition of ZnO . The calculated parameters such as elastic moduli, microhardnes and Debye temperature show similar variations of ultrasonic velocities whereas opposite trend is observed in Poisson's ratio and this is due to the formation of B-O-Zn bonds. The results showed that the Zn^{2+} ions act as network former in the samples above 5mol% of ZnO .

Keywords: DTA, FTIR, ultrasonic velocity, rigidity.

I. Introduction

Boron trioxide is one of the best glass formers with high glass forming ability under normal quenching rates. The structures of pure vitreous borate glass consist of a random network of B_3O_6 and BO_3 triangular units connected by B-O-B linkages. The insulting property of borate glasses turns into a electronics or semiconducting or ion conducting nature when alkali oxides are added to them.

Alkali borate glasses doped with divalent oxide such as MgO , PbO and ZnO have an interesting behavior and draws attention of researchers owing to their dual role and various technological applications. In particular, zinc oxide is a low cost, non-toxic and environmental acceptability material [1-3]. Addition of ZnO into the alkali borate network produces the unique combinations of electrical, optical and magnetical properties and also reduces the coefficient of thermal expansion and make the glass non-hygrosopic, high chemical stability and non-toxic [4,5]. Due to this properties with non-toxic and non-hygrosopic nature, ZnO doped glasses are used in the development of opto-electronic devices, solar convertors, ultraviolet emitting lasers and gas sensors [6,7].

The incorporated zinc oxide in glass structures is expected to acts as a intermediate oxide either as network former or as network modifier. As former, ZnO enters the network with ZnO_4 structural units and as network modifier, zinc ions are octahedrally coordinated and behaves like any other conventional alkali oxides. [8-10]. Dual role of ZnO in zinc borate glasses was reported by Cetinka Ya Colak et al. [11]. Yao et al. [12] have prepared copper- lead and copper zinc borate glasses and discussed that the addition of ZnO enhance the network structure. The elastic properties and spectroscopic studies on $Na_2O-ZnO-B_2O_3$ glasses have indicated that the Zn^{2+} ions incorporated into the network act as a former [13]. The aim of this present work is to investigate the effect of ZnO as a replacement for Na_2O in the B_2O_3 - Na_2O-ZnO glass system on its thermal, structural and mechanical properties by differential thermal analysis, infrared spectroscopy and ultrasonic velocity measurements respectively. Three techniques were incorporated in order to correlate the changes in the properties as a result of ZnO addition.

II. Experimental details

2.1 Preparation of glass samples

Glasses of the composition $70B_2O_3-(30-x)Na_2O-xZnO$, where $x= 0, 5, 10, 15, 20$ and 25 mol\% were prepared by the conventional melt- quench technique. Appropriate amount of Reagent grade B_2O_3 , Na_2O and ZnO was ground repeatedly using an agate mortar to achieve good homogeneity. The mixture was then placed in a silica crucible and heated in a muffle furnace at $1100^\circ C$. The melt which had a high viscosity was then transferred to a stainless steel mold to form circular shape. Then the samples were placed in a oven and annealed

at 300 °C for 1hours. The prepared samples were polished and the surfaces were made perfectly plane and smoothened by diamond disc and diamond powder In this way,6 different compositions of the $B_2O_3 - Na_2O - ZnO$ glasses were prepared. the nomenclature and compositions are shown in table 1. The obtained glasses were then used for characterization purposes.

S. No.	Nomenclature	Composition in mol%	Remarks
1	BN	70-30-0	Mol% of B_2O_3 is constant
2	BNZ05	70-25-5	
3	BNZ10	70-20-10	
4	BNZ15	70-15-15	
5	BNZ20	70-10-20	
6	BNZ 25	70-05-25	

2.2 Glass characterization

X-ray diffraction measurement

Powder X-ray diffraction (XRD) spectra for all the samples in the present investigation were recorded at room temperature using, Dist Focus-Diverg Slit 91.00 mm was used with a scanning step time of 10.138 sec. the sample was firmly pressed into aluminum holder with an area of 10 mm. XRD spectra of Bragg's peak confirm the amorphous nature of the glasses, which is shown in Fig 1.

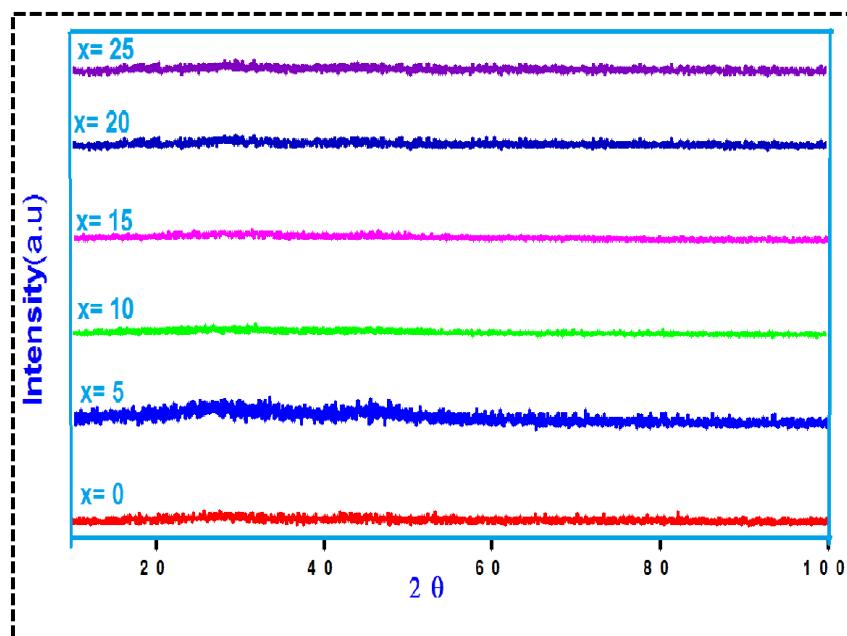


Fig. 1. XRD patterns of BNZ glasses

Differential thermal analysis

The glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) of these glasses were determined by Differential scanning Calorimetric (DSC) traces, recorded using thermal analysis NETZSCH-STA449FS JUPITER instrument at a heating rate of 20 °C/min in nitrogen gas atmosphere.

FTIR analysis

The infrared spectra of the powdered glasses were recorded at room temperature (303K) in the wavenumber range 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹ by SHIMADZU 8400 FTIR spectrometer, using KBr pellet technique.

Density measurements

The density of the glass samples was determined by the standard Archimedes principle. These measurements were done using single pan balance and water as an inert immersion liquid. The density was obtained from the relation

$$\rho = \left(\frac{W_a}{W_a - W_b} \right) \rho_w \quad (1)$$

where, W_a and W_b are the glass sample weight in air, and water respectively, The molar volume (V_m) has been calculated as (M/ρ) , where M is the molar weight. ρ is the glass density were calculated by multiplying X times the molecular weights of the various concentrations

Ultrasonic velocity measurements

The Pulse-echo technique is a key method for making precise measurements of ultrasonic velocities which use a broad band buffered piezoelectric transducer (X-cut transducer for longitudinal wave and Y-cut transducer for shear wave) at room temperature using MATEC model 7700 ultrasonic system. The two velocities and density were utilized in determining elastic constants, Poisson's ratio, microhardness and Deby temperature using the following relations

$$L = \rho U_\ell^2 \quad (2)$$

$$G = \rho U_s^2 \quad (3)$$

$$K = L - \left(\frac{4}{3} \right) G \quad (4)$$

$$\sigma = \left(\frac{L - 2G}{2(L - G)} \right) \quad (5)$$

$$E = (1 + \sigma) 2G \quad (6)$$

$$H = (1 - 2\sigma) \frac{E}{6(1 + \sigma)} \quad (7)$$

$$\theta_D = \frac{h}{K} \left(\frac{9N}{4\pi V_m} \right)^{\frac{1}{3}} U_m \quad (8)$$

$$U_m = \left[\frac{1}{3} \left(\frac{2}{U_s^3} + \frac{1}{U_\ell^3} \right) \right]^{-\frac{1}{3}} \quad (9)$$

where h , k , N , V_m , and U_m are the Planck's constant, Boltzmann's constant, Avogadro number, molar volume and mean ultrasonic velocity respectively.

III. Results and discussion

The scrutiny of Table 2 depicts the values of density and molar volume of the BNZ glasses. Generally, the density of the glasses is explained in terms of a competition between the mass and size of the various structural units present in the glass. In otherwords, density explain how tighty the ions and ionic groups are placed together in the structure [14]. In the present study, the density of the glass system was found to increases from 2.34 kgm^{-3} to 2.86 kgm^{-3} while molar volume decreases from 29.40 to $26.10(\times 10^{-6} \text{ m}^3/\text{mol})$ as ZnO increases at the expense of Na_2O content. The increasing density of the glasses is due to the replacement of lighter Na_2O (molar mass 61.97 kg/mol) by the heavier ZnO (molar mass 81.40 g/mol) together with the decrease in molar volume. The decrease of the molar volume with the addition of ZnO was most likely due to the lower ionic radius of Zn^{2+} ions (~74P pm) Compared to Na^+ ions (~pm) [15]. Besides these variations of the glass samples are attributed to the formation of new linkages in the glass structure.

To understand the effect of ZnO content on the thermal properties of $B_2O_3-Na_2O-ZnO$ glasses, DTA curves were obtained (Fig.2). It is observed that all the curves are similar in nature and the first endothermic hump at $315^\circ C$ (for the binary BN glass) corresponding to glass transition temperature (T_g). Glass transition temperature is very sensitive to know any change in the coordination number of the network forming atoms and also destruction of the network structure brought about by the formation of non-bridging oxygens. Therefore, systematic shifting of T_g to lower values with the incorporation of ZnO ($x=5 \text{ mol\%}$) into the BN glass and then shifted to higher values with increasing zinc ions at the expense of Na_2O content suggest some type of modifications may exists within the borate network. The next peak at $638^\circ C$ is a exothermic peak which is corresponding to crystallization temperature and this followed by another endothermic peak at $873^\circ C$ corresponding to melting temperature (T_m). T_c and T_m also decrease first and then increase with increasing ZnO content. In lower concentration of ZnO ($x=5 \text{ mol\%}$) acts as network modifier, these oxygens break the local structure of B-O-B bonds and may occupy interstitial positions and form weak ionic Zn-O bond. At $x > 5 \text{ mol\%}$,

the Zn^{2+} ions fills the interstitial sites of the BNZ glass structure and increases the T_g , T_c and T_m values, resulting in the formation of bridging oxygen in the place of NBOs through ZnO_4 units. This indicates the dominant role of bridging oxygen atoms in glass structures where ZnO behaves as a network former. From the Table 2, two parameters have been commonly employed to evaluate thermal stability index of glasses,

- (i) Glass stability factor (S) = $T_c \cdot T_g$
- (ii) Hruby's parameter (K_{g1}) = $\frac{T_c - T_g}{T_m - T_c}$.

Hruby's parameter gives the information on the stability of the glass against devitrification. The values of S and K_{g1} shows similar variation of T_g and are found that the glass with the higher ZnO concentration have strong structural units.

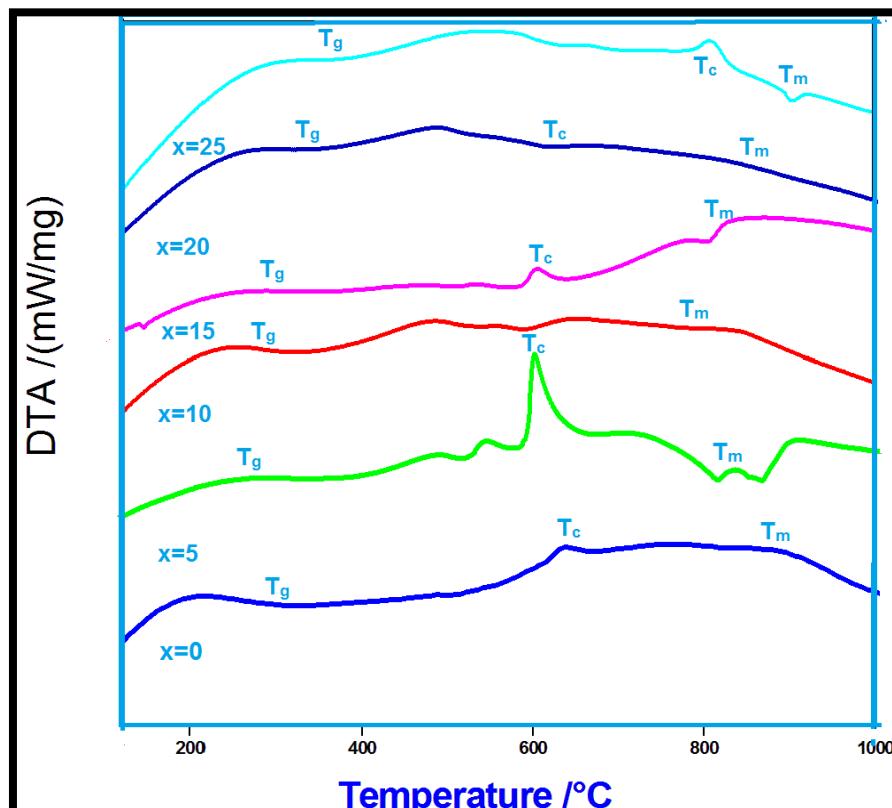


Fig.2.DTA curves of BNZ glasses

Table 2 Physical properties of $B_2O_3-Na_2O-ZnO$ glass system

Parameters	X=0	X=5	X=10	X=15	X=20	X=25
Density (Kgm ⁻³)	2.34	2.46	2.55	2.64	2.79	2.87
Molar volume (x10 ⁻⁶ m ³ /mol)	29.40	28.70	28.30	27.70	26.60	26.10
Glass transition temperature (°C)	315	306	320	332	342	347
Crystallization temperature (°C)	638	565	589	614	725	825
Melting temperature (°C)	873	779	803	820	911	936
Thermal stability (S)	323	259	269	282	383	478
Hruby's parameter (K_{g1})	1.37	1.21	1.26	1.37	2.06	4.31

The FTIR spectra can provide information about molecular vibration or rotation associated with a covalent bond and is usually used to survey the variation of glass structure with change in composition. Fig.3 shows the FTIR spectra of studied glasses. Generally, the vibrational modes of the modified borate glass network are mainly active in three infrared spectral regions. The first region in the range between 1200 and 1600 cm⁻¹ is due to the B-O stretching vibrations of trigonal BO_3 units, the second band which occurs at 800-1200cm⁻¹ is due to the B-O stretching vibration of tetragonal BO_4 units and the third region around 700 cm⁻¹ which corresponds to the B-O-B bending vibration of bridging oxygen atoms [16]. From the Fig.3, the broad band observed at 1380cm⁻¹ is attributed to the B-O bonds due to stretching vibration in the BO_3 units[17] whereas the band at 1021cm⁻¹ is due to symmetric vibration of the B-O bonds in BO_4 units [18] and the another band around 680cm⁻¹ is due to bending vibration of B-O-B [19,20] in the borate network. The bands at lower frequencies (400-500 cm⁻¹) are observed in the spectra and can be attributed to ZnO_4 . ZnO may acts as

a network former or modifier in the glass structures and this can be known from the FTIR spectra. The peak does not appear in the binary glass but the addition of ZnO at the expense of Na₂O, the band around 474 cm⁻¹ appeared at higher concentration of ZnO ($x > 5$ mol%) indicating presence of Zn-O tetrahedral bending vibrations of ZnO₄ units. This confirms that ZnO acts as a network former more than 5 mol% of ZnO concentration. The addition of ZnO to the borate network breaks the B-O-B bonds and creates NBOs, further addition of ZnO gives extra oxygen atoms which are accommodated in the network, forming ZnO₄ and BO₄ units. As the concentration of ZnO increases, the intensity of the band due to [BO₃] decreases corresponding increases in the intensity of [BO₄] units.

The variation of ultrasonic velocities for the glasses as a function of ZnO content as shown in Table 3. The incorporation of 5 mol% of ZnO into the B₂O₃-Na₂O structure shows that ultrasonic velocities decrease and then increase with further addition of ZnO ($x < 5$ mol%), ZnO acts as a network former or network modifier, when acting as a network modifier in the structure, it may break B-O-B bonds and leads to formation of NBOs atom together with the defects known as dangling bonds [21]. In this position, zinc ions are octahedrally coordinated. However it plays a different role when played as a network former, ZnO enters the glass network as ZnO₄ structural units, where Zn²⁺ ions are linked to four oxygen ions in a covalent bond configuration. In the present study, the addition of Zn²⁺ ions rearrange the bonding of BN glass and causing the splitting of B-O-B and B-O-Na linkages, results in the structural rearrangement of glass due to the formation of non-bridging oxygens and this leads to decrease in the connectivity of the glass network as well as ultrasonic velocities. The increase in ultrasonic velocities with ZnO (from 10 to 25 mol%) suggest that Zn²⁺ is incorporated into the network of the BNZ glass system as ZnO₄ structural units and the formation of bridging linkage, B-O-Zn is possible and also it may be due to the conversion of BO₃ units into BO₄ units. As a result, the replacement of Na₂O by ZnO ($x > 5$ mol%) improves mechanical properties and strength of the cross-link between chains in the borate network.

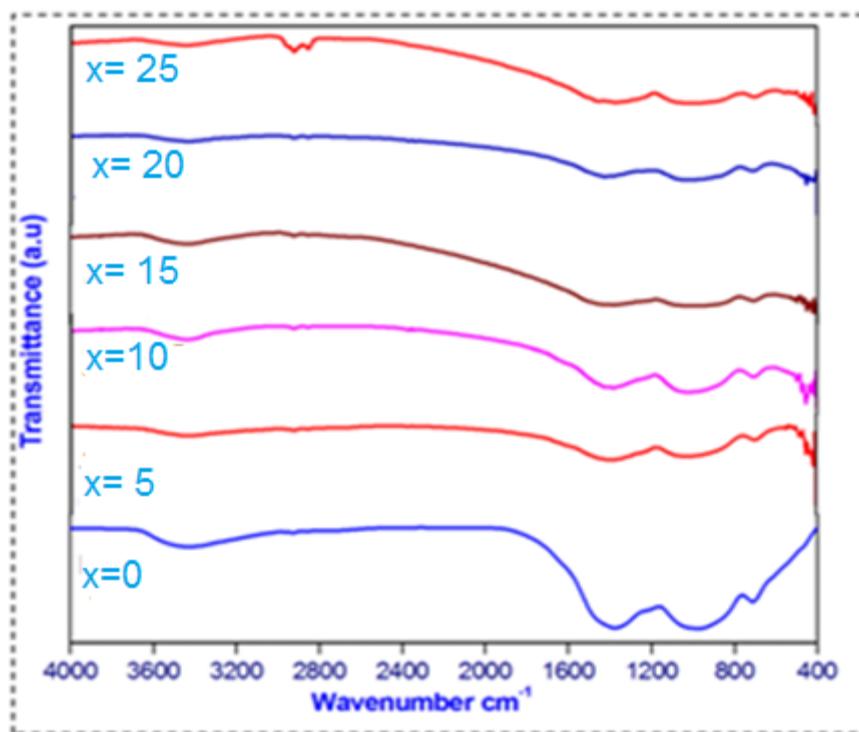


Fig.3.FT-IR spectra of BNZ glasses

The change in elastic moduli, such as longitudinal, shear, bulk and Young's moduli revealed the existence of alteration in stiffness and rigidity of the glass network. The similar behavior as that of ultrasonic velocities is observed that the elastic moduli decrease first and then increase. It confirms weakening of the glass network at 5 mol% due to the addition of ZnO into the borate glass network. Further addition of ZnO, all the elastics moduli found to increase and this leads to strengthening of the glass network. On comparison, the absolute value of longitudinal modulus (L) is always higher than the shear modulus (G) indicating that the glasses can withstand larger longitudinal stress compared to shear stress.

Generally, a low σ value between 0.1 and 0.2 shows higher resistance towards lateral expansion compared to σ value between 0.3 and 0.5 [22]. The replacement of Na₂O with ZnO should decrease cross-link density and

increases. Further replacement of ZnO, there is a sudden decrease of σ which indicate increase in cross-linking of the borate network. The variation of H with ZnO mol% is presented in Table 4. It can be seen that the microhardness has the same attitude as the elastic moduli with increase of ZnO mol%. Hence the observed decrease in BNZ 05 is related to the decrease in the rigidity of glass and beyond 5 mol% of ZnO increases the rigidity of the glass. Thus all these changes in the properties with varying concentration of ZnO indicate that ZnO makes the glass network somewhat less at 5 mol% and for $x > 5$ that stabilizes the glass network.

Debye temperature (θ_D) is associated with the highest allowed mode of vibration and it reflects stability and strength of bonds of a solid [23,24]. In the present study, the decrease in θ_D for 5 mol% of ZnO may be due to the concurrent decrease in ultrasonic velocities while the increase in θ_D at $x > 5$ mol% may be due to increase in ultrasonic velocities. However, the similarity behavior of θ_D with ultrasonic velocities strongly suggests that θ_D is dominant by ultrasonic velocities which indicate strong influence for elastic behavior on θ_D . Thus the increase in θ_D for $x > 5$ mol% is an indicator of the increase in rigidity and stiffness of the glass. Therefore, the results from thermal, FTIR and ultrasonic studies of the glass structure under investigation showed that the structure of glass network changing with composition.

Table 3. Longitudinal velocity, shear velocity, longitudinal modulus and shear modulus of BNZ glasses

Glass samples	Ultrasonic velocities		Longitudinal modulus (GPa)	Shear modulus (GPa)
	Longitudinal(U_L)	Shear (U_s)		
BN	5698.2	3028.7	75.98	21.46
BNZ05	4784.6	2501.9	56.32	15.40
BNZ10	4871.3	2613.2	60.51	17.41
BNZ15	4934.8	2698.5	64.29	19.22
BNZ20	5051.3	2783.4	71.19	21.62
BNZ25	5166.0	2877.7	76.59	23.77

Table 4 Bulk modulus Young's modulus Poisson's ratio microhardness and Debye temperature of BNZ glasses

Glass samples	Bulk modulus (GPa)	Young's modulus (GPa)	Poisson's ratio σ	Microhardness (GPa)	θ_D K
BN	47.36	55.94	0.3031	1.3334	394.4
BNZ05	35.78	40.40	0.3118	1.1770	328.9
BNZ10	37.29	45.20	0.2980	1.2422	344.8
BNZ15	38.66	49.47	0.2867	1.3028	357.8
BNZ20	42.37	55.42	0.2820	1.4093	374.1
BNZ25	44.90	60.61	0.2750	1.4826	423.3

IV. Conclusion

The effect of addition of ZnO with the reduction of Na₂O on thermal, structural and mechanical properties of B_2O_3 -Na₂O-ZnO glasses has been studied. Thermal stability of glasses decreases at 5 mol% of ZnO while on further addition stability of the glasses increase with increasing ZnO concentration. It is found from FTIR spectra that Zn²⁺ cations ($x > 5$ mol%) are incorporated in the glass network or ZnO₄ units and borate structural units also present in the glasses. The introduction of ZnO decrease the ultrasonic (longitudinal and shear) velocities, elastic moduli, microhardness and Debye temperature suggest formation of NBOs while further addition ($x > 5$ mol%) caused an increase in above said parameters due to the formation of BO. Poisson's

ratio shows reverse trend compared to other parameters. The results indicate that ZnO behaves as both network modifier as well as network former in the studied glasses.

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