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RESEARCH ARTICLE

PHYSICAL AND ELASTIC PROPERTIES OF B_2O_3-Bi_2O_3-Na_2O GLASSES

***Ezhil Pavai, R and Thirumal, C**

Department of Physics, Annamalai University, Annamalainagar - 608 002, Tamil Nadu, India

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ABSTRACT

Glasses of the system: $60B_2O_3$-$(40\text{-}x)Bi_2O_3$-xNa_2O (where x= 0, 5, 10, 15 and 20 mol%) have been prepared by melt quench technique. Longitudinal and shear velocities were measured using pulse echo technique. Density of the glass samples were measured by Archimedes principle using water as immersion liquid. Elastic moduli and some parameters such as molar volume, Poisson's ratio, acoustic impedance, microhardness, Debye temperature and thermal expansion co-efficient have been calculated from the measured data. Compositional dependence of the ultrasonic velocities and related parameters are discussed in the light of the rigidity and compactness of the glasses studied.

INTRODUCTION

Glasses based on boron and heavy metal oxides have attracted considerable interest for their potential applications (Takahash, *et al.* 2004; Sugimito, 2002; Dutta and Ghosh, 2007). Borate glasses are very important optical materials because of their low melting point, high transparency and high thermal stability (Huang, *et al.* 2001). It is generally used to make insulating and dielectric materials. On the other hand, glasses containing the heavy metal oxide (Bi_2O_3) have been extensively investigated because of their interesting technological applications. Bi_2O_3 exists in a monoclinic form and has an irregular octahedral arrangement of six oxygen atoms located at distances from 2.14 to 2.8 Å. Three of these are appreciably closer to [2.14-2.29 Å] than the other three [2.48-2.8 Å]. Thus, pure Bi_2O_3 glass due to its low field strength and high polarizability cannot be obtained compared with pure B_2O_3 glass.

Bi_2O_3 is not a classical glass former, due to high polarizability and small field strength of Bi^{3+} ions, in the presence of conventional glass former such as B_2O_3, SiO_2, etc., it may build a glass network of BiO_n (n=3, 6) pyramids. Because of its dual properties, as a modifier with [BiO_6] octahedral and as glass former with [BiO_3] pyramidal units, bismuth ions may influence the electrical properties of oxides glasses (Ablawat, *et al.* 2008).

Borate glasses containing Bi_2O_3 have particular interest because of their long infrared cutoff and high third order non-linear optical susceptibility, which make them ideal candidates for developing internal transmission components, ultrafast optical switching and photonic devices besides the scope for other applications (Dumbaugh, 1978; Simon and Todea, 2006). These glasses also have wide range applications like glass ceramics as subtracts for optical and electronic devices, thermal and mechanical sensor and reflecting windows (Venkataraman and Varma, 2006; Onishi, *et al.* 1991). Bismuth borate glasses have been studied intensively for their electrical, optical and thermal properties (El-Shaarawy and El-Batal, 2002; Shaaban and Shapaan, 2008). Recently considerable attention has been paid to noncentro symmetric bismuth borate based compounds for their possible applications as piezoelectric, ferroelectric and pyroelectric materials (Becker, 1998; Murugan and Varma, 1999). The properties of B_2O_3-Bi_2O_3 glass can be modified either by changing their composition or by adding different additives like alkali or alkaline earth metal oxides which lead to the structural changes in bismuth borate glasses.

The main aim of this work is to study the physical and structural properties alkali of bismuth borate glasses using XRD, density, ultrasonic velocity measurements.

EXPERIMENTAL PROCEDURE

Glass Preparation

A series of glass samples of formula $60B_2O_3$-$(40\text{-}x)Bi_2O_3$-xNa_2O with x varying from 0 to 20 mol% composition were prepared by melt quench technique. The raw materials of boron trioxide (B_2O_3), bismuth oxide (Bi_2O_3) and sodium oxide (Na_2O) were mixed together by grinding to obtain a fine powder. The obtained mixture was melted in a silica crucible for 3 hours in muffle furnace at 1060 ºC until a bubble free liquid is formed. The melt was poured into a brass mould to form samples of dimensions 10mm diameter and 6mm thickness. Glass samples were annealed at 380 ºC for 2 hours to avoid the mechanical strain developed during the quench process. Then the furnace was switched off and glass was allowed to cool gradually to room temperature. The obtained samples of two parallel sides were polished using a polishing machine in order to obtain a suitable sample for the ultrasonic measurements.

The amorphous nature of the samples is confirmed by X-ray diffraction technique using GE-Inspection technology 3003TT model made in Germany copper target operating voltage 40 Kv 300 mA current rate. The density (ρ) of the glasses were determined by Archimedes method with water as a floatation medium. All the weights were measured by digital balance with ±0.001g standard error.

Ultrasonic velocities measurements have been carried out using pulse-superposition techniques at a frequency of 10MHz. By measuring the thickness of the sample (d) the longitudinal (U_l) and shear (U_s) wave velocities were calculated using the relation U=2d/t, where t is the transit time of ultrasonic waves in the glass samples. The molar volume, elastic moduli, Poisson's ratio, acoustic impedance, microhardness and Debye temperature have been calculated using the following relations (Veerannagowda and Anavekar, 2004):

Molar volume $$V_m = \frac{M}{\rho} \quad (1)$$

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

Shear modulus $$G = U_S^2 \quad (3)$$

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

Young's modulus $$E = (1 + \sigma)\, 2G \quad (5)$$

Poisson's ratio $$\sigma = \left(\frac{L - 2G}{2(L - G)}\right) \quad (6)$$

Acoustic impedance $$Z = U_\ell\, \rho \quad (7)$$

Microhardness $$H = (1 - 2\sigma)\frac{E}{6(1+\pm)} \quad (8)$$

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

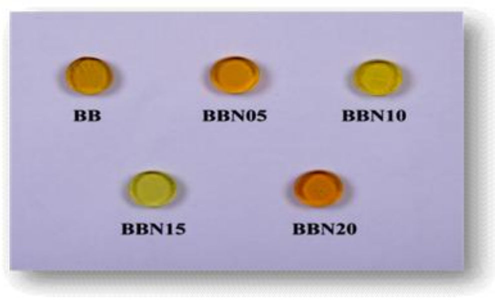
where h, K, N and V_m are the Planck's constant, Boltzmann's constant, Avogadro's number and molar volume of the sample respectively. The mean sound velocity U_m is given by

$$U_m = \left[\frac{1}{3}\left(\frac{2}{U_S^3} + \frac{1}{U_\ell^3}\right)\right]^{-1/3} \quad (10)$$

The nominal compositions in mol% of glasses are present in Table 1.

Table 1 Nomenculture and composition (mol%) of glasses

Nomenculture	Composition in mol%			Remarks
	B_2O_3	Bi_2O_3	Na_2O	
BB	60	40	0	
BBN5	60	35	5	Mol % of
BBN10	60	30	10	B_2O_3 is
BBN15	60	25	15	constant
BBN20	60	20	20	



Photograph of BBN glass sample

RESULTS AND DISCUSSION

XRD studies

The XRD pattern of BB and BBN20 glasses is shown in Fig.1. The X-ray spectrograms show no continuous (or) discrete sharp peak but exhibit broad halo, which reflects the characteristics of amorphous glass structures. The absence of long-range atomic arrangement is a clear indication of amorphous nature of the glass samples (Doweider and Yasser B Saddeek, 2009).

The experimental values of density (ρ), molar volume (Vm), longitudinal velocity (U_ℓ) and shear velocity (U_s) of the different glass specimen with respect to change in mol% of Na_2O are listed in Table 2. The calculated longitudinal modulus (L), shear modulus (G), bulk modulus (K) and Young's modulus (E) are reported in Table 3. Poisson's ratio (σ), acoustic impedance (Z), microhardness (H) and Debye temperature (θ_D) are presented in Table 4.

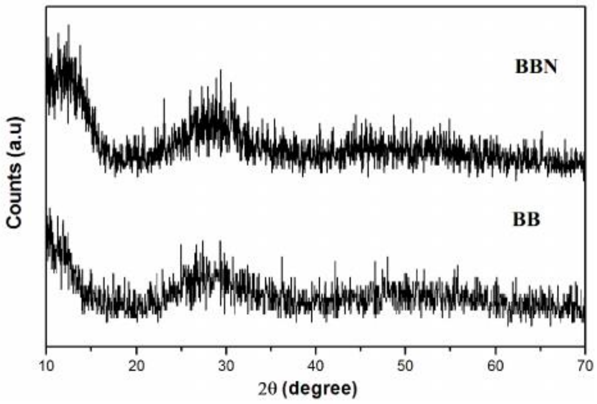


Fig. 1 XRD pattern of BB and BBN20 glass system

The density and molar volume of the glass network depend upon many factors such as structure, coordination number, cross-link density and dimentionality of interstitial space. The variation of density and molar volume is shown in Table 4.2. As can be seen from the table, the density and molar volume decreases linearly with the increase of Na_2O content at the expense of Bi_2O_3 content. The decrease in the density by increasing the modifier is most likely related to the replacement of Bi_2O_3 (atomic mass - 465.95) by Na_2O (atomic mass for Na_2O is 61.98). In short, the decrease in density of the glasses accompanying the addition of Na_2O is probably attributable to a change in cross-link density and coordination numbers.

In general, it is expected that the density and the molar volume should show opposite behaviour to each other, but in the present glasses the behaviour is different. However, this anomalous behaviour was reported earlier for many glass systems (Saddeek, *et al.* 2008; Moustafa, *et al.* 2008; Gao, *et al.* 2009). Similar trend is observed by Dahiya, *et al.* 2013, in their study on the xNa_2O-(50-x)Bi_2O_3-10ZnO-40B_2O_3 glasses, found that the density and molar volume decreases with increase in Na_2O content at the expense of Bi_2O_3 content and conclude that Na_2O acts as a network modifier and modify the glass structure.

It is observed from the Table 2 that both longitudinal (U_l) and shear velocity (U_s) decreases linearly with increasing mol% of Na_2O content, but the rate of decrease of U_l is greater than that of U_s. Addition of Na_2O as a third component into the binary

Table 2 Values of density, molar volume, longitudinal velocity and shear velocity of BBN glasses

Name of the Sample	Density (ρ) ò 10^{-3} kgm^{-3}	Molar volume (V_m) cm^3/mol	Ultrasonic velocity ms^{-1}	
			Longitudinal (U_l)	Shear (U_s)
BB	5.8560	38.96	3821.2	1918.0
BBN05	5.6261	36.96	3530.5	1769.1
BBN10	5.5073	34.09	3354.2	1676.5
BBN15	5.3726	31.18	2789.5	1392.4
BBN20	4.7464	31.04	2609.3	1300.8

Bi_2O_3 - B_2O_3 glass, results in splitting of B-O-Bi bond and hence, the bridging oxygens (BOs) are converted into NBOs. A further addition of Na_2O into glass interstices, more and more ions being open up in the network. Thus weakening of the glass structures or reduction in the rigidity of the network takes place.

Table 3 Values of longitudinal, shear, bulk and Young's moduli of BBN glasses

Name of the Sample	Longitudinal modulus L ò 10^9 Nm^{-2}	Shear modulus G ò 10^9 Nm^{-2}	Bulk modulus K ò 10^9 Nm^{-2}	Young's modulus E ò 10^9 Nm^{-2}
BB	85.51	21.54	56.78	57.37
BBN05	70.13	17.61	46.65	46.92
BBN10	61.96	15.48	41.32	41.28
BBN15	41.81	10.42	27.92	27.79
BBN20	31.43	7.81	21.02	20.85

Longitudinal, shear, bulk and Young's moduli (Table 3) decrease over the entire range of composition of Na_2O in BBN glasses. The decrease in elastic moduli may be attributed to the open nature of the glass network structure with the addition of Na_2O. The alkali (Na^+) ion is a network modifier and they reside in the B_2O_3-Bi_2O_3 glass interstitially and break down some of the bridging bonds in the network and create non-bridging oxygens. The creation of non-bridging oxygen in the network reduced the connectivity and deceased the elastic moduli. The broken bonds are replaced by ionic bonds between the interstitial modifying ions (N^+) and the non-bridging oxygen of the network. Similar conclusion was studied by Marzouk and Gaafar, 2007.

Table 4 Values of Poisson's ratio, acoustic impedance, microhardness and Debye temperature of BBN glasses

Name of the Sample	Poisson's ratio σ	Acoustic impedance Z ò 10^{-7} kgm^{-2} s^{-1}	Microhardness H ò 10^9 Nm^{-2}	Debye temperature θ_D K
BB	0.3316	2.2377	2.4185	72.70
BBN05	0.3324	1.9863	1.9679	66.89
BBN10	0.3335	1.8473	1.7183	63.81
BBN15	0.3341	1.4987	1.1522	53.96
BBN20	0.3346	1.2046	0.8611	48.67

Normally the rigidity decrease in the glasses contributes a decrease in velocity and hence elastic moduli on the other hand causes an increase in Poisson's ratio. According to Rao (2002), Poisson's ratio depends on the dimensionality of the structure and cross-link density. A three dimensional network (eg. SiO_2) has a lower σ value than that of a two dimensional structure (eg. B_2O_3), Since the number of bonds resisting a transverse deformation decreases in that order. The values of Poisson's ratio were found to be increase from 0.3316 to 0.3346 for glass samples (Gaafar, *et al.* 2013). This is due to increase in molar volume, which means that the structure becomes more open.

The acoustic impedance decreases (Table 4) with increase in mol% of Na_2O content as shown in Table 4. The variation of the acoustic impedance confirming the decrease in rigidity of the structure of the glass, thereby increasing the formation of NBO atoms, resulting in lower impedance to the propagation of ultrasonic waves in the specimen (Rajendran 1995 and Sharma, *et al.* 2009). The microhardness is seemingly another property characteristic of solids. It is defined as the resistance of a material to permanent indentation or penetration. Table 4 show the variation of microhardness of the glass systems with Na_2O content. Decreases in microhardness of glasses means reduction in their softening points, as the network modifiers content is increased. Similar trend of variation is also observed by Anand Pal Singh *et al.* (1990).

The results are further confirmed by taking another parameter, Debye temperature (Table 4) which decreases with increase in mol% of Na_2O content. Decrease in θ_D suggests decrease in connectivity of the glass network. This implies that the decrease in the rigidity of the glass is accompanied by a decrease in the lattice vibrations. The observed decrease in Debye temperature in this study is mainly attributed to change in the number of atoms per unit volume and also to the existence of non-bridging oxygens (Abd EI-Malak, 2002).

CONCLUTION

The density, ultrasonic velocities and elastic properties of ternary glasses have revealed the following conclusion:

i. The density as well as molar volume of the BBN glasses decreases with the increase in Na2O content. This is probably attributed to the greater molecular weight of bismuth atom and the coordination numbers of Bi3+ ions.
ii. Ultrasonic velocity (both longitudinal and shear) values decrease with increasing Na2O content which is interpreted as being a decrease in connectivity of the network structure.
iii. The elastic moduli and remaining parameters are decrease and the Poisson's ratio is increase with addition of Na2O, indicating the decrease in rigidity of the glass network.

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