Research Paper

Effect of Bi_2O_3 on Elastic Properties of Silica Bismuthate Glasses by Pulse-Echo Method

Physics

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ABSTRACT
A binary glass system of xBi_2O_3 $(100-x)SiO_2$ with x= 60, 65, 70, 75 and 80 mol% was synthesized by rapid melt quenching method. Longitudinal and shear ultrasonic velocities were measured at room temperature using pulse-echo method at 5 MHz frequency. The densities of the glasses were also measured by Archimedes principle. Elastic moduli, Poisson's ratio, Debye temperature, softening temperature, acoustic impedance, thermal expansion coefficient and micro hardness have been calculated from the measured density and ultrasonic velocity. The above parameters were analysed in terms of structural changes of glasses with composition. The results indicate that the elastic moduli and other parameters of the binary glass system decrease with increasing Bi_2O_3 content.

1. INTRODUCTION

Simple oxides such as SiO_2, B_2O_3 and P_2O_5 are classified as glass forming oxides [1,2] whereas Bi_2O_3 and CuO are the conditional glass formers. Silicate glasses are the most commonly available commercial glasses due to ease of fabrication and excellent transmission to visible light [3]. Since pure and doped silica glasses have excellent optical transmission properties as the core and/or cladding materials of optical waveguides hence they are widely used in optical fibers and planar lightwave circuits [4] for telecommunications.

Pb-containing glasses have excellent properties, such as high refractive indices and low melting temperatures, and hence they have been widely used in various applications, such as table wares, optical lenses and solder glasses for electronic components. As Bi is placed next to Pb on the periodic table both Bi^{3+} and Pb^{2+} ions have the same $6s^2$ electronic configurations. Therefore, a number of similarities have been confirmed in various properties. However, in toxicity, Bi is much safer than Pb. For these reasons, Bi-based materials have been expected as substitutes for the Pb-containing materials, and the novel glass systems have been explored in glass industries. It is well known that Bi_2O_3 does not vitrify itself, but the addition of other oxides enables its vitrification. It has been reported that Bi ions in oxide glasses have 5- or 6-fold coordination state [5].

Glasses based on heavy metal oxide have attracted attention of researcher's community for their excellent IR transmission compared with conventional glasses [6, 7]. The bismuth oxide glasses have wide range of applications for optical and electronic devices, mechanical sensors, and reflecting windows [8]. They have specific properties, which allow to obtain the corresponding nonlinear optical susceptibilities higher even in the similar crystalline state of the same compounds [9,10].

Elastic properties of solid materials are of considerable significance because their measurement yields information concerning the forces that operate between the atoms or ions comprising solids. This is fundamentally important in interpreting and understanding the native bonding in the solid state materials. Hence elastic properties are suitable for describing the glass structure as a function of composition [11].

The prime goal of the present work is to measure the ultrasonic velocity, density for the binary xBi_2O_3 $(100-x)SiO_2$ glass system using pulse-echo technique at a frequency 5MHz. These values have been used to study the elastic moduli, Poisson's ratio, Debye temperature, softening temperature, acoustic impedance, thermal expansion coefficient and micro hardness which will give insight into rigidity and structure of the glasses.

2. EXPERIMENTAL TECHNIQUES

2.1. PREPARATION OF GLASSES

The xBi_2O_3 $(100-x)SiO_2$ with x= 60, 65, 70, 75 and 80 mol% glasses were prepared by conventional melt-quenching method with analytic reagent grade Bi_2O_3 and SiO_2 as raw materials. The required amount (approximately 20g) in mol% of different chemicals in powder form was weighed using single pan balance. The homogenization of the appropriate mixture of the components of chemicals is effected by repeated grinding using a mortar. Mixed batches of 20 g were melted in porcelain crucibles at a temperature from 900 to 1070ºC for all the compositions. The molten sample is cast into a copper mould having dimensions of 10mm diameter and 6mm length. Then the glass samples are annealed for two hours to avoid the mechanical strain developed during the quenching process The prepared glass samples are polished and the surfaces are made perfectly plane and smoothened by diamond disc and diamond powder. The glasses produced were transparent, clear and free from defects.

2.2. MEASUREMENT OF DENSITY

The density of the glass samples is measured using Archimedes principle with water as buoyant liquid. The glass samples are weighed both in air and in water at 303 K. The density is calculated using the formula

$$\rho = \frac{W_A}{(W_A - W_B)} \times \rho_W \qquad (1)$$

where and are the weight of the sample in air and in water, ρ_W is the density of water at 303 K.

2.3. MEASUREMENT OF SOUND VELOCITY

The ultrasonic longitudinal and shear velocities of the specimen have been determined using the conventional pulse echo method at room temperature (303 K) by making use of 5 MHz X-cut and Y-cut transducers. These transducers act as both transmitters and receivers of the ultrasonic pulse. Ultrasonic velocity is calculated using the relation [12]

$$U = \frac{2d}{t}$$

where U is the velocity of the specimen (ms^{-1}), d is the thickness of the specimen(mm) and t is the transit time(μ_s).

Various parameters of the glass specimen are calculated using the standard expressions given below [13, 14]:

Molar volume $(V_m) = \frac{M}{\rho}$ $\qquad (3)$

Longitudinal modulus $(L) = \rho \, U_l$ $\qquad (4)$

Shear modulus $(G) = \rho \, U_s$ $\qquad (5)$

Bulk modulus

$$\ )=L-\left(\frac{4}{3}\right)G \qquad (6)$$

Poisson's ratio

$$(\sigma)=\left(\frac{L-2G}{2(L-G)}\right) \qquad (7)$$

Young's modulus $(E)=(1+\sigma)2G \qquad (8)$

Acoustic impedance $(Z)=U_l\,\rho \qquad (9)$

Microhardness $(H)=(1-2\sigma)\dfrac{E}{6(1+\sigma)} \qquad (10)$

Debye temperature $(\theta_D)=\dfrac{h}{K}\left(\dfrac{9N}{4\pi V_m}\right)^{1/3}U_m \qquad (11)$

Where ρ, and U_s are the measured density, longitudinal and shear ultrasonic velocity and 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

$$U_m=\left[\frac{1}{3}\left(\frac{2}{v_s^3}+\frac{1}{v_l^3}\right)\right]^{-1/3}$$

Softening temperature $(T_s)=\left(\dfrac{M_w}{C\rho}\right)U_s^{\,2} \qquad (12)$

Where M_w the molecular weight of the glass and C, is a constant equal to $0.5074\times10^5 cmK^{-1/2}$ s.

Thermal expansion coefficient $(\alpha_p)=23.2\,(U_l-0.57457) \qquad (13)$

3. RESULT AND DISCUSSION

The silica bismuthate glasses with different concentration of Bi_2O_3 from 60 to 80 mol % have been achieved. The compositions of glass samples are shown in Table 3.1. The glass samples were light yellow in colour. The experimental values of density (ρ), longitudinal velocity (U_l) and shear velocity (U_s) of the different glass samples with respect to change in the mol% of Bi_2O_3 are listed in Table 3.1. The values of longitudinal modulus (L), shear modulus (G), bulk modulus (K), Young's modulus (E) and Poisson's ratio (σ) are also reported in Table 3.2. The acoustic impedance (Z), micro hardness (H), Debye temperature (θ_D), softening temperature (T_s) and thermal expansion coefficient (α_p) are given in Table 3.3.

It can be seen from the Table 3.1 that the density increases from 5.567 to 6.107 10^{-3} kg m^{-3} with increase of Bi_2O_3 concentration. The increase in density is related to the high dense Bi_2O_3 compared to that of SiO_2, i.e., the increase in the density is related to the constitution of the glass rather than to the type of the structural unit, as observed earlier [15]. The change in geometrical configuration, co-ordination number, cross-link density and dimensions of interstitial space of glass decide the ultrasonic velocity and therefore, ultrasonic velocity is a tool in revealing the degree of change in structure with composition of glasses [16]. In general, the decrease of ultrasonic velocity is related to the increase in the number of nonbridging oxygen (NBO) and consequently the decrease in connectivity of the glass network [17].

Table 3.1 Glass composition, density (ρ), longitudinal velocity (U_l) and shear velocity (U_s) of BS glass system

Sample name	Nominal composition (mol %)		Density ($\rho\times10^{-3}$ kg m^{-3})	Ultrasonic velocity (U) ms^{-1}	
	SiO_2	Bi_2O_3		Longitudinal velocity ()	Shear velocity (U_s)
BS1	40	60	5.567	3578.37	1652.70
BS2	35	65	5.672	3498.82	1625.13
BS3	30	70	5.815	3402.76	1588.40
BS4	25	75	5.978	3304.68	1551.87
BS5	20	80	6.107	3225.60	1519.59

Table 3.2 Values of longitudinal (L), shear (G), bulk (K), Young's modulus (E) and Poisson's ratio (σ) of BS glass system

Sample name	Longitudinal modulus (L × 10⁹ Nm^{-2})	Shear modulus (G × 10⁹ Nm^{-2})	Bulk modulus (K × 10⁹ Nm^{-2})	Young's modulus (E × 10⁹ Nm^{-2})	Poisson's ratio (σ)
BS1	71.28	15.20	51.01	41.49	0.364
BS2	69.44	14.98	49.46	40.82	0.362
BS3	67.33	14.67	47.77	39.93	0.360
BS4	65.29	14.39	46.09	39.12	0.358
BS5	63.54	14.10	44.74	38.28	0.357

Table 3.3 Values of acoustic impedance (Z), microhardness (H), Debye temperature (θ_D), softening temperature (T_s) and thermal expansion coefficient (α_p) of BS glass system

(2)

Sample name	Acoustic impedance (Z × 10⁷ $kgm^{-2}s^{-1}$)	Micro hardness (H × 10⁹ Nm^{-2})	Debye temperature (θ_D K)	Softening temperature (T_s K)	Thermal expansion coefficient (ms^{-1})
BS1	1.992	1.374	174.06	299.63	83005.02
BS2	1.984	1.373	167.30	297.21	81159.35
BS3	1.978	1.362	161.47	294.29	78930.82
BS4	1.975	1.357	156.07	289.37	76655.29
BS5	1.970	1.341	150.71	286.71	74820.86

The sound velocities (both longitudinal and shear velocities) decrease with increase in mole fraction of Bi_2O_3. It is well known that Bi^{3+} is highly polarizable due to its large ionic radius, small cation field strength and a lone pair of valence shell. The elec-

tronic shell of O^{2-} is influenced by the high polarization of Bi^{3+}. Therefore, the increase of Bi_2O_3 content resulted in the increase of the non-bridging oxygens which in turn made the glass network loose [18, 19].

The decrease of ultrasonic velocity with increasing Bi_2O_3, indicating that Bi_2O_3 plays a dominant role in the velocity [20]. The addition of more Bi_2O_3 in glass interstices causes more ions to open up in the network. Thus, weakening of the glass structure or reduction in the rigidity of the network takes place. As a consequence, both velocities and U_s decrease with the addition of heavy metal oxide. It can be seen from the Table 3.2 that the decrease in elastic moduli may be due to decrease in oxygen packing density [21, 22], which is a consequence of increasing number of non-bridging oxygen due to which the glass structure has further expanded.

Table 3.2 gives the values of Poisson's ratio. They have decreased from 0.364 to 0.357 with the increase of Bi_2O_3 content from 60 to 80 mol%. This decrease in Poisson's ratio can be explained in terms of covalent bonds that are formed in the glass network. In addition, Rajendran et al. [23] have suggested a close correlation between Poisson's ratio and cross-link density. They reported that high cross link density has a Poisson ratio of the order of 0.1 to 0.2, while low cross link density has a Poisson ratio between 0.3 and 0.5.

Debye temperature (θ_D) plays an important role in solid materials in the determination of elastic moduli and atomic vibrations. θ_D represents the temperature at which all the low frequency 'lattice' vibrational modes are excited. It is known that Debye temperature depends directly on the mean ultrasonic wave velocity [24]. The observed θ_D, obtained from the ultrasonic velocity data, is particularly sensitive with Bi_2O_3 content (Table 3.3). The observed decrease in θ_D with addition of Bi_2O_3 supports that the addition of Bi_2O_3 content indicates the loose packing structure of the glass structure with increasing the creation of NBOs as discussed above.

It can be seen that both microhardness and softening temperature decrease with increasing Bi_2O_3. Afifi and Marzouk [14] have explained that the increase in hardness of glasses means an increase in softening points. In the present glasses the decrease in hardness is noted. This decrease is what may be expected

from the decrease of elastic moduli. The increase in the value of acoustic impedance causes increasing in the propagation of ultrasonic waves in the specimen [27]. The acoustic impedance (Z) was found to decrease from 1.992 to 1.970 $10^7 kgm^{-2} s^{-1}$ with increasing Bi_2O_3 as shown in Table 3.3. Therefore, in this system, the propagation of ultrasonic waves is decreased.

Softening temperature (T_s) is another important parameter defined as the temperature point at which viscous flow changes to plastic flow. In actual practice, it plays a crucial role in determining the temperature stability of the glass. The higher the value of softening temperature of a glass, the greater is the stability of its elastic properties [25, 26]. Values of softening temperature for BS glasses were calculated and presented in Table 3.3. On addition of Bi_2O_3 to SiO_2, the softening temperature decreases from 299.63 K to 286.71 K. This shows that the stability of the glasses decreases as the Bi_2O_3 content increases.

From the Table 3.3 it is noted that the thermal expansion coefficent () decreases with increasing the concentration of Bi_2O_3. Srivastava and Srinivasan [28] have stated that the thermal expansion coefficient of materials depends on the strength of bonds. Therefore, the decrease in number of bonds per unit volume explains the decrease in the value of thermal expansion co efficient, and hence reduction in rigidity of the glass structure.

CONCLUSION
Elastic properties of the glass system have been investigated to ascertain the effect of Bi^{3+} ion in these glasses. The following conclusions have been drawn in the present investigation.

- The densities show an increasing trend with increase in Bi_2O_3 content and this is due to the heavier Bi atoms.
- The ultrasonic velocity (both longitudinal and shear) values decrease with the addition of Bi_2O_3 content. This is due to the presence of non-bridging oxygen which leads to loose structure of network.
- The elastic properties such as Young's modulus, bulk modulus, shear modulus, and longitudinal modulus decrease with increasing Bi_2O_3 content is due to the weakening of the glass network.
- The other parameters such as Poisson's ratio, Debye temperature, softening temperature, acoustic impedance, thermal expansion coefficient and micro hardness suggest that the rigidity of the glasses has been decreased when Bi_2O_3 content is increased.

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