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Elastic Properties of Copper Containing Bismuth Silicate Glasses - an Ultrasonic Study

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ABSTRACT

Oxide glasses with the general formula Bi_2O_3–(60-x)SiO_2–xCuO with different compositions of copper (x = 5, 10, 15, 20 and 25 mol %) have been prepared by conventional melt- quenching technique. Both longitudinal and shear velocities were measured in different compositions of glass using pulse echo technique. Measurements were carried out at 5MHz frequency and room temperature. Elastic moduli and some other parameters such as, acoustic impedance, Debye temperature, softening temperature, microhardness, thermal expansion coefficient and poisson ratio have been calculated as a function of composition. Elastic moduli and all other parameters get decreased when CuO is substituted for SiO_2 upto 10 mol% and above 10 mol% of CuO content, a reverse trend is followed, whereas poisson ratio shows opposite behaviour.

KEYWORDS: Ternary glass, Elastic properties and Debye temperature

1. INTRODUCTION

The bismuthate glasses, a distinct type of noncrystalline materials, having unique structure, are at present the object of intensive investigations. Oxide glasses have been the subject of extensive research for several decades owing to their interesting properties and applications [1]. Various additives such as transition metal oxides (TMOs) are found to modify the properties of oxide glasses considerably. Bismuth oxide (Bi_2O_3) glass is a popular member of the oxide glass family in which selected additives are found to modify its properties significantly.

Since the first report by Dumbaugh [2] on Bi_2O_3 based glasses being thermally stable against crystallization and showing high refractive indices and excellent infrared transparencies, so many studies on structural and optical properties of Bi_2O_3 based glasses such as PbO–Bi_2O_3–B_2O_3 and PbO–Ga_2O_3–Bi_2O_3 have been carried out. For example, it has been found that glasses containing Bi_2O_3 exhibit extremely large third order nonlinear optical susceptibilities $\chi^{(3)}$ of the order 10^{-12} esu [3, 4].

Oxide glasses doped with the TMOs such as CuO, Fe_2O_3, MoO_3, WO_3, V_2O_5, etc. are known to exhibit semiconducting properties [5]. The concentration of TMO plays an active role in semiconducting glasses [6]. Bi_2O_3 glasses containing CuO are interesting materials which form an important constituent of high T_c superconducting glasses [7]. In the CuO–Bi_2O_3 system, it is found that Bi^{3+} ions participate in the network structure above 70 mol% of Bi_2O_3. In these glasses, network structure is formed with Bi_2O_3 pyramidal units as in the case of many other Bi containing glasses [8].

The elastic properties of these glasses are of considerable significance, because their studies yield information concerning the forces that are operative between the atoms comprising a solid. Hence the elastic properties are suitable for describing the compactness of glass structure [9]. The presence of TMO in the matrix of bismuth silicate glasses improves the glass quality, especially when modified by CuO. Ultrasonic non-destructive characterization of materials is a versatile tool for the inspection of their microstructure and their mechanical properties. It was suggested [10] that the addition of Cu_2O in sodium phosphate glasses leads to the formation of P–O–Cu bonds which increase the cross-link density in the glass network.

For technical applications of such attractive Bi_2O_3–SiO_2–CuO glasses, it is obvious that an understanding of elastic properties is necessary, because generally poor elastic properties of glasses limit their use in many applications. From the literature survey, it is understood that the study of the elastic moduli, Debye temperature, acoustic impedance, softening temperature, microhardness, thermal expansion coefficient and poission ratio in Bi_2O_3 based glasses is scarce.

2. EXPERIMENTAL PROCEDURES

The Bi_2O_3–(60-x)SiO_2–xCuO with x = 5, 10, 15, 20 25 mol % glasses were prepared by conventional melt-quenching method with analytic reagent grade Bi_2O_3, SiO_2 and CuO as raw materials. The required amount (approximately 20g) in mol% of different chemicals in powder form was weighed using a 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 1040ºC for all the compositions. The molten sample is cast into a copper mould having dimensions of 10mm diameter and 6mm thickness. 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.

The density (ρ) of the glass samples is measured using Archimedes principle with water as buoyant liquid. The molar volume (V_m) has been determined as M/ρ, where M is the molar weight of the glass. The ultrasonic longitudinal (U_ℓ) and shear (U_s) 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 [11], U=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).

The two velocities besides the density were utilized in determining two independent second-order elastic constants, namely, the longitudinal (L) and shear (G) moduli. L and G describe the elastic strain produced by a small stress in isotropic amorphous solids like glasses. For pure longitudinal waves $G = \rho U_\ell^2$, and for pure transverse waves $G = \rho U_s^2$. The elastic bulk modulus (K), Young's modulus (E), Debye temperature (θ_D) and acoustic impedance (Z) softening temperature(T_s), micro hardness (H), thermal expansion coefficient (α_p) and poisson ratio(σ) can be determined from L and G[12].

3. RESULT AND DISCUSSION

The density is perhaps the most important measure of a glass. Its value is needed in manifold techniques such as neutron, electron and x-ray scattering. Density also stands on its own as an intrinsic property capable of casting light on short range structure. The density is generally affected by the structural softening/compactness, change in geometrical configuration, co-ordination number, cross-link density and dimension of interstitial spaces of the glass [13]. Table 3.1 shows the values of density, molar volume, longitudinal and shear ultrasonic wave velocities with CuO content. It is observed from Table 3.1 that the density increases with increase in CuO content. The increase in density with CuO is obvious since lighter SiO_2 (60.08 g/mol) is being replaced by heavier CuO (79.545 g/mol).

However it must be indicated that it is not the real reason in all cases. For example in $Li_2O–B_2O_3$ [14] or $Li_2O–SiO_2$ [15] glasses the density increases markedly with increasing Li_2O content at the expense of B_2O_3 or SiO_2, which have greater molecular mass. The reason of density increase in those cases is related to the type of structural units that form when Li_2O is incorporated into the glass structure. Depending on the composition of $Li_2O–B_2O_3$ glasses, Li_2O converts symmetric BO_3 triangles into BO_4 tetrahedra or converts the latter into asymmetric BO_3 triangles. Both the BO_4 tetrahedra and asymmetric BO_3 triangles are considerably denser than the symmetric BO_3 triangles [14]. In $Li_2O–SiO_2$ glasses, SiO_4 tetrahedra having one, two, three or four non-bridging oxygen ions are denser than those without non-bridging oxygen ions [15].

It is observed from Table 3.1 that the values of molar volume of the studied glasses are decreased from 51.526 to 46.401 cm^3/mol with increasing CuO mol%. This decrease in the molar volume of the present glasses may be attributed to the increase in ionic radii of the Cu^{2+} ions which fill the interstices of the glass network.

Table 3.1 Glass composition, density (ρ), molar volume (V_m) longitudinal velocity (U_ℓ) and shear velocity (U_s) of BSC glass system

Sample name	Nominal composition (mol %)			Density (ρ x10^{-3} kg m^{-3})	Molar volume V_m (cm^3/mol)	Ultrasonic velocity (U) ms^{-1}	
	Bi_2O_3	SiO_2	CuO			Longitudinal velocity (U_ℓ)	Shear velocity (U_s)
BSC1	60	35	5	5.911	51.526	3545.01	1904.43
BSC2	60	30	10	6.073	50.312	3306.18	1740.548
BSC3	60	25	15	6.292	48.714	3477.837	1844.25
BSC4	60	20	20	6.463	47.575	3498.79	1910.93
BSC5	60	15	25	6.648	46.401	3524.58	1951.73

The addition of CuO into the Bi_2O_3-SiO_2 structure decreases both longitudinal and shear velocities when the CuO content is increased from 5mol% to 10mol%. This indicates that the CuO ions reside in the Bi_2O_3 glass matrix as glass modifier without entering into the glass matrix [16]. Hence results in the structural arrangement of the glasses such that the Bi–O–Bi bonds are broken and the bridging oxygens are transferred into non-bridging oxygens.

Then, the progressive additions of CuO content show an increase in both longitudinal and shear velocities as shown in Table 3.1. The observed increase in the ultrasonic velocity can be explained such that, as Cu^{2+} ions enter interstitially, some type of modification may occur in the already existing Bi–O–Bi and Bi–O–Si linkages into Bi–O–Cu bonds [17]. Thus, an increase in the ultrasonic velocity will contribute to the increase in the rigidity. This behavior indicates that the replacement of SiO_2 by CuO after 10 mol% improves the mechanical properties and the strength of the cross-links between chains of the bismuth silicate glasses.

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

Sample name	Longitudinal modulus (L × 10^9 Nm^{-2})	Shear modulus (G × 10^9 Nm^{-2})	Bulk modulus (K × 10^9 Nm^{-2})	Young's modulus (E× 10^9 Nm^{-2})	Poisson's ratio (σ)
BSC1	74.29	21.44	45.70	55.62	0.297
BSC2	66.38	18.39	41.85	48.14	0.308
BSC3	76.11	21.40	47.57	55.83	0.304
BSC4	79.12	23.60	47.65	60.77	0.287
BSC5	82.59	25.32	48.82	64.77	0.278

Table 3.2 gives the values of the elastic moduli; longitudinal modulus (L), shear modulus (G), bulk modulus (K), young's modulus (E) and Poisson's ratio (σ). It is interesting to note that, a similar decrease in ultrasonic velocity is noticed when the CuO content is 10 mol% and then increased subsequently as more CuO was added into the bismuthate network in all the elastic moduli (Table 3.2) viz. L, G, K, Y. It is evident from Table 3.2 that the elastic constants first decrease with addition of small amount of CuO. This indicates that the CuO reside in the Bi2O3 glass matrix as glass modifier without entering into the glass matrix. With further increase in CuO content, elastic constants increase as CuO ions start taking part in the formation of glass matrix [16].

It is well known that the poisson's ratio of a polycrystalline or amorphous solid is related to the cross linking of the network. As it can be seen from Table 3.2, Poisson's ratio of the studied glasses increases as the CuO content increases from 5 mol% to 10 mol% after that it decreases. According to Bridge et al, [18] the crosslink density of two, one and zero are related to Poisson's ratio of 0.15, 0.3 and 0.4 respectively. Poisson's ratio starts from 0.297 for 5 mol% of CuO and increases to 0.308 when the CuO reaches 10 mol% after that it decreases. It means the cross-link density increases from nearly one to two.

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 BSC glass system

Sample name	Acoustic impedance (Z × 10^7 kgm^{-2} s^{-1})	Micro hardness (H × 10^9 Nm^{-2})	Debye temperature (θ_D K)	Softening temperature (T_s K)	Thermal expansion coefficient (α_p ms^{-1})
BSC1	2.095	2.899	197.839	368.309	82230.78
BSC2	2.007	2.351	183.329	300.397	76689.99
BSC3	2.188	2.791	196.096	326.550	80672.25
BSC4	2.261	3.345	203.653	342.389	81158.49
BSC5	2.343	3.733	209.165	348.345	81756.94

Table 3.3 gives the values of acoustic impedance (Z), micro-hardness (H), Debye temperature (θ_D), softening temperature (T_s) and thermal expansion coefficient (α_p). The values of the acoustic impedance (Z) were found to decrease with the addition of CuO content from 5 mol % to 10 mol%. The variation of the acoustic impedance indicates that the addition TMO ions causes the splitting of the glass network, thereby increasing the formation of non-bridging oxygen atoms, resulting in lower impedance to the propagation of ultrasonic waves in the specimen [19]. After 10 mol% of CuO content, it increases.

Table 3.3 shows the dependence of microhardness with CuO concentration in the glass. With the addition of CuO, glasses showed decrease in microhardness for 10 mol %, reflects the weakening of glass network [20]. Further addition of CuO (x >10 mol %) in the glass, results in a reverse trend in these values, this indicates the stronger bonding in the glass network. Thus all these changes in the properties with varying concentration of CuO indicate that CuO makes the glass network somewhat less rigid up to 10 mol % and beyond that stabilizes the glass network.

Debye temperature plays an important role in solid materials in the determination of elastic moduli and atomic vibrations. It 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 [21]. As we have measured the θ_D values from the ultrasonic wave velocity, the Debye temperature should follow more or less the same variation with the addition of CuO. So Debye temperature decreases for 10mol% CuO content and beyond which it has a tendency to increase (Table 3.3). The increase in θ_D can be attributed to strengthening of the structure as revealed the increase in the hardness. Also increase in the rigidity of the glass is associated with an increase in the lattice vibrations.

The softening temperature (T_s) is the temperature at which viscous flow changes to plastic flow. It plays a crucial role in determining the stability of glasses. It was found that the elastic properties became more stable for high softening temperature [22]. Softening temperature decreases for 10 mol% and this decrease in the softening temperature predicts weakening of glass network. Further the addition of CuO (>10 mol%), softening temperature increases, this indicates more stability of glasses.

The thermal expansion coefficient indicates the relation between the volume of a glass and its temperature. From Table 3.3 it can be seen that the thermal expansion coefficient decrease as the CuO content substitutes from 5 mol% to 10mol% which weakens the network rigidity of the glass system. However, further addition of CuO at x > 10 mol% contributes the formation of more bridging oxygen causing connectivity and rigidity of the glass network to improve. Both the values of acoustic impedance (Z) and the thermal expansion coefficient of the studied glass system support well the earlier conclusions derived from the previous parameters.

CONCLUSION

Investigation on elastic properties of Bi_2O_3–(60-x)SiO_2–xCuO glasses with different compositions of copper (x = 5, 10, 15, 20 25 mol %) have been carried out to elucidate the structural role of CuO. The density, ultrasonic velocities, and elastic properties of ternary Bi_2O_3– 60-x)SiO_2–xCuO glasses have revealed the following conclusions:

(i) the density values of the glass system studied were found to be increased, while the molar volumes decreased.

(ii) ultrasonic velocity (both longitudinal and shear) values decrease with the addition of CuO content at lower concentration. This may be due to presence of non-bridging oxygen and this leads to loose structure of network. At higher concentration of CuO, the velocity values increase and this leads to increase the connectivity of the network structure

(iii) decrease in elastic moduli and other parameters and increase in Poisson's ratio at lower concentration of CuO indicating the weakening of the glass network. Further addition of modifier oxide increases the elastic moduli and other parameters due to increase in rigidity of the network

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