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Investigation of Acoustical Parameters in Ternary $B_2O_3 - MnO_2 - Al_2O_3$ GLASSES

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Abstract: ***Glass samples of composition 60B_2O_3- (40-x)MnO_2-xAl_2O_3 (where x=0, 5, 10, 15 and 20 mol %) were synthesized by melt quench technique. Longitudinal and shear velocities have been measured at 5 MHz frequency by Pulse - Echo Overlap method. The density of the glasses has also been determined. The density increases while their molar volume values decreases with the increase of Al_2O_3 concentration. The amorphous nature of the glass samples were checked by XRD technique. Elastic moduli such as longitudinal, bulk, shear and Young's moduli, Poisson's ratio, acoustic impedance, microhardness and Debye temperature were calculated from the measured data. The variations of the above parameters with change in composition have been discussed in terms of structural changes in the glass network.***

Keywords: XRD, Ultrasonic velocity, elastic moduli, rigidity.

1. Introduction

Among the various non-destructive evaluation techniques, ultrasonic technique is a versatile tool for investigating the changes in microstructure, deformation process and mechanical properties of materials. The ultrasonic waves are closely related with the elastic and inelastic properties of the materials (1). The study of elastic properties of glasses has inspired many researchers (2, 3), because their measurement yields information concerning the forces that are operative between the atoms or ions comprising solid. This is basically important in interpreting and understanding the nature of bonding of the solid state.

B_2O_3 is one of the best glass formers (4) and it exhibits unique structural features. It is well know that the main structural units of the borate network are (BO_3) triangles and (BO_4) tetrahedral, may form different super structural units; boroxol and metaborate rings, metaborate chains, pentaborate, triborate, diborate and pyroborate. (5). Borate glasses containing various transition metal ions have been under extensive investigation of the technological applications especially in microelectronics, optical glasses and solid state laser (6). Transition metal doped borate glasses have been studied by several authors (7-9). Among all transition metal ions, manganese (Mn) ion is particularly interesting because it exits in different valance states in different glass matrices (10). With the composition of glass, the local environment of the transition metal (TM) ion incorporated into the glass network can be changed, leading to the logical legend field homogeneities. Usually, Mn^{3+} ions in the borate glass exits in octahedral coordination whereas they are found in silicate and germinate glasses in Mn^{2+} ionic state with both octahedral and tetrahedral coordination (11). Most Mn^{2+} complexes are octahedral and have a high spin arrangement with five unpaired electrons (12). Manganese ions have been frequently used as paramagnetic probes for exploring the structure and properties of vitreous systems (13).

The aim of the present work included preparation and characterization of $B_2O_3 - MnO_2 - Al_2O_3$ glasses. The structural properties and rigidity of the glasses are analyzed by using calculated values of the elastic moduli, Poisson's ratio, acoustic impedance, microhardness and Debye temperature.

2. Experimental

2.1. Sample preparation

The glass samples under investigations were prepared by the conventional melt quench technique. The required amount in mol% of different chemicals in powder form was weighed using single pan balance having an accuracy of ± 0.0001g. The nominal compositions of BMA glass system are listed in Table-1.

Table 1: Nominal composition of BMA glass samples

S. No	Nomenclature	Compositions in mol%
1	BMA 1	60-35-5
2	BMA 2	60-30-10
3	BMA 3	60-25-15
4	BMA 4	60-20-20

The chemicals were first thoroughly mixed together by grinding the mixture repeatedly to obtain a fine powder. The powder was melted in silica crucible at about 900ºC in muffle furnace for few minutes to homogenize the melts. The molten sample is cast into a copper mould having dimensions 10mm diameter and 6mm length. All these glasses were annealed for three hours at 250ºC to avoid mechanical strain developed during the quenching process. The prepared samples are chemically stable and non-hygroscopic. The glass samples are polished and the surfaces are made perfectly plane and smoothened by diamond disc and diamond powder. Thickness of the samples has been measured using vernier calipers with an accuracy of 0.0001mm.

2.2. Measurements

2.2.1 XRD

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.

2.2.2. Velocity

The longitudinal and shear velocities of the glass specimen were measured using the Pulse – Echo Overlapping method at 303K by making use of 5MHz X-cut and Y-cut transducers. These transducers were brought into contact with each of the samples by means of a couplant, in order to ensure that there was no air void between the transducers and the specimen. By applying constant pressure on the probe, the echo waveforms were obtained on the display unit and stored in the memory.

Ultrasonic velocity is calculated using the relation $U = \frac{2d}{t}$ ………. (1)

where d and t are the thickness of the specimen (mm) and transit time in microsecond

2.2.3. Density

The density of the glass samples was measured using relative measurement technique. Ionized water was used as a buoyant liquid. The glass samples were weighed both in air and after immersing in water at 303K. The weight of the glass samples was measured in a single pan with an accuracy of 0.0001g. The density was calculated using the formula $\rho = \rho_w \frac{W_A}{W_A - W_w}$ (2) W_A and W_w are the weight of the glass samples in air and in water respectively and ρ_w is the density of water at 303K.

3. Theory and Calculation

The elastic moduli and other parameters of the glass specimen are calculated using the measured density, longitudinal velocity and shear velocity as given below:

Longitudinal modulus $(L) = \rho U_l^2$ (3)

Shear modulus $(G) = \rho U_s^2$ (4)

Bulk modulus $(K) = L - \left(\frac{4}{3}\right) G$ (5)

Young's modulus $(E) = (1+\sigma)\, 2G$ (6)

Poisson's ratio $(\sigma) = \left(\frac{L-2G}{2(L-G)}\right)$ (7)

Acoustic impedance $(Z) = \rho U_l$ (8)

Microhardness $(H) = (1-2\sigma)\frac{E}{6(1+\sigma)}$ (9)

Debye temperature $(\theta_D) = \frac{h}{k}\left(\frac{9N}{4\pi V_m}\right)^{1/3} U_m$ (10)

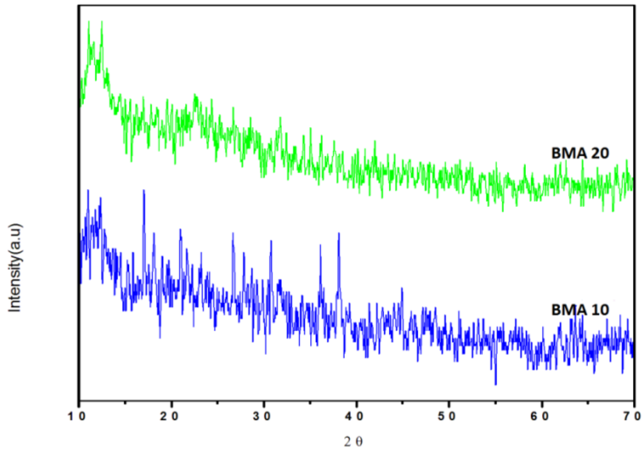
where ρ, U_l, U_s h, k, N and V_m are the density, longitudinal velocity, Shear velocity, Planck's constant, Boltzmann's constant, Avogadro's number and molar volume respectively.

Mean sound velocity $U_m = \left[\frac{1}{3}\left(\frac{2}{{u_s}^3} + \frac{1}{{u_l}^s}\right)\right]^{1/3}$

4. Results and Discussion

XRD Analysis

X-ray diffraction is a useful method to detect readily the presence of crystals in a samples. From the result of X-ray diffraction, the prepared glass system [(Fig1] was found to be in the form of broad halo, which is characteristic of amorphous structure (14). This indicates the absence of long range atomic order and lack of periodicity of the three dimensional network



The density, molar volume, longitudinal velocity and shear velocity, of the different glass specimen with respect to change in the mol% of the Al_2O_3 are reported in Table 2. Elastic moduli and Poisson's ratio are given in Table 3 The, acoustic impedance, microhardness and Debye temperature are presented in Table 4.

Table 2: Values of density, molar volume, longitudinal velocity and shear velocity of BMA glass system

Name of the sample	*Density (ρ) × 10^{3} kgm^{-3}*	*Molar volume (V_m) cm^3/mol*	*Ultrasonic velocity ms^{-1}*	
			Longitudinal (U_l)	*Shear (U_s)*
BMA1	4.2467	18.287	4898.4	2647.5
BMA2	4.3327	17.922	5010.6	2710.2
BMA3	4.4101	17.86	5239.9	2891.7
BMA4	4.5492	17.4868	5358.5	2982.6

Table 3: Values of longitudinal, shear, bulk and Young's moduli and Poisson's ratio of BMA glass systems

Name of the sample	Longitudinal modulus L ´ 109 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
BMA1	101.896	29.766	62.208	77.014	0.2936
BMA2	108.777	31.824	66.344	82.312	0.2932
BMA3	121.086	36.876	71.916	94.481	0.281
BMA4	130.623	40.469	76.664	103.241	0.2755

Table 4: Values of acoustic impedance, microhardness and Debye temperature of BMA glass systems

Name of the sample	Acoustic impedance Z × 10^7 kgm^{-2} s^{-1}	Microhardness H × 10^9 Nm^{-2}	Debye temperature θ_D K
BMA1	2.08	4.094	398.81
BMA2	2.17	4.383	409.67
BMA3	2.31	5.395	437.66
BMA4	2.43	6.055	503.12

The density is a powerful tool, capable for exploring the changes in the structure of glasses and is affected by structural compactness, changes in geometrical configurations, co-ordination numbers, cross-link densities and dimensions of interstitial spaces of the glass system. It can be seen from the table 2 that the density increases while molar volume decreases with increase in mol% of Al_2O_3. The structure of the glass depends on the nature of Al_2O_3 entering in the network and hence the density of the glasses. (15). The addition of Al_2O_3 into the BM glass network caused the density to increase and this indicated that the Al^{3+} ions enter the network of the glass as a glass former in tetrahedral coordination. The presence of AlO_4 leads to the increase in connectivity and rigidity of the network. Similar conclusion was also reported by Rada, (16)

The structural role of Al_2O_3 in oxide glasses is important. This oxide has insufficient oxygen to form a tetrahedral network. Al^{3+} ions become four-coordinated with oxygen if there are sufficient oxygen ions from the modifier oxides in the glass Abd EI-moneim etal. (17) reported that CaO molecule in the TiO_2-30CaO-30Al_2O_3-40B_2O_3 glass system converts Al_2O_3 molecule producing two AlO_4 units and Al^{3+} incorporated into the network resulting in the formation of Al-O-B linkage and they concluded that their is an increase in the connectivity of the glass compared with the parent pure B_2O_3 glasses.

It can be observed from the table 2 that the longitudinal (U_l) and shear (U_s) velocities increase almost linearly with the increase in concentration of Al_2O_3, but the rate of increase is greater than that of U_s. The velocity of B_2O_3-MnO_2 glass is increased by the introduction of Al_2O_3 indicating the conversion of some BO_3 units into BO_4 units. Further the increase of Al_2O_3 content at the expense of MnO_2 cause the increase in ultrasonic velocity and a simultaneous increase in the number of BO_4 units that increase the stability of the glasses. Al^{3+}incorporated in the glasses as a network former and to form AlO_4 tetrahedral and B-O-Al linkages.

Table 3 shows the values of longitudinal, shear, bulk and Young's moduli as a function of Al_2O_3 concentration which varies in a similar fashion as ultrasonic velocities. The increase in the values of elastic moduli has been attributed to an increase in the packing density, rigidity and hence the formation of stronger structural building units in the glass network. The large difference between L and G arises from volume effect. The change in volume due to compressions and expansions involved in longitudinal strain is pronounced while no change in volume is involved in shear strain (18).

In general, Poisson's ratio of the order of 0.1 to 0.2 reveals high cross link density while low cross link density has the Poisson's ratio between 0.3 and 0.5. Ultrasonic velocities can be utilized in the calculation of the Poisson's ratio. The value of the Poisson's ratio decreases from 0.2936 to 0.2755 with the increase of Al_2O_3 content as shown in table 3. This decrease can be explained in terms of the introduction of covalent bond that formed glass network as B-O-Al.

The acoustic impedance increases with increase in mol% of Al_2O_3 content in the glass system confirming the increase in rigidity of the structure of the glass. Further, the increase in microhardness expresses the stress required to eliminate the free volume of the glass in the present study, the increasing microhardness indicated the increase in structural connectivity of the glasses.

The results are further confirmed by another parameter, the Debye's temperature which represents the temperature at which all modes of vibration in solid are excited and its increasing trend implies an increase in the rigidity of glass. From table.4. it can be observed that the increase in Debye temperature values confirms the occurrence of strong ring formation in glasses. Such an enhancement of Debye's temperature is attributed to the increase in the number of atom in the chemical formula of the glass and increase in ultrasonic velocity (19). The continuous increase of Debye temperature also suggests that the compactness and structure leading to increase in mean sound velocity.

5. Conclusion

The density, ultrasonic velocites and other evaluated parameters of studied B_2O_3 – MnO_2 - Al_2O_3 glasses have revealed that;

(i) the density of the studied glass system increases whereas the molar volume decreases with increase in mol% of Al_2O_3 which indicates there is an increase in connectivity of the network structure.
(ii) The elastic moduli and remaining parameters increase while Poisson's ratio decreases indicating the increase in rigidity of the network structure.

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