Elastic Behaviour of Zirconium Doped Manganese Borate Glass by Employing Ultrasonic Pulse Echo Techniques

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Abstract

Glasses of the system $60B_2O_3$-(40-x)MnO_2-xZrO_2 (where x= 0, 5, 10, 15, 20 mol. %) have been prepared by the rapid melt quenching method. The density of each glass samples were determined using Archimedes method with water as a floatation medium. The molar volume have been estimated and analysed for the present study of manganese borate glasses added with zirconium oxide. Ultrasonic velocities, both longitudinal and transverse have been measured using the pulse-echo method at a frequency of 4MHz at room temperature. The elastic moduli, Poisson's ratio, acoustic impedance, microhardness and Debye temperature have been calculated from the measured data. The sound velocity, density, elastic moduli, acoustic impedance, microhardness and Debye temperature increase with increasing ZrO_2 concentration. Poisson's ratio decreases with increasing ZrO_2 concentration. The variation of these parameters have been explaining using structural modify present and the dimensionality of the glass network.

1. Introduction

Borate glasses are very interesting amorphous materials considering their specific structure and physical properties with changes in chemical composition and thus find wide applications. Borate glasses are glasses known for their low glass transition temperature and their boron anomaly which is manifested by the double coordination of the boron which can have either coordination three or coordination four according to the composition of the glass bath and the configuration of the atoms of the neighborhood (1– 4). In pure B_2O_3 glass structure most of the boron is involved in B_3O_6 (boroxol) ring. Addition of modifier breaks boroxol ring and thereby produced BO_3 and BO_4 units (5–7). In addition, modifier also changes the physical properties along with structural modifications.

Recently, a study of borate oxide glasses containing with transition metal ions (TMI) has received considerable attention due to their attractive combination of physical and chemical properties. TMI doped borate glasses have application in microelectronics, optical glasses, solid state laser photoconducting devices, magnetic materials, etc (8–11). It is used to probe glass structure and exhibits different valance states in different glass matrices depending on quantitative properties of glass formers and modifiers, ion size in glass matrices, field strength and mobility of the cations Mn^{3+} and Mn^{2+} are well known paramagnetic ions while Mn^{2+} and Mn^{4+} are luminescent activators. Trivalent manganese ions in glasses exhibit octahedral coordination having large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbit, whereas divalent manganese ion with tetrahedral and octahedral coordination possesses small magnetic anisotropy due to zero angular momentum (12–14).

The addition of metal oxide ZrO_2 bring about desirable changes in the glass network due to their excellent chemical and mechanical stability (15). Zirconium products can be used in a wide range of engineering applications. The highly refractory nature and good resistance to aggressive environments, such as melted glass, are exploited in the high temperature chemical industry (16). For the purpose of maximal toughening, ZrO_2 was often acted as a considerable candidate in laminated composites owing to its excellent toughness, both for strong layers structure and for weak layers structure.

The aim of the present work is to understand the structural role of ZrO_2 in B_2O_3-MnO_2 glasses matrix by studying the ultrasonic and XRD analysis of these glasses.

2. Experimental Details

Glass Preparation

A series of glass samples of formula $60B_2O_3$-$(40-x)MnO_2$-$xZrO_2$ with $0 \leq x \leq 20$ mol. % composition were prepared by using the melt quench technique. The required amount of chemicals, boron trioxide (B_2O_3), Manganese oxide (MnO_2) and Zirconium oxide (ZrO_2) 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 1100 ºC. The melt was poured into a brass mould to form samples of dimensions 10mm diameters 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 two parallel sides were polished using a polishing machine in order to obtain suitable sample for the ultrasonic measurements.

The amorphous nature of the sample is confirmed by X-ray diffraction technique using Philips (Philips PW 1050/51) X-ray powder diffractometer with CuKα radiation. The density of the glasses were determined by Archimedes method with water as a floatation medium, while their molar volume was calculated from the molecular weight (M) and density (ρ) (17-18). All the weights were measured with digital balance with ±0.001g standard error.

Ultrasonic velocities measurements have been carried out using pulse-superposition techniques at a frequency of 4MHz at room temperature. By measuring the thickness of the sample (d), longitudinal (U_l) and shear (U_s) wave velocity were calculated using the relation U=2d/t, where t is transit time taken as ultrasonic waves in the glass samples. The molar volume, elastic moduli, Poisson's ratio, acoustic impedance, micro hardness and Debye temperature have been calculated using the following relations (19):

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

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

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

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

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 composition in mol. % of glasses are present in Table 1.

Table-1: Nominal composition (mol. %) of glasses

Smpales	**Nominal Composition**			**Remarks B_2O_3**
	B_2O_3	**MnO_2**	**ZrO_2**	
BM	60	40	0	Mol. % of B_2O_3 is constant
BMZ05	60	35	5	
BMZ10	60	30	10	
BMZ15	60	25	15	
BMZ20	60	20	20	

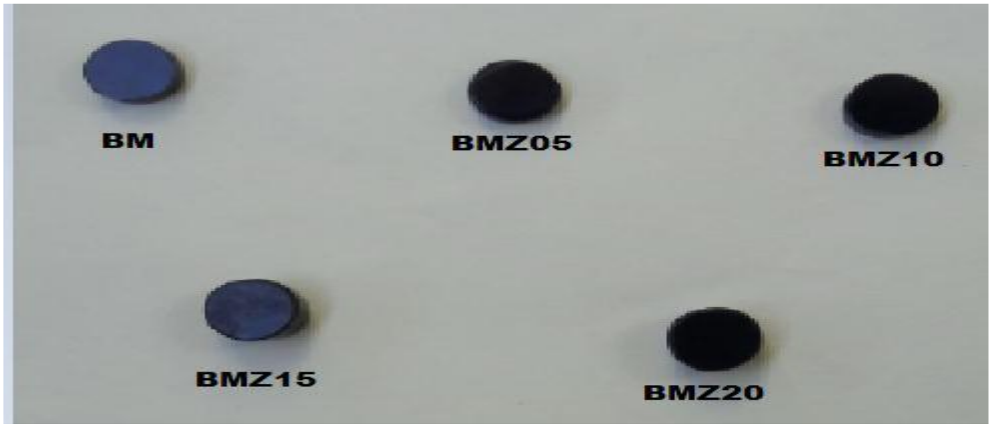

Plate 1 BMZ Glass Specimen

3. Results and Discussion

3.1 XRD analysis

Figure 1 shows XRD spectrum of BM and BMZ20 glass samples. The X-ray diffraction spectra showed the diffused bands characteristic of the X-ray diffraction pattern of amorphous materials. The spectra did not show any sharp peaks and this confirms the fact that glass samples are amorphous in nature (20).

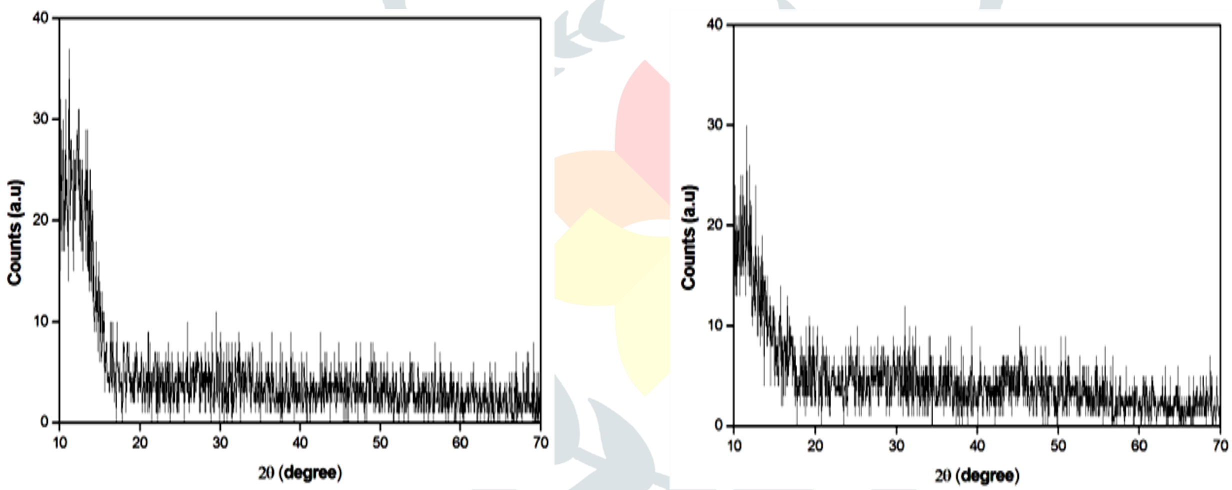

Fig. 1. XRD pattern of BM sample XRD pattern of BMZ20 sample

3.2 Ultrasonic Study

The experimental value of density and molar volume, longitudinal and shear velocity of the different glass specimen with respect to change in mol. % of ZrO_2 are collected in Table 2. The calculated longitudinal modulus, shear modulus, bulk modulus, Young's modulus, Poisson's ratio are reported in Table 3. The acoustic impedance, microhardness, and debye temperature are depicted in Table 4.

Borate glasses exhibit commonly three or four co-ordinated with oxygen and these are exhibited in a wide variety of borate glasses or minerals. The addition of modifier oxide and transition metal ions into the borate glasses brings drastic structural changes in the structural units with the evaluation of four coordinated boron and non-bridging oxygen (NBO) ions in the glass network. The existence of triangular (BO_3) and tetrahedral (BO_4) borate species and their concentrations depend on the relative concentration of the transition metal ions and modifier oxides in the glass network.

The variation of density and the molar volume with respect to ZrO_2 content is shown in Table 2. With increasing ZrO_2 content in the manganese borate glass an increase in density is seen followed by a decrease in molar volume values. This increase in density may be attributed to the heavier molecular weight of the dopant ZrO_2. Also the addition of ZrO_2 in steps leads to the conversion of large number of BO_3 triangles into BO_4 tetrahedra which are denser than that of BO_3 triangle and hence the increase in density of the developed glass system may arise (21). Generally the density and molar volume should be opposite to each other and the same is the case in this system also. Here, the molar volume shows a continuous decrease as ZrO_2 concentration increases opposite to the density trend. As more BO_4 units linked to divalent zirconium ions are much denser, occupying less volume, the formation of more BO_4 causes the decrease in molar volume. Hence the incorporation of ZrO_2 in the manganese borate glass system contracts the glass network, increases the rigidity of the glasses resulting in a causes decrease in interatomic space and close – packing atomic structure (22).

It is observed from the Table. 2 that both longitudinal and shear velocities increases with increase linearly with increase in ZrO_2 concentration. The observed increase in ultrasonic velocities can be explained such that, as Zr^{2+} ions enter interstitially, there is some type of modification occurs in the already existing B-O-Mn linkages into B-O-Zr bond. This behaviour indicates that the replacement of MnO_2 by ZrO_2 improves the mechanical properties and strength of the cross-links between chains of the manganese borate glasses.

Table-2: Values of density, longitudinal, shear modulus and molar volume of BMZ glass system

Sample	Density ($\rho \times 10^3$ kgm^{-3})	Molar volume V_m(x10^{-6}m^3/mol)	Ultrasonic velocity (ms^{-1})	
			Longitudinal (U_ℓ)	Shear (U_s)
BM	4.1523	19.10	4623.4	2466.5
BMZ05	4.3056	18.88	4872.6	2627.4
BMZ10	4.3471	18.62	4988.3	2689.3
BMZ15	4.4102	18.25	5112.7	2750.1
BMZ20	4.5284	18.01	5386.5	3013.6

Table-3 Values of longitudinal (L), shear (G), bulk (K), Young's moduli (E) and Poisson's ratio (σ) of BMZ glass system

Sample	Longitudinal modulus L (GPa)	Shear modulus G (GPa)	Bulk modulus K (GPa)	Young's modulus E (GPa)	Poisson's ratio (σ)
BM	88.76	25.26	55.08	65.73	0.3011
BMZ05	129.24	37.19	79.65	96.55	0.2983
BMZ10	140.21	38.69	88.63	101.32	0.2969
BMZ15	146.34	43.14	88.82	111.39	0.2964
BMZ20	161.55	50.50	94.22	128.54	0.2736

Table .3 Shows the values of longitudinal, shear, bulk and Young's moduli as a function of ZrO_2 concentration which varies in a similar to the ultrasonic velocities. The increase in elastic moduli of the glass systems may be attributed to an increase in the packing density, rigidity and hence the formation of stronger structural building units in the glass network, hence transforming borate triangular units in to denser, stronger tetrahedras which cause the more compact structure (23).

Table-4 Values of acoustic impedance (Z), microhardness (H), Debye temperature (θ_D) BMZ glass system

Sample	Acoustic impedance Z (10^7 kgm^{-2} s^{-1})	Microhardness H (GPa)	Debye temperature θ_D (K)
BM	1.9198	3.3498	148.01
BMZ05	2.7796	5.0092	331.26
BMZ10	2.9380	5.9141	359.62
BMZ15	3.0405	6.0111	372.69
BMZ20	3.2379	7.6545	398.34

The behaviour of the Poisson's ratio is nearly opposite to that observed for the elastic moduli variations, i.e.Poisson's ratio decreases with increase of modifier concentration. Addition of ZrO_2 into B_2O_3–MnO_2 glass, results in an decreases in Poisson's ratio which is attributed to the introduction of covalent bonds B-O-Zr are more bridging oxygens leading to more BO_4 units that formed the more rigid glass network (24). The acoustic impedance (Table .4) increase with increase in mol% of ZrO_2 content in the glass systems. The increase acoustic impedance confirms the increase in rigidity of the glass structure.

Microhardness (H) of the glasses is shown in table 4, which was calculated according to the equation no 8. The Variation of Microhardness has the same attitude as the elastic moduli with increase ZrO_2 content and hence the observed increase in microhardness indicates the increase in structural connectivity of the glasses and the observed variation in H provides further evidence about the rigidity and stability of the glass structure (25).

Debye temperature plays an important role in solid materials in the determination of elastic moduli and atomic vibrations. θ_D represents the temperature at which all modes of vibrations in a solid are excited and its increase implies an increase in the rigidity of glass. In the present glass system the value of θ_D increases from 148K to 398K, as ZrO_2 concentration increases. The observed increase in the Debye temperature supports the claim that the addition of Zr^{2+} ion will strengthen the structure of borate manganese glass which reduces the vibration of the lattice of the formed glasses (26). As it can be seen from table.4, the gradual increase of Debye temperature also suggests increase in the compactness in the structure leading to increase in mean sound velocity (27).

4. Conclusion

The $60B_2O_3$-(40-x)MnO_2-xZrO_2 (with $0 \leq x \leq 20$ mol. %) glass samples were successfully prepared. Based on the result obtained, it demonstrated that the density of the glasses increases whereas the molar volume decreases which indicates the increase in connectivity of the network structure. The ultrasonic velocities and hence the various elastic moduli with the increase in concentration of ZrO_2 implies the conversion of three coordinated boron into four coordinated borons thereby increasing the rigidity and hence the compactness of glass structure**.** The similar results are observed in the Poisson's ratio, micro hardness, acoustic impedance and Debye temperature due to ZrO_2 in doping. Therefore it is concluded that the addition of ZrO_2 improves the strength and stability of manganese borate glass system.

5. References

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