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Research Article

MECHANICAL AND STRUCTURAL PROPERTIES OF BARIUM OXIDE DOPED MANGANESE BORATE GLASS

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ABSTRACT

Ultrasonic velocity and density measurements have been carried out on B_2O_3-MnO_2-BaO glass. The amorphous nature of the glasses was confirmed by X-ray diffraction pattern. Various parameters, viz., molar volume, longitudinal modulus, shear modulus, bulk modulus, Young's modulus, Poisson's ratio, acoustic impedance, microhardness and Debye temperature have been evaluated 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. The FT-IR spectra show that glass network consists of borate structural units and the BO_4 units increase with increasing BaO concentration.

INTRODUCTION

The glass materials are one of the possible alternatives to concrete, because they can be transparent to visible light and their properties can be modified by composition and preparation techniques. The structure of borate glasses was investigated by XRD [1.2], FT-IR [3.4], Raman [5] and NMR [6] spectroscopies. All investigations report that B_2O_3 is composed essentially of BO_3 units forming three-member (boroxol) rings. Boron trioxide is a basic glass former because of its higher bond strength, lower cation size, smaller heat of fusion and valence of (=3) of B. B_2O_3 can be considered to posses highest glass formation tendency because molten B_2O_3 does not crystalline by itself even when cooled at a slowest rate. The size of B^{3+} ion is very small and it can fit into the trigonal void created by three oxide ions in mutual contact, forming a BO_3 units. BO_3 units are the primary building blocks in all borate glasses [7]. The proportion of trigonal and tetrahedral boron depends on both the chemistry and concentration of the added modifier oxide. Borate glasses with various compositions are widely used in different industries.

Oxide glasses containing significant concentrations of transition metal ions or low mobility metal ions such as Zn^{2+} or Ba^{2+} exhibit electronic conductivity and may be regarded as high resistivity semiconductors [8]. Borate glass formulations have been adopted worldwide for immobilization of high – level radioactive liquid waste (HLW), but are not suitable for sulphate bearing HLW. Addition of barium to borate glasses has provided a suitable glass matrix for immobilization of sulphate bearing HLW [9]. Glasses containing barium are also proved to be good radiation shielders [10]. In particular, barium borate glasses demonstrate high refraction, low dispersion, high electric resistance, a low co-efficient of thermal expansion and a relatively low melting point [11-12].

The B_2O_3-BaO glass system is interesting from fundamental point of view, because it exhibits anomalies in the compositional dependence of some physical properties (eg: glass transition temperature, T_g). This phenomenon is widely known as the "boron anomaly". Special interest in glasses with a relatively high BaO content arises from their potential use in optical fibre technology [13].

In the light of above, the aim of the present work is to investigate the role of BaO on mechanical and structural properties in B_2O_3-MnO_2 glass using ultrasonic, XRD and FTIR studies.

Experimental

Sample preparation

The series of glasses containing 5 specimen are prepared from AR grade chemicals (minimum assay 99.9 %) B_2O_3, MnO_2 and BaO. The required amount (approximately 10g) of different chemicals in powder form is weighed using a single pan digital balance having an accuracy of ±0.001 g. The mixtures of

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components of chemicals were mixed together by grinding the mixture repeatedly using a mortar to obtain a fine powder. The homogeneous mixture is put in a platinum crucible and placed in a furnace. The furnace is electrically heated under ordinary atmospheric conditions at a temperature from 900 to 1000°C. The obtained glass samples were cast into a copper mold having dimensions of 10 mm diameter and 6 mm length. Then the glass samples are annealed at a temperature 400°C for two hours to remove any internal stresses. The prepared 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 digital vernier calipers with an accuracy of 0.0001 mm. The samples prepared are chemically stable and non - hygroscopic. All the obtained samples were visually homogeneous and transparent. The nomenclature and the composition in mol% of different glass specimen are listed in Table 1, and the photograph of glasses is shown in plate 1.

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 samples were compressed into thin pellets using KBr for the infrared measurement. The infrared spectra were recorded using Nexus FT-IR at a range of 400 cm^{-1} to 4000 cm^{-1} at room temperature. The ultrasonic velocities (longitudinal and shear) were measured using Pulse Echo Overlap method. The density measurement was based on the Archimedes Principle with deionized as buoyant liquid.

Table 1 Nomenclature and composition of glass samples

Sample No.	Nomenclature	Composition in mol%	Remarks
1	BM	60-40	
2	BMBa 05	60-35-5	Mol% of B_2O_3 is constant
3	BMBa 10	60-30-10	
4	BMBa 15	60-25-15	
5	BMBa 20	60-20-20	

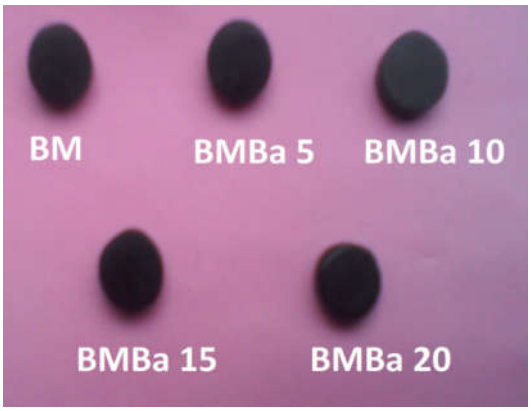

Plate 1 BMBa glass specimen

Theory and Calculation

Ultrasonic study

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.

$$U=\frac{2d}{t} \quad (1)$$

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

Density

The density of the glass samples was measured using relative measurement technique. If density was calculated using the formula

$$\rho=\rho_w \frac{w_a}{w_a-w_b} \quad (2)$$

where W_a and W_b are the weight of the glass samples in air and Density of the water is respectively.

Molar volume **(V_m)** $V_m = \frac{M}{\rho}$ [3]

Longitudinal modulus (L) $L = \rho U_\ell^2$ [4]

Shear modulus (G) $G = \rho U_s^2$ [5]

Bulk modulus (K) $K = L - \left(\frac{4}{3}\right)G$ [6]

Young's modulus (E) $E = (1 + \sigma)\, 2G$ [7]

Poisson's ratio (σ) $\sigma = \left(\frac{L - 2G}{2(L - G)}\right)$ [8]

Acoustic impedance (Z) $Z = U_l \rho$ [9]

Microhardness (H) $H = (1 - 2\sigma)\frac{E}{6\,(1+\sigma)}$ [10]

Debye temperature (θ_D) $\theta_D = \frac{h}{K}\left(\frac{9N}{4\pi V_m}\right)^{1/3} U_m$ **[11]**

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

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

RESULTS AND DISCUSSION

XRD analysis

The XRD pattern of BMBa10 and BMBa 20 glasses are 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 structure. The absence of long-range atomic arrangement is a clear indication of amorphous nature of the glass samples [14, 15].

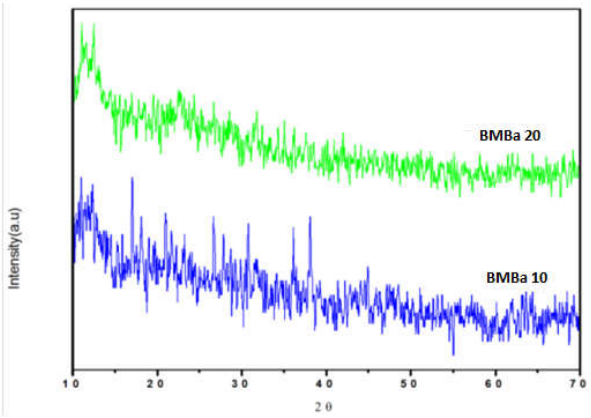

Fig. 1 X-Ray diffractogram for BMBa glass specimen

Ultrasonic Study

The experiment data (density, longitudinal velocity and shear velocity) and molar volume of the different glass specimen with respect to change in mol% of BaO are listed in Table.2. The values of longitudinal modulus, shear modulus, bulk modulus, Young's modulus and Poisson's ratio are reported in Table 2. The acoustic impedance, microhardness and debye temperature are presented in Table 2.

In borate glasses, the main structural units are triangular [BO_3] and tetrahedral [BO_4] which form different super structural units. The addition of transition metal / alkali earth 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/alkali earth ions in the glass network. The dominant role of BaO content in manganese borate glass is observed by ultrasonic and FT-IR studies.

The variation of density and the molar volume with respect to BaO content is shown in Table 2. With increasing BaO content in the manganese borate glass an increase in density is seen followed by a decrease in molar volume values. A possible explanation of the general increase in density is a change in the structure of glass with increasing oxide contents. It is believed that the presence of Ba^{2+} ions, which are situated in cavities in the empty space of the network. The availability of more oxygen from BaO shifts the coordination [BO_3] to [BO_4]. The tetrahedral BO_4 groups are strongly bonded than the triangular BO_3 groups and therefore a compact structure is expected leading to a higher density.

In general, it is expected that the density and the molar volume should show opposite behavior to each other. The molar volume is of greater interest, since it relates directly to the spatial distribution of the oxygen in the glass network. The decrease in molar volume causes decrease in interatomic space and hence increases in packing density.

It can be observed from the Table 2. that the longitudinal U_l and shear (U_s) velocities increase linearly with the increase in concentration of BaO, but the rate of increase of U_l is greater than that of U_s. The progressive additions of BaO content shows an increase in both longitudinal and shear velocities. The observed increase in ultrasonic velocities can be explained such that, as Ba^{2+} ions enter interstitially, there is some type of modification occurs in the already existing B-O-Mn linkages into B-O-Ba bond. This behaviour indicates that the replacement of MnO_2 by BaO improves the mechanical properties and strength of the cross-links between chains of the manganese borate glasses.

Table 2 Values of longitudinal velocity (U_l), shear velocity (U_s), density (ρ) and molar volume (V_m) of BMBa glass system

Name of the sample	Density ρ (10^3 kgm^{-3})	Molar volume V_m (10^{-6}m^3/mol)	Ultrasonic velocity (ms^{-1})	
			Longitudinal (U_l)	Shear (U_s)
BM	4.1523	19.10	4623.4	2466.5
BMBa 05	4.2298	18.88	4672.8	2478.5
BMBa 10	4.2966	18.58	4700.0	2530.6
BMBa 15	4.3931	18.17	4850.3	2661.0
BMBa 20	4.4997	17.74	5064.5	2815.3

Table 3 Values of longitudinal, shear, bulk and Young's moduli and Poisson's ratio of BMBa glass system

Name of the Sample	Longitudinal modulus L (GPa)	Shear modulus G (GPa)	Bulk modulus K (GPa)	Young's modulus E (GPa)	Poisson's ratio σ
BM	88.75	25.26	55.07	65.73	0.3011
BMBa 05	92.35	28.98	58.18	65.85	0.2985
BMBa 10	94.87	29.51	58.54	71.30	0.2957
BMBa 15	103.34	31.10	61.87	79.92	0.2847
BMBa 20	115.41	35.66	67.89	91.04	0.2763

Table 3. Shows the values of longitudinal, shear, bulk and Young's moduli as a function of BaO 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 [16].

Table 4 Values of acoustic impedance, microhardness and Debye temperature of BMBa glass system

Name of the sample	Acoustic impedance Z (10^7 kgm^{-2} s^{-1})	Microhardness H (GPa)	Debye temperature θ_D(K)
BM	1.91	3.349	148.10
BMBa05	1.97	3.405	363.38
BMBa10	2.01	3.746	377.43
BMBa15	2.13	4.464	399.27
BMBa20	2.27	5.316	425.34

It is well known that Poisson's ratio is affected by change in the cross-link density of the glass network [17]. The change in cross-link density of the glass network is well understandable from the variations in Poisson's ratio. The observed decrease in Poisson's ratio with the addition of Ba^{2+} ions indicate the compact or tight packing of the glass structure and the formation of covalent

B-O-Ba linkages.

The acoustic impedance (Table 4) increases with increase in mol% of BaO 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 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 [18].

Debye temperature is associated with the highest allowed mode of vibration and it reflects the stability and strength of bands of a solid. It is known that Debye temperature depend directly on the mean ultrasonic wave velocity. Table 4 shows the values of θ_D of the manganese borate glasses as a function of BaO concentration. The increase in θ_D can be attributed to strengthening of the structure as revealed to increase the hardness. Also increase in the rigidity of the glass is associated with an increase in the lattice vibrations.

FT-IR study

Infrared spectroscopy is one of the most useful experimental techniques available for easy structural studies of glasses. As this technique leads to structural aspects related to both local units constituting the glass network and the anionic sites hosting the modifying cations. The effect of substitution of BaO into manganese borate glasses were investigated by recording their FTIR spectra in the range 4000-400 cm^{-1}. The observed band positions and their corresponding assignments of samples have been tabulated in Table 5.

The well-known characteristic band (at 806 cm^{1}) of vitreous B_2O_3 is assigned to the symmetric stretching vibrations of boroxol rings. The peak at 806 cm^{-1} is found missing in the FTIR spectra of BM glass, which indicates the absence of boroxol rings in the glass network. The addition of MnO_2 to B_2O_3 breaks these rings and hence consists of only BO_3 and BO_4 groups [19]. The obtained broad bands confirm the amorphous nature of the studied glass samples and are in good agreement with XRD.

The FTIR spectra consists of two conventional bands due to the presence of borate group and they are due to stretching vibration of B-O bond of the trigonal [BO_3] units at 1384-1399 cm^{-1} and B-O bond stretching of the tetrahedral [BO_4] units at 1032-1095 cm^{-1}. The relative area of the first group of bands is opposite to the second group of bands when the glasses are doped with BaO. The intensity of band due to BO_3 units decreases and BO_4 structural units increases with increasing BaO concentration, indicating a gradual increase in the formation of BO_4 structural units at the expense of BO_3 units [20].

Since the addition of BaO to the manganese borate glass gives a oxygen atom, which is accommodated in the network, a transfer of some boron atoms from triangular BO_3 to BO_4 occurs and it produce a more polymerized borate network. This can be deduced from the increase in the intensity of band at 1034 cm^{-1} and decrease in the intensity of the band at 1384 cm^{-1}. Similar conclusion is also observed by Lakhwant Singh et al., [21] for their glass systems**.** The third band is observed around 700 cm^{-1} due to bending vibration of B-O-B linkages in the borate network [22]. The band at 425 cm^{-1} is due to the vibration of metal cations in bi-valent state Mn^{2+} [23] which is present is all samples.

The additional bands at lower frequencies (474-550 cm^{-1}) are observed in the spectra and can be attributed to vibration of metal cation (Ba^{2+}). Hence, network modifying behavior is observed in which these ions enter the interstices of the network.

The addition of BaO into BM glass matrix, makes an increase in BO_4 units and decrease in the BO_3 structural units, indicating an increase in the compactness in the glass network.

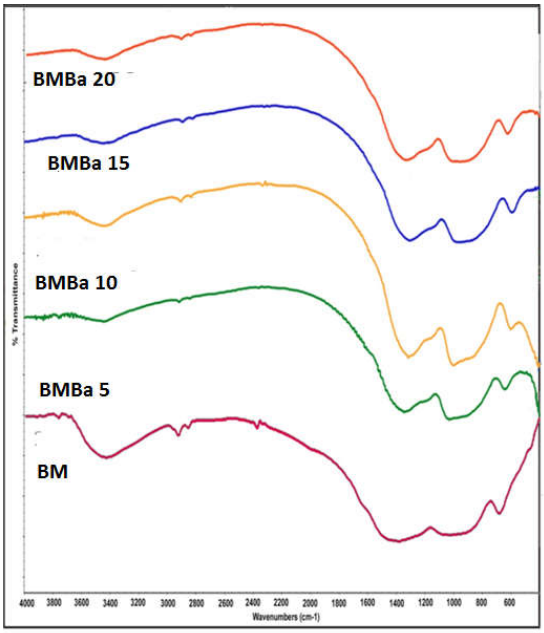

Fig 1 FTIR spectra of BMBa glasses

Table 5 Band positions and their corresponding assignments of infrared spectra and BMBa glass system

Wave number cm^{-1}	Assignment
~1384	B-O stretching vibrations of the trigonal BO_3 units in meta-,Pyro- and ortho-borate groups
1089	B-O stretching vibrations of the tetrahedral BO_4 units in tri-, tetra and penta-borate groups
~690	B-O-B bending vibrations
~425	Specific vibration of Mn – O bonds
~470	Specific vibration of Ba – O bonds

CONCLUSION

- The density of the glasses increases whereas the molar volume decreases which indicates the increase in connectivity of the network structure.
- The velocity, elastic moduli and other parameters increase and Poisson's ratio decreases with the addition of BaO content and favours the increase in bridging oxygen due to the formation of BO_4 units.
- IR spectra of BMBa glasses exhibited BO_3 and BO_4 structural units. With an increase of BaO concentration, BO_3 units are gradually converted into BO_4 units.

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