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Compositional Effect of Barium Ions (Ba^{2+}) on Ultrasonic, Structural and Thermal Properties of LeadBorate Glasses

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Abstract: ***Glasses of the formula $68B_2O_3$-(32-x)PbO-xBaO ($0 \leq x \leq 12$) were synthesized by standard melt quench technique and investigated their properties using XRD, ultrasonic, FT-IR and DTA studies. No sharp peaks are existing in the XRD spectra and the broad halo appeared around $2\theta \approx 30^o$, which reflects the characteristics of amorphous nature. Density decreases due to the replacement of higher molar mass by lower molar mass. The ultrasonic velocity varies with the gradual substitutions of barium ions in leadborate host glass matrix. The variations in elastic moduli such as L, G, K and E), Poisson' sratio(σ), acoustic impedance(Z), microhardness (H) and Debye temperature (θ_D)were observed which resulted in compact glasses. The functional groups of prepared glasses were studied by FTIR analysis and BO_4 structural units enhanced with decreasing BO_3 structural units. Characteristic temperatures of DTA increase because of the higher bond strength of barium ions and also strength of the glasses.***

Kwywords :BPBa glasses, DTA, FTIR, Ultrasonic velocity

I. INTRODUCTION

The borate glasses are studied intensively due to existence of their structural properties. Besides, these glasses are keenly attracted by research community because of their unique and novel properties for instance wide range formation regions, low melting point, high radiation shielding properties and so on [1, 2]. PbO can play dual role in the glass matrices, it exists as a modifier in octahedral (PbO_6) structural units and as a former in tetrahedral (PbO_4) form. The content of Pb^{2+} ions in tetrahedral and octahedral positions developing in the glass matrices are strongly depending upon glass formers, the field strength and the ion size in the structure of the glass [3]. Last few decades, many attempts were made in order to study the significant of PbO in the glass matrices using various methods and techniques [4-6]. In the present investigation, binary B_2O_3–PbO glass is choosing as a parent glass because it exhibits low rate of crystallization, high moisture resistance, refractive index and density.

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Leadborate glasses doped with alkaline earth metal oxide have potential applications in various domains of modern technology and show an interesting behaviour [7]. Though barium oxide is not suitable for preparing glasses by alone, it is used to behave as a network former/modifier in glass matrices and also addition to glass network, stabilizes the glass [8, 9]. Moreover doping with barium ions, these glasses show low dispersion, co-efficeint of thermal expansion and melting point as well as high refraction and electric resistance [10, 11]. The authors were attempted to synthesis and characterize the BaO doped B_2O_3 – PbO glasses by using several techniques such as XRD, ultrasonic velocity, DTA and FT-IR.

II. EXPERIMENTAL

A. Sample preparation

Glasses of formula 68B2O3-(32-x)PbO-xBaO were synthesized by the standard melt-quench technique. BaO was increased form 0 to 12mol%. While the content of PbO was decreased form 32 to 20%. The pure boron trioxide (B2O3), lead monoxide (PbO) and barium oxide (BaO) were mixed with each other by continuous grinding to get a fine powder. The ground mixtures were taken in the crucible and placed in a high temperature furnace at 900 oC. As a result, the mixture was melted homogeneously. The bubble free liquid was casted into prewarmed copper mould to obtain the glass samples of dimension 6mm thickness and 10mm diameter The prepared glasses were sintered at 450 oC for 3 hours in order to remove internal stresses which caused during sample preparation process. Then the glasses were polished using a polishing machine and the polished glasses are ready for ultrasonic characterization. The nomenclature and elemental composition of the prepared glasses are tabulated in Table 1.

The XRD technique (PAN Alytical x' Pert PRO Powder X-ray Diffractometer, 15kVA UPS support) has been performed in order to study the crystal structure of prepared glasses. The density of the prepared glasses was estimated using Archimedes principle with water; it is used as a floatation medium. The Pulse – Echo Overlapping method was used to study the longitudinal and shear velocities of the glasses at 303K with 10MHz X-cut and Y-cut transducers. These transducers were in contact with each of the samples by a couplet to ensure no space between the transducers and the glass. By giving sustained pressure on the probe, the echo waveforms were received and stored in the memory. Velocity is calculated using the relation,

$$U=2d/t \quad (1)$$

The mechanical and elastic properties have been understand from the following relations,

$$\text{Molar Volume} = \frac{M}{\rho} \quad (2)$$

$$\text{Longitudinal Modulus} = \rho U_{\lambda}^{2} \quad (3)$$

$$\text{Shear modulus} = \rho U_{s}^{2} \quad (4)$$

$$\text{Bulk Modulus} = L - \left(\frac{4}{3}\right)G \quad (5)$$

$$\text{Young's Modulus} = (1+\sigma)2G \quad (6)$$

$$\text{Acoustic Impedance} = U_{\ell}\,\rho \quad (7)$$

$$\text{Poisson's Ratio} = \left(\frac{L-2G}{2(L-G)}\right) \quad (8)$$

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

$$\text{Debye Temperature} = \frac{h}{K}\left(\frac{9N}{4\pi V_m}\right)^{1/3} U_m \quad (10)$$

where K is the Boltzmann's constant, N is the Avogadro's number, h is Planck's constant and V_m, molar volume of the prepared glasses. The mean sound velocity estimated by

$$U_m = \left[\frac{1}{3}\left(\frac{2}{U_s^3} + \frac{1}{U_{\lambda}^3}\right)\right]^{-1/3} \quad (11)$$

The FTIR spectrum were studied for the powdered glasses at room temperature in the wavenumber range 400-4000 cm^{-1} with a resolution of 4 cm^{-1} by RX1 Perkin Elemer FTIR spectrometer using KBr pellet technique. The thermal transition parameters such as T_g, T_c and T_m of these glasses were determined by Differential Thermal Analyser NETZSCH-STA449FS JUPITER instrument in inert gas atmosphere at a heating rate of 20°C per minute.

III. RESULTS AND DISCUSSION

A. X-ray diffraction

The synthesized glasses were bubble free, transparent and homogeneous. The non-existence of Bragg's peak in the spectrograms (Fig.1) clearly indicated that the studied samples are non-crystalline and homogeneous in nature. Moreover, the board humps around 2θ indicate that there is a existence of short range order in the glasses [12].

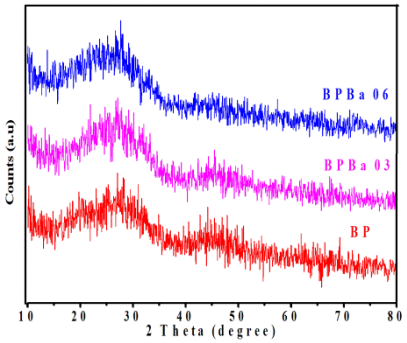

Fig. 1. XRD pattern of BPBa glasses

B. Density and molar volume

Figs. 2 and 3 show the variation of molar volume and density of barium oxide concentration in the prepared glasses. Density of solids is one of the simplest physical parameters to measure. However, it is more informative which will define the crystal structure of the prepared sample. In other words, it is also interpreted in terms of rivalry between the mass and size of the various structural units takes place in the glass. The gradual replacement of lead ions by barium ions and the corresponding variations of density and molar volume cause a monotonic decrease. Density varies from 3.9003×10^{3} kgm^{-3} to 3.7492×10^{3} kgm^{-3} and molar volume varies from $30.43\times 10^{-6}m^{3}$/mol to $29.44\times 10^{-6}m^{3}$/mol.

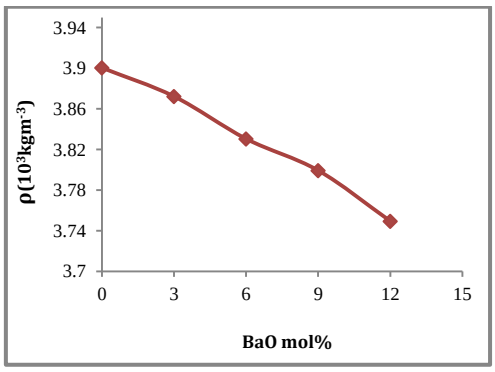

Fig. 2. Deviation of density with BaO mol%

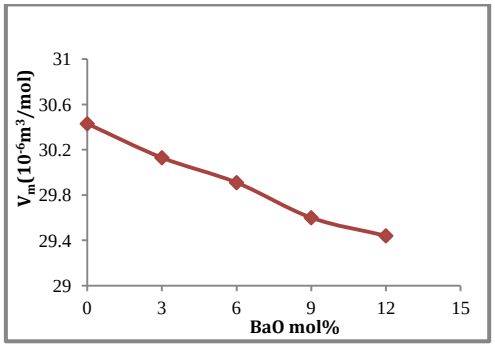

Fig. 3. Deviation of molar volume with BaO mol%

This variation is occurred due to the replacement of heavier cation by lighter and the values of density is well understandable from the deviation in the molar mass of the added components and the molar mass of PbO (223.2 g/mol) is heavier than BaO (153.33 g/mol) causes decrease in density. Similar trends also followed by many researchers [13, 15]. Generally, density and molar volume revealed an opposite attitude. But in the present report, similar trend of variation is also observed in the molar volume and this indicates that a more BO_4 units linked to divalent barium ions are much denser, occupying less volume. Hence the incorporation of BaO in the lead borate glass system contracts the glass network, increases the rigidity of the glasses resulting in a close – packing atomic structure.

Table- I: Values of longitudinal velocity (U_l), shear velocity (U_s) and elastic moduli (L & G)

Sample code	Composition in mol%			Ultrasonic velocity ms^{-1}		Longitudinal modulus L (GPa)	Shear modulus G (GPa)
	B_2O_3	PbO	BaO	Longitudinal(U_l)	Shear(U_s)		
BP	68	32	0	4260.2	2251.4	70.78	19.76
BPBa03	68	29	3	4388.2	2373.0	74.62	21.80
BPBa06	68	26	6	4559.3	2513.1	79.62	24.19
BPBa09	68	23	9	4694.6	2619.7	83.72	26.07
BPBa12	68	20	12	4835.7	2750.2	87.67	28.35

C. Ultrasonic properties

In the view of ultrasonic properties of Ba^{2+} ions doped leadborate glasses is interesting that BaO and PbO converts BO_3 units into BO_4 structural units. The successive replacement of BaO in leadborate glass matrix in the present glass increases both longitudinal and shear velocities. Hence, a modification in the structure of the glasses is resulted such that the B-O-Pb linkages are ruptured to form more covalent B-O-Ba and Pb-O-Ba linkages and also creating number of bridging oxygens [16-20]. Besides, these bridging oxygens creation, cause the trigonal borate units get converted into tetragonal borate units resulting in a decrease in molar volume, contracting the glass network. These phenomena revealed that the replacement of PbO by BaO can increase the strength of the bonds between the chains of atoms in the leadborate glasses. Hence, it is confirmed that BaO act as a modifier.

Elastic moduli are very sensitive to any structural changes in the chemical bonds, strength as well as the cross-link density of the glass matrices. In this system, the values of longitudinal modulus increases from 70.78 to 87.67 GPa and shear varies from 19.76 to 28.35 GPa while the bulk modulus increases from 44.42 to 49.86 GPa and Young's modulus from 51.64 to 71.51 GPa. The rate of fluctuation of elastic moduli is copious pronounced in L and least in G. The modifier cation Ba^{2+} is incorporated into the BP glass matrix, it will disrupt the linkages and form covalent bonding between the broken chains. This behavior increases the connectivity of the glass network as well as elastic moduli.

Table II shows that the Poisson's ratio is drastically drop from 0.3062 to 0.2609 with increasing Ba^{2+} ions. It confirms that structure becomes more compact as tetrahedral coordination of boron increases with the increase in barium concentration [21].

The variations of acoustic impedance conforming the increase in compactness of the structure of the glass. Microhardness is the resistance offered by the material to permanent indentation, a property to study the characterization of solids. It also increases like the increase in elastic moduli which indicate the polymerized glass structure and this may be due to the introduction of strong bonding.

It is well know that Debye temperature depends precisely on the mean ultrasonic velocity. It increases gradually as the BaO increases which indicates the increase in the dimensionality of the glasses. This is due to the increase in the number of atoms in the chemical formula of the glass network and the increase in the values of mean ultrasonic velocity [22].

Table- II: Values of elastic moduli (K and E), Poisson's ratio (σ), acoustic impedance (Z), Microhardness (H) and Debye temperature (θ_D)

Sample code	Bulk modulus K (GPa)	Young's modulus E (GPa)	Poisson's ratio (σ)	Acoustic impedance Z ($10^7 kgm^{-2}s^{-1}$)	Micro hardness H (GPa)	Debye temperature θ_D (K)
BP	44.42	51.64	0.3062	1.6616	2.5536	290.1
BPBa03	45.48	56.41	0.2932	1.6991	3.0056	306.4
BPBa06	47.36	62.01	0.2817	1.7463	3.5191	324.7
BPBa09	48.96	66.42	0.2739	1.7835	3.9300	339.3
BPBa12	49.86	71.51	0.2609	1.8130	4.5191	356.3

D. FTIR studies

FTIR is used to study the structural properties of the prepared glasses and find existence of functional groups present in the sample. The observed band positions and their corresponding assignments of prepared samples are shown in Table III.

The well-known characteristic band (at 806 cm^1) of vitreous boron oxide is associated to the symmetric stretching vibrations of boroxol rings. This peak vanishes in the BP glass it indicates the absence of boroxol rings in the glass structure. The addition of PbO into B_2O_3, breaks these rings and hence have borate structural units [23].

The broad bands exhibit the amorphous nature of the glass samples which is well agreed with XRD.

The FTIR spectra contains of two predictable bands which is due to existence of borate groups and stretching vibration of B-O bond of the trigonal [BO_3] units at 1399-1344 cm^{-1} and B-O bond stretching of the tetrahedral [BO_4] units in the wave number range 870-885 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. Since the substitution of barium ions to the lead borate glass network gives a oxygen atom, which is entered in the network,

it alters the structure of the glass to substantial extent by converting BO_3 trigonal units to BO_4 tetrahedra. This can be known from the raise in the intensity of band at 870 cm^{-1} and fall in the intensity of the band at 1399 cm^{-1}. Similar conclusion is also observed by Lakhwant Singh et al., [24] 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 [25]. The band at 425 cm^{-1} is due to the vibration of metal cations in bi-valent state Pb^{2+} [26] which is present is all samples.

The additional bands at lower frequencies (474-550 cm^{-1}) are observed in the spectra. It is owing to vibration of metal cation (Ba^{2+}). Hence, network modification is found inwhich cation enter the interstices of the glass matrices and resulted in more polymerized.

Table- III: Assignment of IR absorption peaks due to the borate structural units

Wavenumber cm^{-1}	Assignment
~1344	B-O asymmetric stretching vibration of the trigonal BO_3 units
~870	B-O stretching vibration of BO_4 units
~692	Bonding vibration of B-O-B linkage
~500	Vibrations of metal cations Ba-O

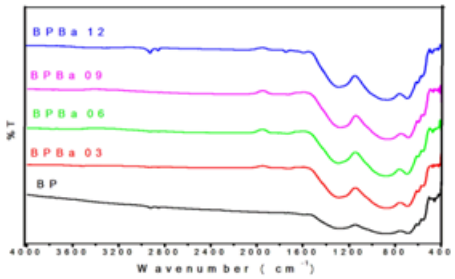

Fig. 3. FTIR spectra of BPBa glasses with

E. Thermal studies

The DTA is very useful for determination of melting points of crystals and glass transformation of glasses [27]. In all the glasses, the DTA curves exhibits a endothermic hump in the lowest region of the temperature corresponding to transition temperature (T_g) and followed by exothermic peak attributed to the crystallization temperature (T_c). Other endothermic events observed at the highest temperature corresponding to melting temperature (T_m). Fig. 4 shows the differential thermal analysis curve for BPBa glasses. The first endothermic hump appears in the region from 232°C to 320°C followed by exothermic peak from 472°C to 583°C and another endothermic peak appears from 717°C to 833°C. The values of above parameters increase with the addition of BaO at the expense of PbO, it shows that number of bridging oxygens raises with closed network structures. These results implies that BaO behave as a modifier and occupies the intrinsic positions.

In general, the variation between the T_g and T_c, gives a measure the hardness of a super cooled liquid which is stability factor. Hruby's parameter shows the strength of the glass against devitrification [28, 29]. The S and K_{gl} raises with increasing BaO content and this revealed that the substitution of BaO with higher bond strength (561.9±13.4) in place of PbO with lower bond strength (382.0±12.6). There by indicating that the incorporation of BaO helps to form more tightly packed glasses.

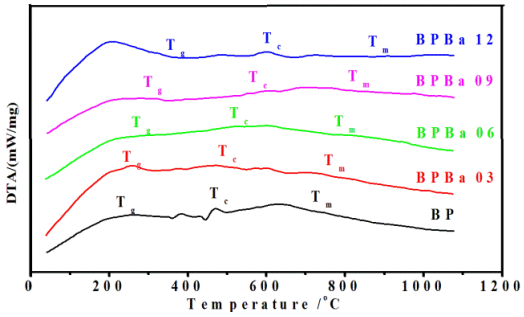

Fig. 4. DTA curves for BPBa glasses different concentrations of BaO

Table- IV: Physical properties of BPBa glasses

Sample Code	Glass transition temperature T_g/°C	Crystallization temperature T_g/°C	Melting temperature T_g/°C	Thermal stability S	Hruby's parameter K_{gl}
BP	232	472	717	209	0.9023
BPBa03	245	491	734	239	0.9287
BPBa06	270	516	775	246	0.9498
BPBa09	290	545	796	254	0.9622
BPBa12	320	583	833	266	1.0513

IV. CONCLUSION

The B_2O_3-PbO-BaO glasses were synthesised and characterized. Based on the results, amorphous nature of glasses was reflected from XRD study. The density decreases which depends on molar mass of added cations. All parameters increase except Poisson's ratio, with the inclusion of BaO content and favours the increase in bridging oxygen due to the creation of BO_4 units. IR spectra indicate that the structural role played by the Ba^{2+} ions is preferentially get incorporated into leadborate glass as modifier.

The interesting conversion of BO_3 into BO_4 structural units were found and thermal stability of the glass is enhanced with barium ions.

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