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Structural interpretation and Elastic properties of barium borate glasses through Ultrasonic Techniques

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Abstract

The binary barium borate glass systems were obtained by using the rapid melt quenching technique. The density of the glass samples was determined using relative measurement method with water as a floatation medium. Ultrasonic velocities, both longitudinal and shear velocities for all the glass samples were measured at room temperature and at a frequency of 4MHz. The different parameters, such as elastic moduli, Poisson's ratio, acoustic impedance, microhardness and thermal expansion coefficient are used to evaluate from the measured data. The results of these parameters were used to attain quantitative information about the structural properties and compactness of these prepared glasses.

Keywords: Ultrasonic velocity, Elastic moduli, XRD, Poisson's ratio, micro hardness.

1. Introduction

The glassy materials have become increasingly important in the field of materials science because of their specific structure and physical properties with changes in chemical composition and thus find important applications in the field of glass ceramics, optical fibers, laser hosts, thermal and mechanical sensors, γ –ray absorbers, photonic devices, and so forth **[1-4].** The longitudinal and shear ultrasonic velocity and the elastic moduli are mainly appropriate for characterizing glasses as a function of composition **[5].** The ultrasonic examination of solid is gaining a lot of significance and concentration in glasses has rapidly increasing because of improving information technology. Elastic characteristics are very information about the structure of solid and they are directly related to inter atomic potential.

Borate based glasses are the focus of interest due to their structure and properties and are very well known for their glass forming ability; boric oxide (B_2O_3) is one of the essential glass former, because of its having higher bond strength, lower cation size and lesser heat of fusion. In pure B_2O_3 glass structure most of the boron is involved in B_3O_6 (boroxol) ring. The conversion between threefold coordinate boron and fourfold coordinated boron with the addition of network modifier oxide like that BO_3 and BO_4 structural units **[6-8].** Furthermore, the modifier oxide also changes the physical properties along with structural modifications.

The barium to borate glasses has provided a suitable glass matrix for immobilization of sulphate bearing HLW **[9]**. 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 **[10]**. However the barium oxide in borate network 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 **[11]**.

The present research intents to study the elastic properties of the binary xBaO –(100-x) B_2O_3 glass system using ultrasonic techniques and to correlate the changes in elastic moduli to the anticipated structural changes in the borate network.

2. Experimental Details

Glass Preparation

The glass samples having the chemical composition (xBaO – (100-x) B_2O_3 mol. %) are prepared by using the conventional melt quench technique. The appropriate amounts of chemicals, boron trioxide (B_2O_3), Barium oxide (BaO) were obtained from Aldrich and S.D. Fine chemicals. The proper required quantity (approximately 20g) in mol% of different chemicals in powder form was weighed using a single pan balance having an accuracy of ± 0.001g. The homogenization of the appropriate mixture of the components of chemicals is effected by repeated grinding using a mortar. The homogeneous mixture is put in a silica crucible and placed in a electrically heated muffle furnace at 1100 ºC. The melting sample was quickly quenched by pouring on to a copper plate to form pieces of samples. The glass samples were annealed at 470 ºC for two hours to avoid the mechanical strain developed during the quench process. The glass samples were polished using a polishing machine in order to obtain appropriate sample for the ultrasonic characterization.

The amorphous nature of the sample 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 density was measured at room temperature using the Archimedes method with water as a immersing medium, **[12-13]**. The weights of the obtained glass samples were measured by using a digital weight balance with ±0.001g standard error.

Longitudinal velocities and shear velocities of the prepared glass samples were determined by using Pulse-Echo superposition techniques at a frequency of 4MHz at room temperature. The thickness of the sample (d), longitudinal velocity (U_l) and shear velocity (U_s) were calculated using the relation U=2d/t, where t is transit time taken as ultrasonic waves in the glass samples. The elastic moduli, Poisson's ratio and other parameters have been calculated using the following relations **[14]**:

Longitudinal modulus: $$L = \rho U_\ell^2 \quad (1)$$

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

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

Young's modulus: $$E = (1 + \sigma)\, 2G \quad (4)$$

Poisson's ratio: $$\sigma = \left(\frac{L - 2G}{2(L - G)}\right) \quad (5)$$

Acoustic impedance: $$Z = U_\ell \rho \quad (6)$$

Microhardness: $$H = (1 - 2\sigma)\frac{E}{6(1+\sigma)} \quad (7)$$

Thermal expansion coefficient $$\alpha_p = 23.2\,(U_\ell - 0.57457) \quad (8)$$

The nominal composition in mol. % of BBaO glasses are present in Table 1.

Table-1: Nominal composition of barium borate glasses

Smpales	Nominal Composition		Remarks
	B_2O_3	BaO	
BBaO 1	60	40	Mol. % of B_2O_3 is decreasing with increasing BaO content
BBaO 2	55	45	
BBaO 3	50	50	
BBaO 4	45	55	

Vol 11, Issue 7,July/2020
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BBaO 5	40	60	

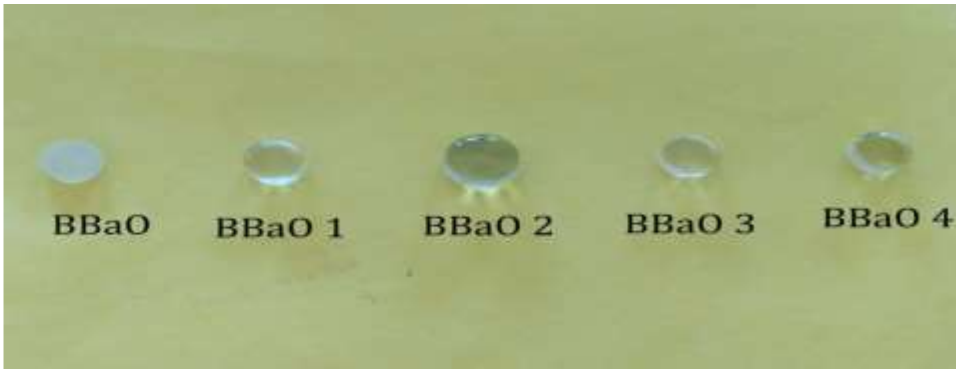


Plate 1 BBaO Glass Specimen

3. Results and Discussion

3.1 XRD analysis

The amorphous nature of glass samples was confirmed by X-ray diffraction technique using an GE-Inspection technology 3003TT. Figure 1 shows XRD spectrum of BBaO1 and BBaO5 glass samples. The XRD spectrum shows the absence of any discrete or no continuous sharp crystalline peaks, this confirms the fact that glass samples are amorphous in nature **[15]**.

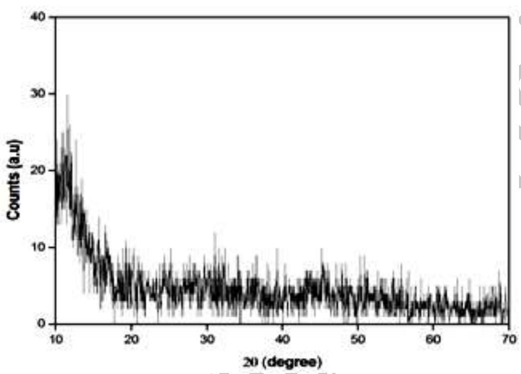
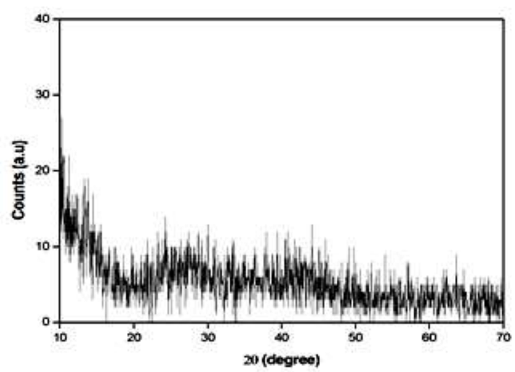


Fig. 1. XRD pattern of BBaO 1 sample



XRD pattern of BBaO 5 sample

3.2 Ultrasonic Study

The experimental values of density (ρ), longitudinal ultrasonic velocity (U_l) and shear ultrasonic velocity (U_s) of the different glass specimen with respect to change in mol. % of BaO are collected in Table 2. The calculated longitudinal modulus (L), shear moduli (G), bulk modulus (K), Young's modulus (E), Poisson's ratio (σ) are listed in Table 2&3. The acoustic impedance (Z), micro hardness (H) and thermal expansion co-efficient (α_p) are presented in Table 4.

Borate glasses conversion between three fold coordinated boron and fourfold coordinated boron with the addition of modifier oxide and these are exhibited in a wide variety of borate glasses or minerals. The addition of modifier oxide into the borate glasses brings drastic structural changes in the structural units with the evaluation of four coordinated boron and bridging oxygen ions in the glass network. The existence of tetrahedral (BO_4) borate species and their concentrations depend on the relative concentration of the modifier oxides in the glass network.

The density is a efficient tool capable of exploring the changes occurring in the structure of glasses. The density is affected by the structural softening or compactness, the changes in geometrical configuration, coordination number of ions and the dimension of intestinal space of the glass. An increasing in the density values with increasing in the concentration of BaO content is shown in Table 2. 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 [BO4]. 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.

It is noticed that from Table. 2 that the longitudinal and shear velocities increases with increase linearly with increase in BaO concentration. The observed increase in ultrasonic velocities can be explained such that, as largest divalent positive ions (Ba^{2+}) enter interstitially and as a result some type of modification of B-O-B linkages into B-O-Ba bond linkages which already exist in the glass may occur. Besides, the conversion of BO_3 unit into BO_4 results in a increase in ultrasonic velocity which affected the rigity of the glassy nature. This behavior indicates the replacement of B_2O_3 by B-O-Ba improves the mechanical properties and strength of the cross-links between chains of the atom in the borate glasses **[16]**.

Table-2: Values of density, ultrasonic velocity (longitudinal and shear) and longitudinal modulus of BBaO glass system

Sample	Density ($\rho \times 10^3$ kgm^{-3})	Ultrasonic velocity (ms^{-1})		Longitudinal modulus L (GPa)
		Longitudinal (U_l)	Shear (U_s)	
BBaO 1	4.0090	4666.7	1933.3	87.31
BBaO 2	4.1872	4798.4	2189.2	96.41
BBaO 3	4.2484	4969.2	2315.5	104.91
BBaO 4	4.4214	5104.0	2482.0	115.19
BBaO 5	4.5621	5223.5	2592.7	124.48

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

Sample	Shear modulus G (GPa)	Bulk modulus K (GPa)	Young's modulus E (GPa)	Poisson's ratio (σ)
BBaO 1	14.98	67.33	39.66	0.3964

BBaO 2	20.07	69.64	54.94	0.3685
BBaO 3	22.77	74.54	62.00	0.3614
BBaO 4	27.25	78.85	73.32	0.3450
BBaO 5	29.98	84.50	80.44	0.3413

From Table 2&3 lists the experimentally estimated values of the elastic moduli; longitudinal modulus, shear modulus, bulk modulus and Young's modulus as a function of BaO concentration. The increase in elastic moduli has been attributed to an increase in the rigidity and increases in the strength of the glass network. Furthermore the increase in elastic moduli is due to increase in network dimensionality and connectivity **[17]**.

Table-4 Values of acoustic impedance (Z), microhardness (H), Thermal expansion co-effieient (α_p) BBaO glass system

Sample	Acoustic impedance Z (10^7 kgm^{-2} s^{-1})	Microhardness H (GPa)	Thermal expansion co-efficient $\alpha_p \times 10^{-6}$ K^{-1}
BBaO 1	1.8709	1.0348	10.82
BBaO 2	2.0092	1.7595	11.13
BBaO 3	2.1111	2.1046	11.52
BBaO 4	2.2567	2.8159	11.84
BBaO 5	2.3830	3.1716	12.11

According to Rao, Poisson's ratio varies as a function of dimensionality of the structure and cross link density **[18]**. The cross link density of the glass decides the Poisson's ratio. In this present study, Poisson's ratio decreases with increase of modifier concentration. Addition of BaO into B_2O_3 glass, results in an decreases in Poisson's ratio which is attributed to the introduction of covalent bonds B-O-Ba are more bridging oxygens leading to more BO_4 units that formed the more rigid glass network **[19]**.

Table 4 summaries the value acoustic impedance of barium borate glass. The increase of acoustic impedance is attributed to the increase in rigidity of the glass structure, which resulting in the higher impedance to the propagation of ultrasonic wave in the glass specimen. From table 4 mention that the increase in the thermal expansion coefficient indicates the connectivity and rigidity of the glass network to improve **[20]**.

Table 4 shows the values of microhardness of the barium borate glasses. The increasing 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 **[21]**.

4. Conclusion

Based on the result obtained, it concluded that:

- The density of the glasses increases which indicates the increase in connectivity of the network structure
- The ultrasonic velocities, elastic moduli and other derived parameters increases and Poisson's ratio decreases with the increase in BaO concentration which implies increase in bridging oxygen due to formation of BO_4 structural unit with increasing the rigidity and compactness of glass structure**.**
- Therefore it is concluded that the addition of BaO into B_2O_3 improves the strength and stability of borate glass system

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