

Acoustic Investigations on Pure and Rare Earth Ion Doped MgO-ZnO-B₂O₃ Glasses

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Abstract: Rare earth ion doped MgO-ZnO-B₂O₃ glasses were prepared by rapid melt quench method. Accurately measured the density of the samples. Ultrasonic velocity measurements were carried on the prepared samples by piezoelectric composite resonance method and investigated acoustic properties. Various acoustic, elastic and mechanical constants were derived from these investigations. All these parameters are found to increase with increasing atomic number Z of the rare earth ions and found to decrease with increasing temperature of measurement. The results of these parameters have been discussed in terms of the structural and physical properties of the prepared glasses.

Keywords: acoustic impedance, borate glass, debye temp., elastic moduli, micro hardness, Poisson's ratio, rare earth ions

1. Introduction

The acoustical properties are particularly suitable for describing microstructure and the dynamics of the glasses. The elastic properties are related to microscopic properties through the behaviour of the network and the modifier giving valuable information about several physical properties like elastic moduli (longitudinal, Young's, bulk and shear), Poisson's ratio, acoustic impedance, micro hardness, Debye temperature and thermal expansion coefficient [1]-[3].

M Rami Reddy et.al [4] reported Acoustic investigations on PbO-Al₂O₃-B₂O₃ glasses doped with Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺ and Yb³⁺. Elastic moduli (E, G), Poisson's ratio (s), microhardness (H) and some thermodynamical parameters such as Debye temperature (θD), diffusion constant (Di), latent heat of melting (□ Hm) parameters were evaluated and found to increase with increasing atomic number Z of the rare-earth ions and found to decrease with increasing temperature of measurement. P. Vasantharani et.al [4] studied physical and elastic properties of the ternary glass system of (50-x) Li₂O-50B₂O₃-xNa₂O (where x =10, 15, 20, 25 and 30 mol%) with different compositions. AN. Kannappan et.al [5] evaluated various elastic and mechanical parameters of Na₂CO₃-ZnO-B₂O₃ (SZB) and Na₂CO₃-PbO-B₂O₃ (SLB) composition glasses from ultrasonic measurements. Their findings reveal that acoustical, elastic and mechanical parameters of the glass specimen (SZB, SLB) throw light on the rigidity and compactness in structural network and the SZB glass possess higher rigidity, strength and compactness in structural network over the SLB glass.

Borate glasses are one of the most popular and excellent glass forming materials. Upon addition of alkali oxides to B₂O₃, the covalent network of amorphous boron oxide causes considerable changes, resulting in the creation of anionic sites that accommodate the modifying alkali cations [4]. With the presence of property modifying salts like ZnO with B₂O₃ glass network could significantly improve different properties like very glass nature, mechanical strength and thermal stability with an extended chemical durability. Such glasses

could be found as more supportive materials for their applications in optical communications (optical fibers), laser hosts, optical filters, γ-ray absorbers, photonic devices etc [7] - [16]. M. Venkateswarlu et.al reported structural, thermal and optical properties of Sm³⁺, Dy³⁺, Eu³⁺ and Tb³⁺ ions doped Borate Zinc Magnesium Glasses (MZB glasses). Their findings reveal that MZB glasses are amorphous, transparent, moisture resistant and stable and brightly luminescent. Under UV light MZB glasses doped with Sm³⁺, Dy³⁺, Eu³⁺ and Tb³⁺ shown bright orange, blue, red and green emissions respectively. They also reported the transformation of BO₃ triangles into BO₄ tetrahedral from the FTIR measurements. [17], [18]. This makes MZB glasses as promising optical luminescent materials with technological importance.

Based on these findings to throw some light on the mechanical strength and elastic nature of the MZB glasses, acoustic investigations were carried out with and without rare-earth dopants in the present work. To the best of our knowledge acoustic investigations on MZB glasses were not reported.

2. Aims and Objectives

Synthesis of pure and rare earth ion doped MZB glasses and to investigate their mechanical strength.

3. Materials and Methods

3.1 Preparation of Samples

The borate zinc magnesium (MZB) glasses in the following chemical composition containing Sm³⁺, Dy³⁺, Eu³⁺, or Tb³⁺ ions in 0.2 mol % each separately, along with a host glass as well were prepared by rapid melt quenching method.

- Host glass: 65B₂O₃-20ZnO-15MgO (MZB)
- (Sm³⁺)0.2: 64.8 B₂O₃-20ZnO-15MgO,
- (Dy³⁺)0.2: 64.8 B₂O₃-20ZnO-15MgO,
- (Eu³⁺)0.2: 64.8 B₂O₃-20ZnO-15MgO, &
- (Tb³⁺)0.2: 64.8 B₂O₃-20ZnO-15MgO,

The starting materials used in the present work were reagent grade of H₃BO₃, ZnCO₃, MgCO₃, Sm₂O₃, Dy₂O₃, Eu₂O₃ and Tb₄O₇. All weighted chemicals were powdered finely and mixed thoroughly before each batch (10g) was melt in porcelain crucibles in an electrical furnace for an hour, at 980°C. These melts were quenched in between two brass plates to obtain 2-3 cm diameter optical glass discs of 0.3 cm thickness. The glasses were then ground and finely polished. These glasses thus obtained were used for further characterizations.

3.2 Measurement of Density

The density (d) of the glasses was determined to an accuracy of 0.001 by the Archimedes' Principle using xylene (99.99% pure) as the buoyant liquid. The weight of the glass samples was measured in a single pan balance with an accuracy of 0.0001g. The density was calculated using the formula

$$d = d_x \frac{W_1}{W_1 - W_2} \quad (1)$$

where W₁ and W₂ are the weights of the glass samples in air and in xylene and dx is the density of the xylene at 303K.

3.3 Measurement of Ultrasonic Velocity

The ultrasonic velocities in the samples were measured with a piezoelectric composite oscillator apparatus (Mittal Enterprises, New Delhi) by resonance method. The final dimensions of the glasses used were (2×0.25×0.25cm) and (2cm long and 0.25cm in diameter) for longitudinal and shear velocity measurements respectively. These dimensions were almost identical to those of X-cut 0.13 MHz quartz transducers used in the measurements. Since the ultrasonic measurements on the present samples were made at 303K and 373K which are far below when compared with the melting temperature of the glasses (≈ 980°C), density of the samples in the entire present experimental range of temperature, was taken as constant. If fq and fc are the resonance frequencies of the transducer and the composite bar, respectively, the resonant frequency (fs) of the glass samples was determined using the relation

$$f_s = f_c + \frac{m_q}{m_s} (f_c - f_q) \quad (2)$$

where m_q and m_s are the masses of the transducer and glass sample respectively.

Using the value of length (l) and density (d) of the specimen, the velocity of ultrasonic waves in the specimen (U) and compressibility (β) can be calculated using the following relations

$$U = 2 * f_s * l \quad (3)$$

$$\beta = \frac{1}{d * v^2} \quad (4)$$

3.4 Theory and Calculations

Longitudinal Modulus $L = dU_f^2$ (5)
 Shear Modulus $G = dU_s^2$ (6)

Bulk Modulus $K = L - \frac{4}{3}G$ (7)

Young's Modulus $Y = (1 + \sigma)2G$ (8)

Poisson's Ratio $\sigma = (L - 2G)/2(L + G)$ (9)

Acoustic impedance $Z = U_f d$ (10)

Micro Hardness $H = (1 - 2\sigma)Y/6(1 + \sigma)$ (11)

The mean sound velocity $U_m = [1/3(2/U^2 + 1/U^3)]^{-1/2}$ (12)

Thermal Expansion Coefficient $\alpha_p = 23.2(U_f - 0.57457)$ (13)

Diffusion Constant $D_i = k_B r_i^2 \theta_D / 96h$ (14)

Debye Temperature $\theta_D = h/k_B (9N/4\pi V_m) U_m$ (15)

coefficient of internal friction $Q^{-1} = \frac{\Delta f}{\sqrt{3}f_r}$ (16)

4. Results and Discussion

From the measured values of density (d) and calculated average molecular weight M, various physical parameters such as Ln³⁺ ion concentration (Ni), mean Ln³⁺ ion separation distance (Ri), and field strength (Fi), which are useful for understanding the elastic properties of these glasses are evaluated and presented in table 1

Table 1: Various physical properties of MZB: Ln³⁺ glasses

Glass	d (g/cm ³)	M	Ni (10 ²²) (ions/cm ³)	Ri (Å)	Fi.10 ¹⁶ (cm ⁻²)	N[EF]-10 ²⁰ (eV ⁻¹ cm ³)
Sm ³⁺	3.005	101.9	1.95	4.01	0.124	4.84
Eu ³⁺	2.99	102.8	1.87	4.09	0.123	4.61
Tb ³⁺	2.844	103.1	1.76	4.12	0.131	4.25
Dy ³⁺	2.715	103.8	1.69	4.19	0.129	3.83

Figure 1A shows longitudinal resonance curves obtained at room temperature for MZB glasses doped with Sm³⁺, Eu³⁺ and Tb³⁺; it is observed that these resonance curves exhibit the sharpening of the peaks with a shift in the resonance frequency towards higher frequencies with ascending peak heights as the atomic number Z of the rare- earth ion is increased.

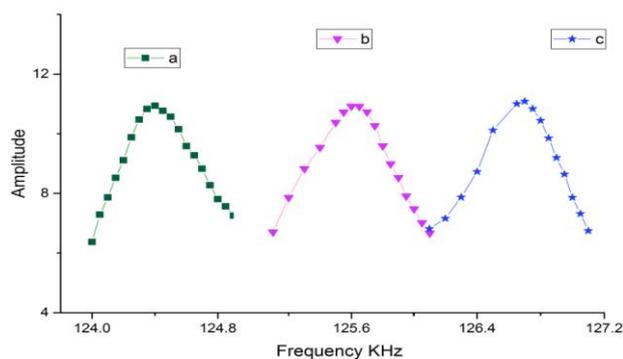


Figure 1A: Longitudinal resonance curves of MZB glass with different rare earth ions (a) Sm³⁺, (b) Eu³⁺ and (c) Tb³⁺

Fig. 1B shows the longitudinal resonance curves of Tb³⁺ doped MZB glasses drawn at different temperatures; we observe the broadening of the resonance curves with resonance frequency being shifted towards the lower frequencies with increasing half widths and descending peak heights, with increase in the temperatures of measurements. Similar observations were made by [4].

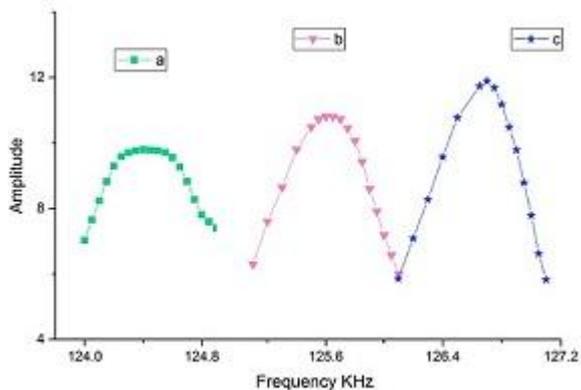


Figure 1B: Longitudinal resonance curves of MZB glass doped with Tb³⁺ at (a) 30°C, (b) 100°C and (c) 160°C.

Fig. 2 depicts the variation of coefficient of internal friction (Q^{-1}) with atomic number (Z) of the rare-earth dopants of MZB glasses at 30°C and 100°C. It is observed that there is a decrease in the coefficient of internal friction at fixed

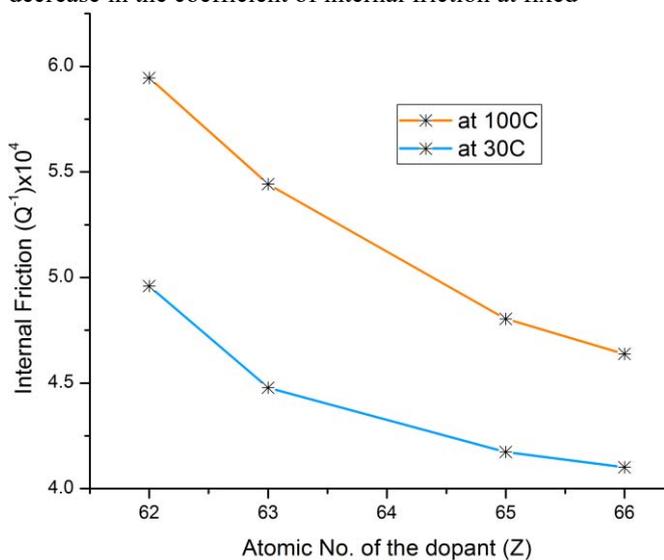


Figure 2: Variation of internal friction with atomic no. of rare-earth ion of MZB glass

temperature with a decrease in the ionic radius (or with increase in the atomic number) of the rare-earth dopant (from Sm³⁺ to Dy³⁺). This is apparently due to the successive decrease in the depolymerisation. This is further confirmed by a slight increase in the microhardness (H) of the MZB: Ln³⁺ glasses with increase in the atomic number (Z) of Ln³⁺ ions as given in table 2 [4].

Table 2: Elastic Properties of MZB: Ln³⁺ glasses

Glass	Y (GPa)		G (GPa)		σ (30°C)	H (GPa)
	30°C	100°C	30°C	100°C		
Pure	57.24		22.86		0.311	2.84
Sm ³⁺	48.71	46.65	18.61	16.85	0.304	2.37
Eu ³⁺	51.39	49.1	19.64	17.98	0.308	2.51
Tb ³⁺	54.44	52.52	20.80	18.24	0.312	2.66
Dy ³⁺	55.65	53.14	21.27	20.04	0.318	2.71

The values of Young's modulus (Y) and shear modulus (G), at room temperature for pure MZB glass are found to be 57.24 and 22.86 GPa respectively. when these glasses are doped with Sm³⁺ ions, the values of Y and G decreased to

48.71 and 18.61 respectively. However, the successive increase in the atomic number (Z) of the dopant caused a gradual increase in these values. Fig. 3 shows the variation of Young's modulus (Y) and shear modulus (G) with atomic number (Z) of the rare-earth dopants of MZB: Ln³⁺ glasses at 30°C.

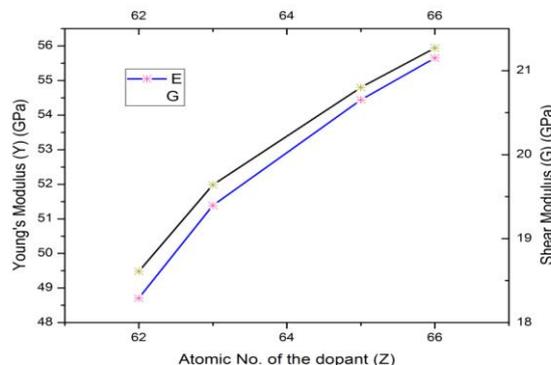


Figure 3: Variation of Young's modulus (Y) and Shear modulus (G) of MZB glass with atomic no. of rare-earth ion

Fig. 4, Fig. 5 and Fig. 6 and Fig. 7 depict the isotherms of Debye temperature (θ_D), latent heat of melting (ΔH_m), mean velocity (U_m) and diffusion constant (D_i) respectively. All of them show increasing behaviour with the increase of atomic number (Z) except debye temperature. This may be due to the decrease of atomic size (known as lanthanide contraction) which in turn causes a decrease in the degree of depolymerisation of glass network; this is also borne out by decrease in the values of density of localized defect states ($N[EF]$) with increase in atomic number (Z) as given in Table 1.

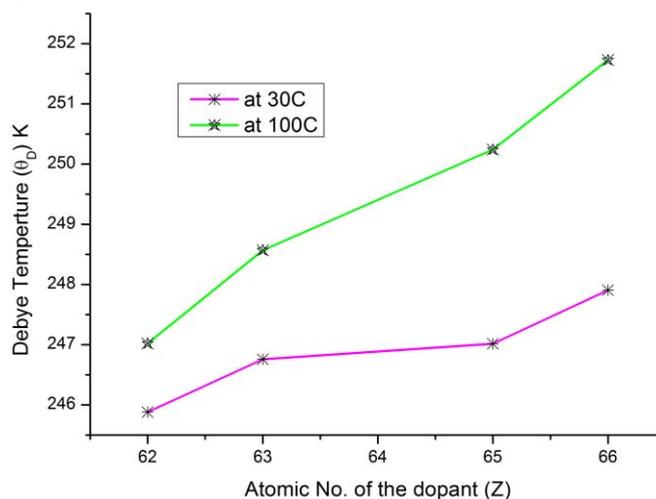


Figure 4: Variation of Debye Temperature (θ_D) of MZB glass with atomic no. of rare-earth ion

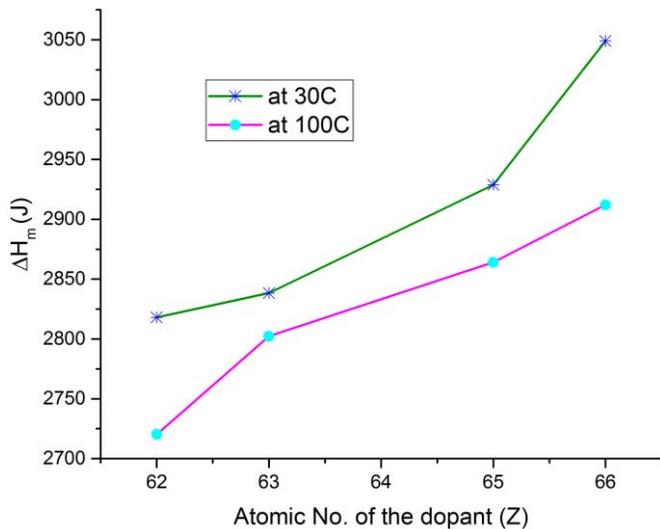


Figure 5: Variation of latent heat of melting (ΔH_m) of MZB glass with atomic no. of rare-earth ion

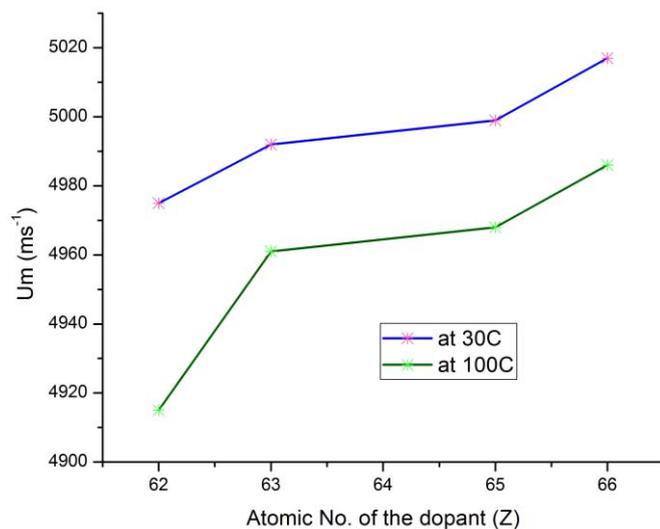


Figure 6: Variation of Mean Velocity (U_m) of MZB glass with atomic no. of rare-earth ion

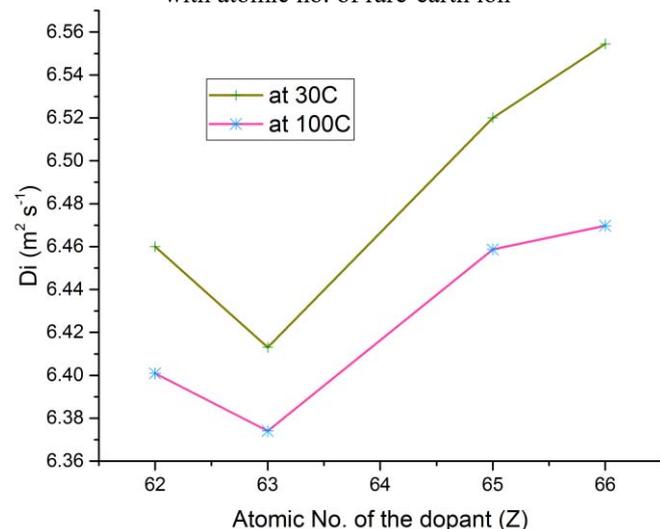


Figure 7: Variation of internal friction with atomic no. of rare-earth ion of MZB glass

In general, in a less disordered glass framework the energy introduced by the vibrator is distributed more rapidly among the vibrational degrees of freedom of the glass framework.

The time required for the establishment of equilibrium distribution of energy goes on decreasing in comparison with the period of oscillation of the vibrator and hence a decrease in the mechanical loss factor or coefficient of internal friction leading to an increase in the elastic coefficients of these glasses (with decrease in the ionic radius of rare earth dopants) is observed in the present measurements. Increase in the temperature of the measurement causes an enhancement of the depolymerisation of the glass network leading to an increase in the mechanical loss factor; such an increase in the loss factor may be responsible for decrease in these values [4].

The observed increasing and decreasing value of θ_D and T_s are related to the changes occur in compactness, thermal stability and cross-link density of the glass network. Srivastava and Srinivasan [20] have stated that the thermal expansion coefficient of materials depends on the strength of bonds. the acoustic impedance increases in the glass system attributed to the presence of bridging oxygens and increase in rigidity of the glass structure. Similar trend is observed by Raghavaiah and Veeraiah [19].

5. Conclusions

Our study on various elastic/acoustic properties of MZB: Ln^{3+} glasses indicates that MZB glasses seemed to be more suitable (as far as mechanical strength is concerned) hosts for the rare-earth ions. Further, the increase in micro hardness (H) and Poisson's ratio (ν) shows that the atoms experience higher transverse contracting strain and hence become more tightly packed. Further the increase of acoustic impedance and thermal expansion coefficient are due to increase in rigidity of the structure of the glass. The increasing trend of Debye temperature values confirms the occurrence of strong ring formation in MZB glasses. To further elaborate the understanding of MZB glasses compositional dependence of acoustic properties are needed and are proposed to carry. It is also important to see how these MZB glasses are useful for other rare earth ions than Sm^{3+} , Eu^{3+} , Tb^{3+} and Dy^{3+} .

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