

Acoustic investigations on $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses doped with certain rare earth ions

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Abstract. Elastic moduli (Y , h), Poisson's ratio (s), microhardness (H) and some thermodynamical parameters such as Debye temperature (q_D), diffusion constant (D_i), latent heat of melting (ΔH_m) etc of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses doped with rare earth ions viz. Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} and Yb^{3+} , are studied as functions of temperatures (in the temperature range 30–200°C) by ultrasonic techniques. 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. From these results (together with IR spectra of these glasses), an attempt is made to throw some light on the mechanical strength of these glasses.

Keywords. $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses; rare earth ions; elastic moduli.

1. Introduction

The study of elastic/acoustic and thermodynamic properties of glasses helps in assessing their mechanical strength. Work along these lines was carried out in recent years on a variety of inorganic glasses giving valuable information (Singh *et al* 1992; Mallawany 1994; Satyanarayana and Buddhudu 1994; Ravikumar and Veeraiah 1997; Kumar and Veeraiah 1999). Several physical properties of alkali/alkaline earth alumino borate glasses, in particular, those containing different transition and rare earth metal ions have also been under extensive investigations in recent years (Nachimuttu and Jagannathan 1995; Khalifa *et al* 1996). However, the alkali free alumino borate glasses like $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses are moisture resistant, possess low rates of crystallization and high electrical resistance. In contrast to alkali or alkaline earth oxides, PbO has the ability to form stable glass due to its dual role, one as the modifier (if Pb–O is ionic) and the other as glass former (if Pb–O is covalent). In addition, aluminium can occupy both tetrahedron (network forming), and octahedral (modifying) states, in these glasses. Further, these glasses are optically transparent to the short wavelength region (necessary for getting optimum efficiency from optical pumping of lasing ions) and high wavelength region (necessary for getting the maximum output intensity from laser radiation); in view of these qualities these glasses are considered as good hosts for lasing rare earth ions (such as Pr^{3+} , Nd^{3+} , Eu^{3+} , Tb^{3+} etc). Thus it is felt useful to throw some light on mechanical strength of

these laser emitting glasses by studying their elastic properties.

Recently, we have reported the results of our studies on electrical and certain optical properties of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses (Nageswara Rao and Veeraiah 2000; Rami Reddy *et al* 2000); these studies have yielded valuable information regarding insulating and other defect controlled properties of these glasses. This paper reports the results of detailed investigations on various acoustic and thermodynamic properties of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses doped with rare earth ions, viz. Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} and Yb^{3+} in the temperature range 30–200°C by ultrasonic techniques.

2. Experimental

For the present study, a particular composition $19\text{PbO-}5\text{Al}_2\text{O}_3\text{-}76\text{B}_2\text{O}_3 : 1\text{Ln}_2\text{O}_3$, (all in mol%) was chosen. Appropriate amounts of Analar grade reagents of PbO, Al_2O_3 , B_2O_3 and Ln_2O_3 were thoroughly mixed and all the samples were melted at about $1150 \pm 10^\circ\text{C}$ in a platinum crucible for about 2 h until a bubble free liquid was formed. The melt was then poured into a brass mould with a narrow rectangular hole for longitudinal oscillation measurements and into a brass mould with a cylindrical hole for torsional oscillation measurements, and they were subsequently annealed at 300°C .

The amorphous state of the samples was checked by X-ray diffraction spectra recorded on a Seifert Diffractometer model SO-Debye Flux 2002 with a copper target and nickel filter operated at 40 kV, 30 mA. The density (d) of the glasses was determined to an accuracy of 0.001

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by the Archimedes' Principle using xylene (99.99% pure) as the buoyant liquid. Since the ultrasonic measurements on the present samples were made in the temperature range below 200°C, which is far below when compared with the melting temperature of the glasses ($\approx 1150^\circ\text{C}$), density of the samples in the entire present experimental range of temperature, was taken as constant. The glasses were then ground and finely polished. The final dimensions of the glasses used for longitudinal ($2 \times 0.25 \times 0.25$ cm) and shear (2 cm long and 0.25 cm in diameter) velocity measurements were almost identical to those of X-cut 0.13 MHz quartz transducers used in the measurements. The ultrasonic velocities in the samples were measured with a piezoelectric composite oscillator apparatus (Mittal Enterprises, New Delhi). If f_q and f_c are the resonance frequencies of the transducer and the composite bar, respectively, the resonant frequency (f_s) of the glass samples was determined using the relation:

$$f_s = f_c + (m_q / m_s)(f_c - f_q), \quad (1)$$

where m_q and m_c are the masses of the transducer and glass sample, respectively. For measuring the temperature variation of f_s , the adhesive used for cementing the glass sample with quartz transducer was a very thin layer of paste containing calcium carbonate and sodium silicate in 1 : 5 ratio by weight and the system worked satisfactorily after it was kept for one full day under pressure at room temperature. The resonant frequencies at high temperatures were measured by keeping the composite bar along with the holder at the centre of an electric furnace whose rate of heating was maintained at 50°C/h with a sensitive PID temperature controller. The accuracy of the temperature control in these measurements was $\pm 0.5^\circ\text{C}$.

3. Results

From the measured values of density (d) and calculated average molecular weight \bar{M} , various physical parameters such as Ln^{3+} ion concentration, N_i , mean Ln^{3+} ion separation distance, R_i , and field strength, F_i , which are

useful for understanding the elastic properties of these glasses are evaluated and presented in table 1.

Figure 1A shows longitudinal resonance curves obtained at room temperature for $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses doped with four different rare earth ions viz. Pr^{3+} , Eu^{3+} , Tb^{3+} and Yb^{3+} ; 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 1B shows the longitudinal resonance curves of Pr^{3+} doped $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ 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 variations in the resonance curves with temperatures were observed for all other samples. The torsional resonance curves have also exhibited similar behaviour.

From the resonance frequencies, the longitudinal (V_l) and shear (V_s) velocities were determined by the relationship $V_{l \text{ or } s} = 2Lf_s$ (where L is the length of the specimen). From the variations of f_s with temperature, the corresponding longitudinal and shear velocities of the sound waves in the specimens were evaluated at different temperatures. Using these velocities, Young's modulus, Y , and shear modulus, h , were determined at different temperatures for all the samples. Further using the relationships

$$\frac{Y}{h} = 2(1+s), \quad (2)$$

and

$$H = (1-2s)Y/6(1+s), \quad (3)$$

the Poisson's ratio, s , and microhardness, H , of the glasses were evaluated and presented in table 2. The variation of mechanical loss factor or the internal friction, Q^{-1} , with atomic number, Z , of rare earth ions, evaluated at two different temperatures (viz. at 30 and 100°C) using

Table 1. Various physical properties of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3 : \text{Ln}^{3+}$ glasses.

Glass	d (g/cm^3)	\bar{M}	N_i (10^{22} ions/ cm^3)	R_i (\AA)	F_i (10^{16} cm^{-2})	$N[E_F]$ (10^{20} $\text{eV}^{-1}/\text{cm}^3$)
Pr^{3+}	3.005	103.0	1.76	3.84	0.138	5.44
Nd^{3+}	2.990	103.1	1.75	3.85	0.138	5.21
Sm^{3+}	2.980	103.2	1.74	3.86	0.137	5.05
Eu^{3+}	2.903	103.2	1.70	3.89	0.135	4.75
Tb^{3+}	2.844	103.3	1.67	3.91	0.134	4.51
Dy^{3+}	2.800	103.4	1.63	3.94	0.132	4.20
Ho^{3+}	2.751	103.5	1.60	3.97	0.130	3.84
Er^{3+}	2.737	103.5	1.59	3.97	0.129	3.48
Yb^{3+}	2.715	103.6	1.58	3.99	0.129	3.33

$$Q^{-1} = \frac{\Delta f}{\sqrt{3}f_r}, \quad (4)$$

(where Δf is the half width of the resonance curves) is shown in figure 2; the value of Q^{-1} is found to decrease with increase in the atomic number, Z , of the doping ion and found to increase with increase in the temperature of measurement.

The values of Young's modulus, Y , and rigidity modulus, h , at room temperature for pure $PbO-Al_2O_3-B_2O_3$ glasses are found to be 58.5 and 26.3 GPa respectively; when these glasses are doped with Pr^{3+} ions, the values of Y and h decreased to 55.3 and 22.7 respectively. However, the successive increase in the atomic number, Z , of the dopant caused a gradual increase in these values (figure 3). Figure 4 shows the variation of Y and h with temperature for some of the samples; with increase in

temperature, the values of Y are found to decrease slowly up to about 60°C and beyond that the rate of decrease is considerably higher for all the samples. However, the decrease in the values of h with temperature up to 200°C is observed to be only about 4–10%.

The average sound velocity for these glasses was determined using the relationship (Lal and Singh 1993)

$$V_m = [V_l^2 - (4/3)V_s^2]^{1/2}. \quad (5)$$

Using this velocity, the Debye temperature, q_D , of the glasses was also determined using the relationship

$$q_D = \frac{h}{K} \left(\frac{3N_A}{4pV} \right)^{1/3} V_m, \quad (6)$$

where h is Planck's constant, K , the Boltzmann's constant, N_A , the Avagadro's number and V , the specific volume (volume occupied by the unit mass of the glass) and its variation with atomic number, Z , of the rare earth ions at five different temperatures is shown in figure 5.

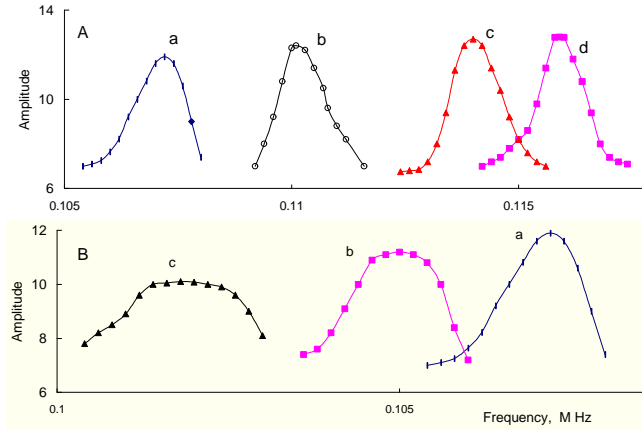


Figure 1. **A.** Longitudinal resonance curves of $PbO-Al_2O_3-B_2O_3$ glasses doped with different rare earth ions (a) Pr^{3+} , (b) Eu^{3+} , (c) Tb^{3+} and (d) Yb^{3+} and **B.** longitudinal resonance curves of $PbO-Al_2O_3-B_2O_3$ glasses doped with Pr^{3+} at different temperatures: (a) 30, (b) 100 and (c) 160°C.

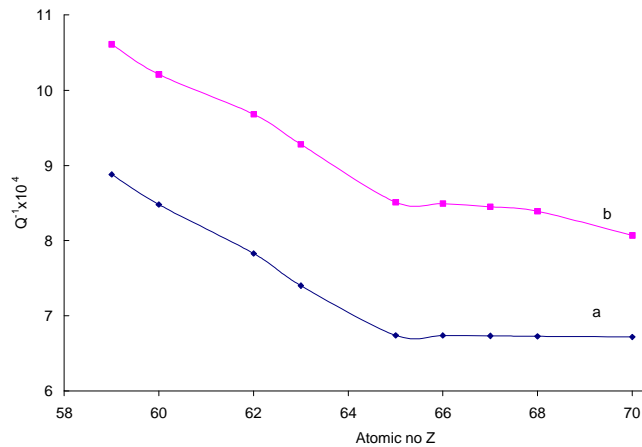


Figure 2. Variation of internal friction, Q^{-1} with atomic number, Z of the rare-earth dopants of $PbO-Al_2O_3-B_2O_3$ glasses at a. 30 and b. 100°C.

Table 2. Data on some elastic properties of rare earth ion doped $PbO-Al_2O_3-B_2O_3$ glasses.

Glass	Y (GPa)		h (GPa)		S 30°C	H (GPa) 30°C
	30°C	100°C	30°C	100°C		
Pure	58.5	—	26.3	—	0.111	6.800
Pr^{3+}	55.3	53.0	22.7	22.0	0.098	6.749
Nd^{3+}	55.8	53.4	25.3	24.4	0.100	6.761
Sm^{3+}	56.3	53.8	25.4	25.7	0.101	6.764
Eu^{3+}	56.3	53.8	25.4	24.6	0.102	6.766
Tb^{3+}	56.5	54.2	25.48	24.7	0.103	6.768
Dy^{3+}	57.5	55.0	25.9	25.3	0.109	6.769
Ho^{3+}	58.2	55.5	26.1	25.5	0.112	6.771
Er^{3+}	58.3	55.9	26.24	25.7	0.112	6.774
Yb^{3+}	58.4	56.1	26.3	25.7	0.113	6.776

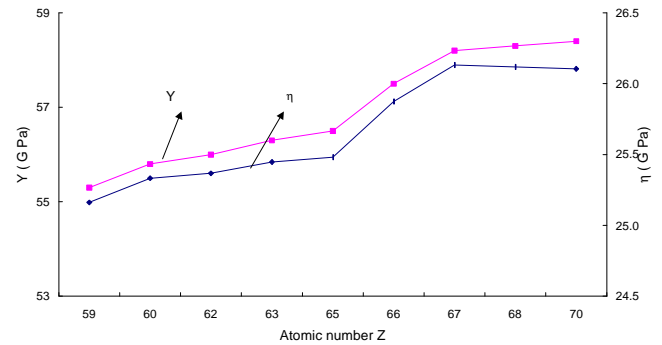


Figure 3. Variation of Young's modulus, Y and rigidity modulus, h with atomic number, Z of the rare-earth dopants of $PbO-Al_2O_3-B_2O_3$ glasses at room temperature.

The acoustic impedance for these glasses was also determined by the relationship

$$Z_i = V_m d. \quad (7)$$

Further, latent heat of melting, ΔH_m and the diffusion constant D_i , given by the relationships

$$\Delta H_m = \frac{9M}{128} \left(\frac{q_D r_i K}{h} \right)^2, \quad (8)$$

$$D_i = K r_i^2 q_D / 96h, \quad (9)$$

were also evaluated for these glasses. All these parameters viz. the average sound velocity, V_m (figure 6), the Debye temperature, q_D (figure 5), the latent heat of melting, ΔH_m (figure 7) and the diffusion constant, D_i (figure 8) were found to increase at faster rates with increase in the atomic number of Ln^{3+} ions in the beginning of the series and seemed to attain saturated values at the end of the series.

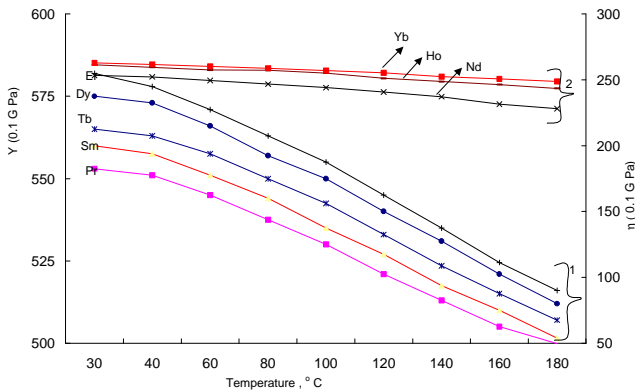


Figure 4. Variation of 1. Young's modulus, Y and 2. rigidity modulus, h with temperature of the rare-earth doped $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses.

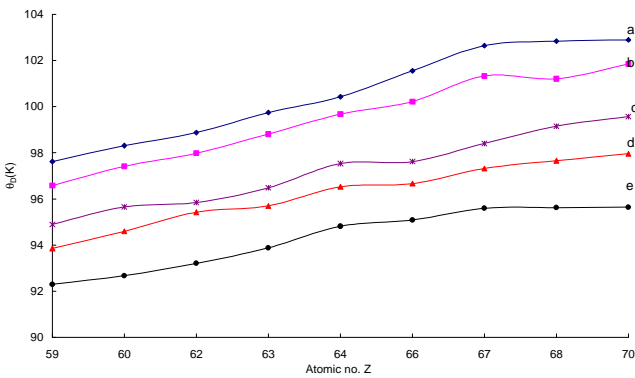


Figure 5. Isotherms of Debye temperature as functions of atomic no. Z of rare-earth dopants in $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses at a. 30, b. 60, c. 100, d. 140 and e. 180°C.

4. Discussion

In general, the properties of glass depends upon its composition and to a considerable extent upon its structure. Lead aluminoborate glasses doped with rare earth ions have complex compositions and are an admixture of network formers and modifiers. B_2O_3 is a well known network former with BO_3 structural units. The presence of BO_4 units in these glasses is also confirmed from the infrared spectra of these glasses (figure 9); IR spectra of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses recorded at room temperature in the frequency range $200\text{-}4000\text{ cm}^{-1}$ have exhibited three groups of bands: (i) in the region $1200\text{-}1600\text{ cm}^{-1}$, due to stretching vibrations of B-O bond of trigonal BO_3 units, (ii) in the region $800\text{-}1200\text{ cm}^{-1}$ which are due to B-O bond stretching of the tetrahedral BO_4 units and (iii) band around 700 cm^{-1} due to the bending of B-O-B linkages in borate network. In addition a weak but a definite band around 550 cm^{-1} is also observed; this is indicative of the presence of PbO_4 units in $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glass network (Ahmed *et al* 1998; Khalifa *et al* 1998). With the introduction of rare earth oxides into the network, the intensity

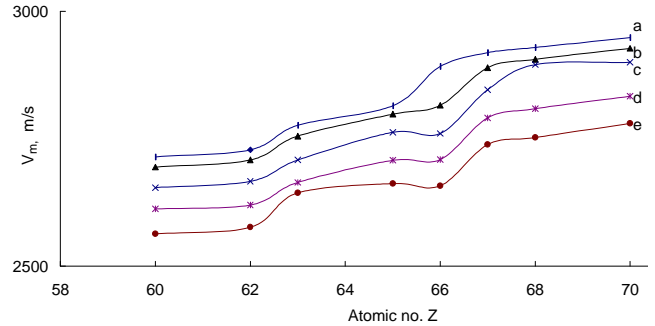


Figure 6. Mean velocity (V_m) isotherms as functions of atomic no. Z of rare-earth dopants in $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses at a. 30, b. 60, c. 100, d. 140 and e. 180°C.

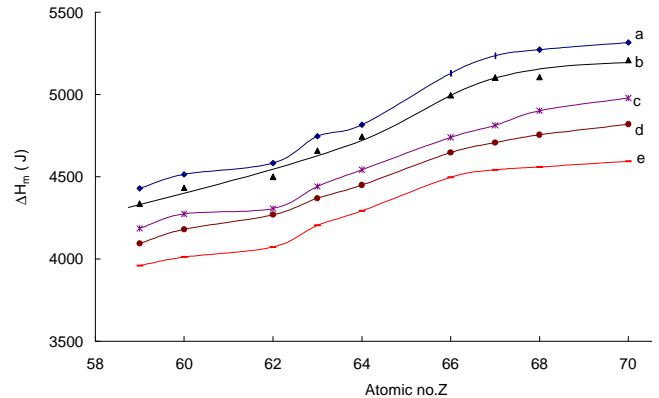
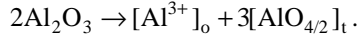


Figure 7. Latent heat of melting (ΔH_m) isotherms as functions of atomic no. Z of rare-earth dopants in $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses at a. 30, b. 60, c. 100, d. 140 and e. 180°C.

of the second group of bands slowly increased and shifted towards slightly lower frequencies with increase in the atomic number, Z , of the rare earth ion.

Further, aluminium can also occupy both tetrahedral (viz. substitutional or network formers) and octahedral sites (viz. interstitial or network modifiers) as (Elliott 1990):



In alumino borate glasses, each BO_4 or AlO_4 unit is linked to two such other units and one oxygen from each unit with a metal ion and this structure leads to formation of long chain of tetrahedra. Ln_2O_3 also enters the glass network as modifier (Shelby 1994) by breaking up tetrahedral bonds (the oxygen of Ln_2O_3 break the local symmetry while Ln^{3+} ion occupy interstitial position) and introduces coordinated defects known as dangling bonds in these glasses. During this process there can be a break of different structural units viz. BO_4 , PbO_4 and AlO_4 units. The reduction in the BO_4 and PbO_4 units may be understood by the observed decreasing trend of intensities of bands corresponding to these units in the IR spectra of

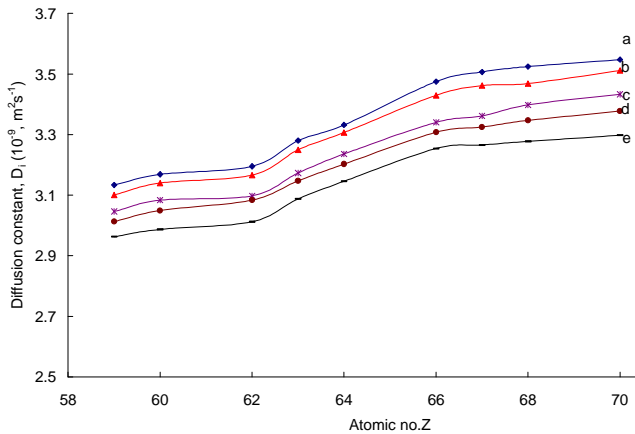


Figure 8. Diffusion constant (D_i) isotherms as functions of atomic no. Z of rare-earth dopants in $PbO-Al_2O_3-B_2O_3$ glasses at a. 30, b. 60, c. 100, d. 120 and e. 180°C.

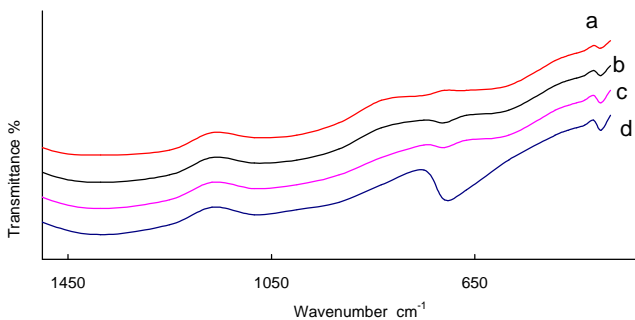


Figure 9. Infrared spectra of $PbO-Al_2O_3-B_2O_3$ glasses doped with a. Pr^{3+} , b. Nd^{3+} , c. Tb^{3+} and d. Yb^{3+} ions.

these glasses with decreasing atomic number (from Yb to Pr) of rare earth ions (figure 9). Further these bonding defects give rise to electron states within the band gap of the material and get localized in that region.

Considering the data on internal friction of these glasses, we have observed that there is a decrease in the logarithmic decrement or coefficient of internal friction at fixed temperature (figure 2) with a decrease in the ionic radius (or with increase in the atomic number) of the rare earth dopant (from Pr^{3+} to Yb^{3+}); this is apparently due to the successive decrease in the depolymerization of the glass network as also observed in IR spectra. This is further confirmed by a slight increase in the microhardness, H of the $PbO-Al_2O_3-B_2O_3:Ln^{3+}$ glasses with increase in the atomic number, Z , of Ln^{3+} ions (table 2).

Recollecting the data on elastic/acoustic parameters of these glasses an increase in the values of these parameters viz. V_m , Y , h , has been observed as we go from Pr^{3+} doped glasses to Yb^{3+} doped glasses. The thermodynamic parameters viz. Debye temperature, q_D , diffusion constant, D_i and the latent heat of melting, ΔH_m , show a similar increase. In the series of rare earth ions from La^{3+} to Lu^{3+} a general decrease in size with increase in atomic number results, because addition of electrons to the shielded $4f$ orbital cannot compensate for the effect of increased nuclear charge. This decrease in general is known as lanthanide contraction. Such a decrease in size from Pr^{3+} to Yb^{3+} causes a decrease in the degree of depolymerization of $PbO-Al_2O_3-B_2O_3$ glass network; this is also borne out by the fact that the values of $N[E_F]$ i.e. density of localized defect states, evaluated using a.c. conductivity values at 1 MHz and 303 K (Nageswara Rao and

Table 3. Data on acoustical properties of rare earth ions doped $PbO-Al_2O_3-B_2O_3$ glasses.

Glass temp (°C)	V_m (m/s)	q_D (K)	$Z_i \times 10^{-6}$ (kg m ⁻² s ⁻¹)	ΔH_m (J)	$D_i \times 10^9$ (m ² s ⁻¹)	
Pr^{3+}	30	2691	97.62	8.08	4429	3.13
	100	2616	94.90	7.86	4186	3.05
Nd^{3+}	30	2714	98.31	8.11	4514	3.17
	100	2641	95.66	7.89	4274	3.08
Sm^{3+}	30	2733	98.88	8.14	4582	3.19
	100	2649.4	95.84	8.00	4307	3.09
Eu^{3+}	30	2781	99.74	8.07	4746	3.28
	100	2690	96.50	7.81	4440	3.17
Tb^{3+}	30	2820	100.43	8.01	4816	3.33
	100	2738	97.54	7.78	4543	3.23
Dy^{3+}	30	2866	101.56	8.02	5129	3.47
	100	2755	97.62	7.71	4739	3.34
Ho^{3+}	30	2914	102.65	8.01	5236	3.50
	100	2794	98.40	7.68	4812	3.36
Er^{3+}	30	2924	102.80	8.00	5273	3.52
	100	2820	99.15	7.71	4901	3.40
Yb^{3+}	30	2934	102.89	7.96	5316	3.55
	100	2839	99.57	7.70	4978	3.43

Veeraiah 2000), are found to decrease with decrease in the ionic radius of rare earth dopants (table 1). 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 depolymerization 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 the values of V_m , Y , h , s , D_i , etc with temperature for these glasses.

Finally, our study on various elastic/acoustic properties of $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3 : \text{Ln}^{3+}$ glasses indicates that $\text{PbO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses seemed to be more suitable (as far as mechanical strength is concerned) hosts for the ions like Ho^{3+} , Er^{3+} which exhibit eye safe lasers (Chicklis *et al* 1971) rather than to the conventional lasing ions like Nd^{3+} , since the parameters like microhardness, H and other elastic parameters are found to be the highest for glasses containing ending ions of the lanthanide series.

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