Bull. Mater. Sci., Vol. 20, No. 5, August 1997, pp. 667–675. © Printed in India.

Elastic properties of ZnF_2–PbO–TeO_2 glasses doped with certain rare earth ions

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MS received 7 February 1997; revised 28 April 1997

Abstract. The elastic moduli (Y, η, σ and H) and some thermodynamical parameters, such as Debye temperature θ_D, diffusion constant D_i and latent heat of melting ΔH_m, of ZnF_2–PbO–TeO_2 glasses doped with some rare earth (Pr^{3+}, Nd^{3+}, Eu^{3+} and Tb^{3+}) ions are determined as functions of temperature using piezo electric composite oscillator technique. All the parameters are found to decrease with increase in the atomic number Z of the rare earth ions and with increase in the temperature of measurement. The results are explained on the basis of the density of localized bonding defect states within the band gap of the material.

Keywords. Elastic moduli; composite oscillator; bonding defects.

1. Introduction

The understanding of the elastic properties of glasses i.e. longitudinal and shear moduli (Y, η), Poisson's ratio σ and microhardness H, and also certain thermodynamical parameters like Debye temperature θ_D, diffusion constant D_i, and latent heat of melting ΔH_m etc are essential for understanding the mechanical strength of the glasses. Work along these lines was carried out on a variety of glasses, yielding valuable information (Kartha *et al* 1983; Swarna Latha and Padmini 1986; Satyanarayana and Bhuddhudu 1994). ZnF_2–PbO–TeO_2 glasses are stable against devitrification and are nontoxic and resistant to moisture. These glasses are well known due to their excellent transparency in the 3–18 μm region and are considered as the best materials for use as optical components, such as IR domes, filters and laser windows.

Quite recently we have reported the results of our studies on the effect of electric field *in situ* with ionizing radiation and the effect of presence of certain transition metal ions, such as copper, chromium etc on electrical and certain optical properties of the tellurite glasses (Ravi Kumar *et al* 1994, 1995, 1997 a, b; Rami Reddy *et al* 1995); all these studies have yielded valuable information regarding the insulating and other defect-controlled properties of these glasses. Doping of rare earth ions (such as Pr^{3+}, Nd^{3+}, Eu^{3+}, Tb^{3+}) in tellurite glasses makes them as good laser materials. Thus, it will be useful to throw some light on mechanical strength of these glasses, by studying their elastic properties. Very few studies are available on elastic properties of tellurite glasses and most of them are restricted to some binary tellurite glasses (Hart 1993; Malla Wany 1993; Malla Wany *et al* 1994). In this paper we report the results of our studies on various elastic coefficients, such as Y, η, σ microhardness H, and other acoustical and thermodynamical properties of ZnF_2–PbO–TeO_2 glasses doped with certain rare earth ions such as Pr^{3+}, Nd^{3+}, Eu^{3+} and Tb^{3+} in the temperature range 30°–200°C by piezoelectric composite oscillator technique.

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2. Experimental

For the present study a particular composition i.e. 45 ZnF_2–9PbO–45·4TeO_2– 0·6 LnF_3 with four lanthanide ions (Pr^{3+}, Nd^{3+}, Eu^{3+}, Tb^{3+}) all by wt % is chosen. Our earlier studies on ZnF_2–PbO–TeO_2 glasses prepared with simultaneous decrease in the PbO and TeO_2 contents (starting from high concentrations of PbO and TeO_2) have indicated that the glasses prepared with this composition i.e. 45 ZnF_2–9 PbO–46 TeO_2 possess high electrical resistance, low thermal expansion coefficient and a high mechanical strength over other glasses of the series (Ravi Kumar *et al* 1997 a–c). We have therefore chosen this composition for Ln^{3+} doping. Appropriate amounts of Analar grade reagents of ZnF_2, PbO, TeO_2 and LnF_3 powders were thoroughly mixed and melted in a platinum crucible until a bubble-free liquid was formed. The resultant melt was poured into a brass mould with a narrow rectangular hole for longitudinal oscillations and into a brass mould with a long hole for torsional oscillations, and they were subsequently annealed at 200°C.

The amorphous state of the samples was checked by X-ray diffraction spectra recorded on Seifert Diffractometer Model SO-Debye Flux 2002 with copper target and nickel filter, operated at 40 kV, 30 mA. The X-ray diffraction spectra recorded for these glasses are shown in figure 1; the curves confirm the amorphous state of the glasses used in the present investigation. The samples were then ground and finely polished. The final dimensions of the glasses used for the longitudinal and shear velocity measurements were almost identical to those of X-cut 0·13 MHz quartz transducers used in the measurements. The details of density measurements at high temperature and ultrasonic velocities in the glasses by composite oscillator technique were reported earlier (Ravi Kumar *et al* 1997c). If f_q and f_c are the resonance frequencies of the transducer and the composite oscillator, the resonance frequency of the glass samples were determined using the relation:

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

where m_q and m_s are the masses of transducer and glass sample respectively. For measuring the temperature variation of f_s, the holder of the sample was immersed in

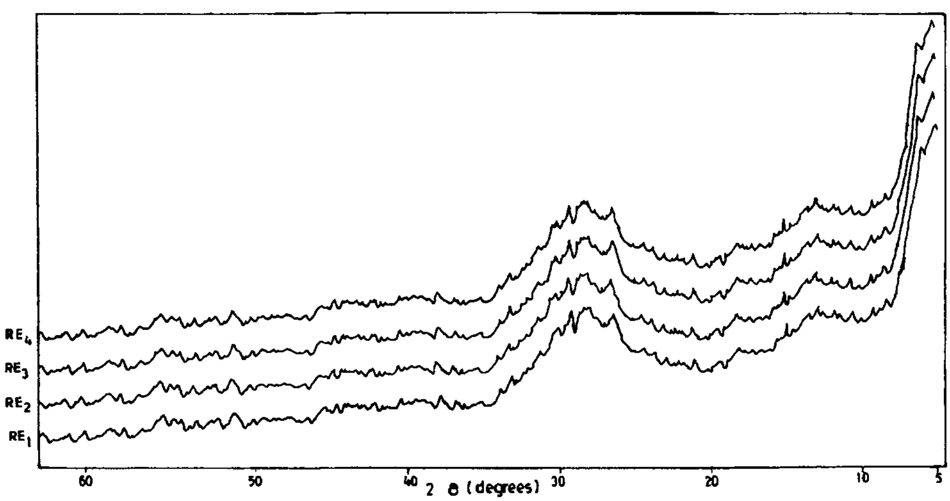

Figure 1. X-ray diffraction spectra of rare earth doped glasses.

Table 1. Data on some elastic properties of rare earth ions doped ZnF_2–PbO–TeO_2 glasses.

Glass	Y(k. bars) 30°C	Y(k. bars) 100°C	η(k. bars) 30°C	η(k. bars) 100°C	σ 30°C	H(k. bars) 30°C
$RE_1(Pr^{3+})$	543	541	74	226	0·1122	63·20
$RE_2(Nd^{3+})$	535	529	77	230	0·1101	62·65
$RE_3(Eu^{3+})$	520	508	82	236	0·1080	61·34
$RE_4(Tb^{3+})$	507	495	85	237	0·1063	60·24

a hot bath whose rate of heating (50°C/h) was maintained with a sensitive temperature controller. The accuracy of the temperature control is $\pm$ 1°C.

3. Results

From the variation of f_s with temperature, corresponding longitudinal and shear velocities (v_l and v_s) of the sound waves in the glasses were evaluated from the plots of resonance curves at different temperatures. With these velocities, using the standard equations, the Young's modulus Y and shear modulus η were determined at different temperatures. Further, using the relations:

$$\frac{v_l^2}{v_s^2} = \frac{Y}{\eta} = 2(\sigma + 1), \qquad (2)$$

and

$$H = (1 - 2\sigma)Y/6(1 + \sigma), \qquad (3)$$

the poisson's ratio σ and microhardness H of the glasses were calculated and presented in table 1 along with the other pertinent data.

The resonance curves, drawn at different temperatures for a particular glass, show the broadening of the resonance peaks with a shift in the resonance frequency towards lower frequencies with descending peak heights as the temperature of measurement is increased. At a particular temperature the resonance curves of ZnF_2–PbO–TeO_2 glasses, doped with different rare earths, exhibit a decreasing trend of quality factor with decreasing sharpness of the resonance as the atomic number Z of the rare earth ions is increased.

Figure 2 shows the variation of internal friction Q^{-1} at room temperature (30°C) and at 100°C calculated from the resonance curves using:

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

The value of Q^{-1} is found to increase with increase in the atomic number Z of the dopant ion and also with the temperature of measurement. Figure 3 presents velocity isotherms (both longitudinal and shear) of ZnF_2–PbO–TeO_2: Ln^{3+} at two different temperatures with atomic number Z of the rare earth ions; both the velocities are found to decrease with increase in Z. The Young's modulus Y and the shear modulus η at room temperature for the pure 45 ZnF_2–9 PbO–46 TeO_2 glasses are found to be 557 and 249 kbars respectively. For Pr^{3+}-doped glasses, these values are decreased to 543

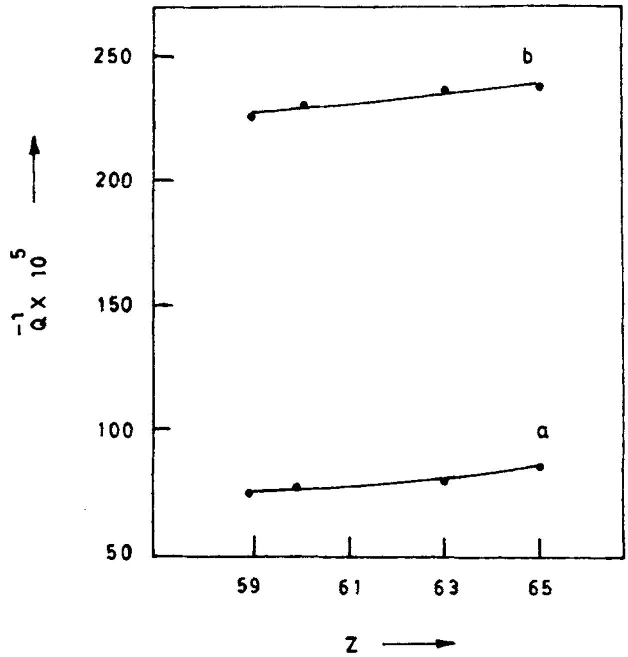

Figure 2. Variation of internal friction Q^{-1} at room temperature: **a.** 100° C and **b.** as a function of atomic number Z.

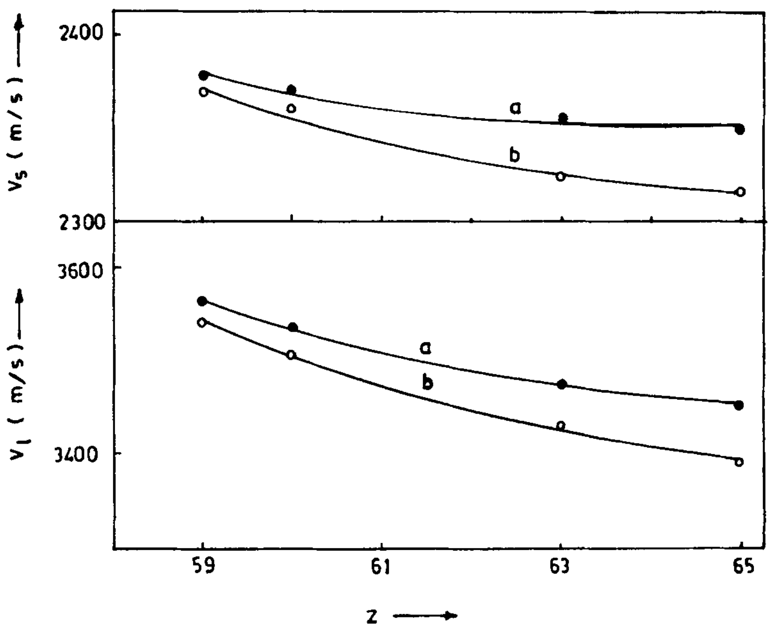

Figure 3. Variation of longitudinal and shear velocities as a function of atomic number Z of rare earth ions (**a**) at room temperature and (**b**) at 100° C.

and 244 respectively, and with increasing the atomic number Z of the dopants these values are found to decrease further. As the temperature of measurement is increased the values of Y and η are found to decrease for all the glasses (figure 4).

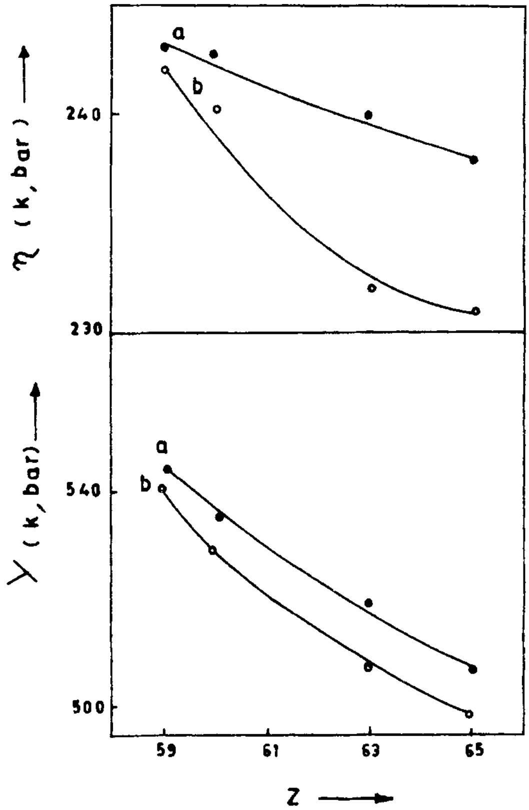

Figure 4. Variation of Young's modulus Y and rigidity modulus η as a function of atomic number Z of rare earth ions (**a**) at room temperature and (**b**) at 100° C.

Further, using the average sound velocity,

$$V_m = [v_l^2 - 4/3\, v_s^2]^{1/2}, \tag{5}$$

another solid state parameter, Debye temperature θ_D of the system, is determined using the relation (Kartha *et al* 1983):

$$\theta_D = \frac{h}{K}\left(\frac{3N_A}{4\pi V}\right)^{1/3} V_m, \tag{6}$$

where h is the Planck's constant, K, the Boltzmann's constant and V, the specific volume.

The acoustical impedance for these glasses is also determined by the relation:

$$Z_i = V_m d. \tag{7}$$

Latent heat of melting ΔH_m and the diffusion constant D_i, given by the relations

$$\Delta H_m = (9M/128)(\theta_D r_i K)^2/h, \tag{8}$$

$$D_i = K r_i^2 \theta_D / 96h, \tag{9}$$

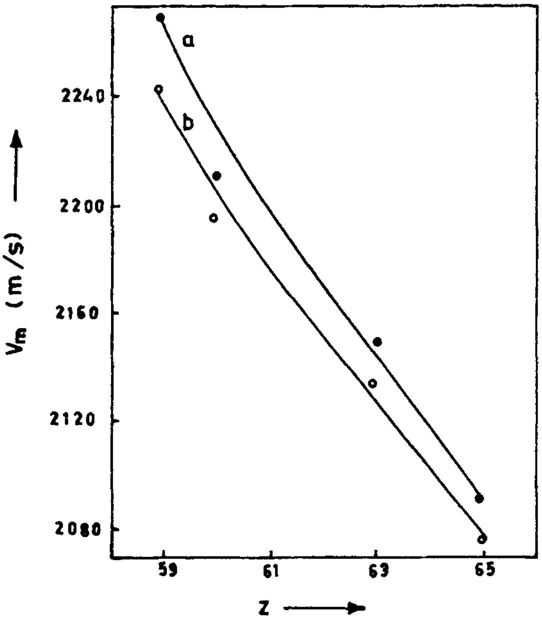

Figure 5. Variation of average velocity V_m as a function of atomic number Z of rare earth ions (**a**) at room temperature and (**b**) at 100° C.

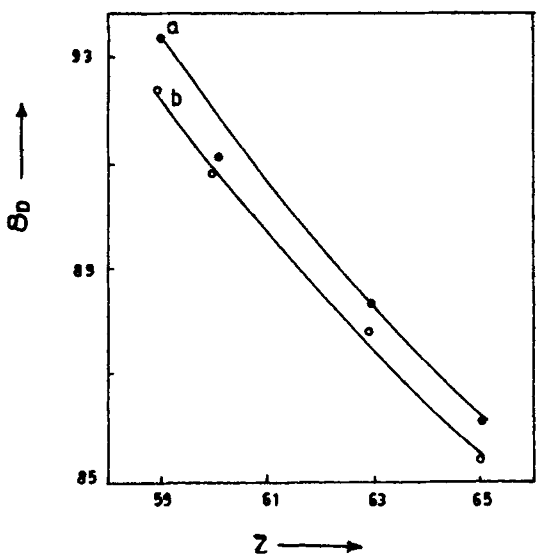

Figure 6. Variation of Debye temperature θ_D as a function of atomic number Z of rare earth ions (**a**) at room temperature and (**b**) at 100° C.

have also been determined for these glasses. All the parameters viz. average velocity V_m (figure 5), the Debye temperature θ_D (figure 6), the acoustical impedance Z_i (figure 7), latent heat of melting ΔH_m (figure 8) and the diffusion constant D_i (table 2) are found to decrease with increase in Z of RE^{3+} ions. All these parameters show a systematic decrease in their values for all the samples as the temperature of measurement is increased.

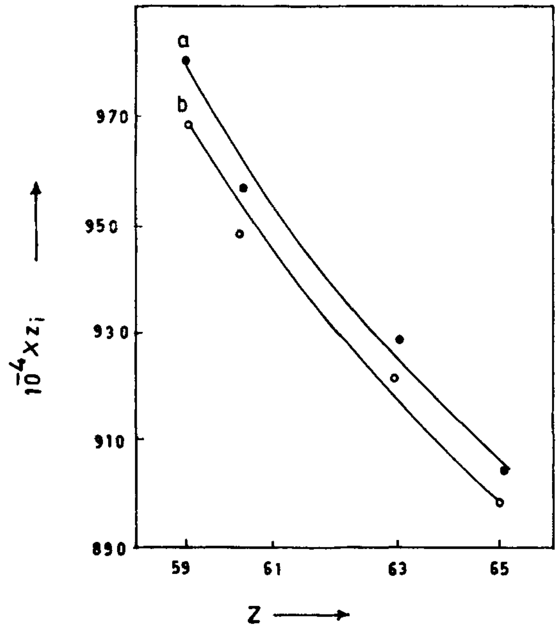

Figure 7. Variation of acoustic impedance Z_i as a function of atomic number Z of rare earth ions (**a**) at room temperature and (**b**) at 100° C.

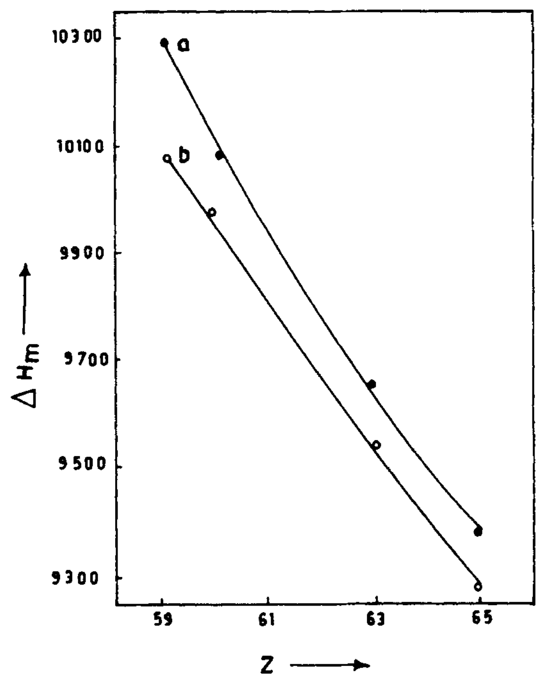

Figure 8. Variation of latent heat of melting ΔH_m as a function of atomic number Z of rare earth ions (**a**) at room temperature and (**b**) at 100° C.

Table 2. Data on accoustical properties of rare earth ions doped ZnF_2–PbO–TeO_2 glasses.

Glass		V_m (km/s)	θ_D	$Z_i \times 10^{-4}$	ΔH_m	$D_i \times 10^9$
$RE_1(Pr^{3+})$	30°C	2·2699	93·40	980·4	10299·36	6·144
	100°C	2·2455	92·38	969·3	10076·40	6·077
$RE_2(Nd^{3+})$	30°C	2·2095	90·91	954·3	9980·26	6·116
	100°C	2·1959	90·93	948·2	9979·15	6·076
$RE_3(Eu^{3+})$	30°C	2·1482	88·47	928·2	9658·40	6·080
	100°C	2·1348	87·84	921·8	9536·11	6·048
$RE_4(Tb^{3+})$	30°C	2·1896	86·00	903·2	9373·70	6·068
	100°C	2·0766	85·45	897·3	9255·48	6·039

4. Discussion

TeO_2 belongs to the intermediate class of glass forming oxides and as such does not readily form glass. But it does form a glass when mixed with modifiers like PbO. Earlier neutron scattering experiments (Brady 1986) and Raman spectral study (Kozhukharov *et al* 1986; Sekiya 1992; Berthareau *et al* 1994) on TeO_2 glasses, containing different alkali oxides as modifiers, have revealed that the basic building block of TeO_2 glass network is a trigonal bipyramid with two axial bonds of length 2·08 Å and two equatorial bonds of length 1·91 Å (Dimitrova *et al* 1989). The modifier PbO enters the glass lattice network by breaking up Te–O–Te bonds, thus introducing coordinated defects known as dangling (broken) bonds which are nothing but the under coordinated bonds denoted by T_3^- and T_{3+1}^0. Further, these bonding defects give rise to electron states within the band gap of the material and will be localized in that region (Mott and Davis 1979). Previous electron spin resonance and optical absorption experiments (Brodbeck and Iton 1985; Sridhar *et al* 1995) indicate that the rare earth ions, when they are present in the glass matrices, impose virtually no specific or narrowly defined site preference in the glass network, but there are reports (Shelby 1994) suggesting that the rare earth ions also enter the glass network as modifiers by breaking up the random network leaving the bonding defects of the type mentioned earlier in the tellurite glass lattice.

The fact that the resonance curves flatten out with increase in atomic number Z of rare earth ion dopant at a given temperature indicates an increase in the logarithmic decrement because of larger coefficient of internal friction; this is apparently due to the progressive depolymerization of the glass network (or due to the increase in the concentration of bonding defects of the type mentioned above) with increase in atomic masses of rare earth ions. This is further confirmed by the decrease in the microhardness H of the ZnF_2–PbO–TeO_2: Ln^{3+} glasses with increase in the atomic weights of Ln^{3+} ions.

Recollecting the data on acoustical and thermodynamical parameters of these glasses, a decrease in the value of these parameters viz. mean velocity v_m of ultrasonic waves, Young's modulus Y, shear modulus η and the Debye temperature θ_D has been observed as we go from Pr^{3+} doped glasses to Tb^{3+} doped glasses. The parameters, acoustical impedance Z_i, the diffusion constant D_i, and the latent heat of melting ΔH_m, show a similar decrease with increasing atomic number Z of the rare earth ions. The raise in temperature of the glass lead to decrease in the values of all the above parameters to a considerable extent. This indicates that as the temperature of measurement approaches the glass transition temperature T_g, there is a further enhancement of the depolymerization in the glass network, causing a slight increase in the width of the localized defect states; this is perhaps responsible for increase in the internal friction and decrease in all the elastic and thermodynamical parameters of the glasses.

Finally, our study on elastic properties of ZnF_2–PbO–TeO_2: Ln^{3+} glasses indicates that though rare earth ions, such as Pr^{3+}, Nd^{3+} etc, are good laser spices in the tellurite glasses these ions are causing a slight decrease in the mechanical strength of the host glass and this decrease is more pronounced in case of rare earth dopants of high atomic number.

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