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Elastic constants of zinc phosphate glasses containing europium

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Abstract : The elastic moduli and the attenuation of the longitudinal ultrasonic wave velocity are studied as a function of composition for the prepared Eu_2O_3–ZnO–P_2O_5 glass system. The density, the ultrasonic wave velocities (longitudinal and shear), the elastic moduli, Poisson's ratio and the ultrasonic attenuation are found to be sensitive to the glass composition. It is found from this ultrasonic data, that the glass system can be divided into 'three compositional regions'. The results are interpreted in terms of changes in the coordination number, the interatomic force constant and the polarizability of the glass network bonds and cations

Keywords : Elastic constants, ultrasonic attenuation, zinc phosphate glasses

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1. Introduction

The structure of binary phosphate glasses has been studied by measurements of the compositional dependence of the refractive index, molar volume, optical dispersion and electrical properties by Kordes *et al* [1], Higazy *et al* [2], Higazy [3] and Khafagy *et al* [4,5]. They divided two component phosphate glasses into normal glasses (which are containing oxides of Na, Ca, Ba and Cd) and anomalous glasses (*i.e.*, phosphate glasses containing oxides of Zn, Mg, Be, Bi and V). In the anomalous phosphate glasses, the properties show discontinuities at about 50 mole % of the metal oxide.

The dependence of elastic constants on glass compositions of a number of phosphate glasses showed discontinuities in elastic constants with metal oxide contents [6–11]. This anomalous behaviour is qualitatively interpreted in terms of coordination numbers, stretching force constants and cross-link densities of network bonds. Elastic moduli data on phosphate glasses containing rare-earth materials are quite rare. However, glasses containing rare-earth ions have considerable potential for applications in optical data

Table 1. Composition, density, molar volume, longitudinal and shear ultrasound velocities, elastic moduli, Poisson's ratio, Debye temperature and attenuation for $ZnO–P_2O_5$ glasses doped with Eu_2O_3 oxide.

Glass	Eu_2O_3 (wt%)	Density (g cm^{-3})	Molar volume (cm^3)	Ultrasonic wave velocity (m s^{-1})		Elastic Moduli * (Kbar)				Poisson's ratio	Debye Temp. (K)	Attenuation (db/cm)
				long	shear	Long	Shear	Bulk	Young's			
ZE1	0 0	2.8515	39 159	4600	2500	603	178	366	459	0 290	341	2.344
ZE2	0.5	2 9512	37 965	4300	2365	546	165	326	423	0.283	326	3 110
ZE3	1.0	2.9814	37.707	4176	2317	520	160	306	409	0.278	318	5 722
ZE4	2.5	2.9418	38 599	4245	2340	530	161	315	413	0 282	321	4 814
ZE5	4.0	2.9401	39.003	4400	2350	569	162	353	416	0 300	322	3 799
ZE6	6.0	2.9812	38 960	3900	2200	453	144	261	365	0.267	300	4.826
ZE7	8.0	3.024	38 892	3650	2150	403	140	216	346	0 234	238	4 785

*1 Kbar = 10^8 N/m^2

change in behaviour of the compositional dependence of all the properties mentioned so far around 1 and 4 wt % Eu_2O_3 content.

Figure 1(a) shows the plot of density versus wt % of europium oxide. The variation of the density with wt % Eu_2O_3 content may be related to the change in the atomic mass and ionic or atomic size of the constituent elements in glasses. The atomic mass of P, Zn and Eu are 30.97, 65.37 and 151.96, respectively, and their respective atomic radii are 1.0, 1.35 and 1.85 Å. The atomic mass and the atomic size of Eu are greater than those of P and Zn atoms. So, the increase in density and the decrease in molar volume in the composition region (0–1) wt % Eu_2O_3 content may be probably attributed to the effect of adding europium cations (atomic mass of 151.96 and atomic radious of 1.85 Å) into the vitreous structure of $ZnO–P_2O_5$. Reisfeld [13] reported that, the rare-earth ions in glasses occupied the center of a distorted cube which is made of four tetrahedra of phosphate glasses. Each tetrahedron contributes two oxygens to the coordination of the rare-earth ions. The overall coordination number is 8, which is the most common coordination number of the rare-earth

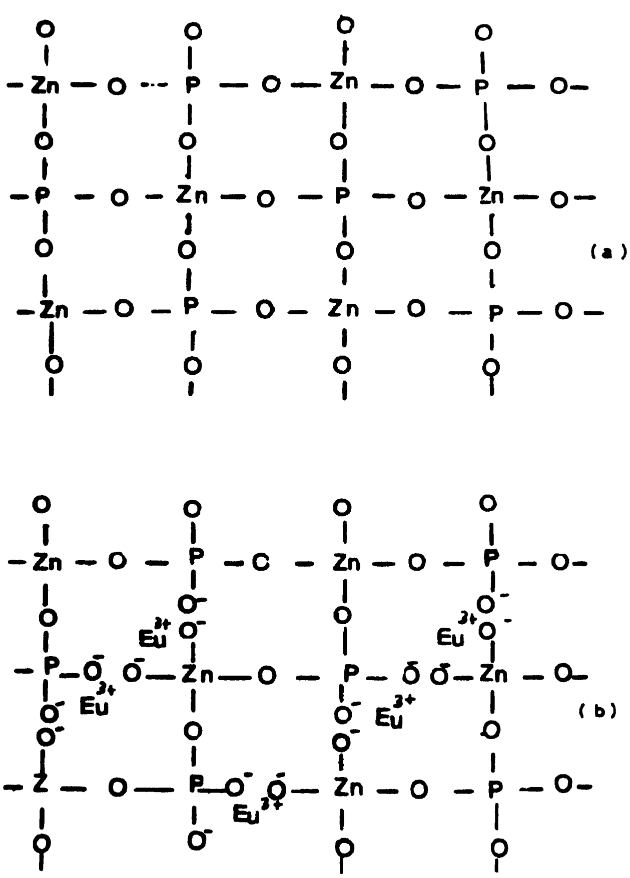

Figure 2. Schematic two-dimensional representation of the effect of Eu_2O_3 oxide on the $ZnO–P_2O_5$ network : (a) the $ZnO–P_2O_5$ network structure and (b) the structure of europium phosphate glasses.

oxides. According to Reisfeld proposal the Eu ions may enter the glass network interstitially (see Figure 2). Hence, some network bonds P–O–P or Zn–O–P are broken and replaced by ionic bonds between Eu ion and singly bonded oxygen atoms. So if one assumed that the only effect of adding Eu cations was to break down the network bonds P–O–P and Zn–O–P then an increase in the molar volume with Eu_2O_3 content would be expected for the entire vitreous range of the present glass system. Experimentally, this effect increase the molar volume in the glass compositional range from 1 to 4 wt % Eu_2O_3 content and as a consequence the values of the density are decreased (see Figures 1(a) and (b)). However beyond 4 wt % Eu_2O_3 content, the addition of Eu_2O_3 increased the values of the density. This increase may be due to simultaneous filling up of the vacancies amidst the network by the interstitial Eu ions (*i.e.* increased packing density) and will reduce the averaged interatomic spacing, which decreases the molar volume (see Figures 1(a) and (b)).

The addition of Eu_2O_3 to the vitreous $ZnO–P_2O_5$ structure decreases both the longitudinal and the shear wave velocities upto 1 wt % europium oxide content (Figures 3(a) and (b)).

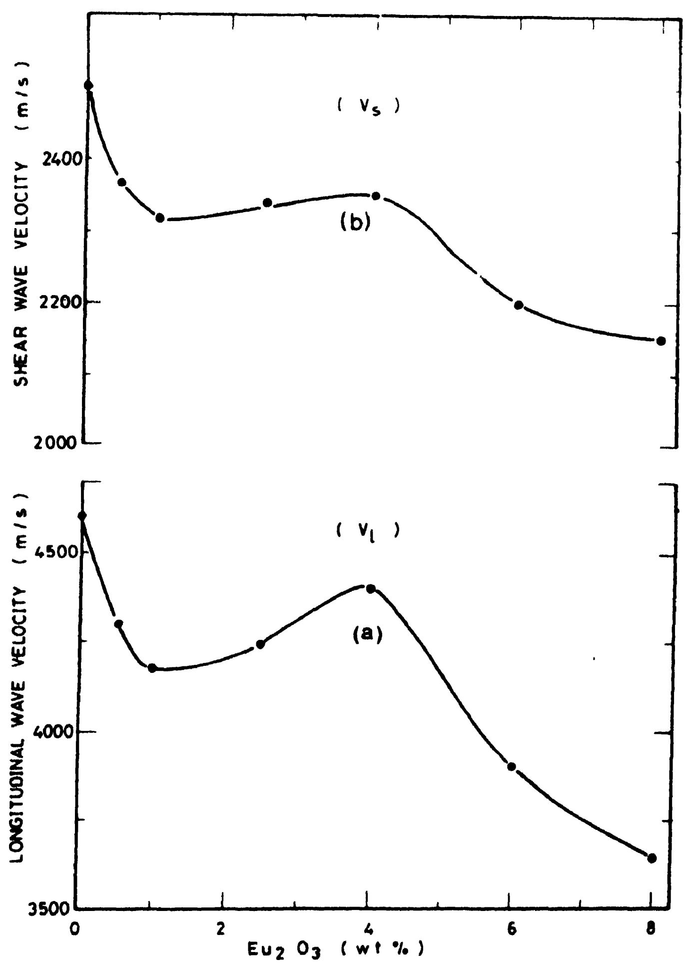

Figure 3. Dependence of (a) longitudinal wave velocity V_l and (b) shear wave velocity V_s on the wt % Eu_2O_3 content.

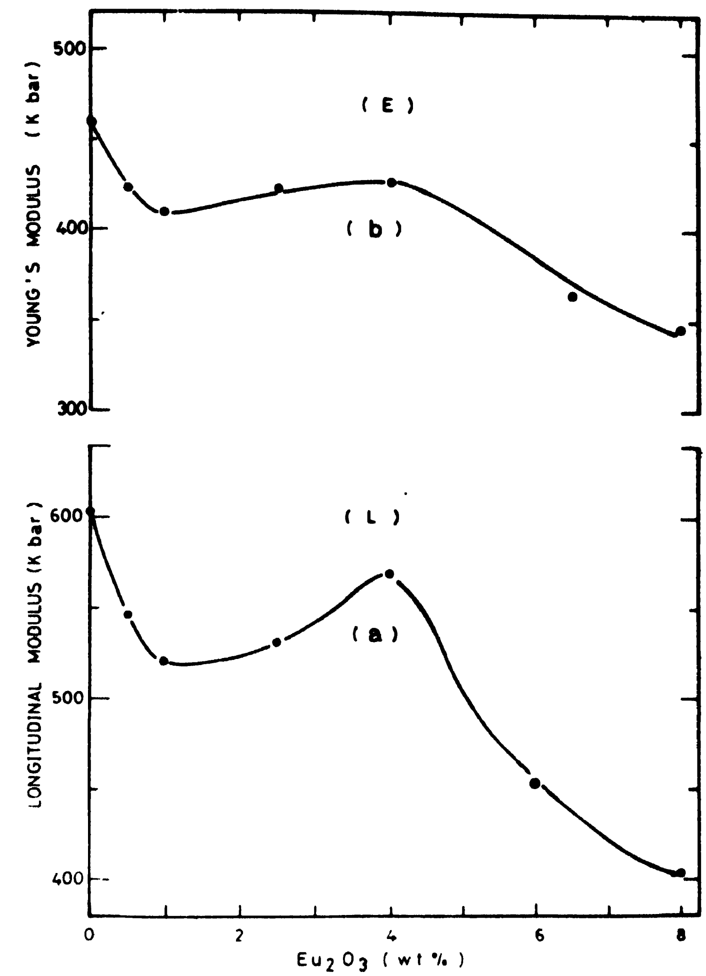

Figure 4. Compositional dependence of (a) longitudinal modulus *L* and (b) Young's modulus *E* in Eu_2O_3–ZnO–P_2O_5 glasses

Then beyond 1 wt % there is an increase in both the ultrasonic velocities with further addition of Eu_2O_3 oxides upto 4 wt %. For high Eu_2O_3 percentages *i.e.* > 4 wt %, the ultrasonic velocities decrease again (see Figures 3(a) and (b)). All the elastic moduli, *viz.* longitudinal, shear, bulk and Young's modulus show the same trend as the acoustic wave velocities (see Figures 4 and 5), *i.e.* they exhibit the same '3-composition-regions' behaviour that identified in the density, the molar volume and the ultrasonic wave velocities for the studied glass system.

All of the anomalous behaviour in the above mentioned properties may be a result of mere combination of some effects provided by the glass elements with different characteristics, particularly different effective radii, weights, coordination numbers, bond strengths cross-link densities and polarizability of ions. Also in the certain rare-earth elements (Ce, Sm, Eu, Tm and Yb) the occupation number of the 4*f* shell can take on more

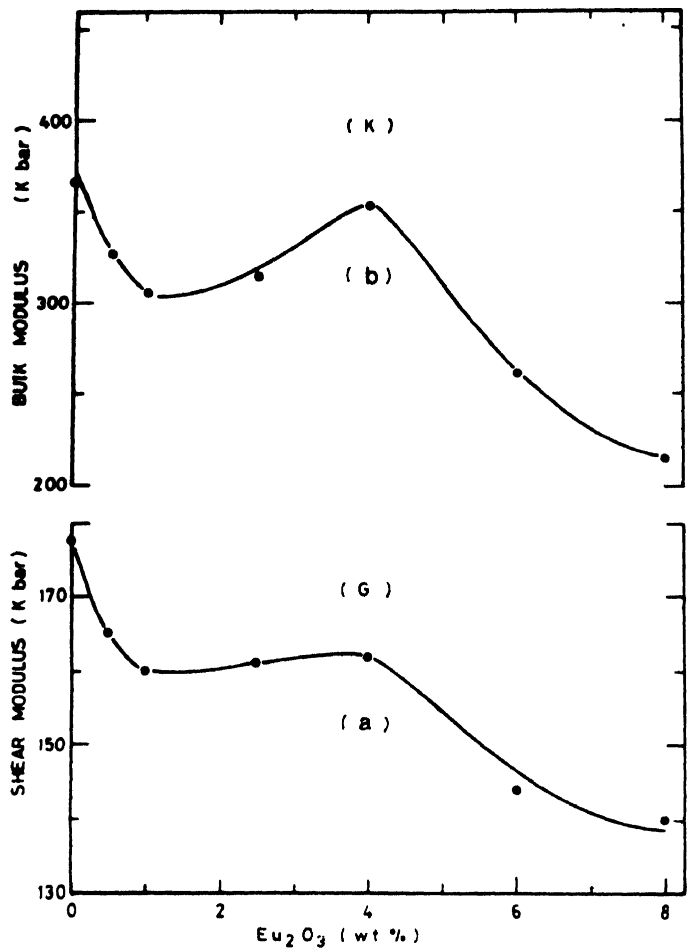

Figure 5. Compositional dependence of (a) shear modulus G and (b) bulk modulus K in Eu_2O_3–ZnO–P_2O_5 glasses.

than one value. The variable valence leads to a rich variety of anomalies in the physical properties of glasses containing these elements [14]. As a consequence of atomic screening, the europium ion-size depends strongly on the valence. Transition of the valence state from 2 to 3 causes a change in the effective ionic radius from 1.17 to 0.95 Å and leads to an abrupt contraction in the europium ion size [15]. Hence, the anomalous elastic properties of the present glass system may be ascribed to the variable valence of europium ions in addition to the structural feature of glass network.

To interpret the present results, we may use the compositional dependence of the elastic moduli of polycomponent oxide glasses model which put forward by Bridge and Higazy [9] in the from

$$K = \text{const.}\ \Sigma_i\left((n_f)_i\ (N_f)_i\ r_i^2 F_i\right)/9x(1/n)\ \Sigma_i\left((n_c)_i\ (N_c)_i\right) Z$$

where for bond type i :

$(n_f)_i$ = number of network bonds per formula unit,

$(N_f)_i$ = number of formula units in which the bond resides per unit volume,

r_i = network bond length,

F_i = stretching force constant,

n = the total number of cations per glass formula unit,

$(n_c)_i$ = number of cross-link per cations,

$(N_c)_i$ = number of cations per glass formula unit.

From the above expression, one can argue that the elastic moduli tend to increase with both cross-link density and the bond stretching force constants. So, according to different characteristics of P, Zn and Eu cations in the studied glass system, one may expect that the addition of Eu_2O_3 oxide to $ZnO–P_2O_5$ glass leads to three different processes which

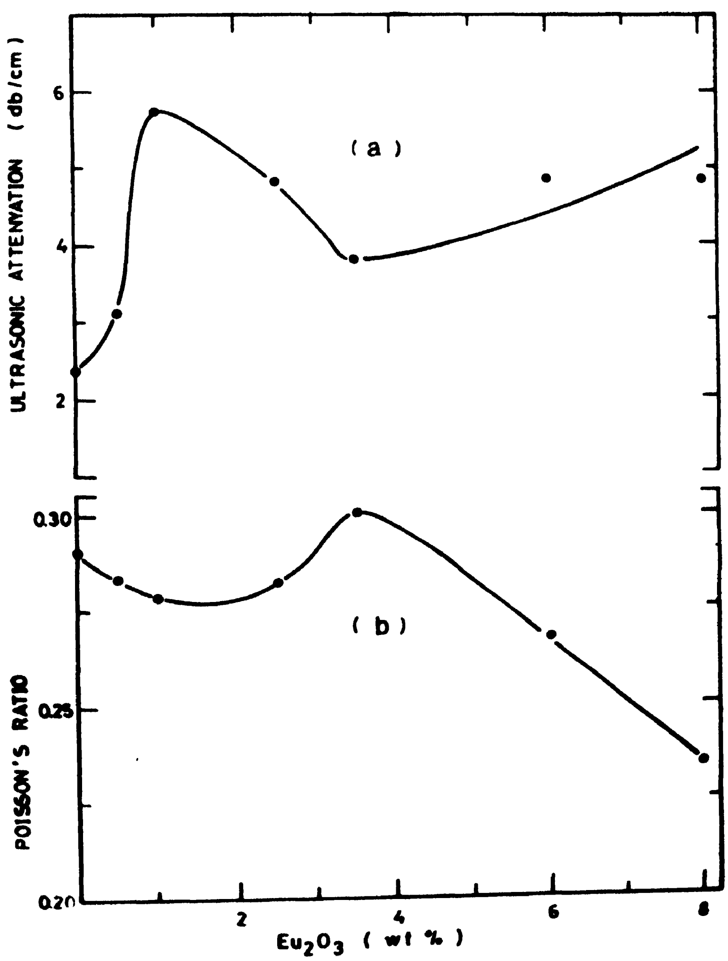

Figure 6. Variation of (a) ultrasonic attenuation α and (b) Poisson's ratio σ with Eu_2O_3 wt %.

are taking place simultaneously. An increase in cross-link density (coordination numbers of P, Zn and Eu are 4, 4 and 8 respectively), increase the number of weaker Eu–O ionic bonds compared with P–O and Zn–O bonds (unit bond strength of P, Zn and Eu are 1.25, 0.50 and 0.33 respectively) and an increase in the polarizability of glasses (polarizability of P, Zn and Eu are 0.05, 0.71 and 1.23, respectively). This may take place in addition to the effect of the variable valence of the europium ions.

In the region 0–1 wt % Eu_2O_3 content, the decrease in elastic moduli (Figures 4 and 5) and the increase in the ultrasonic attenuation 'α' (Figure 6(a)) may be attributed to the increase of the number of weaker Eu–O ionic bonds *i.e.* the effect of other factors are overridden by that of weaker Eu–O bonds.

As the Eu_2O_3 oxide increases from 1–4 wt% an increase in the elastic moduli and decrease in the ultrasonic attenuation are observed. This is probably attributable to a gradual change in the cross-link density in glasses due to introduction of Eu ions with coordination number 8. Also, the simultaneous filling-up of the vacancies amidst the network by the interstitial Eu ions (*i.e.* the increased packing density), this will cause increase the elastic moduli.

The increased amount of Eu_2O_3 in the third composition region (4–8 wt % Eu_2O_3 content) causes the elastic moduli to decrease and the ultrasonic attenuation to increase in spite of the fact that the cross-link density and the filling-up of the vacancies of the glass network still increased. This behaviour might indicate that there are other opposing processes taking place in this composition region. One of these processes is the polarizability effect. The modulus of elasticity has shown decreasing effect with increasing polarizability of glasses [16]. So, the pronounced decreases in the elastic moduli and increases in the ultrasonic attenuation in the third composition region may be due to the effect of adding Eu cations with higher polarizability value of 1.23 compared with the polarizability values of 0.05 and 0.71 for P and Zn cations, respectively. The behaviour of the elastic moduli and the attenuation in the third composition region may also arise from valence changes for the europium ions; *i.e.* the transition of the valence state from 2 to 3 causes an abrupt contraction in the europium ion size (ionic radii of Eu^{2+} and Eu^{3+} are 1.17 Å and 0.95 Å, respectively). This effect leads to reduce the glass packing density which cause a decrease in the elastic moduli values. Unfortunately, we have no independent proof of this valence change of Eu cations in the present glass system.

The variation of Poisson's ratio with wt % Eu_2O_3 content shows the same trend as the elastic moduli [Figure 6(b)]. To interpret our data on the compositional dependence of Poisson's ratio, we try to isolate the possible variable affecting the Poisson's ratio of glass and we next consider the relationship :

$$\sigma = (E/2\,G) - 1.$$

For a glass system where both the degree of cross-linking and the relative proportions of different types of bonds may be changed with composition, it has been reported that [8] as the cross-link density is increased, the value of E for tensile stress applied in the chain direction will remain constant whilst the value of G for shearing force applied parallel to the chains will increase with the cross-link density. Thus, one can argue that Poisson's ratio decreases as the ratio E/G decreases. Also there is another possible way in which Poisson's ratio might change is related to the bond force constant. E will increase with bond stretching force constants, whilst G will increase with bond bending force constant. Thus, as the ratio of bond bending force constant to stretching force constant increases, E/G decreases and so Poisson's ratio decreases. According to the above arguments, the variation of Poisson's ratio in the present study may be related to the change in E/G values *i.e.* the changes in cross-linking density and the bond bending and stretching force constants. In the composition region 0–1 wt % Eu_2O_3 content, the ratio E/G showed a decrease from 2.58 to 2.55 (Table 1) this leads to a decrease in the values of Poisson's ratio [see Figure 6(b)]. However, in the second composition region (1–4 wt % Eu_2O_3 content), the values of E/G increase from 2.55 to 2.57·and then in the third region (4–8 wt % Eu_2O_3 content), the values of E/G decrease again from 2.57 to 2.47; this is consistent with the variation of Poisson's ratio in these compositional regions.

The variation of Debye temperature with Eu_2O_3 content (see Figure 7) showed the same three compositional region which had been found in the compositional dependence of the above mentioned properties.

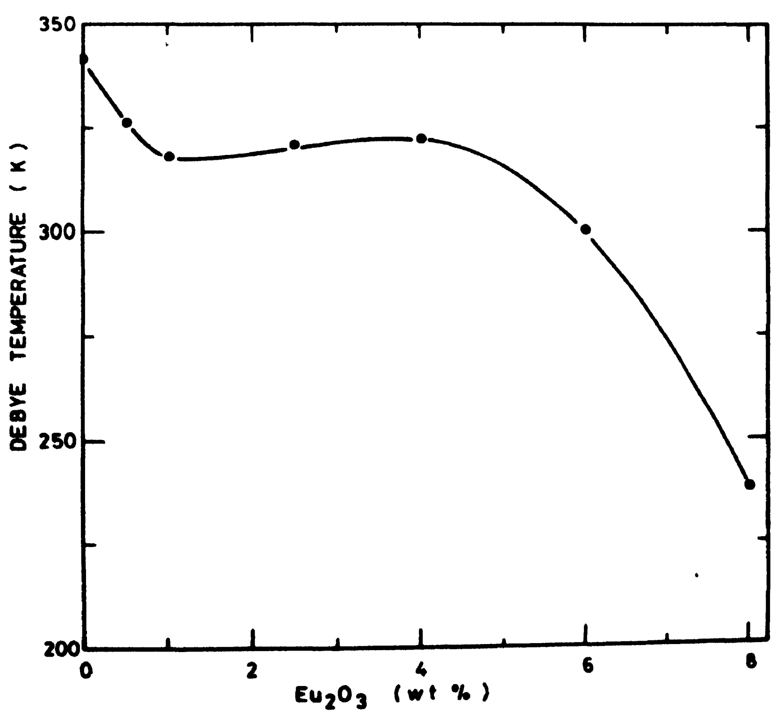

Figure 7. Variation of Debye temperature with Eu_2O_3 wt %.

4. Conclusion

The results have led to some understanding of the structure of these rare-earth phosphate glasses. It is found that all the properties studied in the present investigations are found to be sensitive to the additions of the Eu_2O_3 dopant. On this basis, the ultrasonic data reveals that the present glass system can be divided into three distinct compositional regions.

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