Sci. J. Fac. Sci. Menoufia Univ., Vol. (XI), (1997). 1-28

ULTRASONIC PROPAGATION AND TESTS FOR PHASE SEPARATION IN THE VITREOUS SYSTEM MnO-P_2O_5 DOPED WITH Eu_2O_3 OXIDE.

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ABSTRACT

The compositional dependence of the elastic moduli and the attenuation of the longitudinal ultrasonic wave velocity are studied for a series of Eu_2O_3-MnO-P_2O_5 *glasses. The density, the elastic moduli, the attenuation, Poisson's ratio and Debye temperature are found to be rather sensitive to the glass composition. It is found from this data, that the present glass system can be divided into " three compositional regions". The ultrasonic results are qualitatively interpreted in terms of .changes in the crosslink densities, interatomic force constants and the polarizability of the glasses.*

The application of Voigt-Reuss and Hashin-Shtrikman theoretical boundaries for the elastic moduli, to test for phase separation has shown that there is no evidence that immiscibility is exist in the studied glass system

INTRODUCTION

Several authors (Farley and Saunders[1], Patel and Bridge[2], Higazy and Bridge [3], Bridge and Higazy[4], Higazy et al[5] and Higazy[6] have investigated the dependence of elastic constants on glass compositions of a number of phosphate glasses. It has been found that, the anomalous behaviour is qualitatively explained in terms of coordination numbers, stretching force constants and cross-link densities of network bonds. Elastic constants data for phosphate glasses containing rare-earth materials are quite rare; in spite of, these glasses have considerable potential for applications in optical data transmission, detection, sensing and laser technologies[7].

Phase separation has been observed in many oxide glasses (for example Li_2O-Na_2O-SiO_2, Li_2O-K_2O-SiO_2, Pb-SiO_2, B_2O_3-GeO_2, SiO_2-GeO_2, PbO-GeO_2 and PbO-P_2O_5 glass systems)[8-12]. It has been reported that, this phase separation results from liquid-liquid immiscibility, which is widespread in glass-forming systems. Glass melts whose compositions correspond to a single component (for example SiO_2, P_2O_5, B_2O_3 etc.) or defined and stable chemical compounds (for example sodium metaphosphate, i.e. contain a single kind of structural element only) solidify homogeneously. However, glass melts consisting of two or more oxides whose compositions are intermediate between two stable compounds may tend to phase separation. The tendency is at least in part determined by the relative strengths and coordination numbers of the different types of bond present in the melt.

In earlier literature a number of investigators[13-18] have considered theoretically the problem of expressing the bulk elastic behaviour of a two-phase material interms of the amounts and properties of the end-member materials. generally they discussed the upper and lower bounds between which the various elastic properties must lie.

Voigt and Reuss put forward the following expressions to calculate the upper and the lower limits of buk modulus K*, shear modulus G* and Young's modulus E*, using the experimental elastic moduli of the first and second end-member components. For the upper limits the moduli become

$$K^*_u = (1-V_2)\,K_1 + V_2K_2 \qquad \text{.......(1)}$$

$$G^*_u = (1-V_2)\,G_1 + V_2G_2 \qquad \text{.......(2)}$$

$$E^*_u = (1-V_2)\,E_1 + V_2E_2 \qquad \text{.......(3)}$$

for the lower limits the elastic moduli become

$$\frac{1}{K_L^*} = \frac{1 - V_2}{K_1} + \frac{V_2}{K_2} \quad \text{...(4)}$$

$$\frac{1}{G_L^*} = \frac{1 - V_2}{G_1} + \frac{V_2}{G_2} \quad \text{...(5)}$$

$$\frac{1}{E_L^*} = \frac{1 - V_2}{E_1} + \frac{V_2}{E_2} \quad \text{...(6)}$$

where V_2 refer to the volume fraction of the second end-member components.

Hashin and Shtrikman derived narrower upper and lower theoretical bounds for the bulk modulus, using the expressions

$$K_U^* = K_2 + \frac{1 - V_2}{1/(K_1 - K_2) + 3V_2 / (3K_2 + 4G_2)} \quad \text{............(7)}$$

$$K_L^* = K_1 + \frac{V_2}{1/(K_2 - K_1) + 3(1 - V_2) / (3K_1 + 4G_1)} \quad (8)$$

The slopes and curvatures of these relations (Equations 1-8) show that:

(a) The slopes of the modulus-volume fraction curves depend only of the relative values of the end-member moduli.

(b) The curvatures of such plots are always positive i.e. concave upward; and.

(c) No maxima, minima or points of inflection or discontinuities.

Phase separation studies in glasses mainly have been performed by means of electron microscopy. It is perhaps less well known that is possible to make a test for the presence or absence of two phase systems ultrasonically, from an appropriate theoretical analysis of the compositional dependence of the elastic moduli found experimentally. The ultrasonic method gives information on the interiors of bulk specimens whereas the electron microscope probes only the surface layers of bulk specimens or thin sections by transmission. In hygroscopic glasses, like some phosphate glasses, the surface structure has not the same structure as the rest of the specimen; layers rich in water may give indication on electron micrographs which obscure signs of phase separation and the same problem may also arise with transmission sections. Therefore, it seems well worth while to apply the ultrasonic technique to the present manganese-phosphate glasses doped with europium oxide. Also the ultrasonic data are used to investigate the effect of adding the rare-earth oxide to MnO- P_2O_5 glass on the elastic constants of this glass system.

EXPERIMENTAL TECHNIQUE

Glass Preparation

MnO-P_2O_5 glasses containing europium were prepared by melting the appropriate mixture of Analar phosphorous pentoxide, P_2O_5, manganese oxide, MnO and, europium oxide, Eu_2O_3, using alumina crucibles heated in an electric furnace held at 350°C for one hour. This allowed the P_2O_5 to decompose and react with other components before melting would ordinary occur. After this treatment the mixture was placed for one hour in a second furnace at between 1000-1150°C, the highest temperature being applicable to the mixes richest in Eu_2O_3. The glass melt was stirred occasionally to ensure homogeneous melt. Each metal was cast into two mild-steel molds to form glass rods 1 cm long by 1.6 cm diameter. After casting, each glass was immediately transferred to an annealing furnace held at 350°C for one hour. After this time, the furnace was switched off and the glass samples were allowed to cool to room temperature at an initial cooling rate of 3°C per minute. This procedure was employed to prepare glass sample of the composition 50 mole % MnO-50 mole % P_2O_5 doped with Eu_2O_3 ranging from 0 to 8 wt%. Specimens used for ultrasonic measurements were in the form of cylindrical rods of 1.6 diameter and 0.5 cm thickness with polished and parallel. faces.

The densities of the samples were measured by the Archimedes method using toluene as the immersion liquid and comparison of the different glasses only they are accurate to ±0.001g cm^{-3}.

Ultrasonic Measurements

The ultrasonic compressional and shear wave velocities and attenuation measurements were made by the pulse-echo techniques using commercial transducers (longitudinal transducer 2 MHz, 1.6 cm active diameter, and shear-Krautkramer 2 Mhz, 1.3 cm active diameter) actuated by an ultrasonic flaw detector (ultrasonoscope ML 32). Details of the technique are presented elsewhere[3].

The elastic constants of the studied glasses were calculated at room temperature using the measured densities, ρ, and the velocities of longitudinal, V_L, and sheer, V_S, waves using the following expressions:

Longitudinal modulus $L = \rho V_L^2$,

Shear modulus $G = \rho V_S^2$,

Bulk modulus $K = L - (4/3) G$,

Poisson's ratio $\sigma = (V_L^2 - 2 V_S^2) / 2 (V_L^2 - V_S^2)$

Young's modulus $E = (1 + \sigma) 2G$.

The procedures for calculating the Debye temperatures are presented elsewhere[5].

The total maximum error in the measurements of elastic module due to changes in specimen thickness, velocity, density and phase shift is about 0.09%.

RESULTS AND DISCUSSION

The compositions, the densities, the molar volumes, the elastic constants and the attenuation of the longitudinal ultrasonic wave for the studied glasses are listed in Table 1. The data of this table has shown that there is a change in behaviour of the compositional dependence of all the properties examined in this work around 1 and 4 wt % Eu_2O_3 content.

The plot of density versus wt% Eu_2O_3 oxide (see Fig. 1(a)) showed an increase up to 1 wt% Eu_2O_3 content, which is probably attributable to the effect of adding europium cations (atomic mass of 151.96) into the vitreous structure of $MnO-P_2O_5$. This also may be glass molar volume (see Fig. 1 (b)).

Upon further increase in Eu_2O_3 content, the variation of the density is seen to display slightly decrease up to 4 wt % Eu_2O_3 content (see Fig. 1[a]). This decrease in density indicates a structural change in the glass network which is accompanied by an increase in the molar volume (see Fig. 1[b]). However beyond 4 wt% Eu_2O_3 content substantial increase in density occurs which may be due to an increase in the packing density of glasses. This leads to a decrease in the molar volume (see Fig. 1[b]).

The ultrasonic wave velocities measured in this work are found to be sensitive to the glass composition (see Fig.2). The addition of Eu_2O_3 to the vitreous $MnO\text{-}P_2O_5$ structure decreases both the longitudinal and the sheer wave velocities up to 1 wt% Eu_2O_3 oxide content. Beyond 1 wt % there is an increase in the ultrasonic wave velocities with further addition of Eu_2O_3 oxide until about 4 wt%. For high Eu_2O_3 percentages i.e. > 4 wt% the velocities decrease again (see Fig.2). All the elastic moduli, viz. Young's modulus shear, bulk and longitudinal show the same trend as the acoustic wave velocities (see Figs.3 and 4), i.e. they exhibit the same 3- composition-regions behaviour.

The anomalous behaviour in the elastic meduli in the present work (Fgs. 3 and 4) may be a result of more combination of some effects provided by the glass elements with different characteristics; particularly different coordination numbers, bond strengths, cross-link densities and polarizability of ions. Also it has been reported[19] that, in the certain rare-earth elements (Ce, Sm, Eu, Tm and Yb) the occupation number of the 4F shell can take more than one value. This variable valence leads to a rich variety of anomalies in the physical properties of glasses containing these elements. For example, the europium ion size depends strongly on the valence values. The transition of its valence state from 2 to 3 causes a change in the effective ionic radius from 1.17 A° to 0.95 A°, leads to an abrupt contraction in the europium ionic size[20].

From the above argument, one may expect that the addition of Eu_2O_3 oxide to the studied glass system $MnO-P_2O_5$ leads to an increase in cross-link density (cross-link densities of P, Mn and Eu are 2,2 and 6, respectively), increase the number of weaker Eu-O ionic bonds (unit bond strength of P, Mn and Eu are 1.25, 0.35 and 0.33, respectively, and an increase in the polarizability of glasses (Polarizability of P, Mn and Eu are 0.05, 0.16 and 1.23, respectively).

The increased amount of Eu_2O_3 from 0-1 wt% in first composition region causes the elastic moduli to decrease (Figures 3 and 4) and the ultrasonic attenuation and the internal friction to increase (Figures 5-a and 6-a, respectively). This may be attributed to the increase of the number of weaker Eu-O ionic bonds.

As the Eu_2O_3 oxide increases from 1-4 wt% an increase in the elastic moduli and decrease in the ultrasonic attenuation and the internal friction are observed. This is probably attributable to the increase of the cross-link density in the studed glasses due to introduction of Eu ions with coordination number 8; this beside the simultaneous filling-up of the vacancies amidst the glass network by the interstitial Eu ions.

In the third composition region (4-8 wt % Eu_2O_3 content), the decrease in elastic moduli and the increase of the ultrasonic attenuation and internal friction may be attributed to the polarizability effect. It has been reported that the modulus of elasticity has shown decreasing effect with increasing polarizability of glasses[21]. So, the pronounced decreases in the elastic moduli and increases in the ultrasonic attenuation and internal friction my be due to the effect of adding Eu cations with higher polarizability value compared with the polarizability values of P and Mn cations.

The variation of Debye temperature (Figure 5-b) and Poisson's ratio (Figure 6-b) showed the same trend as the elastic moduli (Figures 3 and 4).

Inspection of the compositional dependence curves of all the elastic moduli for the studied glass system in the light of criterion (c) Section (1) suggests that there can be no two-phase immiscibility gaps traversing compositions 1 and 4 wt% Eu_2O_3 oxide content. So the next stage is to look for possible gaps in between or to either side of these compositions i.e. the ranges 0 to 1 wt%, 1 to 4 wt% and 4 to 8 wt%. The variation of experimental and predicted (using Equations 1-8) values of bulk, shear and Young's moduli with weight percent of Eu_2O_3 content are plotted in Figs 7-12.

It is seen from Figs 7-12 that the experimental elastic moduli data of K,G and E lie outside the upper and lower bounds of the Voigt and Reuss boundaries except the bulk modulus in the compositional range 0 to 1 wt% (Fig. 7). When the upper and lower bounds of the Hashin and Shtrikman boundaries are displayed for bulk modulus it is observed that the experimental values of the bulk modulus lie outside the Hashin-Shtrikman boundaries. So examination of Figs. 7-12 shows that there is no evidence for two-phase immiscibility gaps covering the three compositional ranges in the studied glass system. This is because all experimental values of the elastic moduli lie well outside the Hashin and Shtrikman boundaries.

Table (1): Composition, density, molar volume, longitudinal and shear ultrasound velocities elastic moduli, Poisson's ratio, Debye temperature and attenuation for MnO-P_2O_5 glass doped with Eu_2O_3 oxide.

Glass	Eu_2O_3 (wt%)	Density (9 cm^{-3})	Molar volume cm^3	Ultrasonic wave velocity (ms-1)		Elostic Moduli (Kbar)*				Possion's ratio	Debye Temp. (K)	Atten-uation db/cm	Q^{-1}
				Long	Shear	Long	Shear	Bulk	Young's				
ME_1	0.0	2.660	42.676	4812	2196	616	128	445	350	0.368	305	2.792	0.444
ME_2	0.5	2.708	42.071	4232	2160	485	126	317	334	0.324	299	3.516	0.560
ME_3	1.5	2.747	41.604	3509	1760	338	85	225	218	0.283	245	5.089	0.810
ME_4	2.0	2.743	41.942	4318	1794	511	88	394	246	0.396	251	4.134	0.660
ME_5	4.0	2.738	42.570	5118	1932	717	102	581	289	0.417	270	3.070	0.489
ME_6	6.0	2.775	42.540	4330	1817	520	92	397	256	0.393	253	3.947	0.628
ME_7	8.0	2.816	42.436	2795	1424	220	57	144	151	0.325	197	5.023	0.799

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

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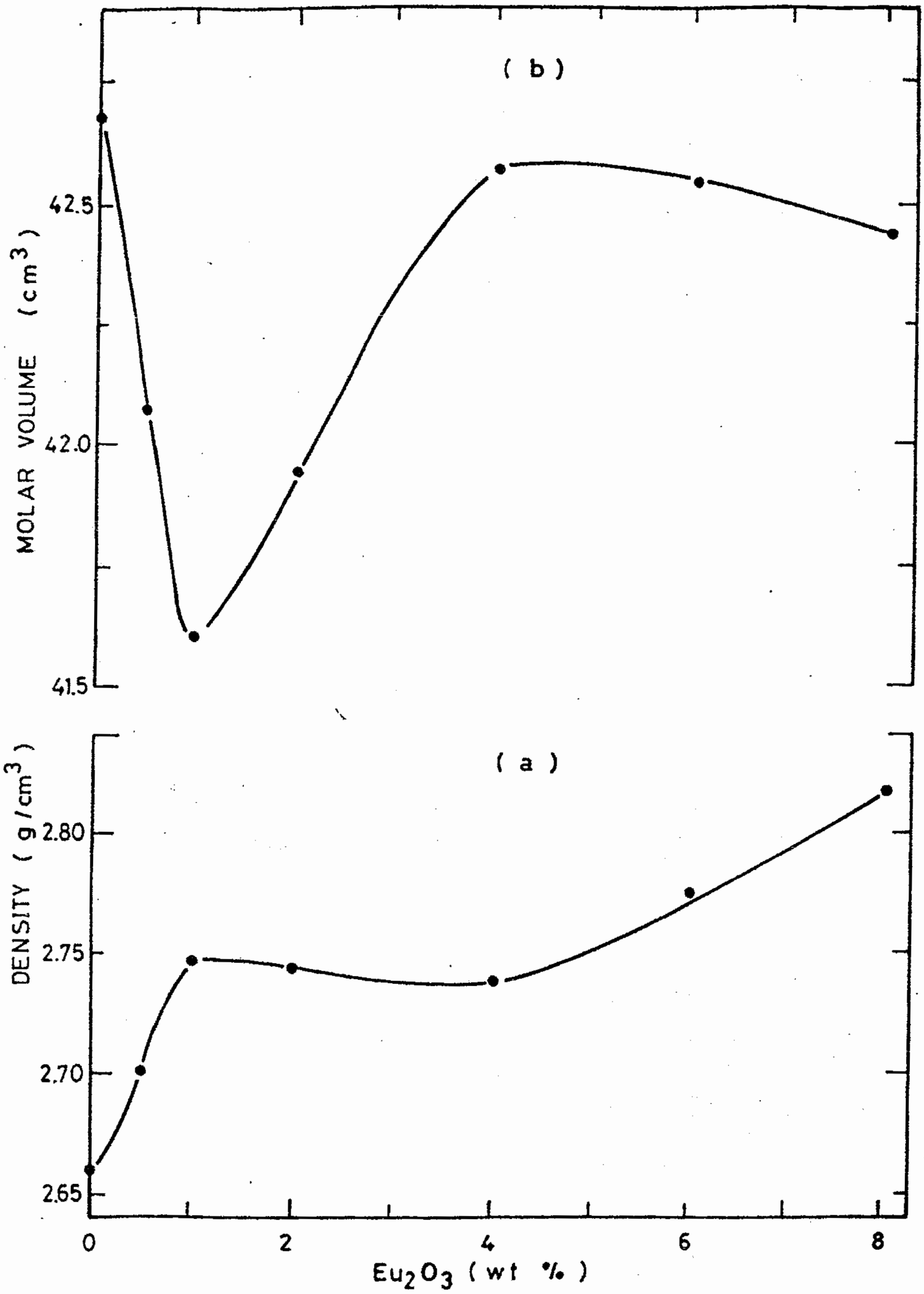

Figure 1 Variation of (a) density and (b) molar volume with Eu$_2$O$_3$/wt %.

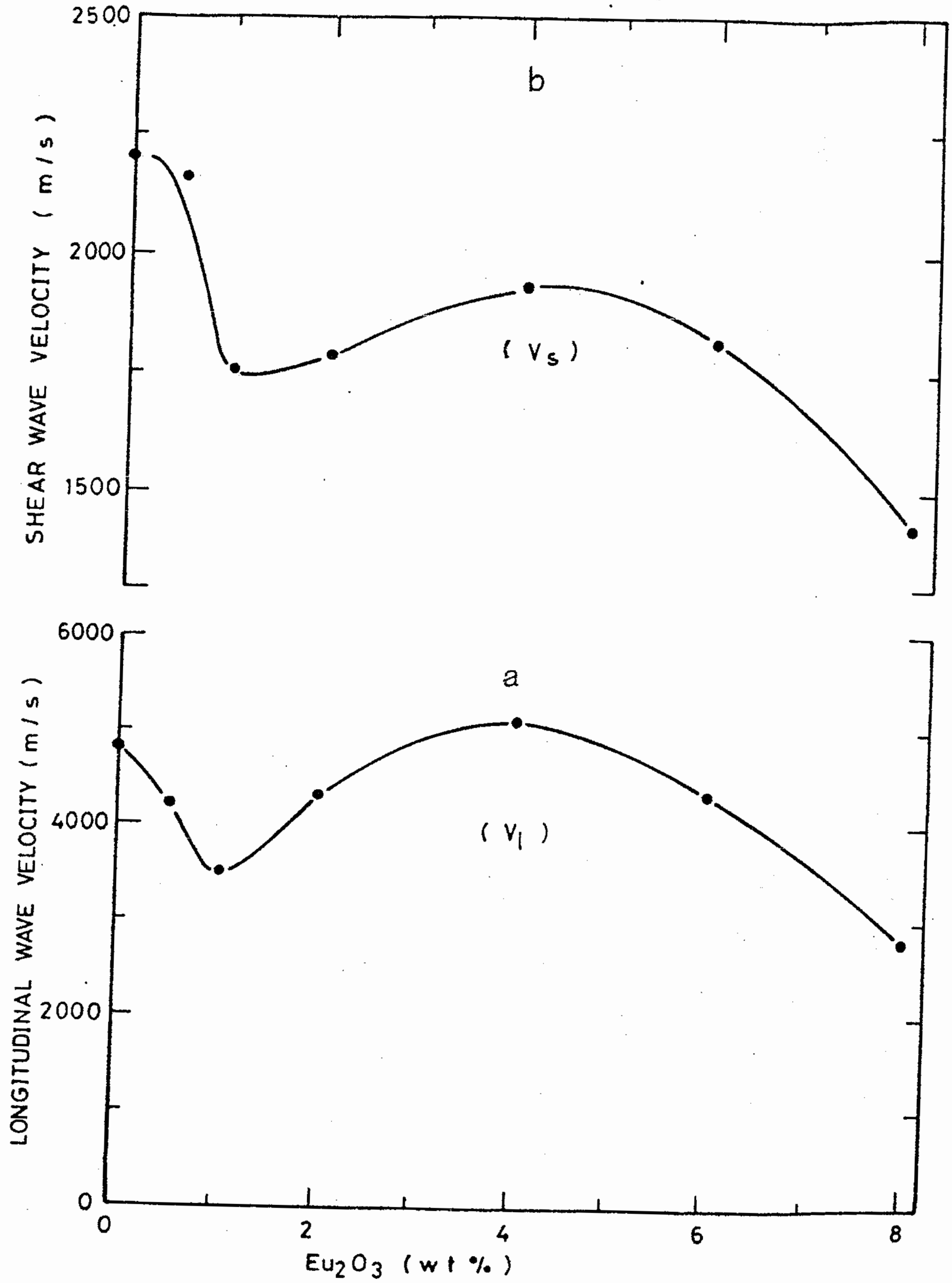

Figure 2 Dependence of (a) longitudinal wave velocity, V_l and (b) shear wave velocity, V_s on the Eu_2O_3 content.

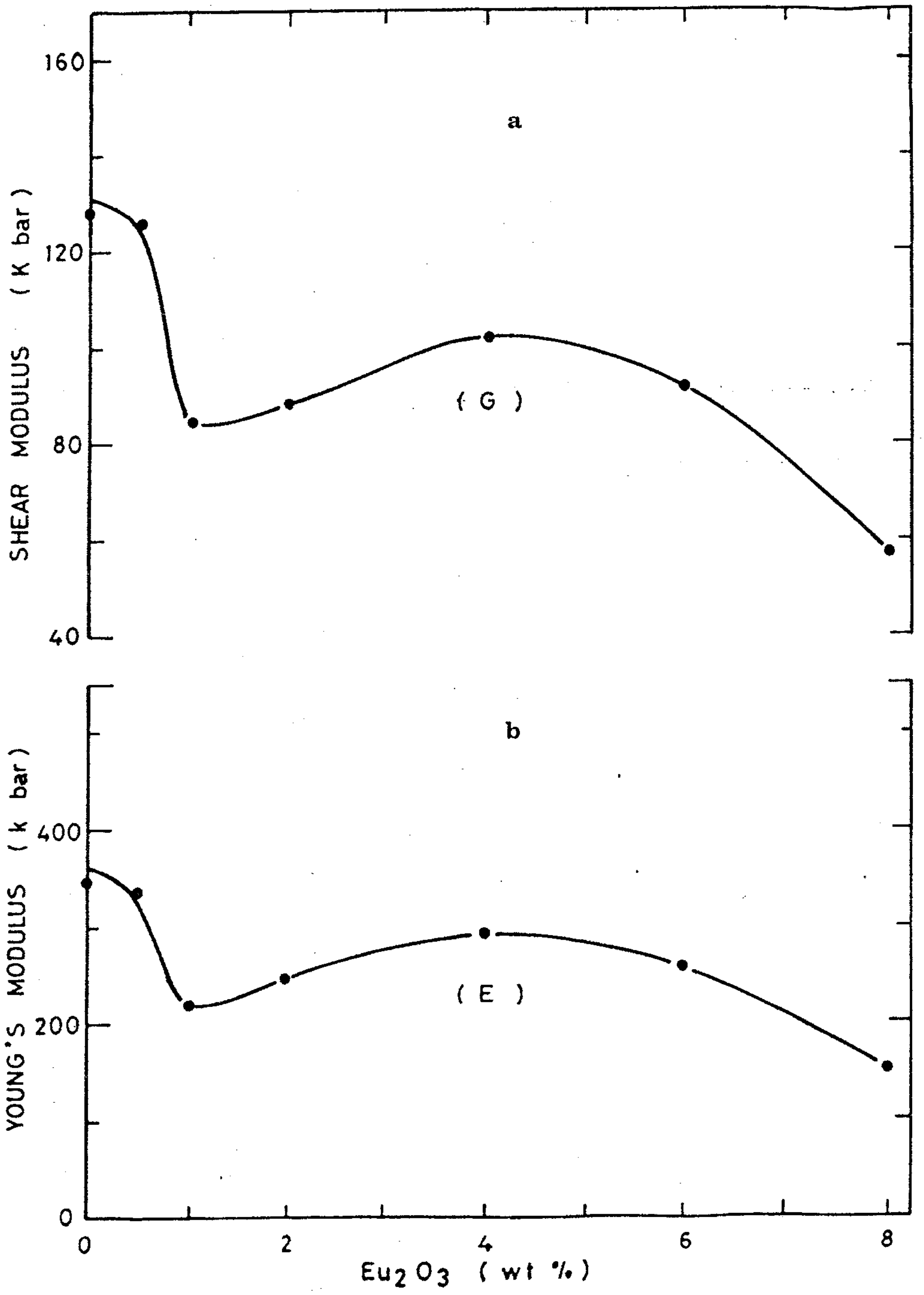

Figure 3 Compositional dependence of (a) shear modulus and(b)Young's modulus for Eu_2O_3-MnO-P_2O_5 glasses.

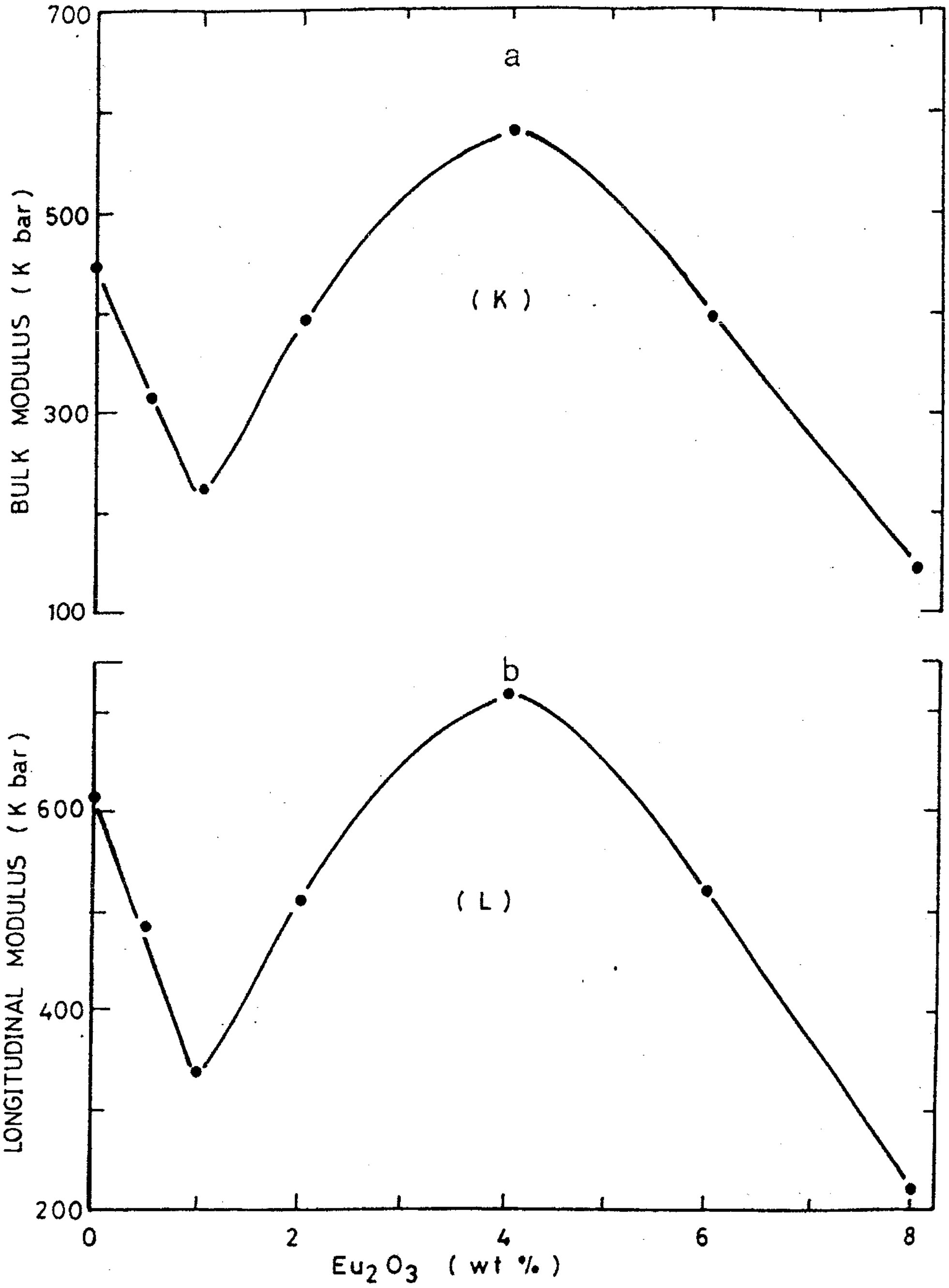

Figure 4 Compositional dependence of (a) bulk modulus, K and (b) longitudinal, L for Eu_2O_3-MnO-P_2O_5 glasses.

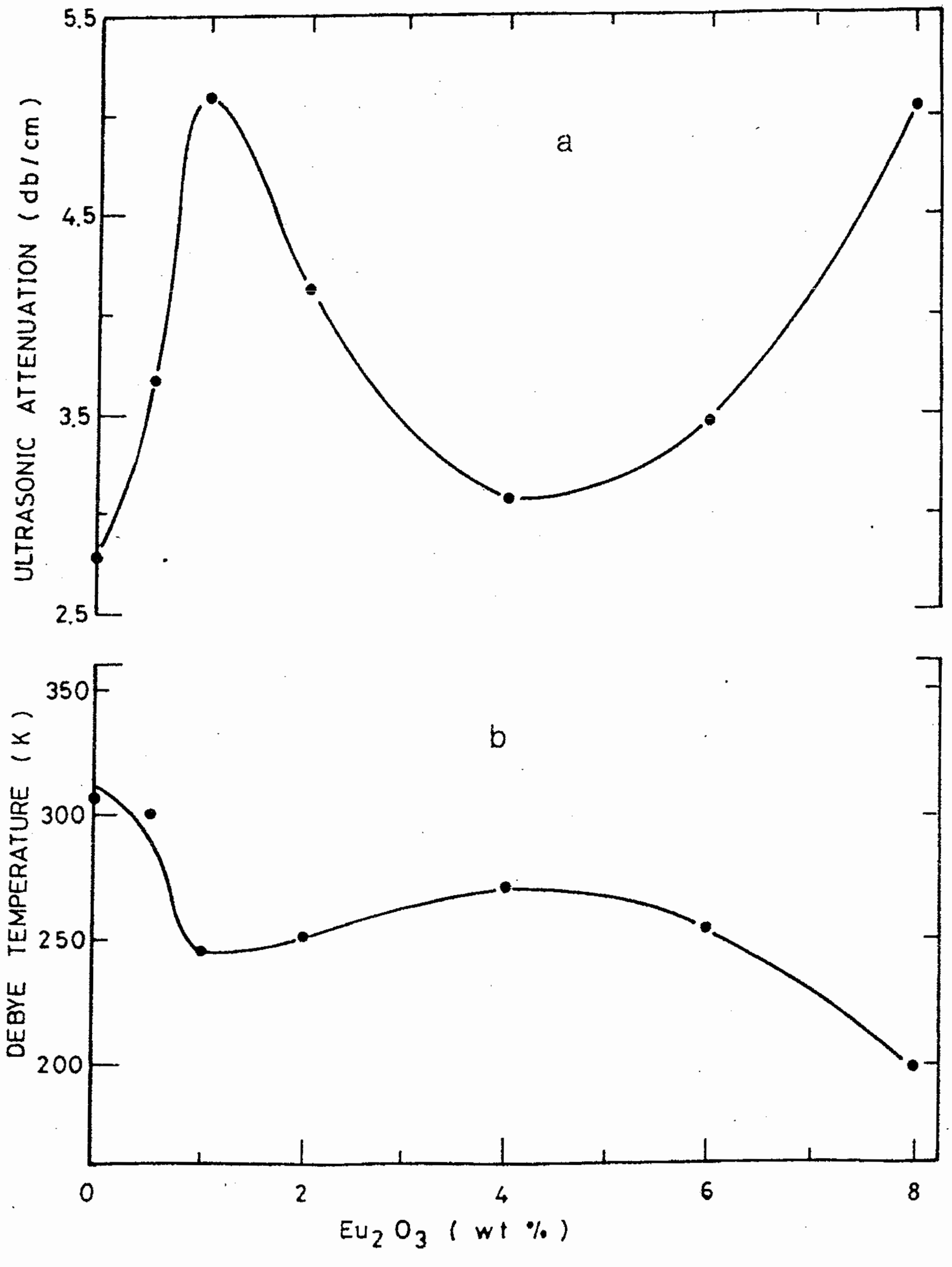

Figure 5 Variation of (a) ultrasonic attenuation, α and (b) Debye temperature with Eu_2O_3 wt%.

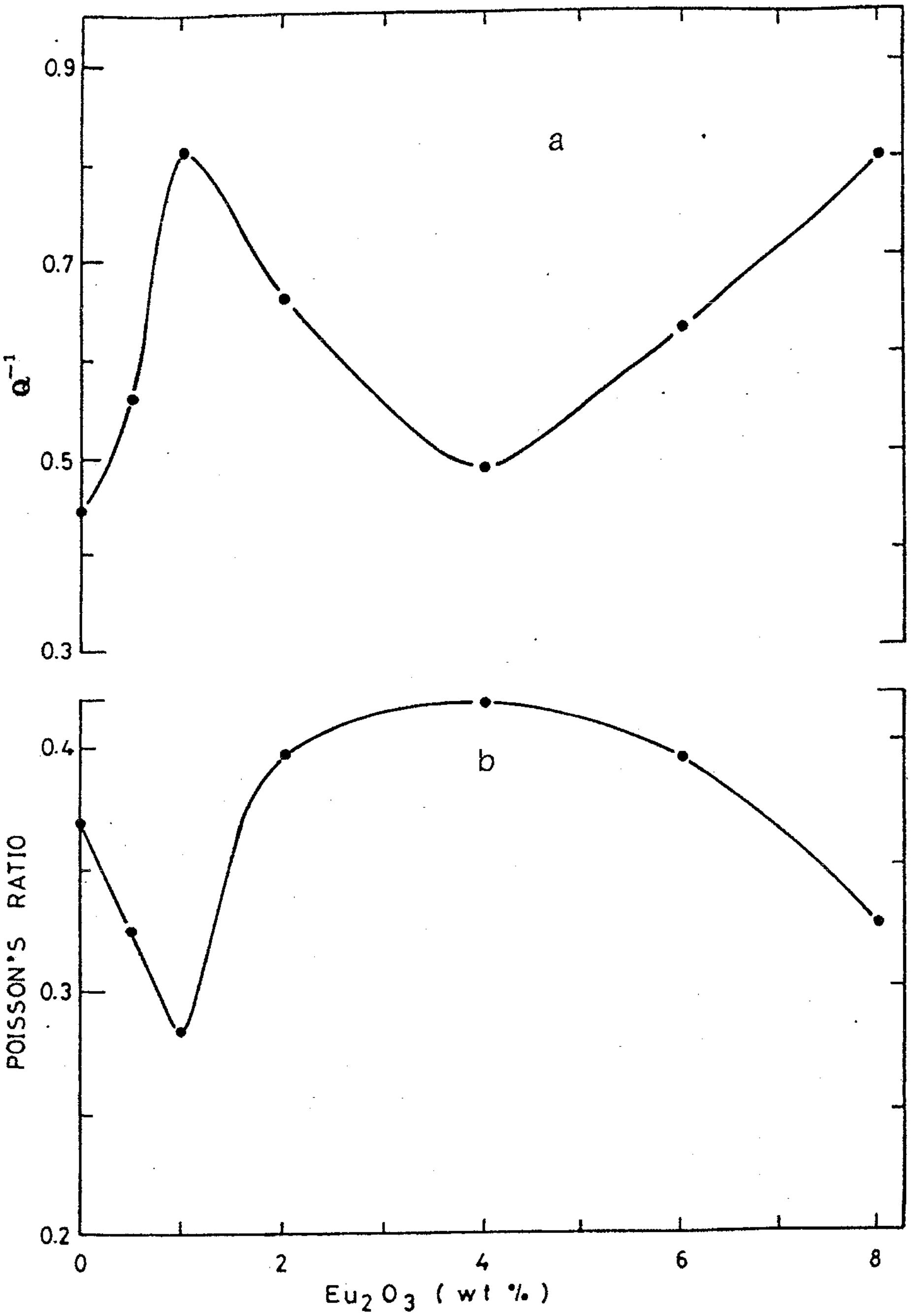

Figure 6 Variation of (a) the internal friction, Q and (b) Poiss-on's ratio with Eu_2O_3 wt%.

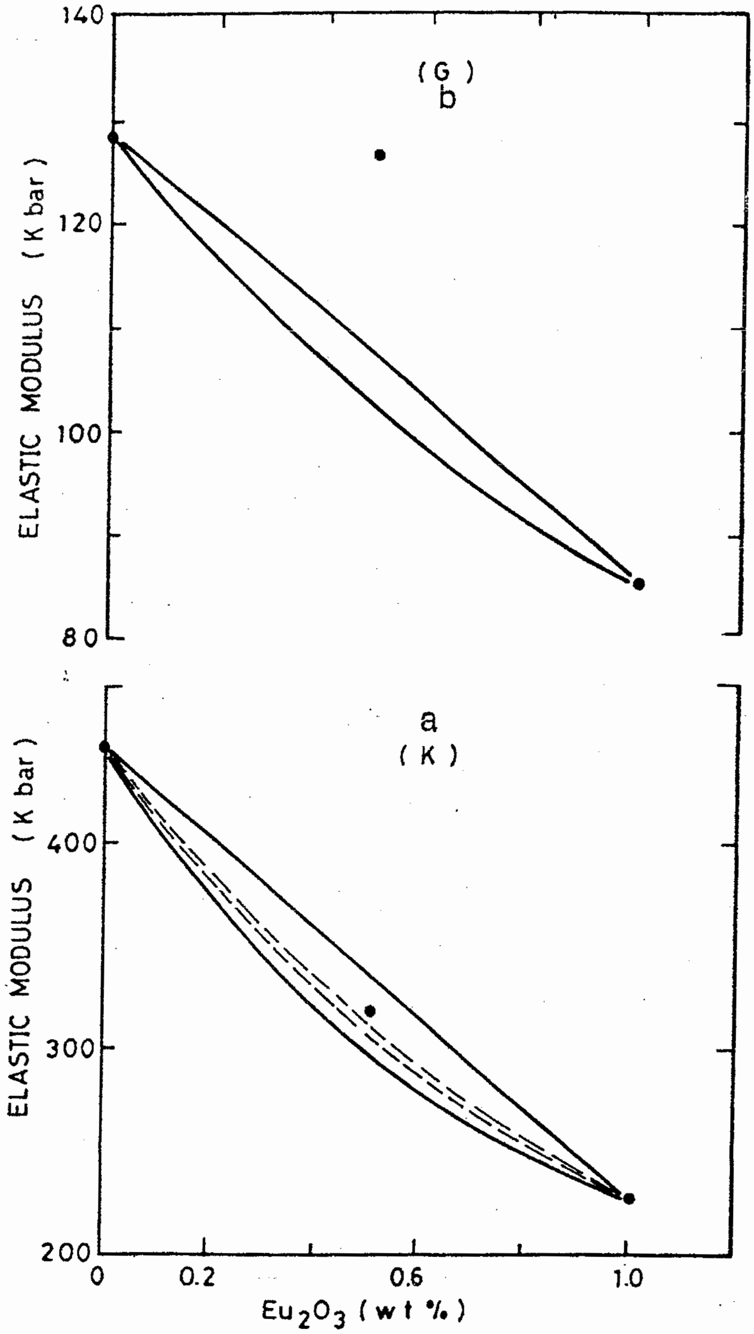

Figure 7 Variation of the observed and predicted (a) bulk modulus and (b) shear modulus with Eu_2O_3 wt% (in the region 0-1 wt%).

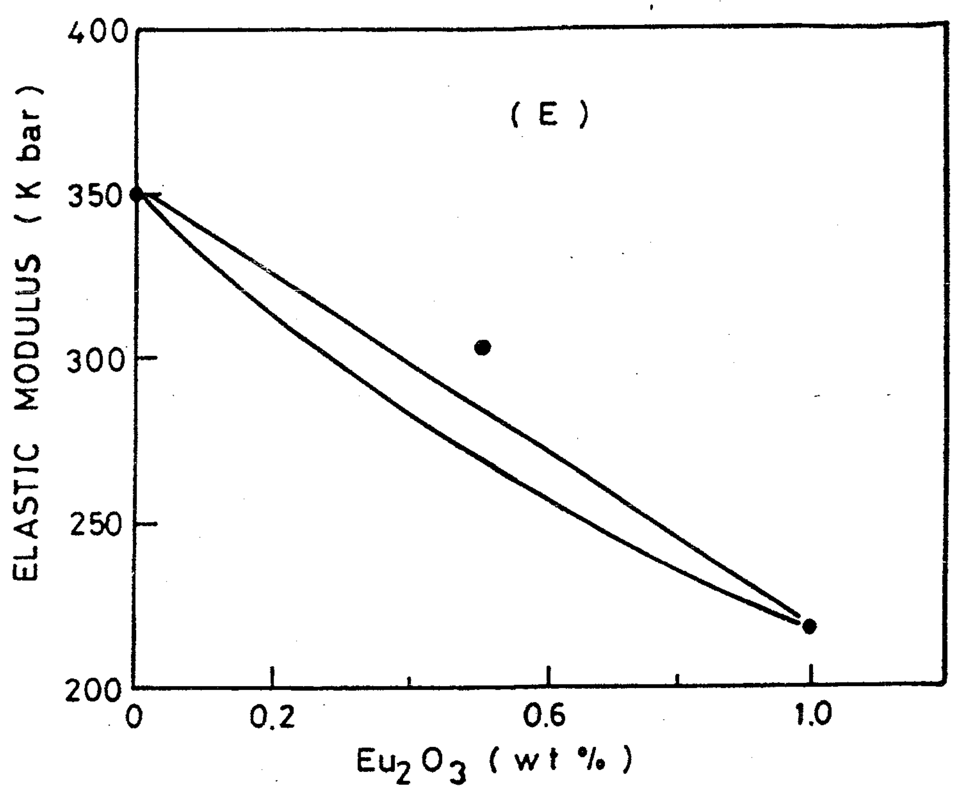

Figure 8 Variation of the observed and predicted Young's modulus with Eu_2O_3 % (in the region 0-1 wt%).

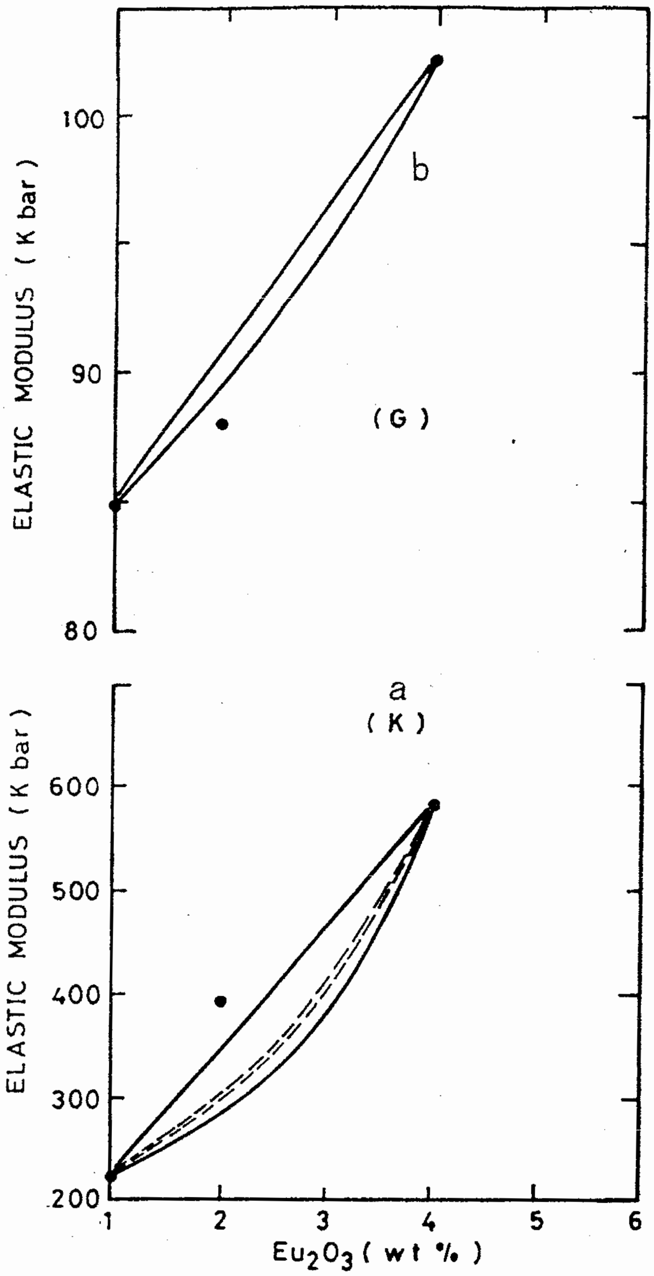

Figure 9 Variation of the observed and predicted (a) bulk modulus and (b) shear modulus with Eu_2O_3 wt% (in the region 1-4 wt%).

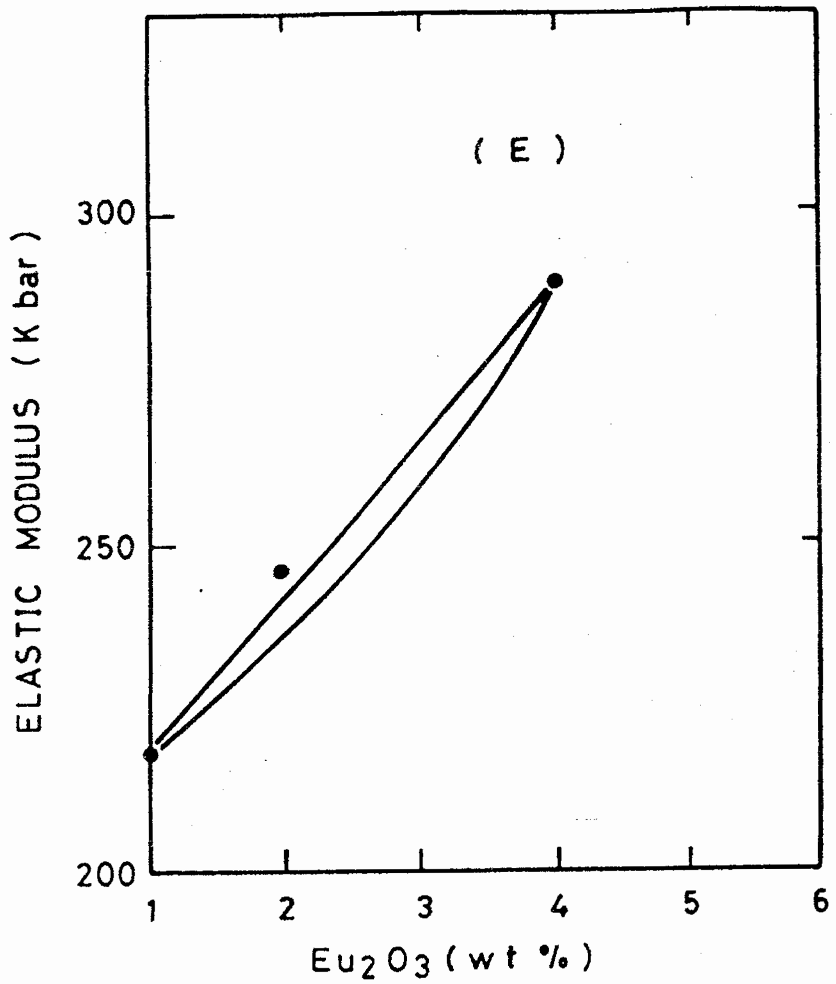

Figure 10 Variation of the observed and predicted Young's modulus with Eu_2O_3 wt% (in the region 1-4 wt%).

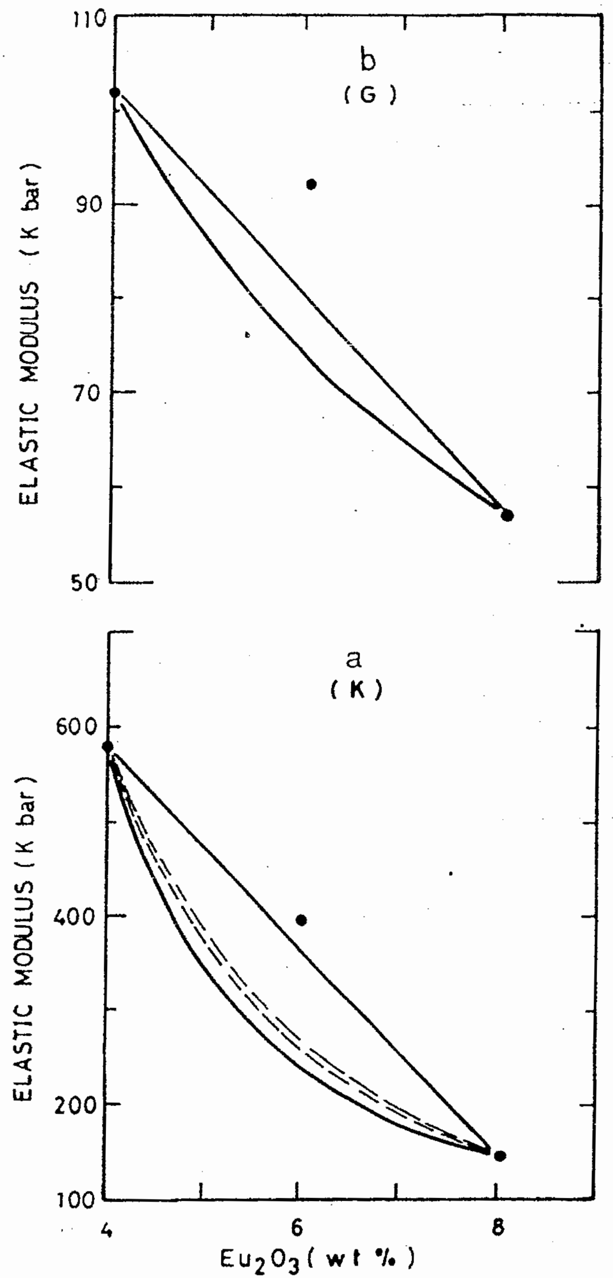

Figure 11 Variation of the observed and predicted (a) bulk modulus and (b) shear modulus with Eu_2O_3 wt% (in the region 4-8 wt%).

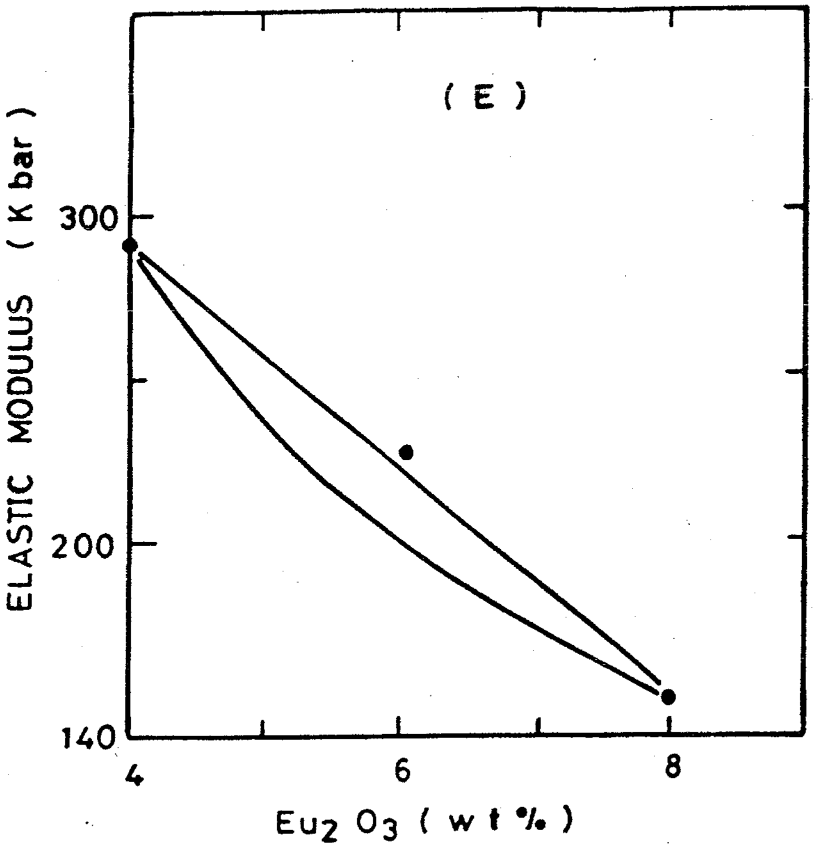

Figure 12 Variation of the observed and predicted Young's modulus with Eu_2O_3 wt% (in the region 4-8 wt%).

انتشار الموجات الفوق صوتية واختبارات الانفصال الطورى في النظام الزجاجي لفوسفات المنجنيز المطعم بأكسيد الأوروبيوم

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الملخص العربي :

في هذا البحث تم دراسة اعتماد معاملات المرونة وتوهين الموجات الفوق صوتية الطولية لسلسلة من عينات زجاج فوسفات المنجنيز المطعم بأكسيد الأوروبيوم بتركيزات مختلفة من ٥و٠٪ الي٨٪) ۰ وقد تم قياس سرعة الموجات الفوق صوتية الطولية والمستعرضة ومعامل التوهين للموجات الطولية وقيست الكثافة الكتليه لجميع العينات قيد البحث ۰ وباستخدام قيم الكثافة والسرعات أمكن حساب معاملات المرونة الطولي والحجمي والقصى ومعامل ينج وكذلك تم حساب حرارة ديباى ونسبةبواسون ۰ وقد أظهرت النتائج أن جميع القيم المقاسة والمحسوبة تتغير مع تغيير تركيزات أكسيد الأوروبيوم مما يدل علي حدوث تغيير في التركيب البنائي للعينات كما لوحظ وجود ثلاث مناطق في المدي التركيزى لأكسيد الأوروبيوم وذلك نتيجة للتغيير في عدد الروابط التساهمية لأيون الأوروبيوم وتكسير الرابطة التساهمية الثنائية لأيون الفوسفور P = O تحويلها الي روابط أحادية P-O-Eu: P-O-P هذا بالاضافة الي تغيير في قوى الربط بين الذرات وتغير في استقطابية الأيونات للعينات قيد البحث ۰

وفي هذه الدراسة تم أيضا تطبيق نموذج فوت وروس وكذلك نموذج هاشين واستريكمان لايجاد الحد الأقصي والأدني لمعاملات المرونه نظريا للعينات الحالية وبمقارنتها بالقيم العملية لنفس العينات وجد أنه لاتوجد أطوار مختلفة في العينة الواحده مما يدل علي التجانس الكامل للعينات المحضرة قيد البحث ۰