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Elastic properties of phosphotungstate glasses

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Elastic properties of potassium and lead phosphotungstate glasses have been investigated using ultrasonic velocity measurements. The composition dependence of elastic moduli in WO_3–K_2O–P_2O_5 glasses suggests that at low alkali oxide concentrations the atomic ring size increases by network modification, which results in the decrease of elastic moduli. In the highly modified regime, due to the presence of coulombic interaction, the rate of decrease of elastic moduli is reduced. In the WO_3–PbO–P_2O_5 glasses the behaviour of elastic moduli suggests that PbO behaves both as a network former and network modifier. The incorporation of PbO into the network is quantitatively determined by the concentration of P_2O_5 in the system. The results are consistent with the structural model proposed earlier, based on characterization studies.

1. Introduction

Transition metal oxides such as MoO_3 and WO_3 form glasses with P_2O_5 over a wide range of compositions [1–4]. In these glasses, transition metal ions have oxygen coordination higher than four and hence they may be considered as non-Zachariesen. We have previously reported glass formation in the ternary system MO_3–RO–P_2O_5 (M = Mo, W; RO = alkali oxides, PbO). These glasses have been characterized in detail and spectroscopic studies of these glasses have been reported earlier [1–3]. We have also investigated elastic properties of MoO_3–RO–P_2O_5 (RO = alkali oxides, PbO) glasses [5, 6]. Based on all these experimental data, a structural model for these glasses has been proposed. According to this model, binary MO_3–P_2O_5 glasses consist of corner-sharing $[MO_{6/2}]$ octahedra and $[POO_{3/2}]$ tetrahedra. The network, therefore, consists of M–O–M, M–O–P and P–O–P linkages, whose energies increase in the same order. Addition of alkali oxides to the system causes degradation of the network through successive breaking of linkages in the order of increasing energy. As a result, structural units such as $[MO_{5/2}O]^-$, $[MO_{4/2}O_2]^{2-}$, $[POO_{2/2}O]^-$ etc., whose connectivities are lower than the progenitors in the unmodified glass, are created in the system [1–3]. The network dimensionality also decreases. An equivalent description of the structure is through the atomic rings which have direct relevance to the elastic properties [5–7]. From the measurement of elastic properties of alkali phosphomolybdate glasses we have inferred that atomic ring reformations occur during modification of the network by alkali oxides. Ring reformation takes place in such a way that in the process the alkali ions achieve their preferred oxygen coordination. However, investigations on MoO_3–PbO–P_2O_5 glasses have shown that PbO acts as a network former and network modifier in different composition regions [2]. It has been suggested that incorporation of lead in the network implies formation of $[PbO_{4/2}]^{2-}$ units in the structure and that the requirements of additional oxygen and charge balance are satisfied by the conversion of $[POO_{3/2}]$ units into $[PO_{4/2}]$ units.

Molybdenum and tungsten compounds possess many similarities due to their chemistry. Therefore, we expect that lead will also be incorporated into the WO_3–PbO–P_2O_5 glass network in a very similar manner and the extent to which PbO is incorporated in the network may again be quantitatively determined by the concentration of P_2O_5 in the system. Because elastic properties exhibit sensitive variation in relation to the structural changes [5–10], we have investigated the phosphotungstate glasses whose structure is altered by K_2O and PbO, using ultrasonic measurements. Our results, which are discussed in this paper, support the structural model proposed earlier for these glasses.

2. Experimental procedure

2.1. Sample preparation and measurement of elastic properties

For this investigation, glasses were prepared with two fixed concentrations of P_2O_5. Glasses with the formula $(80 - x)WO_3$–xRO–$20P_2O_5$ (RO = K_2O, PbO) are referred to as low P_2O_5 glasses (LPG) and glasses with the general formula $(60 - x)WO_3$–xRO–$40P_2O_5$ are referred to as high P_2O_5 glasses (HPG). In both series, WO_3 was progressively replaced by K_2O and PbO in steps of 10 mol %.

Reagent-grade WO_3, K_2CO_3, Pb_3O_4 and $(NH_4)_2HPO_4$ were used as starting materials. Pb_3O_4 was used to give an oxidizing atmosphere which prevented a possible reduction of PbO into metallic lead. (It is well known that Pb_3O_4 decomposes into PbO at

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TABLE I Elastic properties of potassium phosphotungstate glasses

Glass composition (mole fraction)	Density ($g cm^{-3}$)	Molar volume (cm^3)	Sound velocity ($m sec^{-1}$)		Elastic moduli (GPa)				Poisson's ratio	Debye temperature (K)
			v_l	v_s	L	G	K	E		
$80WO_3-20P_2O_5$	5.56	38.52	4188.1	2538.6	97.4	35.8	49.7	86.6	0.21	347.6
$70WO_3-10K_2O-20P_2O_5$	5.07	39.51	3736.7	2242.9	70.7	25.5	36.8	62.1	0.22	302.5
$60WO_3-20K_2O-20P_2O_5$	4.71	39.55	3579.0	2073.0	60.3	20.2	33.4	50.5	0.25	278.3
$50WO_3-30K_2O-20P_2O_5$	4.33	39.86	3467.0	1917.7	52.0	15.9	30.8	40.7	0.28	255.8
$40WO_3-40K_2O-20P_2O_5$	3.93	40.42	3481.2	1885.7	47.6	14.0	29.0	36.1	0.29	248.8
$60WO_3-40P_2O_5$	4.69	41.79	4233.3	2580.5	84.0	31.2	42.4	75.2	0.20	357.9
$50WO_3-10K_2O-40P_2O_5$	4.07	44.71	3794.8	2252.43	58.7	20.7	31.1	50.7	0.23	304.3
$40WO_3-20K_2O-40P_2O_5$	3.70	45.55	3490.0	2008.3	45.0	14.9	25.1	37.4	0.25	268.6
$30WO_3-30K_2O-40P_2O_5$	3.38	45.71	3372.7	1838.4	38.5	12.2	22.2	30.9	0.27	252.4
$20WO_3-40K_2O-40P_2O_5$	3.07	45.90	3360.5	1880.0	34.7	10.8	20.2	27.6	0.27	248.6

673 K.) Appropriately weighed starting materials were thoroughly mixed and kept in a platinum crucible first at 373 K and then 673 K in an electric furnace for several hours for removal of water and ammonia, the decomposition of K_2CO_3 or Pb_3O_4, as the case may be, and for sintering of the charge. The batches were melted between 1173 and 1473 K, depending on the composition, for 30 min in air with periodic stirring to ensure homogeneity. Samples were obtained by quenching the melt into preheated (~ 400 K) brass moulds to avoid shattering of samples due to thermal shock. Later they were annealed just below their respective glass transition temperatures, cut and polished to obtain end faces parallel and flat, suitable for ultrasonic experiments.

Density measurements were performed using the standard pyknometric method using xylene as the displacement liquid. Values reported here were accurate to 0.005 $g cm^{-3}$. Molar volume (V) was calculated from molecular weight and density ($V = M/\varrho$) and mean atomic volume, $V_A = V/q$ where q is the number of atoms in the formula unit.

Ultrasonic velocity measurements were performed at 10 MHz, using quartz X- and Y-cut transducers. Salol (phenyl salicilate) was used as the bonding material. McSkimin's pulse superposition method was employed [11]. A Systems Dimensions (Bangalore, India) ultrasonic pulse echo interferometer was used for this purpose. Different parameters obtained and the relations used are [12]

$$\text{longitudinal modulus } L = \varrho v_l^2 \qquad (1)$$

$$\text{shear modulus } G = \varrho v_s^2 \qquad (2)$$

$$\text{bulk modulus } K = L - (4/3)G \qquad (3)$$

$$\text{Poisson's ratio } \sigma = (L - 2G)/2(L - G) \qquad (4)$$

$$\text{Young's modulus } E = 2(1 + \sigma)G \qquad (5)$$

$$\text{Debye temperature } \theta_D = (h/k)[(3N_0/4)(q/M)]^{1/3} v_m \qquad (6)$$

where ϱ is the density, v_l and v_s are the longitudinal and shear sound velocities, respectively. ($M/q\varrho$) is the mean atomic volume. The mean sound velocity, v_m, is defined by the relation

$$3/v_m^3 = [1/v_l^3 + 2/v_s^3] \qquad (7)$$

3. Results and discussion

The measured elastic properties of potassium and lead phosphotungstate glasses are listed in Tables I and II, respectively.

3.1. Density and molar volume

Composition dependence of density, molar volume and mean atomic volume for potassium and lead phosphotungstate glasses are presented in Figs 1 and 2, respectively. In alkali oxide-substituted glasses, density decreases with the concentration of K_2O, both in LPG and HPG. Molar volume is almost constant in LPG but shows a slowly increasing trend in HPG. Mean atomic volume increases with the concentration of K_2O both in LPG and HPG. In PbO-substituted LPG, density increases and molar volume decreases with the concentration of PbO, but in HPG the

TABLE II Elastic properties of lead phosphotungstate glasses

Glass composition (mole fraction)	Density ($g cm^{-3}$)	Molar volume (cm^3)	Sound velocity ($m sec^{-1}$)		Elastic moduli (GPa)				Poisson's ratio	Debye temperature (K)
			v_l	v_s	L	G	K	E		
$70WO_3-10PbO-20P_2O_5$	5.67	37.59	3880.2	2300.5	85.3	30.0	45.3	75.1	0.23	313.5
$60WO_3-20PbO-20P_2O_5$	5.90	35.98	3647.5	2119.5	78.4	26.4	43.1	66.2	0.25	289.1
$50WO_3-30PbO-20P_2O_5$	6.19	34.11	3482.3	1970.9	75.1	24.1	43.0	60.6	0.26	269.8
$40WO_3-40PbO-20P_2O_5$	6.40	32.87	3321.3	1790.0	70.6	20.5	43.3	53.1	0.295	253.2
$30WO_3-50PbO-20P_2O_5$	6.754	31.02	3196.4	1657.3	69.0	18.6	44.3	48.8	0.32	227.6
$50WO_3-10PbO-40P_2O_5$	4.62	42.26	3842.0	2288.0	68.1	24.2	35.9	59.4	0.23	312.8
$40WO_3-20PbO-40P_2O_5$	4.71	41.24	3612.0	2124.1	61.4	21.2	33.1	52.7	0.24	289.1
$30WO_3-30PbO-40P_2O_5$	4.84	39.88	3426.6	1980.8	61.4	21.2	31.6	47.5	0.24	289.1
$20WO_3-40PbO-40P_2O_5$	5.02	38.31	3280.8	1863.5	54.1	17.4	30.8	44.0	0.26	253.3
$60PbO-40P_2O_5$	5.43	35.12	3117.1	1648.1	52.7	14.8	33.1	38.5	0.31	224.6

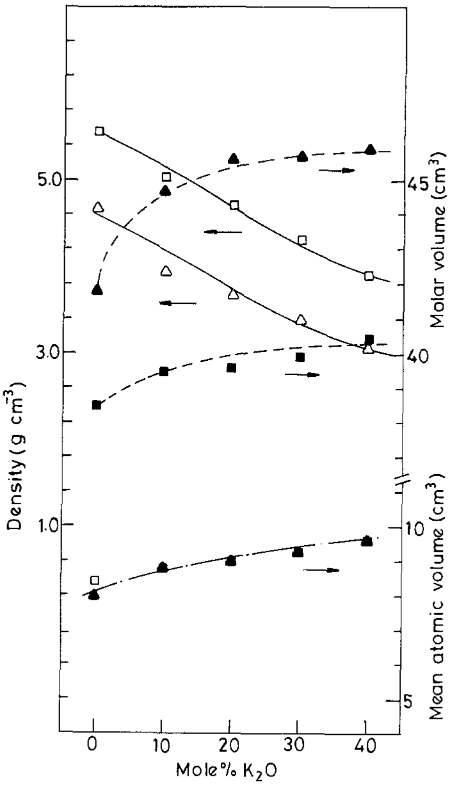


Figure 1 Composition dependence of density, molar volume and mean atomic volume in WO_3-K_2O-P_2O_5 glasses. (■, □) LPG [(80 − x)WO_3-xK_2O-$20P_2O_5$ glasses], (▲, △) HPG [(60 − x)WO_3-xK_2O-$40P_2O_5$ glasses].

density plot suggests a decrease and a corresponding increase in molar volume at low concentrations of PbO. In PbO-substituted LPG, mean atomic volumes remain almost constant while in HPG it remains constant after an initial increase.

The structural units formed in LPG on modification by K_2O ($[WO_{5/2}O]^-$, $[WO_{4/2}O_2]^{2-}$, etc.) do not add significantly to molar volume. In HPG, formation of more $[PO O_{2/2}O]^-$ units which are two-connected, having higher specific volume, contributes to the increase in molar volume [3]. In PbO-substituted LPG at low concentrations of PbO, $[WO_{6/2}]$ units are replaced by $[PbO_{4/2}]^{2-}$ units, when lead acts as a network former. When lead acts as a network modifier, it remains as Pb^{2+} which has high field strength (greater than even Li^+). This causes increase in packing density and decrease in molar volume. The behaviour of molar volumes of HPG to which PbO is added is similar, but there is a slightly anomalous variation around 10 mol % PbO, the origin of which is unclear to us.

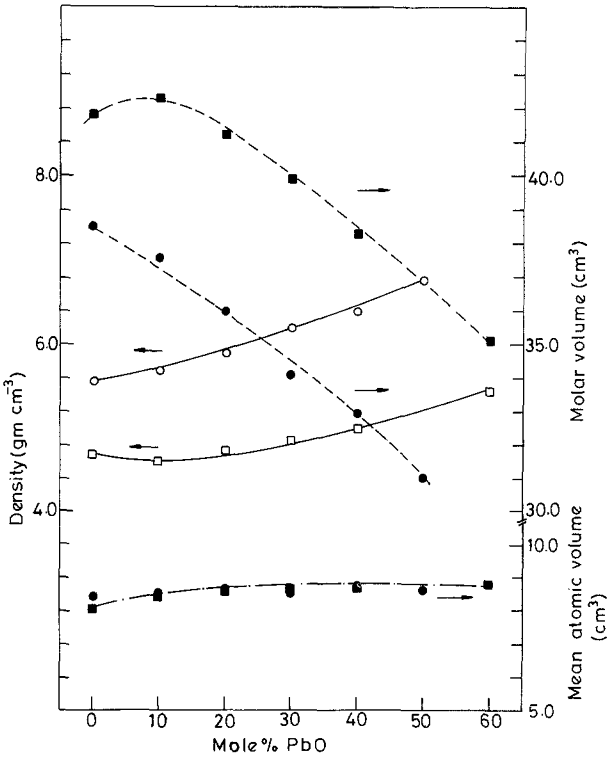


Figure 2 Composition dependence of density, molar volume and mean atomic volume, in WO_3-PbO-P_2O_5 glasses. (●, ○) LPG, (■, □) HPG.

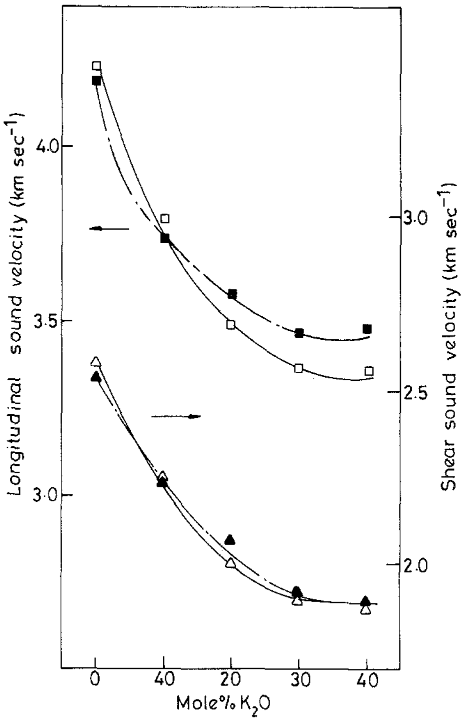


Figure 3 Composition dependence of sound velocities in WO_3-K_2O-P_2O_5 glasses. (■, ▲) LPG, (□, △) HPG.

3.2. Sound velocities

The composition dependence of longitudinal and shear sound velocities are shown in Figs 3 and 4. Sound velocities decrease with increasing concentration of K_2O and PbO. In alkali-substituted glasses, both in LPG and HPG, velocities tend to level off, while no such trend is observed in PbO-substituted glasses.

3.3. Elastic moduli

Variation of Young's (E), shear (G) and bulk (K) moduli with composition in K_2O-substituted glasses is shown in Fig. 5. Variation of Young's and shear moduli with composition for PbO-substituted glasses is shown in Fig. 6 and that of bulk modulus is shown in Fig. 7, in which the variation of Poisson's ratio (σ) with composition is also shown.

In K_2O substituted glasses, all elastic moduli decrease and tend to level off at high alkali oxide concentrations. The effect of K_2O substitution for WO_3 is more severe in E than in other moduli and

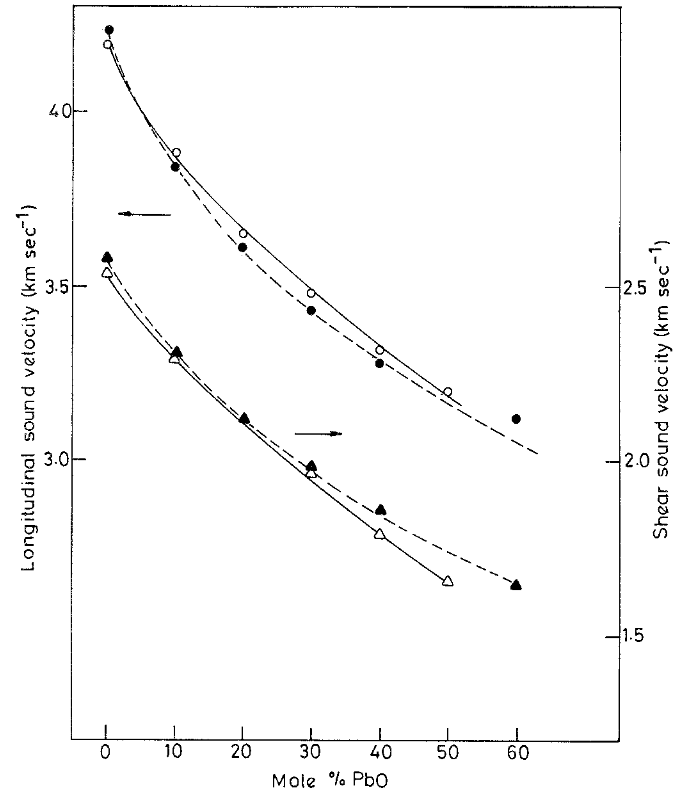


Figure 4 Composition dependence of sound velocities in WO_3-PbO-P_2O_5 glasses. (○, △) LPG, (●, ▲) HPG.

particularly, in the initial stages. A general decrease of the moduli is expected for at least two reasons. Firstly, the overall specific energy, which is directly related to the moduli, decreases when WO_3 is replaced by K_2O. Secondly progressive modification of $[WO_{6/2}]$ units to $[WO_{5/2}O]^-$ and $[WO_{4/2}O_2]^{2-}$ units decrease the overall connectivity in the glass structure. Towards the high alkali end the rate at which the moduli decrease also decreases, in spite of the continued modification, because the now severely modified structure is dominated by coulombic interactions and is characterized by somewhat more efficient packing as corroborated by the diminished rate at which molar volumes increase in this region. However, more importantly, modification by K_2O alters the atomic ring structure quite drastically. As we have noted elsewhere [5], in the case of phosphomolybdate glasses the modification

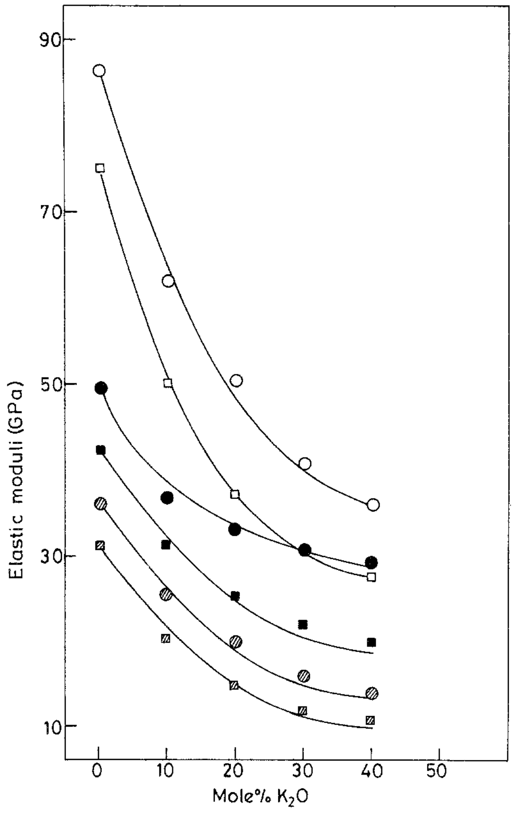


Figure 5 Composition dependence of Young's (*E*), bulk (*K*) and shear (*G*) moduli in WO_3-K_2O-P_2O_5 glasses: (○) *E* (LPG); (□) *E* (HPG); (●) *K* (LPG); (■) *K* (HPG); (⊘) *G* (LPG); (▨) *G* (HPG).

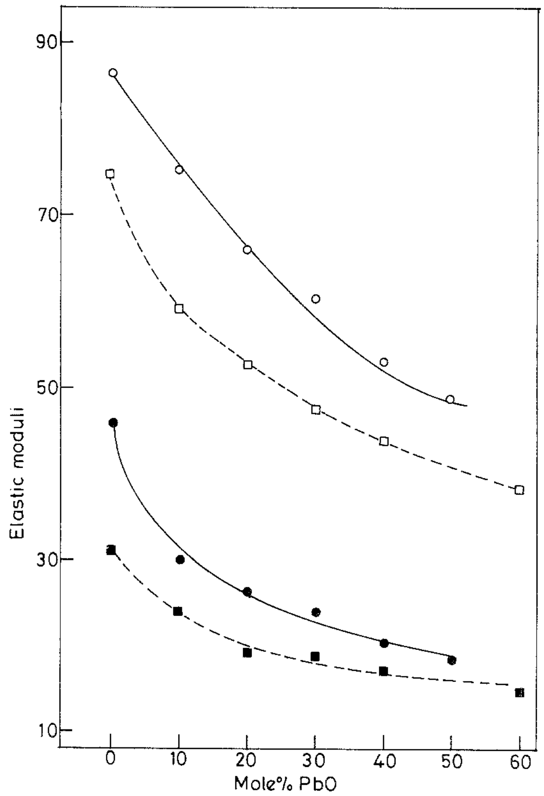


Figure 6 Composition dependence of Young's (*E*) and shear (*G*) moduli in WO_3-PbO-P_2O_5 glasses: (○) *E* (LPG); (□) *E* (HPG); (●) *G* (LPG); (■) *G* (HPG).

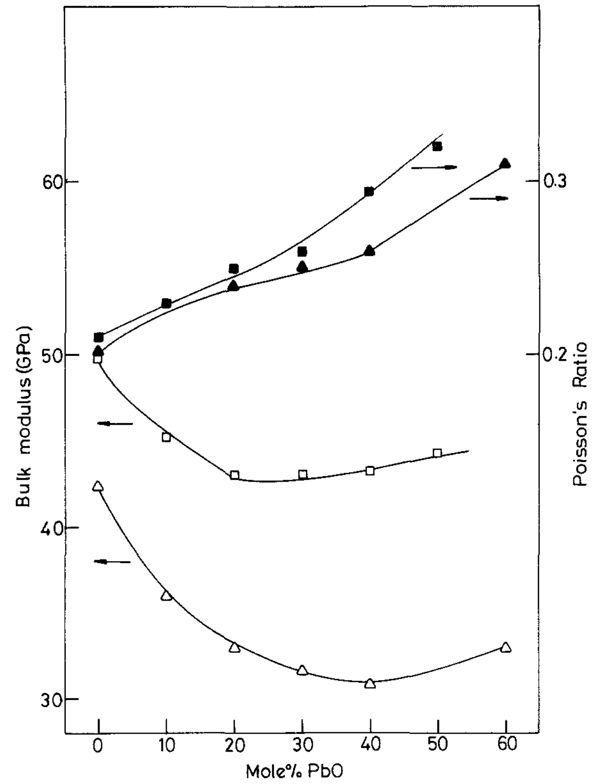


Figure 7 Composition dependence of bulk modulus (K) and Poisson's ratio (σ) in WO_3-PbO-P_2O_5 glasses. (■, □) LPG, (▲, △) HPG.

by K_2O may be represented schematically as in Fig. 8a.

The initial stages of modification involve formation of rather large rings. These have little effect on the three-dimensional nature of connectivities. Thus the most sensitive modulus will be the Young's modulus which exhibits the largest response. At the higher K_2O end the modification involves breaking of W–O–P and P–O–P linkages. Because phosphorus is only two-connected with 120° O–P–O angles, it easily regenerates the smaller rings (reformation of rings) and thus ameliorates the decrease in modulus. This is also intuitively evident because, unless there was reformation of smaller rings the decreased dimensionality due to the transformation of $[POO_{3/2}]$ to $[POO_{2/2}O]^-$ would have been manifested by more severe reduction in modulus at the K_2O-rich end. The reformation can be schematically represented in the form shown in Fig. 8b.

The tendency to form smaller rings where P–O–P linkages are involved may be attributed to the generic effect of P_2O_5 which tends to have smaller ring molecular P_4O_{10} structures. Although the moduli are uniformly lower for HPGs, this tendency for smaller ring formation is manifested in its lower-than-LPG values of the Poisson's ratio shown Fig. 9. The cross-over in the initial stages of modification in values of LPG and HPG appears to be merely due to the relative effects of large ring formation in the initial stages of modification.

The behaviour of the moduli of glasses where WO_3 has been substituted by PbO is even more interesting. The variations of E and G are shown in Fig. 6, which are quite similar to the variation of corresponding moduli of potassium phosphotungstate glasses. They decrease with increasing concentration of PbO and generally tend to a lower rate of variation in the high-PbO regions. The variation of bulk moduli and Poisson's ratio (σ) shown in Fig. 7 is significant. While K decreases with PbO content up to ~20 mol % PbO in LPG and ~40 mol % PbO in HPG, they begin to increase beyond these concentrations, exhibiting a clearly different trend. This behaviour of bulk modulus very clearly demonstrates the structural role of lead is different in these two regions. Further, the concentration of PbO at which this change in trend occurs is quantitatively related to the concentration of P_2O_5 in the glass. In related investigations of phosphomolybdate glasses using several of the physical measurements including electron spin resonance, we

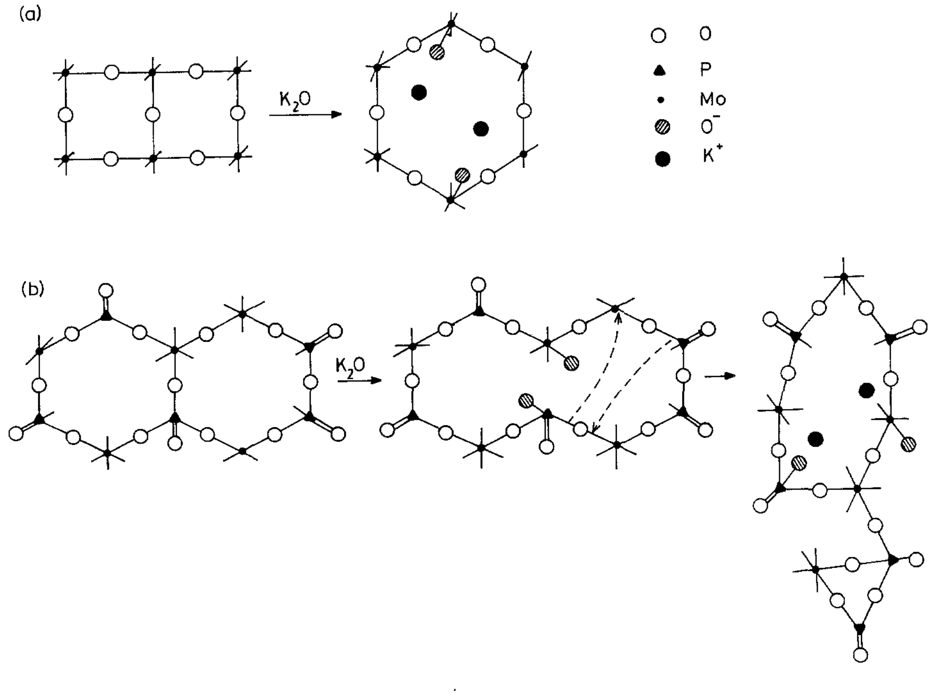


Figure 8 Schematic representation of possible atomic ring reformations in phosphotungstate glasses in the presence of (a) K_2O in the low alkali oxide regime where larger rings are formed, (b) K_2O in the high alkali oxide regime where reformation of smaller rings takes place.

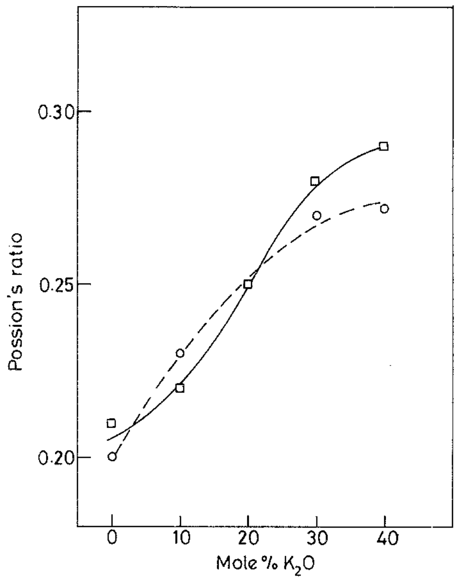


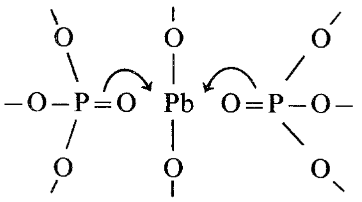
Figure 9 Composition dependence of Poisson's ratio in WO_3–K_2O–P_2O_5 glasses: (□) LPG, (○) HPG.

have shown that lead acts as network former until the additional covalently bonded oxygen coordination requirements of lead are met by the conversion of $[POO_{3/2}]$ units into $[PO_{4/2}]^+$ units [2, 13]. The incorporation of lead into the phosphotungstate network may be represented as follows

$$P_2O_5 \equiv 2[POO_{3/2}] \tag{8}$$

$$PbO \equiv [PbO_{2/2}] \tag{9}$$

$$[PbO_{2/2}] + 2[POO_{3/2}] \leftrightharpoons [PbO_{4/2}]^{2-} + 2[PO_{4/2}]^+$$



$$\leftrightharpoons [PbO_{4/2}]^{2-} + 2[PO_{4/2}]^+ \tag{11}$$

Equation 11 clearly implies the extent of PbO incorporated into the glass network should be 20 and 40 mol %, respectively, in LPG and HPG. Above these concentrations, the excess PbO should be expected to act as a network modifier like an alkali oxide. Because the ionic potential of Pb^{2+} (2/1.2 in e/r units) is higher than even that of Li^+ (1/0.67 in e/r units), in the regions where PbO acts as a modifier, increase of bulk modulus (K) should be expected [14, 15] as in the case of Li_2O-modified phosphomolybdates [5]. The decrease in bulk modulus in the composition region where PbO acts as a network former is to be expected because somewhat stronger six-connected, three-dimensional $[WO_{6/2}]$ units are being substituted by much weaker four-connected three-dimensional $[PbO_{4/2}]^{2-}$ units. Thus, in spite of increasing the dimensionality of the network through the conversion of $[POO_{3/2}]$ into $[PO_{4/2}]^+$ units, the bulk moduli decrease.

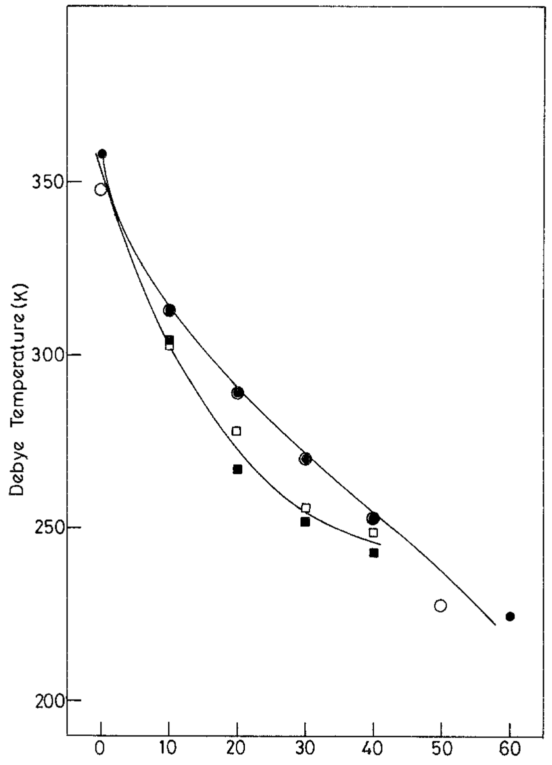


Figure 10 Composition dependence of Debye temperature (θ_D) in phosphotungstate glasses: (□) $(80 - x)WO_3$–xK_2O–$20P_2O_5$; (■) $(60 - x)WO_3$–xK_2O–$40P_2O_5$; (○) $(80 - x)WO_3$–$xPbO$–$20P_2O_5$ and (●) $(60 - x)WO_3$–$xPbO$–$40P_2O_5$.

That the moduli G and E do not as sensitively respond to the structural role of lead as seen in Fig. 6 should be attributed to the reasons given earlier in the case of K_2O-modified glasses. While G and E decrease for the same reason as K in the network-forming region of PbO, namely, due to the general weakening of the network. They continue to decrease in the PbO-modified region, though less significantly, due to the creation of highly modified $[WO_{4/2}O_2]^{2-}$ and $[PO_{4/2}O_2]^-$ units which lower the dimensionality of the network. We may add parenthetically that bulk modulus is responsive to the isotropic compression while E and G are not, and their sensitivity can be quite different during structural variations.

3.4. Poisson's ratio

The variation of Poisson's ratio with composition presented in Fig. 7 also bears out the structural role of lead. Poisson's ratio increases with the concentration of PbO, both in LPG and HPG. The composition region where lead acts as modifier, is evident from the apparent increase in the slope in the composition dependence of Poisson's ratio.

3.5. Debye temperature

The Debye temperatures calculated from the sound velocities for both potassium and lead phosphotungstate glasses are shown in Fig. 10. The highest Debye temperatures are registered by pure phosphotungstates. Because the binary $60WO_3$–$40P_2O_5$ glass has a larger concentration of higher energy W–O–P linkages than in $80WO_3$–$20P_2O_5$ glass, the former has higher θ_D value. Substitution of WO_3 by either PbO or K_2O results in a monotonic decrease in the total vibrational energy of the system because any of the conceivable vibrational units resulting from the substitution will be of lower energy. It may also be noted from the figure that in the ternary compositions Debye temperature is insensitive to the concentration of P_2O_5, particularly the PbO-containing glasses.

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