

Investigations of Glasses in the System PbO–PbF₂

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Glass formation in the system PbO–PbF₂ has been investigated. The structure of these glasses has been studied using X-ray diffraction. Densities, heat capacities, glass-transition and crystallization temperatures and Vicker's microhardnesses have been measured. D.c. conductivities of these glasses have also been measured as a function of temperature. A structural model has been developed which suggests the existence of [PbO₂F₄]-type units over the entire composition range. It is suggested that covalent linkages of the type —O—Pb—O— play a crucial role in determining the composition limits to glass formation. The structural model has been shown to be consistent with other physical properties of the glasses.

Lead oxide is not a glass-forming oxide by itself, but it can be incorporated¹ in substantial quantities into other glass-forming oxide systems such as silicates, borates and phosphates. Lead fluoride has also been used as a constituent of some glass-forming binary and ternary fluoride systems.^{2,3} However, there has been no report to our knowledge of any study of glasses made from the binary system PbO–PbF₂. We have previously reported⁴ glass formation in the similar system PbO–PbCl₂. Recently fluoride ions have been reported to participate in network formation in silicate glasses,⁵ while it is known that fluoride ions act as bridges in BeF₂ glasses.⁶ Hence we suspect that glass formation in the PbO–PbF₂ system may be even more extensive than in the PbO–PbCl₂ system. The phase diagram⁷ for the PbO–PbF₂ system is very simple, with a single eutectic at 54 mol % lead oxide; the eutectic temperature is 767 K. There is no indication of compound formation in the entire binary phase field.⁸ Glass formation may therefore be expected to be easier in this system because of the absence of any tendency towards crystallization. From the chemical point of view also glass formation in the PbO–PbF₂ system should be interesting because PbO is known to be highly covalent whereas PbF₂ is typically ionic. In pure (both yellow and red) PbO lead atoms are bonded to four oxygen atoms, giving rise to a puckered layer structure⁹ with large van der Waals (Pb–Pb) interactions. In yellow PbO it has been suggested that an overlap of empty and filled *sp³d²* hybridized orbitals from neighbouring lead atoms also occurs. PbF₂, on the other hand, has a structure⁹ in which lead ions are coordinated to nine fluoride ions at typically ionic distances. Thus the glasses formed in this system may be expected to be characterized by a continuous decrease in covalent linkages as the PbF₂ content increases unless two chemically distinct types of lead atoms are present. For glass compositions rich in lead fluoride, which may be suspected to be quite ionic, the similarity in the sizes of the O²⁻ and F⁻ ions may be expected to become a contributing factor in increasing the configurational entropy and hence the glass-forming tendency. It is also possible that the structural roles of the fluoride and oxygen ions in such glass compositions become very similar. A study of glass formation in this system should therefore be very interesting.

In this paper we report and discuss various characterization studies of PbO–PbF₂ glasses, *i.e.* glass formation, molar volume, microhardness, glass-transition and crystallization temperatures, temperature variation of the d.c. conductivity and heat capacity for various compositions. We have also performed a structural characterization of these glasses by X-ray diffraction using Cu K_α radiation. We have developed a structural model which is very similar to that of PbO–PbCl₂ glasses and which is consistent with the physical properties of glasses discussed in this study.

EXPERIMENTAL

PREPARATION

The starting materials used in the preparation of the glasses were Pb₃O₄ (A.R.) and PbF₂ (A.R.). It was first confirmed that the Pb₃O₄ decomposes to yellow PbO completely at *ca.* 840 K. Appropriately weighed quantities of Pb₃O₄ and PbF₂ were mixed thoroughly and melted in short quartz tubes using an oxyacetylene flame till a uniformly clear melt was obtained. The melt was kept at this temperature (*ca.* 900–1000 K) for a short time (2–3 min), poured on to a polished steel plate and pressed quickly with a polished steel block. Small drops of the melt were also found to quench easily into shiny, slightly yellow transparent beads which were used for density measurements. There was no noticeable reaction of the melt with the walls of the quartz tube. However, the infrared spectra of these glasses show a peak at *ca.* 860 cm⁻¹ which may be attributed to Si—O stretching as in PbO·*x*SiO₂ glasses¹⁰ where *x* is very low. We have measured the weight loss of the quartz tube used for the preparation. It is estimated that, in deliberately prolonged heating of the melt at *ca.* 1000 K, a maximum of *ca.* 4 mol% SiO₂ is incorporated into the resulting glass. Our attempts to obtain these glasses by melting the batch in a platinum crucible were not successful as the melt was almost always partially reduced to metallic lead upon heating. We have listed the nominal compositions of these glasses in terms of PbO and PbF₂ and have ignored the SiO₂ content, which is treated here as an unavoidable impurity.

DENSITIES AND MICROHARDNESSES

Densities were determined by pycnometry with xylene as filling liquid. Glass beads free of any detectable bubbles were used for density determination. Microhardnesses were determined by Vicker's method, employing a Carl Zeiss (Jena) m.h.p. 160 microhardness tester. A uniform load of 100 g was applied to make indentations on *ca.* 1 mm thick flat discs of glass. The results reported here are averages of measurements made with 4 or 5 distinct symmetrical indentations for each glass composition.

X-RAY DIFFRACTION

A standard Philips diffractometer equipped with a goniometer of the type PW1373 was used for recording X-ray intensities. The scanning rate was 0.5° min⁻¹ and the intensities were recorded in the range 10 ≤ 2θ/° ≤ 120 with Cu K_α radiation using an Ni filter. Details of the procedure adopted for data treatment have been reported in our earlier paper.¹¹ The pair distribution functions were calculated using the following formula:

$$2\pi^2 r \rho^e(r) \sum_{\text{u.c.}} Z_j = 2\pi^2 r \rho_0^e \sum_{\text{u.c.}} Z_j + \int_0^{k_m} ki(k) \sin(rk) dk \quad (1)$$

where

$$i(k) = A \left[I(k) - S(k) - \left\{ \sum_{\text{u.c.}} f^2(k) + \sum_{\text{u.c.}} I_{\text{inc}}(k) \right\} \right] / g^2(k) \quad (2)$$

and

$$g(k) = \frac{\sum_{\text{u.c.}} f(k)}{\sum_{\text{u.c.}} f(0)} \quad (3)$$

In eqn (1)–(3) $k = 4\pi \sin \theta / \lambda$, k_m is its maximum value (in the present case $k_m \approx 7.0 \text{ \AA}^{-1}$), $f(k)$ is the scattering factor, I_{inc} is the incoherent intensity, Z is the atomic number, $I(k)$ is the

Table 1. Density, molar volume, Vicker's microhardness, d.c. conductivity, activation energy and σ_0 value for different glass compositions

composition PbO:PbF ₂	density /g cm ⁻³	molar volume /cm ³	Vickers microhardness /kg mm ⁻²	activation energy /eV	$\sigma_0/10^4 \Omega^{-1} \text{cm}^{-1}$
30:70	7.21	33.09	186 ± 10	0.67	3.84
40:60	7.32	32.29	204 ± 10	—	—
50:50	7.40	31.74	210 ± 10	0.68	1.95
60:40	7.54	30.77	244 ± 10	—	—
70:30	7.73	29.73	230 ± 10	0.74	1.57
80:20	7.88	28.88	235 ± 10	0.91	4.77

X-ray intensity function corrected for background, absorption and polarization and u.c. indicates that the summation is over unit composition. The average electron density, ρ_0^e , is calculated from the density of the glass. A in eqn (2) is a normalizing constant. The constants in parametrized $S(k)$ were determined by methods described earlier.¹¹ The ripples in the low- r region (up to 1.5 Å) were minimized.

HEAT CAPACITIES

Heat capacities were determined using a Perkin-Elmer DSC-II scanning calorimeter employing sapphire as standard. For these measurements *ca.* 100 mg of the samples annealed at a temperature 20 K below T_g were used. A uniform heating rate of 10 K min⁻¹ was employed. Measurements were made over the temperature range 400–580 K. The intersection point of the extended linear regions around the glass-transition elbow was taken as the glass-transition temperature, T_g . The change in the heat capacities, ΔC_p , at T_g was measured for all the samples. The first crystallization temperature for each glass has also been noted.

D.C. CONDUCTIVITY

For conductivity measurements the glasses were prepared as thin discs of 0.5 mm thickness. The conductivity cell and measuring technique have been discussed elsewhere.¹² The resistances were calculated by measuring the current through the sample for a known applied voltage (5 V) using a Keithley 616 digital electrometer. The current was passed for only very brief periods (< 30 s) in order to avoid polarization. Conductivities were measured beyond the glass transition and up to temperatures at which the samples were either deformed under the load of the springs on the electrodes or crystallized, rendering further measurements inaccurate.

RESULTS AND DISCUSSION

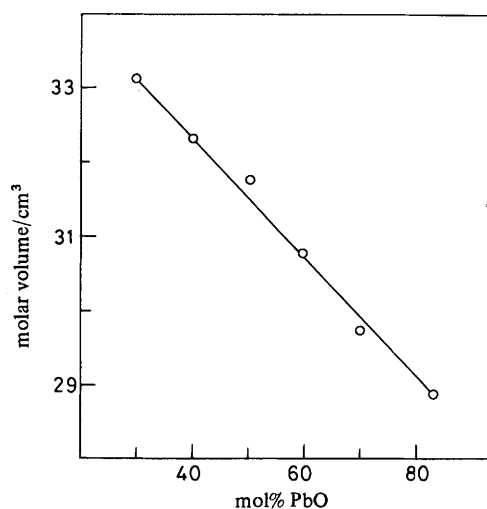
Density, molar volume, Vicker's microhardness, activation energy of conductivity and values of σ_0 are listed in table 1. The thermodynamic quantities, such as the glass-transition temperature (T_g), crystallization temperature (T_{cr}), heat capacity (C_p) at 20 K below T_g and change in heat capacity (ΔC_p) at T_g for various compositions are listed in table 2. The quantity ($T_{cr} - T_g$) is also been listed in table 2.

GLASS FORMATION

The range of glass formation extends from 80 to 30 mol% PbO. This range is considerably larger than in the PbO–PbCl₂ system, particularly on the lead-halide-rich side. Therefore it appears that the fluoride system is a better glass-former than the chloride system. This experimental observation is consistent with the structural features of these glasses discussed below. Fluorine may tend to occupy the bridging position at high PbF₂ compositions, helping glass formation.

Table 2. Thermodynamic quantities for various glass compositions

composition PbO:PbF ₂	T _g /K	T _{cr} /K	(T _{cr} - T _g)/K	C _p below T _g /J mol ⁻¹ K ⁻¹	ΔC _p /J mol ⁻¹ K ⁻¹
30:70	460	545	85	78.7	38
40:60	487	609	122	77.9	36
50:50	491	584	113	75.0	34
60:40	514	588	74	72.0	33
70:30	537	574	37	73.0	30
80:20	545	574	29	72.6	28

**Fig. 1.** Variation of molar volume with glass composition.

DENSITIES AND MOLAR VOLUMES

The molar volumes of the glasses were evaluated from their densities and are plotted against glass composition in fig. 1. The extrapolated molar volumes give the densities of the hypothetical glasses PbO and PbF₂ as 8.12 and 6.92 g cm⁻³, respectively, values which are lower than the densities of the corresponding crystalline components (9.53 g cm⁻³ for tetragonal PbO and 8.24 g cm⁻³ for PbF₂). It is surprising that the ratios of the densities of the extrapolated glasses to those of the corresponding crystalline phases are 0.85 for PbO and 0.84 for PbF₂. These values correspond to the ratio of the space-filling efficiency of random close packing (0.63) to the space-filling capacity of the ordered face-centred cubic or hexagonal close packing (0.74) arrangement of simple spheres. In this context note that the radii of the Pb²⁺ (1.20 Å), O²⁻ (1.32 Å) and F⁻ (1.33 Å) ions are rather similar. A simple random close packing arrangement of such ions increases the volume by *ca.* 15% compared with a close-packed crystalline arrangement. Such an increase in volume lowers the cohesive energy by *ca.* 5%. This energy is *ca.* 146 kJ for a typical 50PbO · 50PbF₂ glass (lattice energies of PbO and PbF₂ are 3251 and 2469 kJ mol⁻¹, respectively). Such a large energy difference between crystalline and glassy states of the same material may be

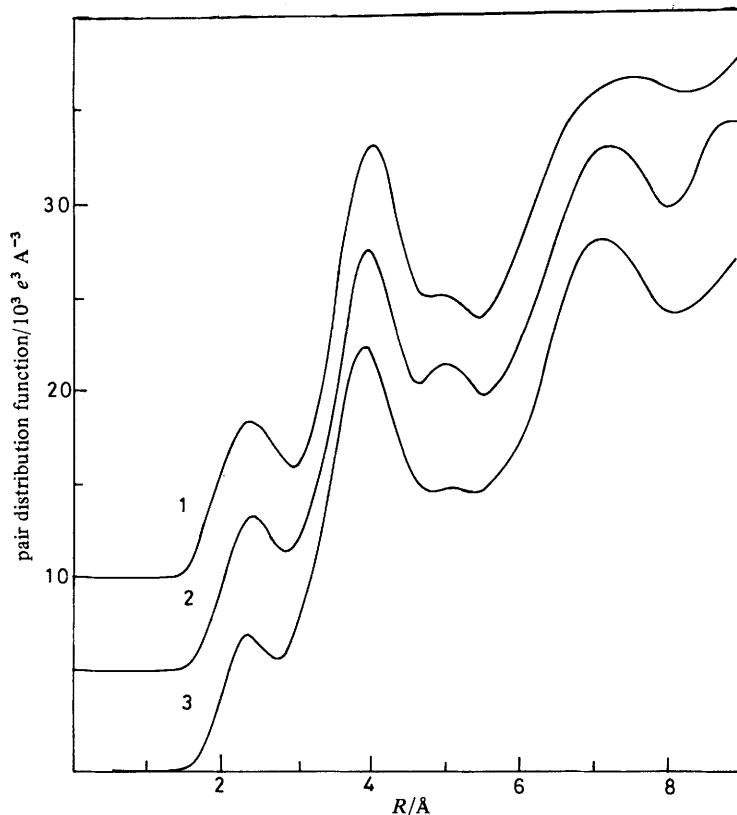


Fig. 2. Pair distribution functions for various glass compositions: (1) 30PbO·70PbF₂, (2) 50PbO·50PbF₂ and (3) 80PbO·20PbF₂. The plots are displaced systematically by 5 units on the y-axis from (2) to (1).

considered as unphysical. Therefore we feel that the observed correspondence to the random-close-packing volume may arise from the presence of small atomic groupings of higher cohesive energy, which in turn are probably present in a random-close-packed assemblage. X-ray diffraction results discussed below support this possibility.

X-RAY DIFFRACTION AND STRUCTURAL MODEL FOR THE GLASSES

The pair distribution functions (p.d.f.) determined in the manner described earlier are given in fig. 2 for three compositions, 30PbO, 50PbO and 80PbO, which span the entire range of glass composition investigated here. The p.d.f. for other compositions are very similar. Upon a cursory examination we note that the most striking feature of these p.d.f. is their similarity to those of PbO–PbCl₂ glasses, the structure of which has been reported by us elsewhere.¹³ The positions of the first four peaks around 2.3, 4.0, 5.0 and 7.0 Å remain largely unaltered. The intensity of the first peak increases with increasing PbF₂ content. The intensity of the second peak is high and remains almost constant for all compositions. The third peak is of rather low intensity and the fourth peak is intense and broad. The positions of the third and fourth peaks also remain unaffected by variations in composition.

From a knowledge of the crystal structures⁹ of PbO and PbF₂, the first peak at

ca. 2.30 Å can be attributed to the Pb–O and Pb–F distances, as the Pb–O distance in PbO is *ca.* 2.30 Å and the Pb–F distance in PbF₂ varies between 2.41 and 2.69 Å (mean 2.55 Å). Pair distances of the type O–F may also contribute to the intensity of the first peak. The second peak at *ca.* 4.0 Å, being the most intense, can be attributed to Pb–Pb. While the integrated intensity of the first peak increases by a factor of two on increasing the PbF₂ content from 20 to 70 mol%, the intensity of the second peak remains almost constant. The substitution of PbO by PbF₂ introduces twice the number of (fluoride) anions, thereby increasing the number of scattering pairs contributing to the first peak (the scattering factors of O²⁻ and F⁻ ions being very similar). Hence the intensity of the first peak increases with PbF₂. The intensity of the second peak remains almost constant because the concentration of lead ions remains constant for all compositions. The third and fifth peaks may contain contributions from various pair distances such as Pb–Pb in different [FPb_x] units where *x* may vary from 3 to 6 (as discussed later). Guided by the close similarity of the general features of the p.d.f. of these glasses to those of PbO–PbCl₂ glasses,¹³ we propose the following structural model. (1) Covalent —O—Pb—O— linkages are crucial for glass formation and are present in all glasses. (2) Oxygen atoms are present in [OPb₄]-type tetrahedra because the former is primarily responsible for establishing network features through covalent bonding using their *sp*³ hybridized orbitals. (3) Lead atoms possess an anion coordination of six (a value between those in crystalline PbO and in PbF₂) in all glasses. EXAFS and XANES studies^{14, 15} of PbO–PbCl₂ glasses have shown that six-coordinated lead is quite consistent. As the lead ion is usually connected to two oxygens, the other four ions surrounding it must be fluoride ions. Hence [PbO₂F₄]-type octahedra are assumed to be present in the entire range of glass composition. (4) The coordination number of the fluoride ion varies with composition, being high in PbO-rich glasses and low in PbF₂-rich glasses.

PbO itself does not have enough lead atoms to provide a three-dimensional network of the type OPb₂ (analogous to SiO₂) built with corner-shared oxygen tetrahedra as the base. However, with the addition of PbF₂ it is possible to consider that the structure is built up towards [OPb₂]F₂, in which a tetrahedral network can exist. The fluoride ions are suitably distributed around the lead ions while the network is formed by [OPb₂]²⁺. Indeed, for this particular composition of glass, corresponding to 50PbO·50PbF₂, the coordination number of the fluoride ion will also be four if we consider that the lead ion is present in an octahedral coordination of the type [PbO₂F₄]. This ensues from the following relation, which is based on one of Pauling's bonding rules.¹⁶ For a glass of composition (1 - *x*)PbO · *x*PbF₂:

$$n_{\text{Pb}} = (1 - x)n_{\text{O}} + 2n_{\text{F}} \quad (4)$$

where *n* is the number of bonds reaching (or emanating from) the subscripted atom. With < 50 mol % PbF₂ we consider that distorted [OPb₄] tetrahedra share edges. Since the ratio of the number of lead ions to fluoride ions is quite high, fluoride ions occupy positions that enable them to acquire high coordination numbers (with Pb atoms). Indeed, it can be calculated from eqn (4) for the specific case of 75PbO · 25PbF₂ that the coordination number for the fluoride ion is six. For compositions with > 50 mol % PbF₂, [OPb₄] tetrahedra must have unshared corners and the dimensionality of the network is gradually reduced. On addition of 60 mol % of PbF₂ we would expect that [OPb₄] tetrahedra would have only three shared corners, so that the glasses possess a two-dimensional structure analogous to that of chalcogenide glasses. By the same argument, addition of 66.6 mol % PbF₂ would lead to a structure where only the integrity of the —O—Pb—O— chains is retained. Further addition of PbF₂ would degrade the chains to shorter lengths, and for a composition with *ca.* 71.5 mol % PbF₂

the structure would possess only corner-shared dimers of $[\text{OPb}_4]$ tetrahedra. Hence this composition corresponds to an extreme limit where the degradation of network features is almost complete. Note from fig. 6 (see later) that $(T_{\text{cr}} - T_g)$, which is considered¹⁷ as a measure of glass stability and indirectly glass formation, is highest at *ca.* 50–60 mol % PbF_2 . $(T_{\text{cr}} - T_g)$ decreases sharply on either side of this region. The highest percentage of PbF_2 for which a reasonably good glass could be obtained is *ca.* 70%, in remarkable agreement with the composition limit to the presence of network features in the model. However, we suspect that fluorine begins to play the role of oxygen in PbF_2 -rich compositions where the fluoride-ion coordination decreases rapidly to *ca.* 3.5.

Such a model is consistent with the observed pair distribution functions of the glasses. Since the Pb—F and Pb—O distances in the model should remain unaltered except for PbF_2 -rich glasses (where fluoride ions may play the part of oxygens) a slightly greater distribution of distances and hence a slightly broader peak results. However, both the nature of the $[\text{PbO}_2\text{F}_4]$ octahedra and the possible effects of composition on the covalency of the —O—Pb—O— linkages should be established by the further experiments.

D.C. CONDUCTIVITY

The variation in d.c. conductivity with temperature for different glass compositions is shown in fig. 3. Curve-fitted values of the activation energy (ΔE) and σ_0 for the linear portion of the graph for various compositions are listed in table 1. Note that $\log \sigma T$ varies quite linearly with $1/T$ up to a temperature a few degrees (40–50 K) below T_g . (T_g values for different compositions are marked by arrows in the figure). Note also that the conductivities are quite high and are comparable to those of fast ion conducting glasses.¹⁸ The isothermal conductivity also increases systematically with increasing PbF_2 content in the glass. Since F^- ions may be considered as dominant charge carriers in these glasses, such a variation in conductivity is quite expected. Activation energies also decrease monotonically with PbF_2 content in the glass and this variation is consistent with our structural model discussed in the earlier section. With the addition of > 50 mol % PbF_2 , the glass structure becomes more open as additional PbF_2 breaks the —O—Pb—O— linkages. The coordination number of F^- ions also decreases. Hence the activation energy decreases with the addition of PbF_2 . Values of σ_0 are comparatively high and are of the same order for all the compositions, suggesting that the environment which mobile F^- ions explore during transport is common to all glass-forming compositions. This is in agreement with the existence of $[\text{PbO}_2\text{F}_4]$ -type octahedra at all glass-forming compositions.

HEAT CAPACITIES AND GLASS TRANSITIONS

Heat capacities obtained from d.s.c. measurements are plotted in fig. 4 as a function of temperature for various compositions. Up to T_g the increase in C_p is very marginal, suggesting that the Debye temperatures of these glasses are well below T_g . Heat-capacity values 20 K below their respective T_g are plotted in fig. 5 for the various glasses. Variation of the Dulong–Petit heat capacity with composition is also shown in fig. 5 for comparison. The heat-capacity behaviour clearly brings out the following points. (1) C_p varies very little with composition. (2) The true C_p below T_g being higher than the Dulong–Petit heat capacity reflects the fact that a part of the liquid configurational heat capacity is frozen into glasses at their respective glass-transition temperatures. (3) The magnitude of the excess heat capacity, which we thus attribute to a configurational origin, is systematically higher in PbO-rich glasses. We consider the latter observation to be significant because the PbO-rich glasses may be expected to

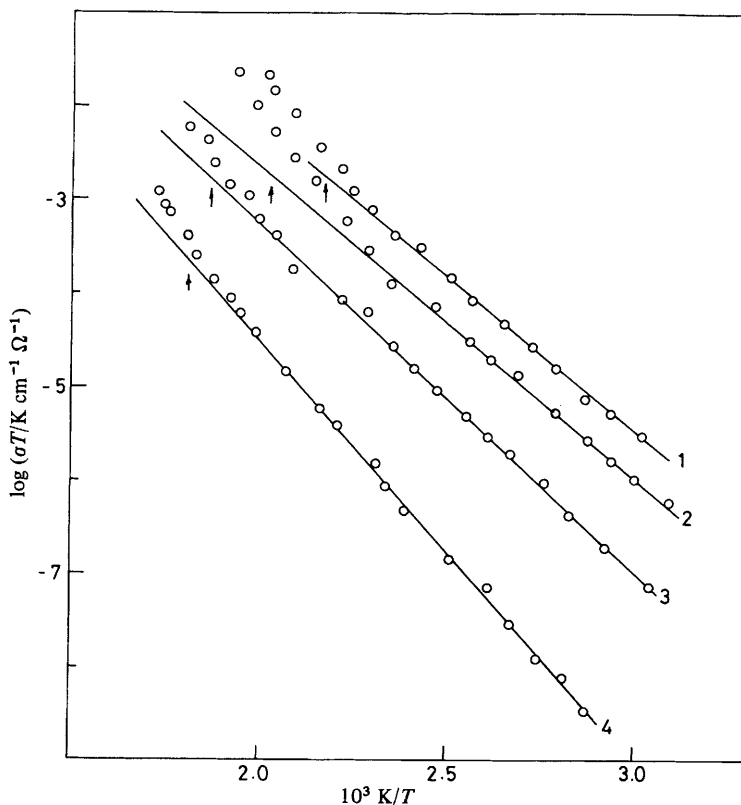


Fig. 3. Temperature variation of d.c. conductivity for various glass compositions: (1) 30PbO·70PbF₂, (2) 50PbO·50PbF₂, (3) 70PbO·30PbF₂ and (4) 80PbO·20PbF₂.

be more covalent and hence are characterized by larger magnitudes of frozen configurational heat capacity. This is in keeping with similar observations made by Angell and Sichina¹⁹ with regard to covalently bonded glasses.

The change in heat capacity at T_g is also plotted against mol% PbO in fig. 5. ΔC_p is higher for PbF₂-rich glasses and decreases with mol% PbO. This may again be interpreted as due to higher covalency of bonding in PbO-rich glasses because highly covalent glasses are known to exhibit weak step-like increases in C_p at their glass transitions.

The variation of T_g with composition is shown in fig. 6. T_g values are generally high, although lower than those of PbO–PbCl₂ glasses, and increase with PbO content. A systematic rise of 85 K in T_g is registered between extreme compositions. Note that T_g varies linearly, although the liquidus temperature exhibits a minimum at 767 K for the eutectic composition 54 mol% PbO. The approximate constancy of the ratio between T_g and liquidus temperature observed in many glass-forming systems with a variety of bonding characteristics is not obeyed by the glasses in this system. However, the molar cohesive energy calculated to a first approximation as a sum of lattice energies of the components weighted by their molar percentages varies in the same manner as T_g . Variation of the glass-transition temperature may also be considered in the light of the cluster model.²⁰ Briefly, in the cluster model glass is considered to be made up of clusters, which form a large part of the glass, and tissue

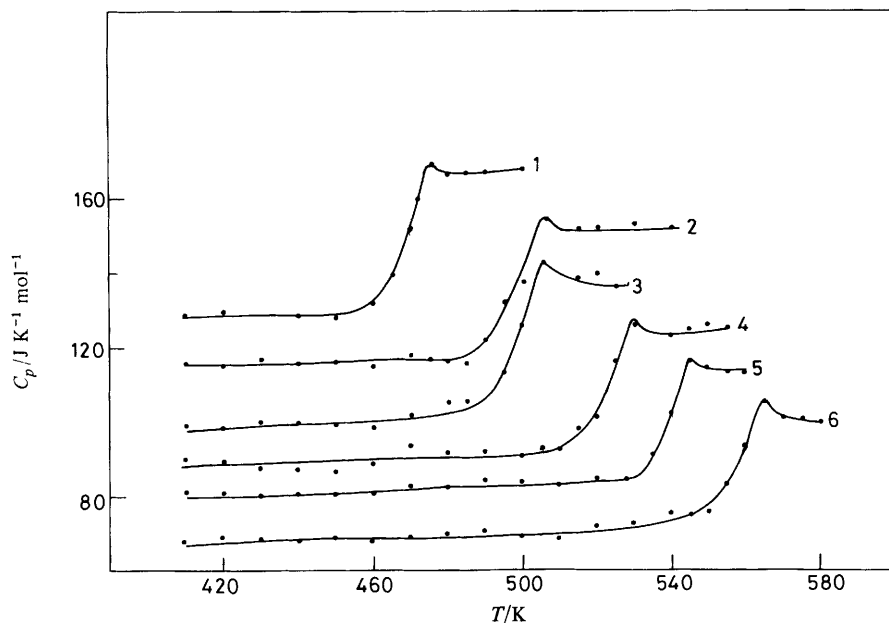


Fig. 4. Temperature variation of heat capacity for various glass compositions: (1) 30PbO·70PbF₂, (2) 40PbO·60PbF₂, (3) 50PbO·50PbF₂, (4) 60PbO·40PbF₂, (5) 70PbO·30PbF₂ and (6) 80PbO·20PbF₂. The plots are displaced systematically by 40 units on the y-axis from (5) to (1).

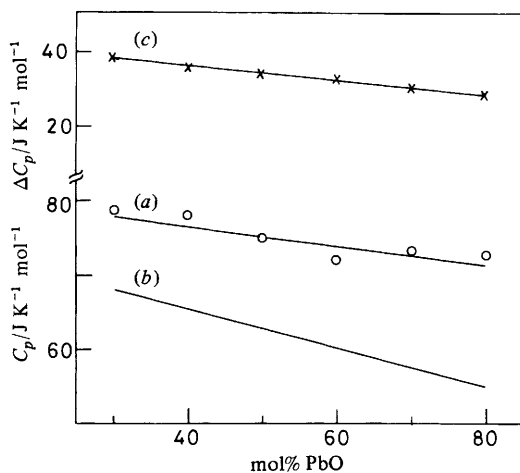


Fig. 5. (a) Variation of heat capacity 20 K below T_g with glass composition. (b) Variation of calculated Dulong-Petit ($3nR$) heat capacity with glass composition. (c) Variation of change in heat capacity with composition.

material of the same composition, which binds the clusters. Clusters in highly ionic glasses possess ordered structures and their sizes are *ca.* 50–100 Å. Particles in the tissue region are in a state of complete positional disorder and vibrate in highly anharmonic potential wells, and their vibratory motion ultimately evolves into translation. Particles in the cluster gradually populate the vibrational manifold of the tissue

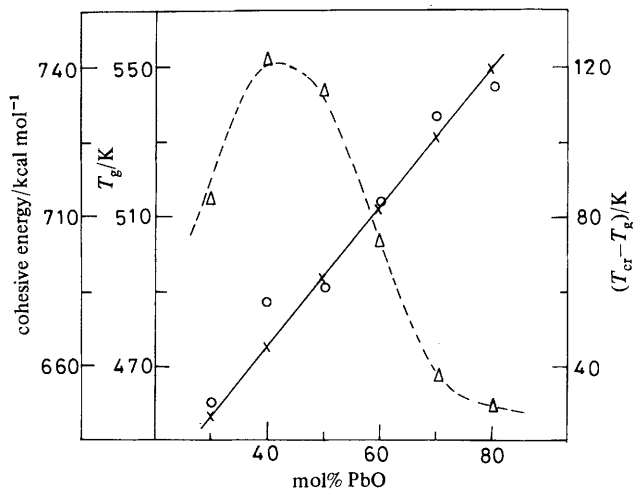


Fig. 6. Variations of glass-transition temperature (○), cohesive energy (×) and the quantity $(T_{cr} - T_g)$ (△) with glass composition.

material and the glass transition occurs when the clusters melt. The quantity which determines T_g in this model [see ref. (20) for details] is the vibrational frequency of the most mobile ion, which we may assume in the present case to be F^- . We presume that the clusters are made up of a suitable and small conglomerate of $[PbO_2F_4]$ units. That T_g decreases as the PbO content decreases in the glass suggests that the vibrational frequency of the F^- ion (in the cationic cage of Pb^{2+} ions) also decreases. This is possible since the coordination number of the F^- ions is highest in PbO-rich glasses and decreases from 6 to 3 in PbF_2 -rich glasses, as discussed in an earlier section. The decrease in coordination number results in a corresponding decrease in force constant and hence affects T_g in the observed manner.

MICROHARDNESSES

Vicker's microhardnesses for various glass compositions listed in table 1 show a slight increase with PbO content up to 60 mol% PbO and the values are roughly constant with higher percentages of PbO. The values are comparable to (but lower than) the values reported for silicate and borate glasses containing very high percentages of PbO^{21, 22} and higher than the values reported for purely ionic glasses.²³ As addition of PbF_2 to the glass is expected to make the glass structure more open, particularly on the PbF_2 -rich side, the decrease in microhardness with increasing PbF_2 content is expected. This variation is also in agreement with the general observation that the addition of ionic constituents into network glasses reduces their microhardnesses. Note also that the microhardness values are slightly higher than those of PbO-PbCl₂ glasses.⁴

CONCLUSIONS

PbO-PbF₂ glasses have been obtained in the range 20–70 mol% PbF_2 . X-ray diffraction studies indicate that the structures of these glasses are similar to those of PbO-PbCl₂ glasses. A structural model has been proposed for these glasses which suggests the presence of $[PbO_2F_4]$ -type units in the entire range of glass compositions.

In glasses with high percentages of PbF_2 , fluoride ions are considered to play the role of oxygen ions in these glasses. All the thermodynamic properties studied vary in a manner consistent with the structural model and with the possible role of partly covalent —O—Pb—O— linkages. Isothermal variations of d.c. conductivity and activation energies as a function of composition are also consistent with the structural model.

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