JOURNAL OF MATERIALS SCIENCE 20 (1985) 1678–1682

Glass formation in the system $PbO–PbCl_2$*

K. J. RAO, B. G. RAO
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

S. R. ELLIOTT
Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK

The preparation of glasses in the system $PbO–PbCl_2$ is described. The behaviour of the glass transition temperatures, heat capacities and microhardnesses as a function of glass composition has been investigated. The variations are discussed in terms of the structural features of the glasses.

1. Introduction

Lead oxide has been used [1] as a constituent in several borate, silicate, phosphate and other glasses in order to achieve useful mechanical and optical properties. Though it is not a glass-forming oxide, it can be incorporated in large percentages into other glass-forming oxide systems such as silicates and borates. There are, however, very few reports on the inclusion of lead chloride as a constituent in glasses. Lead chloride has been used [2] in small amounts in some lead oxide based multi-component glasses to study the effect of chloride ions on different properties of the glass. However, there is no report to our knowledge of any study of glasses made from the binary system $PbO–PbCl_2$. A number of oxychlorides of lead occur in nature [3], notable examples being mendipite ($2PbO \cdot PbCl_2$), matlockite ($PbO \cdot PbCl_2$) and perfieldite ($PbO \cdot 2PbCl_2$). Several other oxychloro-compounds have been reported to form in the binary phase field of $PbO–PbCl_2$, but structures of only very few oxychlorides are known with certainty [4, 5]. Ionic binary systems with such complex phase diagrams are often found to be good glass-formers [6, 7].

We have thus been motivated by two important and related considerations in investigating $PbO–PbCl_2$ glasses, besides the fact that such a simple ionic glass-forming system has not been reported in the literature. The first is that the Pb–O bond is more ionic in lead silicate glasses than in PbO, as revealed by ultraviolet reflectance studies [8] and also the ionic nature of the Pb–O bond changes with lead oxide content in lead borate glasses [9]. Therefore, it is of interest to find out the nature of the bonding of lead in $PbO–PbCl_2$ glasses in which one of the components ($PbCl_2$) is a typically ionic compound of lead. Also of interest is the role of the –O–Pb–O type of covalent linkage. Such linkages may be crucial to sustain amorphicity in $PbO–PbCl_2$ glasses, because the constituent ions are expected to be simple spheres. Finally, it would be interesting to study the structure and properties of such glasses as a function of composition.

In this communication we report and discuss the glass-forming region, molar volumes, microhardnesses, and the glass-transition and crystallization temperatures.

2. Experimental procedure

The starting materials used in the preparation of the glasses were analytical grade Pb_3O_4 and $PbCl_2$. It was first confirmed that Pb_3O_4 decomposes to yellow PbO completely around 850 K. Appropriately weighed quantities of Pb_3O_4 and $PbCl_2$ were mixed thoroughly, and melted in short fused quartz tubes using an oxyacetylene flame till a

---

*Communication No. 256 from the Solid State and Structural Chemistry Unit.

0022–2461/85 $03.00 + .12

TABLE I Molar volume, Vickers microhardness and thermal characterization data for various compositions.

Composition $PbO:PbCl_2$	Molar volume (cm^3)	Vickers microhardness ($kg\,mm^{-2}$)	T_g (K)	T_{crys} (K)	C_p at 20 K below T_g ($J\,deg^{-1}\,mol^{-1}$)	ΔC_p ($J\,deg^{-1}\,mol^{-1}$)	T_l (K)	T_g/T_l
90:10	31.72	200 ± 10	600	655	76	37	1123	0.534
80:20	33.65	175 ± 10	582	665	75	36	1023	0.567
70:30	35.66	210 ± 10	590	663	76	32	1023	0.577
60:40	37.72	200 ± 10	554	647	77	44	973	0.569
50:50	39.78	185 ± 10	525	588	70	43	923	0.569
40:60	40.60	165 ± 10	490	538	78	–	823	0.595

uniformly clear melt was obtained. The melt was kept at that temperature (900–1200 K) for a short while (2–3 min) and then poured on to a polished steel plate and pressed quickly with another polished steel block. The thin disks of glass thus obtained generally shatter into pieces unless they are small in area. However, small drops of melt were 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 $860\,cm^{-1}$ which may be attributed [10] to Si–O stretching in $PbO{\cdot}xSiO_2$ systems when x is extremely small. We have measured the loss in weight of the quartz tube used in the preparation. A maximum of 2 to 4 mol% of SiO_2 is likely to enter into the resulting glass. Attempts to obtain these glasses by melting the batch in a platinum crucible were not successful, as part of the melt was reduced to metallic lead when heated in an electric furnace. We have treated the SiO_2 as primarily an impurity and given the compositions of glasses in terms of PbO and $PbCl_2$ only.

Densities were measured using a density bottle, and xylene was used as the displacing liquid. Glass-transition and crystallization temperatures (T_g and T_{crys}) were determined using a Perkin-Elmer DSC–II scanning calorimeter. Heat capacities were measured as a function of temperature. For this measurement about 80 mg of the samples annealed at a temperature 20° C below T_g were used. The heating rate used during these measurements was $10°\,C\,min^{-1}$.

Microhardnesses of the glasses were measured using a Carl Zeiss (Jena) mhp–160 microhardness tester. A uniform load of 100 g was applied for making the indentations. The diagonals of the symmetrical indentations were measured and Vickers microhardnesses of the samples were determined. The results reported here are averages of measurements using four to five distinct symmetrical indentations for each glass composition.

3. Results and discussion

Glass compositions, molar volumes, glass-transition temperatures, crystallization temperatures and Vickers microhardnesses are given in Table I.

Glasses in the PbO–$PbCl_2$ system could be obtained containing very high percentages of PbO. On the other hand, the upper limit of $PbCl_2$ in the melt composition that could be quenched into a glass was only 60 mol%. Glasses having extreme compositions were often not X-ray amorphous. We have therefore restricted our discussion to the relatively easily glass-forming compositions which range from 90 down to 40 mol% PbO.

The molar volumes of the glasses were evaluated from their densities. The variation of molar volume with composition is shown in Fig. 1. The extrapolated molar volumes give densities of hypothetical $PbCl_2$ and PbO glasses as $5.7\,g\,cm^{-3}$ and

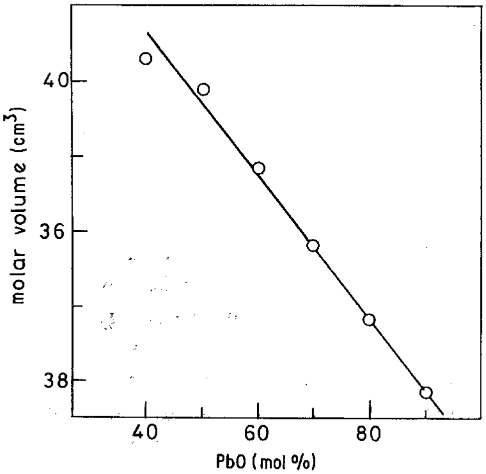

Figure 1 Molar volume against mol% of PbO.

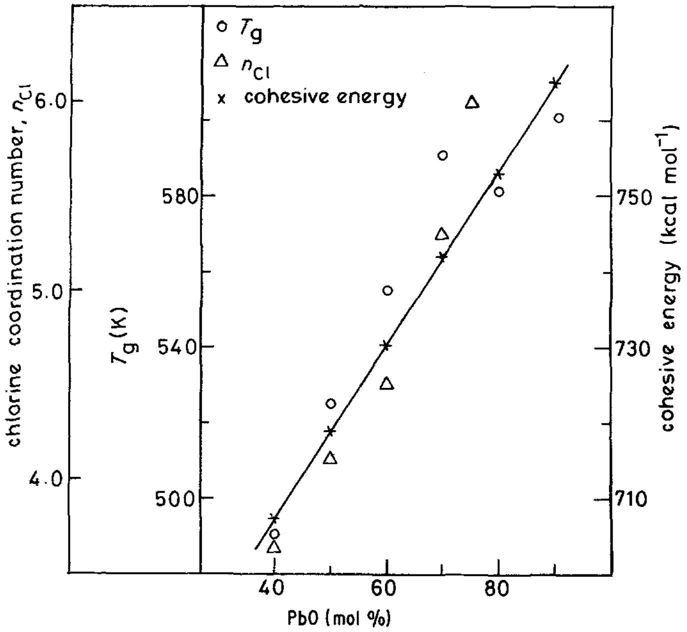

Figure 2 Glass transition temperature (O), cohesive energy (X), and chlorine coordination number n_{Cl} (△) against mol% of PbO. 1 kcal = 4184 J.

7.02 g cm^{-3} respectively, which are lower than the densities of the corresponding crystalline compounds (5.85 g cm^{-3} for $PbCl_2$ and 9.53 g cm^{-3} for PbO). The molar volume variations are quite linear, indicating ideal mixing of the corresponding melts.

The variation of T_g with composition is shown in Fig. 2. It is interesting to note that T_g values are generally high, and increase rapidly with PbO content in the glasses; indeed a rise of almost 110 K in T_g is noted between the extreme compositions. The effect on the coulombic field of substitution of monovalent chloride ions by an equivalent proportion of oxide ions is not sufficient to account for such a large increase in glass-transition temperatures. We suspect that a large variation in the nature of the bonding is responsible for such an increase in T_g. While in PbO-rich glasses the nature of bonding is predominantly covalent, it becomes largely ionic in glasses with a higher percentage of $PbCl_2$. We have shown elsewhere [11] that X-ray absorption near-edge spectra (XANES) are consistent with a large change in the nature of the bonding. It is, however, noteworthy that the molar cohesive energy, calculated to a first approximation as a sum of the lattice energies of the components weighted according to their molar percentages, also varies sharply in the same manner as T_g. Since the melting points scale with the cohesive energies, the values of T_g should also scale roughly with the liquidus temperatures, T_l. The values of T_g/T_l are listed in Table I. While they are uniformly less than 2/3, they are essentially constant for all the glasses.

The conventional models for the glass transition unfortunately do not provide a means of directly correlating T_g with any measurable physical quantities. The problem of the glass transition has recently been treated by using a cluster model for glasses [12]. In this model, glass is considered to be made up of clusters with a high degree of positional correlation and bounded by connective disordered tissue of slightly lower density. The configurational properties relevant to the glass transition evolve rapidly over a narrow region of temperature around T_g. In ionic glasses the clusters may be considered as quasi-crystalline (para- or micro-crystallites) with typical dimensions of 5 to 10 nm, and the parameter which determines the glass transition is the vibrational frequency of the most mobile ion in the tissue region of the glass. The variation of vibrational frequency or the related force constants would affect T_g. In the present system of glasses we assume that the chloride ion is the most mobile, and hence its vibrational frequency determines the transport properties as well as T_g.

In an earlier paper [13] we have discussed the structure of these glasses based on X-ray diffraction studies, and we have suggested that one of the structural characteristics of these glasses is that the chloride ion coordination changes with glass

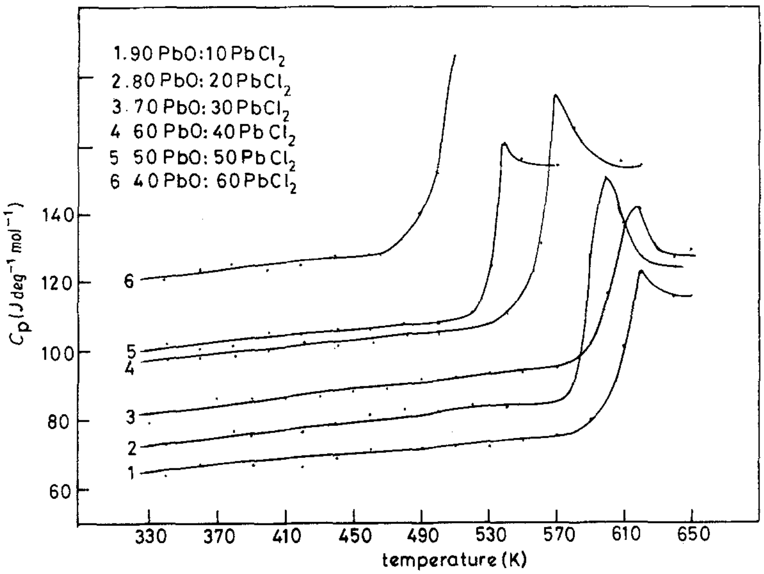

Figure 3 Heat capacity, C_p against temperature for various compositions.

composition. While in low $PbCl_2$-containing glasses chloride ions are coordinated to as many as six lead ions, this decreases to three in $PbCl_2$-rich compositions. This is dictated by the dominance of a $[PbO_2Cl_4]$ type of pseudo-octahedral unit in the glass structure. Such a variation in the coordination number would naturally entail a concomitant decrease in effective force constants and associated vibrational energies. We should therefore expect that increasing the proportion of $PbCl_2$ will decrease the glass transition temperature very sharply. In Fig. 2 we have also plotted the coordination number of chloride ions, n_{Cl} calculated from the model [13] with glass composition to demonstrate that T_g varies in nearly the same manner as n_{Cl}.

Heat capacities obtained from calorimeter measurements are shown in Fig. 3. The increase in C_p up to T_g is very marginal, suggesting that the glasses attain Dulong–Petit heat capacities well before T_g. Values of C_p for the glasses 20 K below their respective values of T_g are plotted in Fig. 4. It is interesting to note that C_p varies very little with composition. The expected variation of the Dulong–Petit capacity with composition is also shown in Fig. 4 for comparison. The heat-capacity behaviour clearly brings out two points: (a) the actual C_p of these glasses below T_g has a definite component of configurational C_p frozen into the glasses at the respective T_g, and (b) the magnitude of the frozen configurational C_p is much higher in PbO-rich glasses than in $PbCl_2$-rich glasses. We consider the second observation as significant because the PbO-rich glasses are highly covalent, and they correspond to a larger magnitude of frozen configurational heat capacities in keeping with the observation made by Angell and Sichina [14]. The ΔC_p values at T_g for various glass compositions are listed in Table I. The uncertainties in ΔC_p are unfortunately very large because several compositions crystallize rapidly just above T_g. However, the trend suggests that ΔC_p is larger for the more ionic $PbCl_2$-rich glasses.

Microhardnesses listed in Table I may be seen to be almost the same for all the glasses. These values are comparable to (and lower than) the values reported for very high percentage PbO-containing borate [15] and silicate [16] glasses. PbO addition into these glasses is known to bring

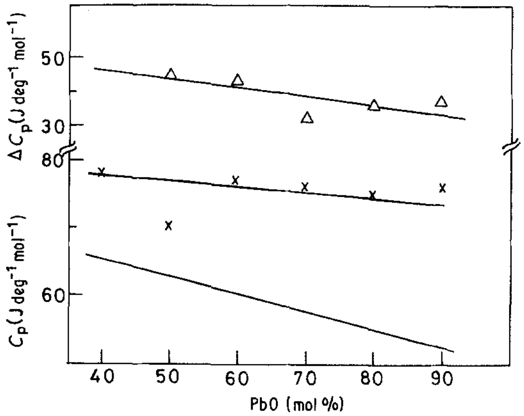

Figure 4 Heat capacity at 20 K below T_g against composition (X). The straight line in the lower part of the figure indicates the variation of calculated Dulong–Petit heat capacities with composition. Changes in heat capacity, ΔC_p against temperature (Δ) are in the upper part of the figure.

down the microhardness [16]. However, it is very difficult to provide a microscopic theory for the hardness of glasses. In many glass systems the microhardness generally ranges with the average cohesive energy of the glass. We should therefore like to think that the resistance to indentation is determined by the binding energy of particular bonds which are present in the entire composition range. However, the structural model of these glasses suggests that no such simple unmodified bonds are present in the entire range of glass compositions. On the other hand the common presence of PbO_2Cl_4 units in the entire range of glass composition may be responsible for the constancy of microhardnesses. The indentation hardness may therefore be related either to the deformation or breaking strengths of these units.

4. Conclusions

$PbO-PbCl_2$ melts containing 40 to 90 mol % PbO can be quenched to form glasses. The variation of T_g is consistent with the structural features of these glasses and with a cluster model of the glass transition. Heat capacities of these glasses prior to T_g are consistent with a higher degree of covalency of bonding in PbO-rich glasses.

Acknowledgements

The authors are thankful to Professor J. M. Thomas, Department of Physical Chemistry, University of Cambridge, UK and to Professor C. N. R. Rao, Solid State and Sturctural Chemistry Unit, Indian Institute of Science, Bangalore, for their kind encouragement.

References

1. H. RAWSON, "Inorganic Glass Forming Systems" (Academic Press, London, 1967).
2. A. PAUL and S. GROLKA, *Phys. Chem. Glasses* **16** (1975) 57.
3. E. W. ABEL in "Comprehensive Inorganic Chemistry", Vol. 2, Edited by J. C. Bailor, J. J. Emeleus, R. Nyholm and A. F. Trotman-Dickenson (Pergamon Press, Oxford, 1973).
4. J. W. MELLOR, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 8 (Longmans, London, 1927) p. 736.
5. A. F. WELLS, "Structural Inorganic Chemistry" (Clarendon Press, Oxford, 1975).
6. C. H. L. GOODMAN in "The Structure of Non-crystalline Materials", edited by P. H. Gaskell (Taylor and Francis, London, 1977) p. 197.
7. K. J. RAO, *Bull. Mater. Sci.* **1** (1979) 181.
8. A. J. BOURDILLON, F. KHUMALO and J. BORDAS, *Phil. Mag.* **B37** (1978) 73.
9. P. TARTE and M. J. POTTIER in "The Structure of Non-crystalline Materials", edited by P. H. Gaskell (Taylor and Francis, London, 1977) p. 227.
10. T. FURUKAWA, S. A. BRAWER and W. B. WHITE, *J. Mater. Sci.* **13** (1978) 268.
11. K. J. RAO and J. WONG, *J. Chem. Phys.* **81** (1984) 4832.
12. K. J. RAO and C. N. R. RAO, *Mater. Res. Bull.* **17** (1982) 1337.
13. B. G. RAO and K. J. RAO, *Phys. Chem. Glasses* **25** (1984) 11.
14. C. A. ANGELL and W. SICHINA, *Ann. N.Y. Acad. Sci.* **279** (1976) 53.
15. N. SHINKAI, R. C. BRADT and G. E. RINDONE, *J. Mater. Sci.* **18** (1983) 2466.
16. J. D. MACKENZIE, "Mechanical Behaviour of Materials IV" (Society of Materials Science, Japan, 1972) p. 347.

Received 17 May
and accepted 6 July 1984