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PbCl₂ conducting glasses with mixed glass formers

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Abstract. Glasses of the formula $x\text{PbCl}_2-(30-x)\text{PbO}-40\text{B}_2\text{O}_3-30\text{P}_2\text{O}_5$ ($0 \leq x \leq 30$ mol%) were prepared and their physical properties have been studied. To enhance the conductivity of these glasses, the 'mixed former effect' and the halide salt (PbCl_2) doping effect have been combined.

The decrease in T_g and increase in both the thermal expansion coefficient and the molar volume with increasing amount of PbCl_2 support the idea of expansion of the glass network by chlorine ions. Because of this expansion, a more open and weaker network is formed. The electrical properties can be well described by the open network model. The experimental data suggest that Cl^- ions form additional migration pathways which are important for the conduction mechanisms.

1. Introduction

Glasses containing halogen ions [1–7] are of practical interest because these materials may serve as the solid electrolyte in a wide variety of electrical devices, such as primary and secondary batteries, sensors and electrochromic displays. Therefore, the field of use of these materials as high-conductivity amorphous solids has become important in the broader field of solid state ionics, since the enhancement of conductivity with a dopant salt is achieved.

Besides the enhancement of conductivity with a halide dopant salt, the mixing former has proved to be useful as a means of achieving enhanced conductivity [1, 2, 6, 7]. It has been shown [7–9] that technologically interesting products can be obtained with competitive network formation (using more than one glass former).

Most of the previous studies on lead-halide-containing glasses [5, 10, 11] have considered lead fluoride as the dopant salt, while research on lead-chloride-containing glasses, to our knowledge, has been limited. Therefore, the present work completes our previous studies [3, 4], aiming to investigate the physical properties of lead chloroborophosphate glasses and the role of chlorine ions in such glasses.

2. Experimental details

2.1. Sample preparation

The glasses of composition given in table 1 were prepared using reagent-grade materials. The raw materials PbCl_2 , PbO , B_2O_3 as orthoboric acid (H_3BO_3) and P_2O_5 as ammonium dihydrogen orthophosphate ($\text{NH}_4 \text{H}_2\text{PO}_4$), were of pure analytical grade. Except for PbCl_2 and P_2O_5 , the components were mixed together and then melted in porcelain crucibles in an electric furnace at a temperature ranging from 900 to 1050 °C, depending on the

composition. The crucible was covered with a lid in order to reduce volatilization losses. After homogenization of the melt, PbCl_2 and P_2O_5 were added and the melting process was extended for 20 min at 800°C in the covered crucible to minimize probable chlorine or phosphorus loss. The melted samples were cast in the form of a rectangular shape (1×1 cm in cross section and 4–5 cm length) using pre-heated steel moulds. The samples used for the thermal expansion measurements were prepared in cylindrical form. The glassy samples were then immediately transferred to the annealing furnace for 1 h at 250°C and then allowed to cool normally to room temperature.

Table 1. Glass composition for the glasses studied.

Glass	Composition (mol%)			
	PbCl_2	PbO	B_2O_3	P_2O_5
1	0	30	40	30
2	5	25	40	30
3	10	20	40	30
4	15	15	40	30
5	20	10	40	30
6	25	5	40	30
7	30	0	40	30

The x-ray diffraction of the glass samples showed them to be amorphous, with no crystalline phases present for the different amounts of PbCl_2 .

2.2. Conductivity measurement

DC conductivity measurements were carried out using samples of thickness 0.2–0.3 cm. The parallel surfaces of the samples were coated with graphite. The coated area had a 0.5 cm radius. The resistance was measured using an insulating tester type (TM 14, Electronic Ltd, England) with a range of 10^3 – $10^{13} \Omega$. As a rule, three samples of each glass were measured. The measured conductivity σ was fitted to an Arrhenius equation.

$$\sigma = \sigma_0 \exp(-E/RT)$$

where σ_0 is the pre-exponential factor, E is the activation energy for ionic conduction, R is the universal gas constant and T is the absolute temperature.

The polarization and space-charge effects on the results have been minimized using electrodes with perfectly flat interfaces and a guard ring. In addition, the DC voltage (10 V) applied to the sample was just for a short time scan (the time necessary for recording the result corresponding to each temperature). So, the effect of the polarization and/or the space charge on the present data could be neglected.

2.3. Thermal expansion, molar volume and T_g

Thermal expansion measurements were carried out using a dial gauge with 0.01 mm sensitivity. The temperature of the specimen was measured with a NiCr–Ni thermocouple in contact with the surface. The same heating rate (5°C min^{-1}) to just above the softening point was used for all the measurements. The average thermal expansion coefficient was determined over the temperature range which is below T_g in all glasses. The accuracy of the measured value of the thermal expansion coefficient was found to be within $\pm 2\%$.

A small sample of the glass was placed in the differential scanning calorimeter to determine the glass transformation temperature T_g .

The molar volume V_m is defined as the mean molecular weight m of the glass divided by its density D :

$$V_m = m/D.$$

To determine the molar volume of glasses, density measurements were carried out at room temperature (using the standard Archimedes method) with xylene as the immersion fluid. Three samples of each glass were measured. The random error in these measurements was $\pm 0.01 \text{ g cm}^{-3}$.

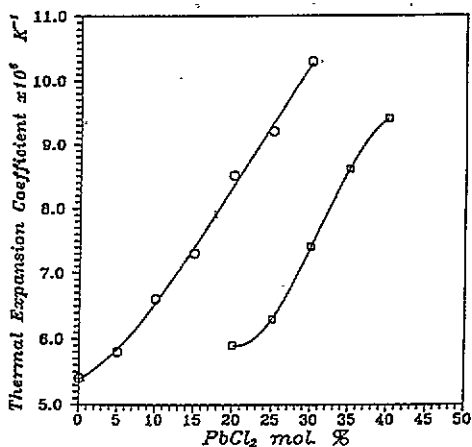


Figure 1. Effect of PbCl₂ content on the thermal expansion coefficients of PbCl₂-PbO-B₂O₃-P₂O₅ glasses (O) and for the lead chloroborate glasses (□) [4].

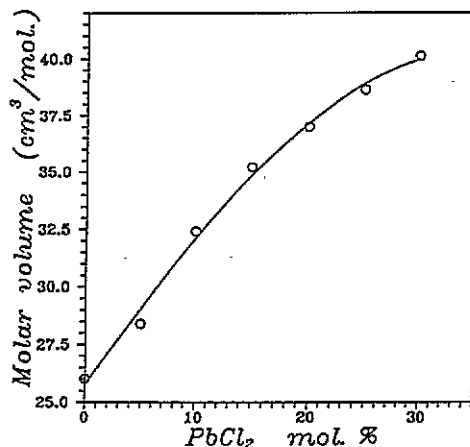


Figure 2. Change in molar volume of the glasses studied on PbCl₂ content.

3. Results

The dependence of the average thermal expansion coefficient on the glass composition is presented in figure 1 as open circles. It is found that the thermal expansion coefficient increases as the amount of PbCl₂ increased. The thermal expansion coefficient for the previously studied PbCl₂-PbO-B₂O₃ is represented in figure 1 as open squares [4]. The effect of substitution of PbO by PbCl₂ on the molar volume of the studied glasses is given in figure 2. The molar volume increases as PbCl₂ replaces PbO. The glass transformation temperature is found to decrease with the increase in the amount of PbCl₂; this is presented in figure 3.

Figures 4 and 5 show the changes in conductivity and the activation energy for conduction of the glasses studied in the system PbCl₂-PbO-B₂O₃-P₂O₅ as a function of PbCl₂ content. The conductivity increases while the activation energy E decreases with increase in PbCl₂ concentration. The experimental error in determining the activation energy for conduction is estimated to be less than 0.02 eV, whereas the relative error of conductivity is about $\pm 5\%$.

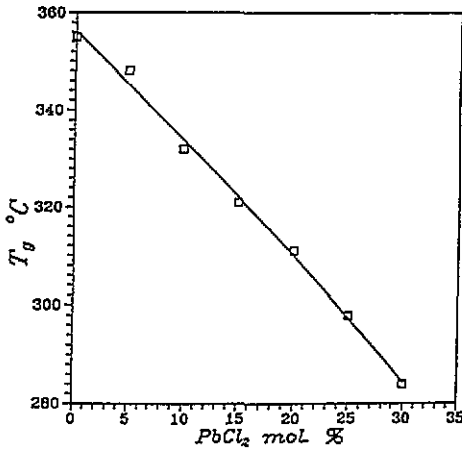


Figure 3. Effect of glass composition on the glass transformation temperature.

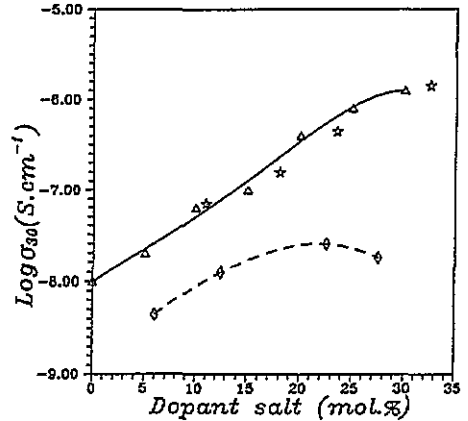


Figure 4. Variation in room-temperature conductivity with halide salt content (PbCl_2 (present study)) (Δ) and LiBr [1] (open star) and for borophosphate glasses containing LiF [1] (\diamond).

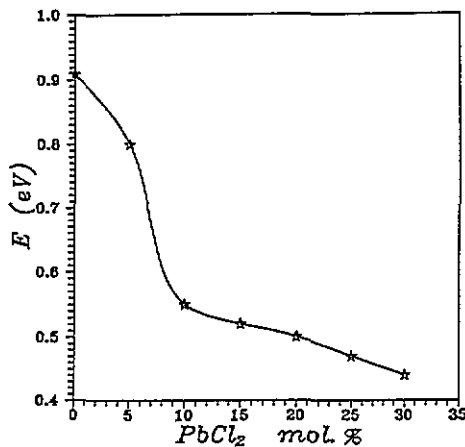


Figure 5. Change in the activation energy E for conduction with PbCl_2 content.

4. Discussion

Glass, in common with other substances, expands with any increase in temperature [12, 13]. On the other hand, several studies [3–5, 12–14] have reported that the thermal expansion depends also on the glass composition, particularly on the nature of the added ions. Further, the thermal expansion is mainly governed by the bond strength and nature of this bond [15]. In addition, the replacement of one ion with another of larger size, i.e. lower bond strength (e.g. oxygen by chlorine as in the case of the present work) will increase the thermal expansion of the glassy network [3, 4, 16]. This is probably because the binding energy decreases with decreasing field strength, i.e. increases the size of the added atoms [17]. Also, the nature of the network structure may affect the thermal expansion of the glass.

As an example, on comparison of the open circles and open squares in figure 1, it can be observed that the thermal expansion coefficient of the mixed glass formers (present work) is higher than that of a single glass former [4]. Another important factor that affects the thermal expansion of the glass is decreasing the glass transformation temperature T_g since, in most known cases, it is the generally accepted rule that the thermal expansion increases when the softening point and transformation temperature decreased [18].

In the light of the above criteria, one can expect that both the thermal expansion and the molar volume of the glasses studied here increase on the replacement of PbO by PbCl₂, while T_g decreases. This is because the Cl⁻ ion is larger than the oxygen atom, (Cl, 0.183 nm; O, 0.132 nm). figures 1, 2 and 3 represent the dependence of the thermal expansion coefficient, molar volume and glass transition temperature T_g , respectively, on PbCl₂ content. Substitution of PbCl₂ for PbO means exchange of one bridging oxygen atom by two chlorine ions; increasing the latter in the glassy matrix should expand the network. Consequently an open, less rigid or looser structure can be formed upon Cl⁻ addition which favours expansion of the network (see figure 1). The increase in molar volume (figure 2) and decrease in T_g (figure 3) with increasing PbCl₂ content support the present results of the thermal expansion, indicating that the structure is opened up, weakened and expanded.

The expansion of the glass network may affect the electrical behaviour of the present borophosphate glasses. This effect appears in the enhancement of the ionic conductivity. The enhancement of σ in the present borophosphate glasses containing PbCl₂ is comparable with borophosphate glasses containing LiBr [1], (figure 4, open triangles and stars). The value of conductivity in both systems increased by about two orders of magnitude upon addition of 30 mol% PbCl₂ from the dopant salt (PbCl₂ or LiBr), while the conductivity of borophosphate glasses which contain LiF is found to be lower than that of glasses containing PbCl₂ and LiBr (see figure 4). Such comparison between the conductivities of the above systems may be considered to be important in elucidating the role of different halide ions in enhancing the electrical behaviour in borophosphate glasses.

There are some models which are considered to be important for interpretation of fast ion conduction especially in halide-containing glasses [3,4,19,20]. In our previous work [3], we have summarized and taken into consideration the models which are pertinent to our work. On the basis of the present elastic data (discussed above), the open network model [21] is considered to be the more acceptable of those proposed to discuss the enhancement of ionic conductivity when doping the glasses with PbCl₂. This model shows that the network is expanded by the halide salt, keeping its connectivity but containing large holes due to the expansion. The migration of the charge-carrying species, e.g. Pb²⁺ or Li⁺ or Ag⁺ [3,22,23], is then thought to occur in preferential pathways of low activation energy made up by the halogen ions. The open network model demonstrates also that the dopant salt does not participate in the network formation, i.e. there no possibility of the formation of clusters from the dopant salt [24,25].

In the PbCl₂-PbO-B₂O₃-P₂O₅ glasses studied, B₂O₃ can enter the structure by forming three types of unit [2,26], as shown in figure 6. The negative charge of the BO₄⁻ units is compensated in figure 6(a) by the coupled positively charged PO₄ tetrahedron, while in figure 6(b) and 6(c) it is compensated by the Pb²⁺ ion. The formation of such units may be useful in explaining the present results.

The substitution of PbCl₂ for PbO can affect the concentration of the above-formed units in the glass matrix, e.g. increasing lead as the charge carrier and decreasing its concentration as a network former. This is because there is no extra added oxygen atoms during this substitution. Furthermore, increasing the PbCl₂ content causes the structure to become progressively crowded with Cl⁻ ions that play the role of weakening and expanding the

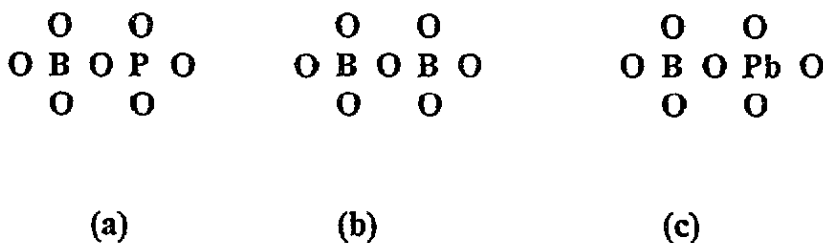


Figure 6. Three types of unit that B_2O_3 can form in $PbCl_2$ - PbO - B_2O_3 - P_2O_5 glasses.

network. Consequently, the mobility of Pb^{2+} as the charge-carrying species increases. Then the overall effects of $PbCl_2$ substitution for PbO appear to increase not only the number of Pb^{2+} as charge carriers but also its mobility. This may be mainly due to the reduction in the cross-linking density of the network. Therefore, the conductivity is increased and enhanced with $PbCl_2$; this can be seen in figure 4.

The activation energy E associated with $PbCl_2$ substitution is decreased. The addition of $PbCl_2$ gives evidence that the B-O network is expanded by Cl^- ions and contains large holes that allow for chlorine accommodation. Then, the structure is weakened and this is evident in the production of easily conducting pathways for Pb^{2+} cations. The migration of Pb^{2+} is thus thought to occur in this preferential pathway of low activation energy made up by Cl^- ions. Therefore, the activation energy associated with jumping Pb^{2+} cations will be decreased. This can be observed from figure 5. The decrease in E with increasing $PbCl_2$ content confirms that the jumps of Pb^{2+} cations in the vicinity of Cl^- ions are relatively easy. However, increasing the additional migration pathways is considered to be the dominant factor affecting not only the increment in conductivity but also the decrease in activation energy for Pb^{2+} cations. In detail, the activation energy drops significantly for low dopant content (up to 10 mol%) and then decreases almost linearly in the range 10–30 mol%. The decrease in E with low $PbCl_2$ content is probably due not only to the increase in both the mobility and the concentration of Pb^{2+} as charge carriers but also mainly to the decrease in the number of PbO_4 pyramids formed. The compactness of the glass structure decreased as the number of PbO_4 pyramids decreased [27]. Hence the ionic charge carriers are allowed to be transported more easily, which leads to a significant decrease in E . The linear decrease in E in the range 10–30 mol% $PbCl_2$ is considered to be mainly due to the subsequent expansion of the glassy network by Cl^- ions.

5. Conclusion

The decreasing trend of T_g and the increase in both the thermal expansion coefficient and the molar volume upon replacing PbO by $PbCl_2$ can be explained not only by a reduction in the degree of polymerization but also by the more opened, weakened and expanded network which results when the Cl^- ion replaces the O^{2-} ion. The expanded and opened network structures of the present borophosphate glasses seem to be the main reason for the large enhancement of the ionic conduction. Therefore, the open network model was proposed to explain the enhanced conductivity and is considered to be the more acceptable model for explaining the results of the present study.

The conductivity of borophosphate glasses containing $PbCl_2$ or $LiBr$ is higher than those of glasses containing LiF .

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