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Electrical and elastic properties of binary lead chloroborate glasses

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Abstract. Various comparative experiments on $x\text{PbCl}_2-(100-x)\text{B}_2\text{O}_3$ ($20 \leq x \leq 45$ mol%) glasses reveal that the PbCl_2 does not enter the B–O network, but is inserted into interstices or voids in the glassy matrix. However, the network becomes systematically weakened and expanded with increasing PbCl_2 concentration; this is observed as a decrease in T_g , and an increase of both the molar volume and thermal expansion coefficient.

The electrical conductivity measurements of these glasses demonstrated a marked enhancement in the ionic conductivity (σ). The maximum enhancement in σ is by eight orders of magnitude as PbCl_2 replaces B_2O_3 (45 mol%). The drastic increase in σ leads us to suggest that the Cl^- ions form additional migration pathways for Pb^{2+} ions, which are important for the conduction mechanisms. In addition, the activation energy associated with jumping Pb^{2+} ions decreases with increasing PbCl_2 content; this indicates that jumps of the Pb^{2+} ions in the vicinity of the Cl^- ions are relatively easy.

1. Introduction

Borate glasses containing alkali and/or halogen ions have attracted much attention because of their higher ionic conductivity [1–3]. This property combined with the ease of preparation of such glasses makes them interesting for technological applications; they may serve as the solid electrolyte in a wide variety of electrical devices. However, fast ion conducting glasses have been found [2–4]; amorphization of glass formation has been reported to be very useful for achieving higher conductivities. Besides the feature of the higher conductivity of glasses, fast ion conducting glasses have a higher potential for use as solid electrolytes.

In order to improve the conductivity of glasses, several authors proposed doping by lithium halides LiX [5–8] or lead halides PbX [9–12] ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$). In a previous work [13] we have already discussed the enhancement of conductivity by substitution of PbO by PbCl_2 in the ternary lead chloroborate glass system.

The present study completes the previous work, to shed more light on the role of the Cl^- ion in binary lead chloroborate glasses. To conclude this introduction we must note that it is of both academic and practical importance to know which ionic species (Cl^- or Pb^{2+}) is most responsible for an observed conductivity.

2. Experimental procedure

2.1. Glasses

The compositions of the glasses prepared were in the binary system $x\text{PbCl}_2-(100-x)\text{B}_2\text{O}_3$ where the PbCl_2 content was between 20 and 45 mol% in steps of 5 mol%. The raw

materials used, PbCl_2 and B_2O_3 as orthoboric acid (H_3BO_3), were of pure analytical grade. It is noticed that a considerable vapour loss (Cl_2) occurs during the melting process. To minimize such loss, the samples were made by firstly melting the desired amount of H_3BO_3 using porcelain crucibles in an electric furnace at 1000°C for complete delivery of water (from H_3BO_3). Then PbCl_2 was added to the melt and the melting process was continued for 15 min in a covered crucible. The melt samples were poured into stainless steel in the form of discs of diameter 2 cm and thickness 0.5 cm. The samples were therefore annealed at 300°C and allowed to cool normally to room temperature.

2.2. Conductivity

DC electrical conductivity measurements were carried out using samples with 0.2–0.3 cm thickness. The parallel surfaces of the samples were coated with graphite. The coated area has 0.5 cm radius. The resistance was measured using an insulator tester type TM 14 (Level Electronics Ltd, UK) with a range of 10^3 – $10^{13} \Omega$. As a rule, three samples of each glass were used to measure the resistance.

The polarization and space charge effects on the results have been minimized by using electrodes with perfectly flat interfaces and a guard ring. In addition to this the applied DC voltage (10 V) on the sample was only applied for a very short time (the time necessary to record the result corresponding to each temperature), so neither the polarization nor the space charge has any effect at all on the present data.

Over a temperature range from about 423 K to 653 K, the measured conductivity obeyed the Arrhenius equation

$$\sigma = \sigma_0 \exp(-E/RT) \quad (1)$$

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.

2.3. T_g , thermal expansion and molar volume

Thermal expansion coefficients were determined using a thermal-mechanical analyser (TMA). Samples ranging from 7 to 13 mm in length were heated at 6 K min^{-1} to just above the softening point. The average thermal expansion coefficient was determined over the temperature range 313–433 K, which is below T_g in all glasses. A small sample of the glass was placed in the differential scanning calorimeter (DSC) 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):

$$V_m = M/D. \quad (2)$$

To determine the molar volume of glass, density measurements were carried out at room temperature, using a standard Archimedes method with xylene as immersion fluid. Three samples of each glass were taken to measure the density. Density values are precise to $\pm 0.01 \text{ g cm}^{-3}$.

3. Ion transport models

It is important in this study to review, in a qualitative manner, the theories or models proposed for discussing the conduction process and the ion transport mechanism in glasses. These models include weak/strong electrolyte [14], random site model [15], diffusion path or dopant salt model [16], percolation theory [17, 18] and open network model [4]. Each model contains some specific picture of the microscopic structure of glasses ranging from a perfect random matrix to a clustering formation of AgI embedded in the host glass network structure.

The weak electrolyte model considers that the change in conductivity with composition is controlled by the change in the carrier concentration, while the random site model considers that the change in conductivity is mainly controlled by the change in the mobility. Replacement of B_2O_3 with $PbCl_2$ in the studied glasses is considered to increase both the number of the charge carriers and also its mobility. This in turn implies that the above two models are not applicable to these glasses.

The diffusion path model is proposed to explain the high ionic conduction of AgI doped oxide glasses. Recent studies [19, 20] confirm the presence of small AgI clusters when the glass is doped with AgI. It has suggested that such AgI microclusters form diffusion pathways for the Ag^+ ion and therefore are important for the conduction mechanism.

The percolation approach for hopping conduction in a disordered system is based on the assumption that electron motion between localized states can be treated as a problem of current flow through a network of impedance Z that connects the different lattice sites. The conductivity of the material is then characterized by the critical impedance, which interconnects small clusters of low impedance through the percolation paths in the samples.

The open network model is proposed to discuss the enhancement of ionic conductivity when doping borate and/or phosphate glasses with halide salt, e.g. LiX, AgX [19, 21], and PbX ($X = F, Cl, Br$) [13, 22, 23]. This model shows that the network is weakened and expanded by doping with halide salt, keeping its connectivity, but containing large holes due to the expansion. The migration of the charge carrying species, e.g. Li^+ or Pb^{2+} or Ag^+ , is then thought to occur in preferential pathways of low activation energy made up by the halogen ions. This phenomenon has been attributed to the expansion of the network upon introduction of the dopant salt. However, the open network model evidences that the dopant salt does not participate in the network formation, i.e. there is no possibility of the formation of any cluster from the dopant salt [7, 24].

On the basis of the marked decrease in activation energy, the increase of both thermal expansion coefficient and molar volume and the decreasing T_g with $PbCl_2$ concentration, our elastic and transport data lent support to the open network model rather than other models (e.g. dopant salt and percolation models), which are applicable in the cases of glasses that contain microclusters with the dopant salt. Consequently the conduction processes in our glasses are discussed in terms of the open network model.

4. Results

The conductivity data for all glasses exhibit Arrhenius behaviour. The effect of glass composition ($PbCl_2$ content) on the electrical conductivity σ_{473} (at 473 K) for the studied glasses is represented in figure 1(a). The conductivity slightly increases with $PbCl_2$ content (up to 30 mol%), then rapidly increases with increasing $PbCl_2$ concentration (> 30 mol%). The associated activation energy for conduction (E) decreases as $PbCl_2$ content increased

(see figure 1 inset). The activation energy at 20 mol% PbCl_2 is slightly lower than that at 25 mol%. The difference is not so much (~ 0.03 eV). The experimental data along with the arbitrary solid line (figure 1 inset) show maximum value at 25 mol% of PbCl_2 , which is absolutely not the case. One could say that within the experimental errors, the activation energies at 20 and 25 mol% PbCl_2 are almost the same. The glass transformation softening temperature and its dependence upon composition are shown in figure 2. The dependence of the average thermal expansion coefficient for the $\text{PbCl}_2\text{-B}_2\text{O}_3$ system on the glass composition is presented in figure 3. It is found that the thermal expansion coefficient increases significantly as the PbCl_2 increases. The effect of substitution of B_2O_3 by PbCl_2 on the molar volume for the present system is shown in figure 4. It is clear that the molar volume increases as PbCl_2 replaces B_2O_3 , which indicates that the network is almost expanded upon addition of PbCl_2 .

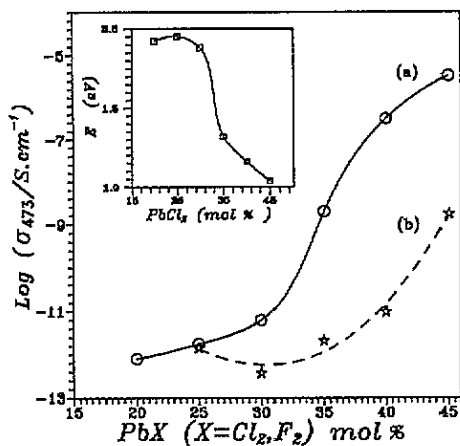


Figure 1. The change of electrical conductivity at 473 K with PbX ($X = \text{Cl}_2, \text{F}_2$) content for the studied lead chloroborate glass (plot a) and for lead fluoroborate glasses (plot b) [10]. The inset shows the dependence of activation energy on PbCl_2 concentration. The lines were drawn as guides for the eyes.

5. Discussion

In order to understand the results of the present study, it is necessary to give a brief review of discussion on the structure of vitreous B_2O_3 and modified B_2O_3 .

The structure of vitreous boron oxide (B_2O_3) has been a much debated issue for many years [25]. Although it is generally accepted that the molecular building block of vitreous B_2O_3 is the planar BO_3 groups the manner in which the BO_3 triangles are connected is much discussed [26]. Some experimental observations of B_2O_3 give strong indication of well defined molecular entities in the structure suggested to be boroxol rings (B_3O_6) [27, 28].

Considerable structural differences caused by introduction of any type of modifier, e.g., the adding of network modifier M_2O to B_2O_3 ($M = \text{alkali}$ or $\text{alkaline earth ion}$) results in the change of coordination number of B from three to four. Various complicated structural units containing BO_3 and BO_4 groups are then formed, such as di-, tri-, and tetraborate [24], without changing the short-range order (the B-O distance remains constant). Another

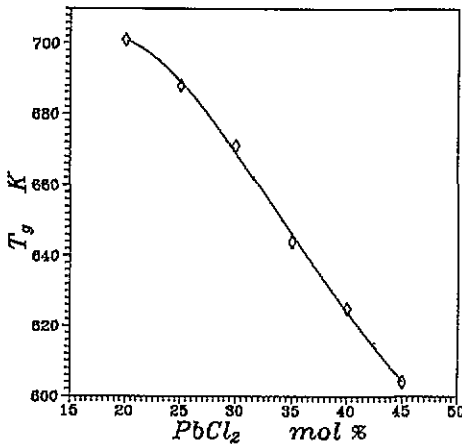


Figure 2. The effect of glass composition on the glass transformation temperature (T_g) of lead chloroborate glasses. The line was drawn as a guide for the eyes.

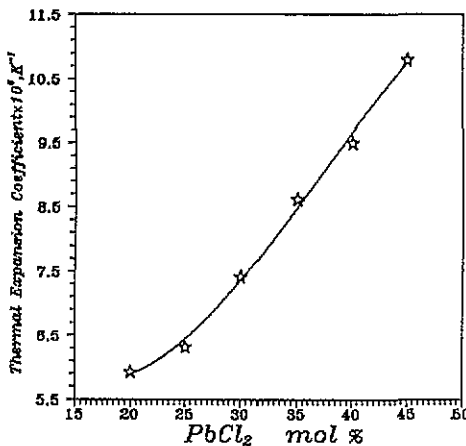


Figure 3. The dependence of the thermal expansion coefficient on composition for lead chloroborate glasses. The line was drawn as a guide for the eyes.

type of modifier such as Ag_2O and almost of all the halogen containing glasses [5–12], causes expansion of the network. The initial B_2O_3 network expands by about 20% for a modification by $2Ag_2O$ [24]. Also, a random introduction of halogen ions (Cl, Br, I) into interstices of the borate network results in the disorder of BO_3 groups. The overall disordering in the halogen doped glass is mainly due to the expansion of the B–O network [9–13].

The results for the present glass system are explained on the basis of modification of B_2O_3 used (by the expansion of the network) upon introduction of $PbCl_2$.

The presence of $PbCl_2$ in borate glasses has a strong influence on both the ionic conductivity (σ) and the activation energy for conduction (E). As seen from figure 1, the increasing value of σ and decreasing value of E with increasing $PbCl_2$ content can be explained under the following aspects.

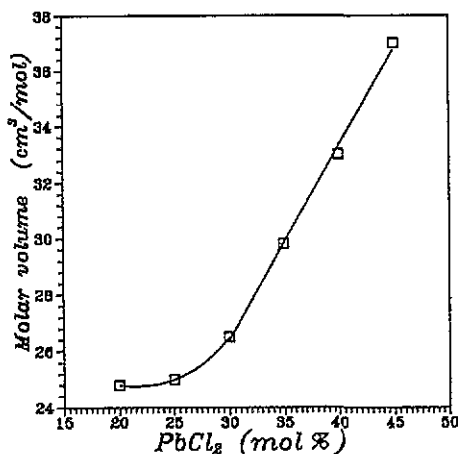


Figure 4. The effect of glass composition on the molar volume. The line was drawn as a guide for the eyes.

In such a glass system, it is by no means obvious whether the Pb^{2+} or Cl^- are the primary carriers. This is of particular importance in the case of the $\text{PbCl}_2\text{-B}_2\text{O}_3$ glass system in which it was initially supposed that the Pb^{2+} ion was the mobile species. In $\text{PbCl}_2\text{-B}_2\text{O}_3$ glasses, there are no extra O ions added during the replacement of B_2O_3 by PbCl_2 , so it is thought that Pb^{2+} ions do not participate in the network formation. Consequently, most of the added Pb^{2+} ions are assumed to enter the glass network as charge carriers. The concentration of the modifier Pb^{2+} ions should increase with increasing PbCl_2 , which should lead to an increase in σ . In these glasses, the enhancement of the electrical properties is considered to be due not only to increasing Pb^{2+} concentration but also mainly to the presence of Cl^- ions, since Cl^- have a good tendency to expand the B-O network, resulting in a more open structure and consequently increasing the mobility of Pb^{2+} ions.

Glasses with low concentration of PbCl_2 (< 30 mol%) consist mainly of BO_3 units, which have a relatively open structure. The large added Cl^- ions can easily be accommodated interstitially in the network. In such glasses an important contribution to the excess of conductivity probably originates from the increased number of charge carriers only. The activation energy in this composition range is really changed very little and can be considered constant; this may be due to the tight bonding of Pb to the network O (Pb-O bond). However, further addition of PbCl_2 (> 30 mol%) at the expense of B_2O_3 gives us evidence that the B-O network is expanded by PbCl_2 , keeps its connectivity, but contains large holes, which allow for Cl^- accommodation. The expanding of the B-O network and consequently the progressive weakening of the structure is evident in the large increase in both molar volume and thermal expansion coefficients and also in a considerable decrease of the glass transition temperature, T_g , which changes from 708 to 504 K. In such a case we propose that the large Cl^- ions present in these glasses can produce easily conducting pathways, which can be considered to be due to the expansion of the glassy network. The migration of Pb cations is then thought to occur in these preferential pathways of low activation energies made up by Cl^- ions. In line with this proposition, the activation energy associated with the jumping Pb^{2+} ions will be lower than that in the corresponding glasses containing small amounts of PbCl_2 . This can indeed be observed from figure 1 (inset). Then the decrease of E with increasing PbCl_2 content confirms our assumption and indicates that the jumps of Pb^{2+} ions in the vicinity of the Cl^- ions are relatively easy. In this composition

range ($\text{PbCl}_2 > 30$ mol%), the drastic increase of σ can be considered not only to be due to increasing the numbers of Pb^{2+} ions during PbCl_2 substitution for B_2O_3 but also to be mainly due to the increase of their mobilities. Increasing the additional pathways is considered to be the dominant factor affecting the increase of the mobility of Pb^{2+} ions. In general, as clearly seen from our conductivity measurements and in comparison with previously reported observations [10] for the binary $\text{PbF}_2\text{-B}_2\text{O}_3$ glass system (figure 1(b)), the corresponding value of σ for the present work is much greater than that for the lead fluoroborate glasses.

Addition of PbCl_2 and halogen ions [9–11] to the borate network not only improves the electrical properties but also softens the elastic properties. The elastic data of the present study, including T_g measurements, thermal expansion coefficient and density, together with reported Raman [29] and NMR [30] observations of the unchanged local structure of the B–O network, suggest that it is the intermediate-range ordering structure that is affected by the introduction of halogens.

Measurements of T_g , thermal expansion coefficients, and molar volume do indeed reveal remarkable changes with PbCl_2 content (see figures 2–4). As is proposed above, the PbCl_2 does not enter the B–O network, but is inserted into interstices or voids in the glassy matrix. However, the network becomes systematically weakened and expanded (a more open network is formed) upon increasing the concentration of PbCl_2 , which is observed as a decrease in T_g (see figure 2) and an increase of both molar volume and thermal expansion coefficient (figures 3 and 4). The more open network is considered more favourable for Pb^{2+} ion migration, which is consistent with conductivity observations for increasing PbCl_2 .

6. Conclusion

Measurements of the elastic properties revealed that the glassy network becomes systematically weakened and expanded upon increasing PbCl_2 concentration. The expanded and open network structure of the present glass system seems to be the main reason for the large enhancement of the ionic conduction. The presence of Cl^- ions in these glasses can produce easily conducting pathways, which leads to an increase of the mobility of charge carriers (Pb^{2+} ions). The glasses containing high PbCl_2 content appear to be much better in terms of fast ion conducting than lead fluoroborate glasses.

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