

Mixed cation effect in silver borate ion conducting glass

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The partial replacement of silver iodide in ion conducting silver borate glass ($\text{AgI-Ag}_2\text{O-B}_2\text{O}_3$) by sodium iodide has been carried out and its effect on the properties of the glass system has been studied. Conductivity studies show that with the simultaneous presence of two cations (Ag^+ and Na^+), mixed cation effect is observed. There is also lower solubility of AgI which crystallised out. The results obtained have been explained by data from X-ray diffraction, FTIR spectroscopy and conductivity vs. temperature studies. © 1999 Kluwer Academic Publishers

1. Introduction

Silver ion conducting glasses with high value of ionic conductivity are important materials due to their possible applications in solid state batteries and electrochromic display devices [1–3]. Here we study the $\text{AgI-Ag}_2\text{O-B}_2\text{O}_3$ system. Pure B_2O_3 glass has been reported to contain BO_3 units and the addition of glass modifying oxide (Ag_2O) has been reported to change the coordination of boron from 3 to 4 with the help of oxygen provided by Ag_2O and as a result BO_4 units start forming in the glass network for low modifier content. At higher modifier content, the formation of BO_3 units with non-bridging oxygen atoms opens the borate units and consequently the degree of linkage of the network is decreased [4, 5]. Raman measurements on $\text{AgI-Ag}_2\text{O-B}_2\text{O}_3$ glass system has shown that the glass matrix is not strongly modified by the addition of doping salt (AgI) [6]. The anions are generally localised leaving the small Ag^+ cation as the only mobile species. The larger the anion, the stronger is its interaction with the host network [7]. EXAFS studies have shown that alkali metal ions have a strong preference to reside in the vicinity of negatively charged non-bridging oxygens [8]. However if two mixed-alkali ions are present, then the smaller ions occupy the lowest energy positions close to non-bridging oxygens and force the large ions to reside in energetically less favorable positions [9].

The effect of the presence of two mixed glass formers (mixed former effect) [10, 11] and mixed alkalis (mixed alkali effect) [12, 13] has been studied for different glass systems. Apart from mixed alkali system, the effect of the presence of two different cations has been studied for a system with both Ag^+ and Cu^+ [14]. In this case, CuI has been said to change to AgI by an exchange reaction. This system also exemplifies the effect where two cations belonging to the same group in the periodic table like the mixed alkali case. The

present study has been undertaken with a view to see mixed cation-effect in ion conducting glasses where the cations belong to different subgroups in the periodic table i.e. Na^+ (Group IA) and Ag^+ (Group IB).

In the present study, glass system having composition $x\text{NaI} \cdot (60-x)\text{AgI} \cdot 20\text{Ag}_2\text{O} \cdot 20\text{B}_2\text{O}_3$ with $0 \leq x \leq 20$ has been chosen to study the effect of partial replacement of AgI by NaI by keeping the amount of glass former (B_2O_3) and glass modifier (Ag_2O) as constant. The various changes in the properties of the glass due to the presence of mixed cations have been studied by using X-ray diffraction, FTIR spectroscopy and transference number measurements.

2. Experimental

Glass samples having composition $x\text{NaI} \cdot (60-x)\text{AgI} \cdot 20\text{Ag}_2\text{O} \cdot 20\text{B}_2\text{O}_3$ with $x = 0-20$, were prepared by the melting and quenching method [15]. Stoichiometric quantities of the starting materials taken as per above formula and mixed thoroughly to get a uniform mixture. The powder was taken in a crucible and heated in a furnace till a uniform melt is obtained, which was then quenched between two air-cooled copper blocks. The samples so prepared were grinded to a fine powder which was then used for different experimental studies.

The ionic transference number measurements were made by using Wagner's polarisation method [16]. A constant dc potential ~ 0.5 V was applied across the cell $\text{C}^+|\text{glass}|\text{Ag}^-$ and current was monitored as a function of time till the saturation is reached. Knowing the initial values of current at the start ($t = 0$) i.e., i_T and current on reaching saturation which is electronic current i.e. i_{el} , the ionic transference number (t_{ion}) can be calculated by using the expression.

$$t_{ion} = \frac{i_T - i_{el}}{i_T}$$

The electrical conductivity of the glass samples was measured by ac impedance spectroscopy method by using HP 4284 A Precision LCR Meter operating in the 20 Hz–1 MHz frequency range. Glass sample taken in the pellet form was placed between two gold disc electrodes which was placed in the sample holder, where sample was pressed by spring pressure. The impedance/admittance plots were drawn for each sample and then conductivity was calculated by using the relation:

$$\sigma = \frac{G\ell}{A}$$

where G is the conductance to be determined from admittance/impedance plot, ℓ is the thickness of the sample, measured by using micrometer and A is the area of cross section of the sample.

For studying the variation of conductivity with temperature, the sample holder containing the sample was placed in a temperature controlled furnace and measurements were made in the 300–500 K temperature range in steps of 20 K.

FTIR spectra for all the glass samples was recorded by KBr powder method in the 200–4000 cm^{-1} range by using Shimadzu 8101 FTIR spectrometer. All the spectra were recorded at room temperature under identical conditions.

X-ray diffraction studies on all the samples were carried out by using computer-controlled X-ray powder diffractometer (Jeol Fdx 8030). Powder pattern of all samples alongwith that of AgI used in the glass preparation was recorded under similar conditions.

3. Results and discussion

Ionic transference number measurements made on all glass samples by Wagner's polarisation method [16] gave a value near unity which shows that these glasses are principally ionic conductors.

Fig. 1 shows the variation of room temperature conductivity with composition (x). The conductivity falls with an initial substitution of NaI in place of AgI, then again increases and shows a peak at around $x = 8$ and then decreases with further increase in the value of x . With the increase in the value of x from 0, some of the AgI is being replaced by NaI which results in a decrease in the concentration of AgI and hence the conductivity falls [17]. However with further increase in the value of x , although the concentration of AgI falls, but the added NaI can significantly supply the ionic charge carrier of Na^+ apart from Ag^+ coming from AgI. As a result, a mixed cation effect [18] is observed which results in a conductivity maxima. At higher values of x , the solubility of AgI in the glass may decrease and as a result some of AgI may get crystallised which will result in a decrease in the conductivity values. It may be noted that our conductivity values are the total contributions due to Na^+ and Ag^+ . It would be interesting to separate out the contributions of Na^+ and Ag^+ separately. This, in principle, can be done by combined ac-dc techniques [19, 20]. However, we have not attempted such a study in the present work.

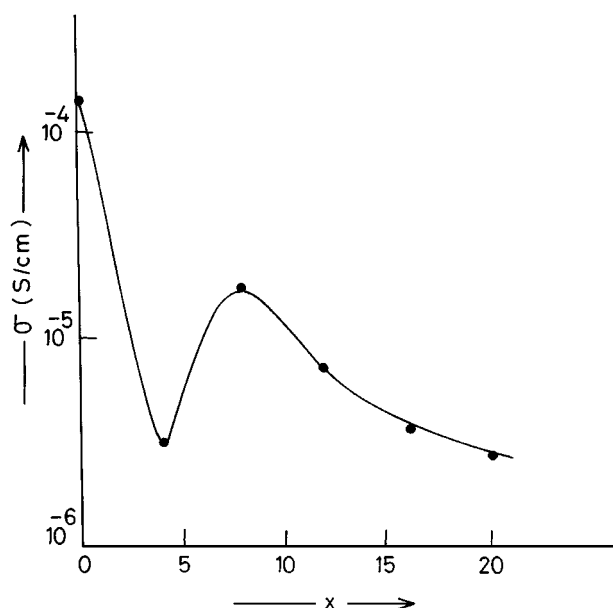


Figure 1 Variation of conductivity of $x\text{Na}_2\text{O} \cdot (20-x)\text{Ag}_2\text{O} \cdot 20\text{B}_2\text{O}_3 \cdot 60\text{AgI}$ with composition (x).

Fig. 2 shows the variation of $\log \sigma$ vs. reciprocal temperature ($1000/T$) for different values of x . For $x = 0$, a straight line behaviour is observed between $\log \sigma$ vs. $1000/T$ which suggests an Arrhenius law behaviour.

$$\sigma = A \exp(-E_a/kT)$$

where E_a is the activation energy and A is the pre exponential factor.

As the value of x increases i.e. some AgI is being replaced by NaI, a change in the slope is observed in $\log \sigma$ vs. $1000/T$ at temperature of 147 °C which corresponds to the $\beta \rightarrow \alpha$ phase transition temperature of AgI [21]. The extent of increase in conductivity at this in our glass system is more for higher values of x . This is because of the fact that as x increases, the solubility of AgI in glass matrix decreases and some AgI as separate entity is present in the glass system. This has been confirmed by XRD measurements described in the next paragraph. For very high values of x , the $\log \sigma$ vs. $1000/T$ behaviour approaches that of polycrystalline AgI for which $\log \sigma$ vs. $1000/T$ results are also shown in Fig. 2.

Fig. 3 shows the X-ray diffraction powder pattern of glass samples with different values of x alongwith that of polycrystalline AgI which was used in the glass preparation. Fig. 3 shows that for small values of x , no sharp peaks are observed which suggest that glass formation has taken place. However, with an increase in the value of x , some peaks start appearing at 2θ values corresponding to that of AgI. These peaks become more and more pronounced with further increase in the value of x which suggests that more AgI is getting crystallised in the glass network. These results are also consistent with the results obtained from $\log \sigma$ vs. reciprocal temperature studies as given in Fig. 2.

The room temperature FTIR spectra indicated that, there is not much change in BO_3 or BO_4 related peaks (1200–1400 cm^{-1} and 900–1100 cm^{-1} respectively)

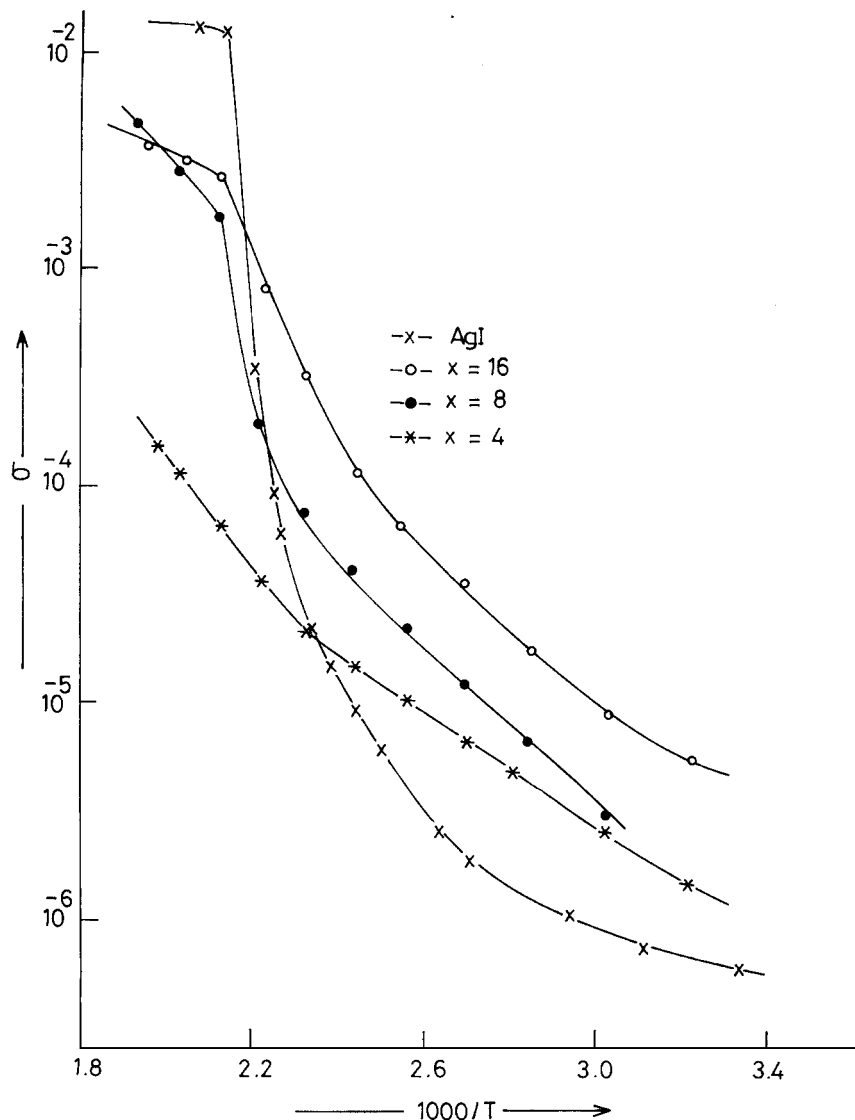


Figure 2 Variation of conductivity with reciprocal temperature ($1000/T$) for samples with $x = 4, 8, 16$ and AgI.

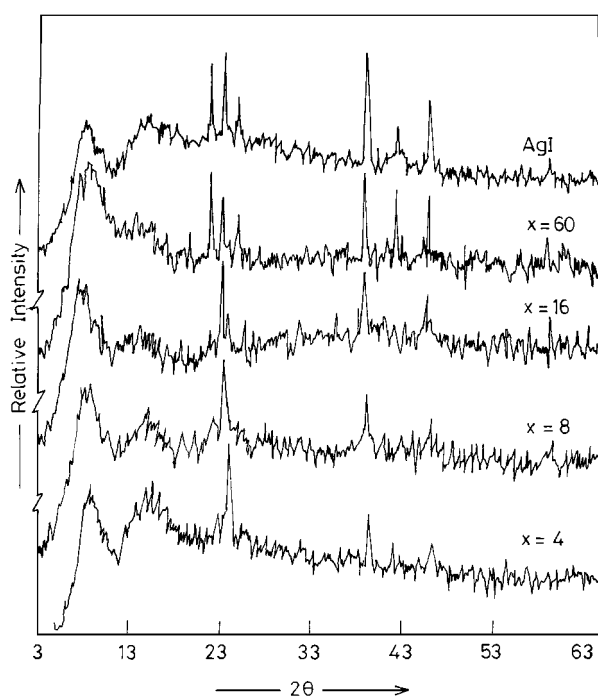


Figure 3 X-ray diffraction pattern of glass samples for values of $x = 4, 8, 16, 60$ and AgI.

which points out that the glass network does not change with NaI addition [6, 7]. This seems logical, since in the glass system under investigation only the amount of the doping salt is being varied by substituting it with NaI, but B/O ratio is being kept constant as the amount of glass forming oxide (B_2O_3) and glass modifying oxide (Ag_2O) is same in all the compositions. In spite of glass network structure remaining same, we had earlier seen (in XRD and $\log \sigma$ vs. $1000/T$ studies) the presence of undissolved AgI. This indicates that NaI is preferentially getting into the glass network leaving a part of AgI undissolved.

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