JOURNAL OF MATERIALS SCIENCE 30 (1995) 3457–3462

Experimental studies and space charge mechanism for the conductivity/mobility enhancement due to SnO_2 dispersion in Ag^+ ion conducting borate glass

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The enhancement in ionic conductivity of a Ag^+ ion conducting borate glass of molar % composition 55.5 AgI–22.25 Ag_2O–22.25 B_2O_3 is reported with the dispersion of SnO_2. X-ray diffraction (XRD), i.r. and optical microscopy reveals that the SnO_2 addition yields a dispersed phase material and not a new glass. The material is essentially a Ag^+ ion conducting ($AgI + Ag_2O + B_2O_3$) glass in which SnO_2 is dispersed. The direct measurement of mobility of the mobile ions reveals that the enhancement in conductivity is controlled by the enhancement in mobility. A space charge model based on the mechanism of adsorption–desorption of mobile ions near/at the interface in the space charge region creating a certain type of mobile ion concentration gradient is introduced to explain the results.

1. Introduction

Ion conducting glasses have recently acquired importance because of their possible use in solid state batteries, sensors, display devices etc. [1–5]. The most studied are those of Li^+ and Ag^+ ion conducting glasses. A large number of glass formers/modifiers/intermediates have been tried in order to prepare high conductive compositions. High conductivity has been attained in Ag–borate glasses [6–9]. In this paper we have investigated the possible enhancement in conductivity of $AgI + Ag_2O + B_2O_3$ glass on addition of SnO_2. The reasons for choosing SnO_2 are: (i) it may act as glass modifier and enhance the conductivity, (ii) it may not actually go into the glass structure, but provide a "dispersed phase" system leading to enhancement of conductivity. Most of the earlier studied dispersed phase systems consist of some poorly conducting ionic solid (first phase) + insulator (second phase) such as $AgI + Al_2O_3$, $LiI + Al_2O_3$ etc. [10–17]. In the present study the dispersion medium (first phase) is actually a good ionic conductor (glass) in which insulating SnO_2 is dispersed. Further, it has been reported in the literature that SnO_2 introduces porosity in ZnO sintered pellets [18]. The degree of porosity (and hence connectivity of grains) was found to be dependent upon sintering temperature. Therefore, SnO_2 seems promising to be explored for heterogeneous doping or to develop a dispersed phase system in which the conductivity enhancement may be achieved as a result of space charge and/or enhanced intergrain connectivity. Here we are reporting our studies on the conductivity enhancement of a Ag^+ ion conducting Ag–borate glass in which SnO_2 is either being (i) added during glass preparation itself or (ii) dispersed physically in already formed Ag^+ ion conducting glass. It is found that SnO_2 does not go into the glass matrix but remains as a separate phase. So the conductivity behaviours of samples prepared by either of the above two procedures are almost similar though the first procedure has an edge as far as conductivity is concerned. A suitable mechanism is suggested for the enhancement of conductivity which is principally due to the enhanced mobility (and not "n" as envisaged earlier in many other heterogeneously doped dispersed phase systems).

2. Experimental procedure

Chemicals used for preparing the samples were anhydrous B_2O_3, Ag_2O, AgI and SnO_2. A mixture of 55.5% AgI + 22.25% Ag_2O + 22.25% B_2O_3 was prepared by taking the respective amounts as 2.35, 0.93 and 0.28 g. To this mixture different amounts of SnO_2, namely 0.1 g, 0.2 g ..., 1 g were added.

To study the effect of different preparation methods on the conductivity of the dispersed phase systems, we have undertaken three methods for sample preparation:

(i) Pre-weighed chemicals were mixed in an agate mortar and transferred to a silica ampoule of ~ 5 ml volume and heated gradually up to ~ 950 °C and quenched into liquid nitrogen after keeping it at ~ 950 °C for ~ 5 h (hereafter referred to as preparatory method I)

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(ii) The glass AgI + Ag_2O + B_2O_3 was first prepared without adding SnO_2. This glass was well powdered and mixed with SnO_2 in an agate mortar until the mixture was homogenized. This physically mixed sample is used without any heat treatment (hereafter referred to as preparatory method II).
(iii) The sample as obtained from method (II) above is given the same heat treatment as for the first method (heated at ~ 950 °C for ~ 5 h and then quenched). This sample is hereafter referred to as preparatory method III.

The well powdered samples so prepared were used for further characterization. For electrical measurements pellets have been prepared with a 10^9 Pa pressure.

The X-ray diffraction (XRD) patterns on powdered samples were taken using an X-ray diffractometer (Philips Model PW 1710). The optical micrographs of sample surfaces were recorded using an optical microscope type Leitz Metallux 3.

The ionic transference number of the conducting ions t_i was determined by (i) Wagner's d.c. polarization technique [19] in which potentiostatic current across the cell configuration (+) graphite/electrolyte/silver (−) was measured as a function of time and the ionic transference number was estimated using the relation

$$t_i = (i_T - i_e)/i_T \qquad (1)$$

where i_T is the initial total current and i_e is the final residual current. (ii) By the e.m.f. method [20] using the cell configuration Ag/electrolyte/C + I_2 + electrolyte. The e.m.f. developed across the cell (E_0) is monitored and the Ag^+ ion transference number t_{Ag^+} is calculated using the equation

$$t_{Ag^+} = E_0/E_t$$

where E_t is the theoretical (thermodynamic) value of e.m.f. across the cell.

The transient ionic current (TIC) measurement technique has been used to evaluate the mobility of the mobile ion [21]. In this method, the sample is first polarized between graphite blocking electrodes using a fixed d.c. voltage. After stabilizing the polarization current, the polarity is reversed and the ionic current is monitored as a function of time. The mobility μ can then be calculated using the formula

$$\mu = d^2/\tau V \qquad (2)$$

where d is the thickness of the sample, V is the applied voltage and τ is the time at which the depolarization current peaks. The peaks are generally broad. The time τ corresponds to the average time for ions to cross from one electrode to the other and hence the above expression gives the average mobilities.

The d.c. electrical conductivity has been deduced from the complex impedance/admittance plots for different compositions, using a computer-controlled Schlumberger Solartron 1250 Frequency Response Analyzer coupled with Solartron (1286) Elctrochemical Interface between the frequency range 1 Hz to 65 kHz with a signal input of 20 mV. Vacuum coated silver was used as electrode.

The i.r. spectra of the samples in KBr pellets have been recorded using a Perkin-Elmer IR Spectrometer model 883.

3. Results and discussion

3.1. Structure and method of preparation

The XRD of AgI + Ag_2O + B_2O_3 glass obtained by quenching the homogeneous melt in liquid nitrogen is shown in Fig. 1(a). There are no sharp peaks and the XRD is typical of a glass.

The effect of adding SnO_2 to AgI + Ag_2O + B_2O_3 during preparation was interesting. No eutectic melting was observed even up to 950 °C although the AgI + Ag_2O + B_2O_3 mixture melts at ~ 600 °C. It was observed that at 400–500 °C the mixture shrunk and it appeared as if melting was going to occur but soon the mixture turned into a 'paste'. As the temperature was raised, the 'paste' started to swell. If the temperature was raised quickly then swelling was accompanied by excessive frothing and spilling of the material. Therefore, the temperature was raised slowly to 950 °C. This sample was quenched in liquid nitrogen. The "as-prepared" sample seen under optical microscopy shows porous regions (see Fig. 2) possibly as a consequence of the frothing occurring during preparation. Such porous structures have also been seen in ZnO sintered SnO_2 [18]. Thus it is expected that such samples will show more grain boundaries. The surface structure of pellets prepared by the material so obtained are shown in Fig. 3 for two different compositions of SnO_2. It is obvious that the higher the SnO_2 content, the higher are the grain boundary regions. XRD results are shown in Fig. 1 (b, c, d). Interestingly SnO_2 peaks appear and their intensity increases as SnO_2 content increases. This suggests that SnO_2 has not gone into the glass matrix and remains as a separate dispersed phase. To check this, a pure AgI + Ag_2O + B_2O_3 glass was prepared first and then SnO_2 was physically dispersed. This was given

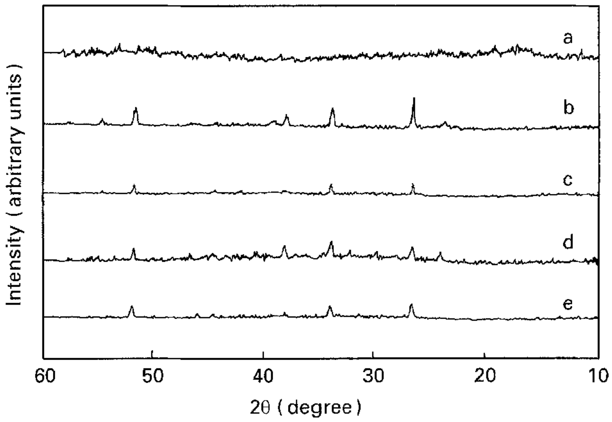

Figure 1 Powder X-ray diffraction patterns for (a) pure glass with molar composition 55.5% AgI–22.25% Ag_2O–22.25% B_2O_3; (b), (c) and (d) are respectively of glass/composite obtained by the addition of 1.0 g, 0.35 g and 0.2 g of SnO_2 to the 3.56 g of above mentioned glass composition during preparation (see preparatory method I in text), (e) for the thermally treated pure glass (3.56 g) + 0.3 g SnO_2 composite mixture (see preparatory method III in text).

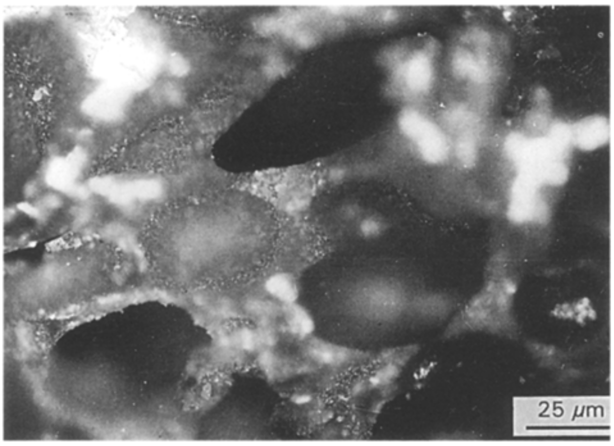

Figure 2 Optical micrograph on the surface of the as prepared sample of glass/composite with SnO_2 (See preparatory method I).

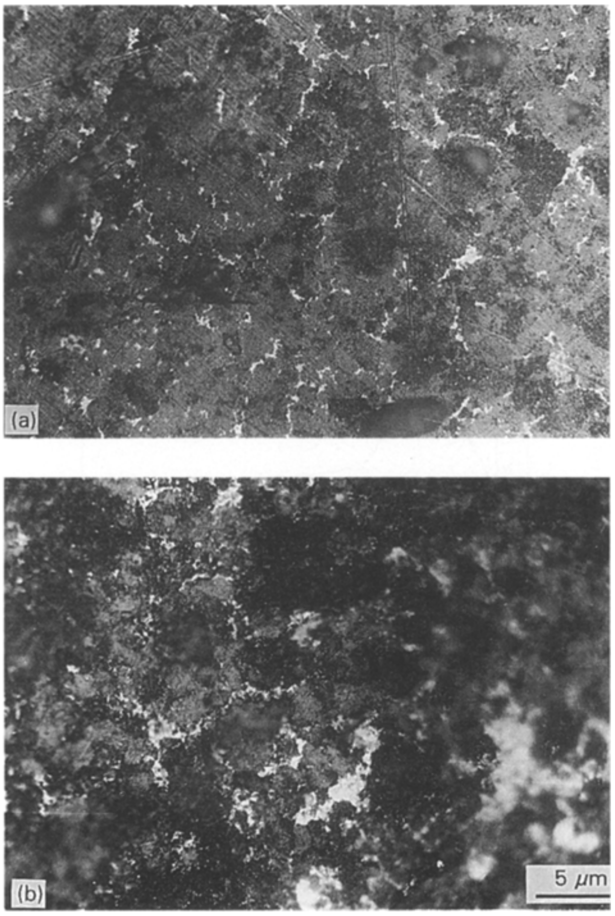

Figure 3 Optical micrograph of the surface of the pellets prepared by method I (see text); (a) and (b) are for sample with 0.25 g and 1.5 g of SnO_2 dispersion to the basic 3.56 g glass.

a thermal treatment as previously described. Again the XRD for this sample was taken (Fig. 1(e)). This also showed the separate SnO_2 phase in the sample.

The i.r. spectra of pure SnO_2, $AgI + Ag_2O + B_2O_3$ glass without SnO_2 and with different amounts of SnO_2 are shown in Fig. 4. It can be seen that SnO_2 characteristic peaks in the region 500–750 cm^{-1} are present and their intensity is higher for sample with higher SnO_2 content. The presence of many overlapping peaks in this region precludes us from finding out whether there is a shift in peak position or not.

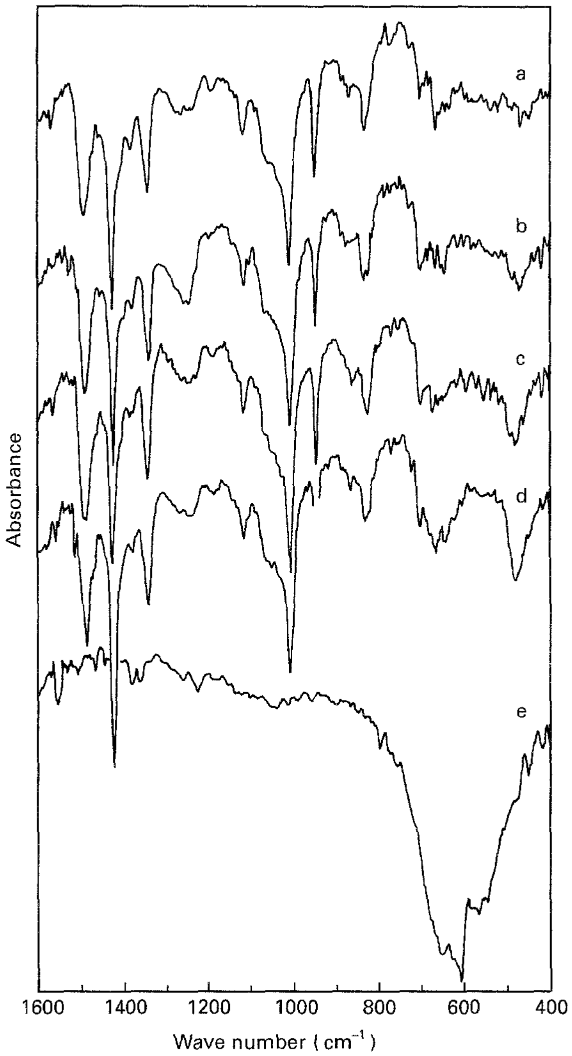

Figure 4 Room temperature i.r. spectra for (a) pure glass; (b), (c) and (d) glasses with 0.1, 0.2 and 0.4 g SnO_2, respectively, added to 3.56 g of its original composition, (e) for pure SnO_2.

Therefore, at best this result is indicative that SnO_2 remains as a separate phase but the real check comes from XRD as discussed earlier.

3.2. Conductivity and method of preparation

The three methods of preparing samples are as given in Section 2. The conductivity of samples obtained by these methods are shown in Fig. 5. The first method gives the highest conductivity for all the compositions. This is due to the uniform mixing obtained due to the frothing occurring during the heat treatment which allows the glass matrix to penetrate into the agglomerated SnO_2 particles leading to better mixing and the formation of intimate interface between dispersoid and the glassy matrix. Of course, it is obvious that formation of intimate interface by simple physical mixing (method II) is less possible and lower conductivity is expected. Further, in method III, the heat treatment does not lead to frothing as in method I and hence uniform mixing of SnO_2 particles in the glassy matrix is not as effective as in the first case and the conductivity of the sample prepared by the third method does not reach values as obtained for samples

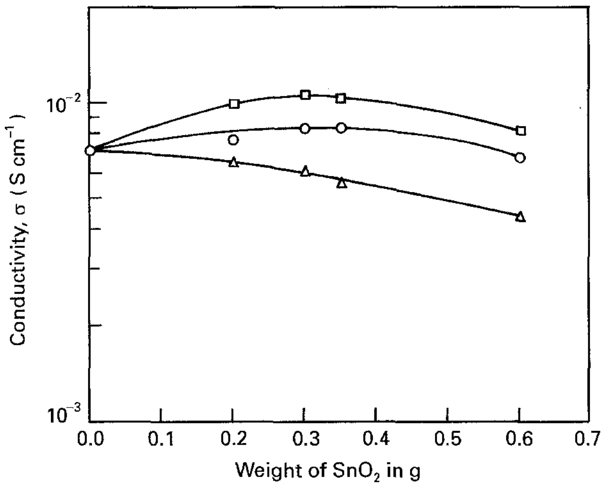

Figure 5 Conductivity for samples prepared by three different preparatory methods (I (□), II (Δ) and III (○)) as detailed in text.

prepared by method I. The detailed studies reported below are for the samples prepared by method I.

3.3. Ionic transference number

The total ionic transference number was measured by Wagner's polarization method [19]. Typical I versus time plots for $V = 0.6$ V for different samples are shown in Fig. 6. Curve (a) is for pure silver borate glass with molar composition 55.5% AgI + 22.25% Ag$_2$O + 22.25% B$_2$O$_3$ (weight ratio 2.35:0.93:0.28 g). Curves (b) and (c) are for samples in which 0.3 g and 1 g of SnO$_2$ is added to the (2.35 g AgI + 0.93 g Ag$_2$O + 0.28 g B$_2$O$_3$). The ionic transference number in all cases is ~ 1 and hence we conclude that addition of SnO$_2$ does not change the ionic nature of the basic composition.

The electrochemical e.m.f. method is used to measure the Ag$^+$ ion transference number [20]. The cell configuration Ag/electrolyte/C + I$_2$ + electrolyte gives a voltage of 686 mV(± 1 mV for different compositions) while the theoretical Ag/I$_2$ cell voltage is 689 mV. This gives $t_{Ag^+} \sim 1$. We conclude, therefore, that the materials studied are effectively Ag$^+$ ion conductors.

3.4. Dependence of conductivity and mobility on SnO$_2$ concentration

The room temperature mobility and conductivity are plotted in Fig. 7 for different compositions. The carrier concentration (as calculated from the measured conductivity and mobility values from the expression: $\sigma = nq\mu$) is also shown in Fig. 7. Some interesting observations are:

(i) σ (without SnO$_2$) can be increased by about twice by addition of SnO$_2$. At a higher SnO$_2$ concentration, σ decreases.

(ii) μ also shows an increase (and decrease) similar to σ.

(iii) n decreases slightly with SnO$_2$ addition. This is an "inherent artefact" due to our method of sample preparation in which weighed amounts of AgI, Ag$_2$O and B$_2$O$_3$ are kept constant and then the additional amount of SnO$_2$ is changed. This in effect, would reflect as a net decrease of Ag (and hence n) per gram of the sample.

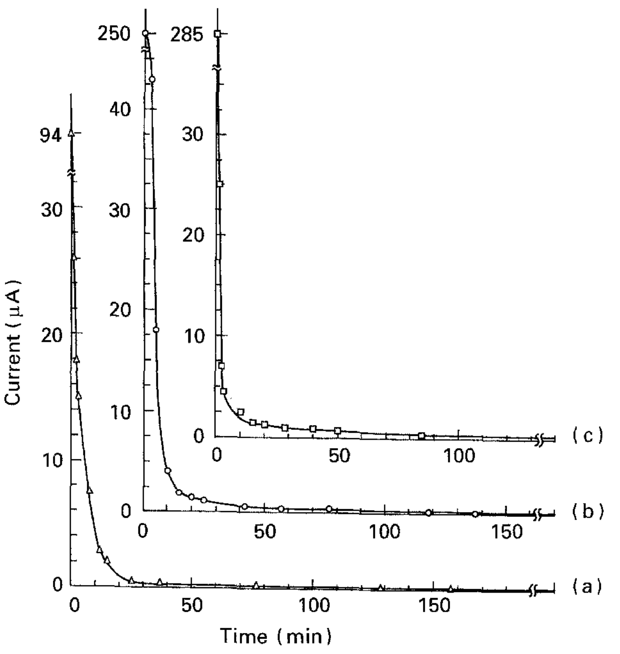

Figure 6 Typical I versus time plots for different samples; (a) for pure glass (Δ, $i_{\text{final}} = 0.10$ μA); (b) (○, $i_{\text{final}} = 0.25$ μA) and (c) (□, $i_{\text{final}} = 0.35$ μA) for glasses with 0.3 and 1.0 g SnO$_2$ added to 3.56 g of original borate glass composition (preparation method I).

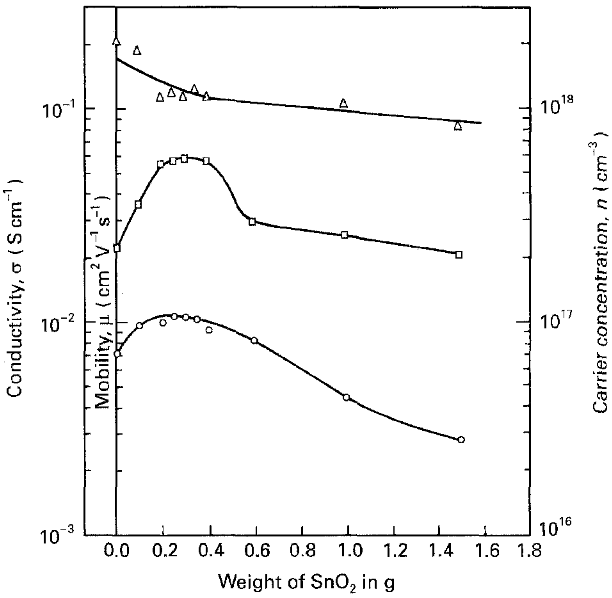

Figure 7 Variation of electrical conductivity (σ, ○), mobility (μ, □) and carrier concentration (Δ, n) as a function of amount of SnO$_2$ dispersed in the 3.56 g of basic glass with composition 55.5 AgI–22.25 Ag$_2$O–22.25 B$_2$O$_3$ (in mol. %), (preparation method I).

Now we address ourselves to explain first the initial enhancement of conductivity and mobility with SnO$_2$ content and second a subsequent decrease in σ and μ with increasing SnO$_2$ content in the high compositional range as shown in Fig. 7. The latter is easy to understand in terms of the blocking effect of insulating SnO$_2$ due to the loss of inter-grain connectivity and resulting enhanced grain boundaries. The presence of

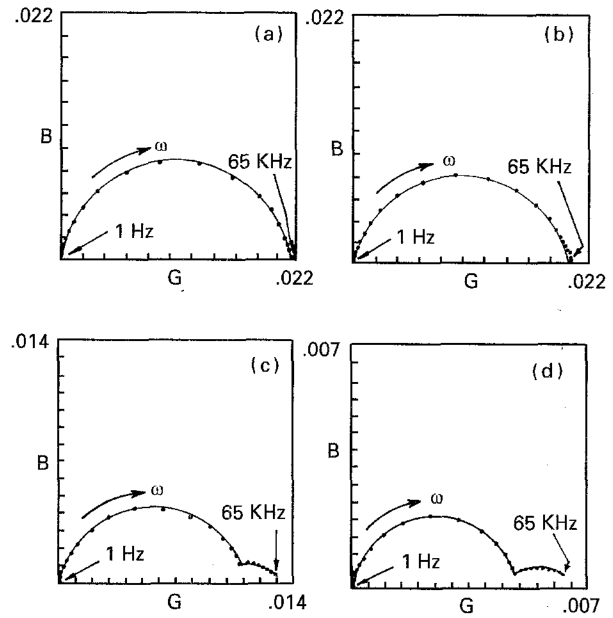

Figure 8 Typical complex admittance plots recorded from 1 Hz to 65 kHz for samples having different weights of SnO_2 in 3.56 g of silver borate glass; (a) for pure glass ($l/A = 0.3290\ m^{-1}$); (b) ($l/A = 0.5378\ m^{-1}$), (c) ($l/A = 0.3549\ m^{-1}$) and (d) ($l/A = 0.5726\ m^{-1}$) with 0.25, 1.0 and 1.5 g, respectively, to the basic glass composition.

grain boundaries can be seen in the complex admittance plots given in Fig. 8 for different SnO_2 content in the sample. It is obvious that for high SnO_2 content, (more than 0.35 g in ~ 3.56 g of glass) the grain boundary semicircle starts to appear as expected from the above argument. The aspect of our study which needs further attention is the initial increase in mobility and its correlation with the increase in conductivity. Increase in ionic conductivity in dispersed phase systems have been seen by many authors [10–17].

Jow *et al.* argued that the dispersed phase creates a space charge region around the dispersoid [16]. This results in the formation of excess compensating defects around the immediate neighbourhood of the space charge region. Maier modified this space charge model by considering the possible surface interactions of the dispersoid [12–14]. According to Maier's model the surface active oxides (added as dispersed material) can adsorb the cation from its regular site (sucked out of the volume of the ionic phase) if the interaction between them is attractive, increasing the vacancy concentration. The cations are driven to interstitial positions (or desorption takes place) if the interaction between the space charge region and the cation is repulsive, resulting an enhanced interstitial concentration. These two processes can be represented as

$$M_M + V_A = M_A^{\cdot} + V'_M \quad \text{(adsorption)}$$

$$M_A^{\cdot} + V_i = M_i^{\cdot} + V_A \quad \text{(desorption)}$$

where M_M, V_A, V_i are cations on the regular site, vacancies at the interface and the interstitial sites respectively. The superscripts "$\cdot$" and "$'$" respectively represent one positive or negative effective charge, respectively. The consequence of both the adsorption and desorption processes is an increase in the carrier concentration which leads to a build up of concentration gradient of carrier ions through the space charge region extending into the bulk. The reasons for enhanced conductivity taken so far are increase in mobile ion concentration [12–17] or concentration gradient at the interface [22]. These explanations seemed quite satisfactory since no direct determination of mobility (or n) was available. Our experimental results in "ionic glasses" as dispersion medium indicate that for such systems the enhanced mobility along the interface (space charge region) may have a decisive role in the conductivity enhancement. One of the possible causes for such an enhancement in the mobility may be a "blanket" argument that SnO_2 anchored in the glassy matrix changes the free volume of the glass. The measurements reported in this paper were carried out on "pellets" after powdering the as-prepared glass ingot. Therefore, there is a possibility of the existence of interfaces between SnO_2 and glassy grains. In the following paragraphs, we propose a mechanism for the creation of a concentration gradient in the space charge region near and around the glassy grains and dispersed SnO_2 which may ultimately lead to an enhancement in the ionic mobility obtained experimentally for our system.

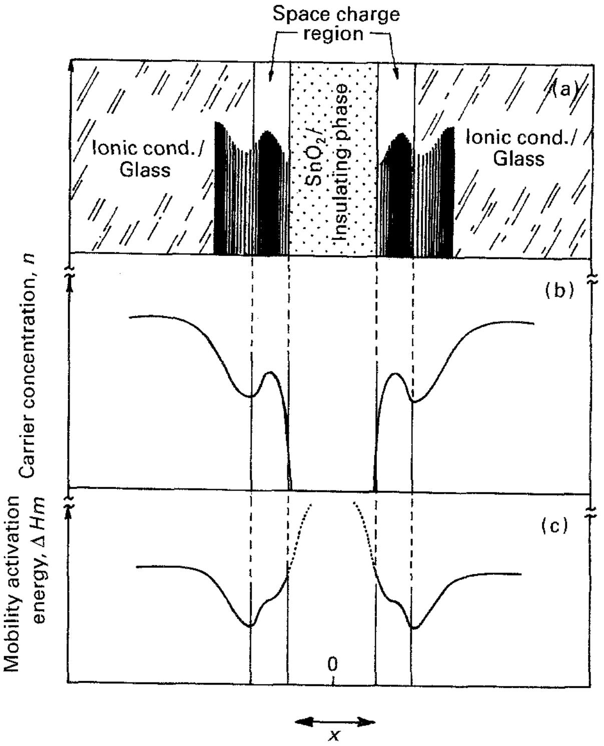

Figure 9 The space charge model for enhanced mobility. (a) Schematic representation for a dispersoid which is in between two clusters of ion conducting material. (b) Representation of the mobile ion concentration near/at the interface in the space charge region. (c) Representation of the Ag^+ ion migration energy near/at the interface in the space charge region.

Consider a situation in which the dispersoid (in this case SnO_2) is in between two clusters of ion conducting material (Ag–borate glass in this case) as shown schematically in Fig. 9(a). The space charge around the dispersoid can adsorb the free carrier ions from the glass towards its surface and a concentration gradient can establish accordingly within the glass but near the interface as shown in Fig. 9(b). This process effectively changes the concentration of the carrier ions from the surface of the dispersoid extending towards the bulk of the ionic phase. It may be noted that the creation of interstitials/vacancies due to adsorption/desorption in the dispersion medium as suggested by Maier [12–14] is more relevant to normal alkali or silver halides but may not be applicable to the non-crystalline or disordered glass as studied in this paper. Nonetheless, a large number of free ions ($\sim 10^{18}\,\mathrm{cm}^{-3}$) are still available for transport in the glassy dispersion medium and hence, the amount of ions pumped/adsorbed to the space charge region or to the surface of the dispersoid can be high. Some of the ions pumped into the space charge region reach the dispersoid (SnO_2) surface and will have a tendency to accumulate since the penetration of Ag^+ ions in SnO_2 bulk is zero or negligible. This, in turn, will give rise to a repulsive force to the further ions coming towards the dispersoid surface (like a Debye–Hückel type shielding) and also drive them away from the immediate neighbourhood of the surface of the dispersoid. This would result in a maxima within the space charge region where the two processes effectively balance. Having hypothesized the concentration gradient model (see Fig. 9(b)) we now consider what will be the energy of Ag^+ ion migration in the different regions. In SnO_2, the Ag^+ migration energy would be obviously very large as it is not a Ag^+ conducting material. In bulk glass, it would be small and is ~ 0.2 eV as experimentally determined by many workers from their results on pure glasses. In the space charge region towards and near the ion conductor/glass surface, the space charge effect would lower the mobility activation energy of carrier ions as an effect of the concentration gradient but inside the space charge region Debye–Hückel type of shielding may occur with increasing mobility activation energy. So, qualitatively, we can draw the mobility activation energy as shown in Fig. 9(c).

The mobility activation energy profile of the interface shown in Fig. 9(c), would mean that silver ions can move in the space charge region near the glass surface with a lower energy. Thus we can expect an increase in net mobility. The migrating ions emanating from ion conducting glass falling inside/near the space charge region find a relatively free migration pathway in the above mentioned region. The initial increase in the amount of the dispersoid results in an increased "connectivity" between neighbouring space charge regions and hence initially both the mobility and the conductivity increases with the increase in SnO_2 dispersoid concentration. However, for large concentrations of SnO_2 the inter-grain connectivity would be lost and the dispersoid will have a greater role in acting as blocking pathways. As a result, the "overall" mobility and hence conductivity would decrease at higher SnO_2 contents as seen earlier in Fig. 7.

4. Conclusions

Enhancement in ionic conductivity of $AgI + Ag_2O + B_2O_3$ glass has been studied on the addition of SnO_2 powder; (i) as one of the inherent constituents of the glass before starting the procedure of glass preparation and (ii) as dispersoid medium in already formed glass powder. It is found that the first method gives higher conductivity. However, SnO_2 remains as a separate dispersed phase even in this sample as revealed by XRD, i.r. and optical micrographs. The enhancement in conductivity is attributed to the formation of intimate interfaces due to the "frothing" observed during the first method of sample preparation. The conductivity enhancement is directly related to the experimentally measured *mobility enhancement.* A space charge model for explaining the mobility enhancement is proposed which introduces the concept of mobile ion concentration gradient of a certain type near or at the interface in the space charge region.

Acknowledgements

We thank the Department of Non-Conventional Energy Sources (Government of India) for financial support. Our sincere thanks are due to Dr D. Pandey, Department of Materials Science and Technology, Banaras Hindu University for providing the optical microscopy facility.

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Received 23 February
and accepted 14 November 1994