MEASUREMENTS OF TRANSFERENCE NUMBER OF 60B₂O₃-(40-x)PbO-xMCl₂ and 50B₂O₃-(50-x) PbO-xMCl₂ (M=Pb, Cd) GLASSES

5.1 Introduction

Historically, human endeavours in search of new materials along with their applications in devices have been the story behind the scientific and technological advancements of mankind. Prior to 1960s, most of the devices were based on electron conducting materials and a few devices like aqueous batteries (Leclanche cell) were based on ion conducting materials. Aqueous batteries have certain drawbacks such as limited temperature range of operation, device failure due to electrode corrosion, bulky size, etc. These drawbacks of aqueous batteries necessitated the search for new solid electrolyte materials exhibiting high ionic conductivity.

Solid electrolytes are solid-state materials that possess an electric conductivity partially or wholly due to ionic displacements. Though alkali halides and silver halides are ion conducting solids, due to poor ionic conductivity (σ approximately 10⁻⁷-10⁻¹² S cm⁻¹) they remain unsatisfactory choice for solid electrolyte applications. Ionic materials with high electrical conductivity comparable with those of liquid electrolytes are termed as superionic solids. In 1967 two new kinds of solid systems, MAgI₃ (M=rb,K,NH₄) and Na-β-alumina, exhibiting very high Ag⁺ and Na⁺ ion conduction (σ approximately 10⁻¹ S cm⁻¹) respectively at room temperature and moderately high temperatures, were discovered. Since then a large number of fast ion conducting solids with different ion species, namely H⁺, Li⁺, Na⁺, K⁺, Ag⁺, Cu⁺, F⁻, O₂⁻, etc. have been reported.
Super ionic solids have immense technological applications such as solid state batteries, sensors, fuel cell, electrochromic display devices, memory devices, supercapacitors, etc. In implantable heart pace maker, Li\(^+\) ion conducting solid state batteries are used with reliable performance. In addition to the above-mentioned applications, the major advantages of solid electrolyte based devices are their utility over a wide range of temperatures (below 0\(^0\) C to 100\(^0\) C) and the possibility of miniaturization.

For electrochemical applications, solid electrolyte systems should possess the following properties\(^7\):

1. Electric conductivity should be very high \((10^{-1} - 10^{-4} \text{ S cm}^{-1})\)

2. The principal charge carriers should be ions which means that ionic transference number \((t_{\text{ion}})\) is almost equal to 1 (\(t_{\text{ion}}\) is the fractional contribution of ionic conductivity to the total conductivity).

3. The electronic conductivity should be small which means electronic transference number \((t_{e})\) should be negligibly small (less than \(10^{-4}\))

Most of the super ionic solids attain a high electrical conductivity above a certain temperature, which may or may not be well defined.\(^1\)

Various structural and non-structural factors are responsible for high ionic conductivity in superionic solids.\(^8\) The important factors which influence high ionic conductivity include the crystal structure, high degree of lattice disorder, high mobile ion concentration, size of mobile ions, ionic polarizability, ion-ion interactions, bonding characteristics, vibrational amplitudes or rotational motions of neighbouring ions, number and accessibility of occupancy sites and presence of high conduction path ways.

In crystalline and polycrystalline solid systems, the structure is probably the main controlling factor for high ionic conduction.\(^7\) A perfect ionic crystal has no defects and it behaves like an insulator. Point defects,
namely Frenkal or Schottky defects, are necessary for ion transport in crystalline solids. Due to thermal vibrations, ions sometimes receive enough energy to be pushed into an interstitial site or to a nearby vacant lattice site leading to ion conduction.

In comparison with crystalline materials, the understanding of transport processes in glasses is complicated by the inherent structural disorder in these materials. But as solid electrolytes, glasses show many advantages over their crystalline or poly crystalline counter parts. The ionic conductivity in glasses are isotropic and avoids the problems associated with grain boundaries in polycrystalline materials. In glasses, there is a possibility for continuously varying the composition of the constituents. The variation of conductivity with composition is a very useful tool for investigating the conduction mechanism of glasses. There is also a possibility for changing the structure of the glasses by manipulating the thermal history.

When solid electrolytes possess conductivity due to both ionic and electronic transport, it is necessary to know the fraction of the conductivity due to ions and electrons. There are numerous applications where understanding of the dynamic behavior of ions in glasses is important. Glasses used in electronic devices should have negligible ionic conductivity, where as in glasses used as solid electrolytes for battery applications, the electronic contributions to the total conductivity should be minimized. The use of solid electrolyte materials in practical devices usually requires that they exhibit little or no electronic conductivity. i.e, \( t_{\text{ion}} \) values should be grater than 0.99 where \( t_{\text{ion}} \) is the transference number of ions.

In this chapter the study of ionic transference number of the mobile ions in \( 60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{MC}_2 \) and \( 50\text{B}_2\text{O}_3-(50-x)\text{PbO}-x\text{MC}_2 \) (M = Pb, Cd), glass systems of different composition (x=10,15 and 20 mole percentage) is presented. The transport of mobile ions in the glass system is discussed in
comparison with the reported ionic transference numbers of ternary borate and silicate glasses systems.

5.2 Theory

In solid electrolytes, the total conductivity is the sum of the ionic and electronic contributions. The fraction of the conductivity due to ions or electrons is given by

\[ t_{\text{ion}} = \frac{\sigma_{\text{ion}}}{\sigma_{\text{tot}}} \quad \text{and} \]
\[ t_{e} = \frac{\sigma_{e}}{\sigma_{\text{tot}}} \]

where \( t_{\text{ion}} \) and \( t_{e} \) are referred as the ionic and electronic transference numbers respectively. \( \sigma_{\text{ion}}, \sigma_{e}, \) and \( \sigma_{\text{tot}} \) are conductivity due to ions, electrons and total conductivity respectively. For a purely ionic conductor \( t_{\text{ion}} = 1 \) and for a purely electronic conductor \( t_{e} = 1 \). For mixed conductors \( t_{\text{ion}} \) and \( t_{e} \) have values between 0 and 1.

There are three different methods for determining the ionic transference number of mobile ions.\(^7\) They are

5.2.1 Tubandt’s Electrolysis Method

The principle of this method\(^{11,12}\) is based on Faraday’s law of electrolysis. A potential is applied across the solid electrolyte. The positive ions would move towards the cathode and negative ions would move towards anode. Hence mass of anode and cathode would increase to the extend of the respective type of charges transported. If the total amount of charge passed through the electrolyte is known from an independent measurement with a coulometer, the respective transference number can be obtained from the increase in mass of the electrodes.
5.2.2 Electrochemical Potential Measurement

In this method\textsuperscript{14,15} the solid electrolyte is sandwiched between two electrodes with different chemical potentials \( \mu_1 \) and \( \mu_2 \). The electrochemical potential across the cell is given by

\[ E = \frac{t_{\text{ion}} (\mu_1 - \mu_2)}{|Z|} F \]

where \(|Z|\) is the absolute vacancy of the mobile ions in the electrolyte, \( F \) is the Faraday's number and \( t_{\text{ion}} \) is the ionic transference number.

For a pure ionic conductor \((t_{\text{ion}} = 1)\), the theoretical value of the electrochemical potential is

\[ E_{\text{theor}} = \frac{(\mu_1 - \mu_2)}{|Z|} F \]

hence

\[ E = E_{\text{theor}} t_{\text{ion}} \]

Thus from measurement of \( E \) and a prior knowledge of \( E_{\text{theor}} \) the value of \( t_{\text{ion}} \) can be calculated.

5.2.3 Wagner's Polarization Method

The most important and apparently simple technique used for the evaluation of ionic transference number is the Wagner's Polarization Method\textsuperscript{16}. The extent of ionic transport in solids is obtained by direct measurement of the electrical conductivity given by

\[ \sigma = \text{Gi} \text{ A ohm}^{-1}\text{cm}^{-1} \]
where \( G \) is the conductance \((1/\text{resistance})\) of the sample having thickness \( L \) (cm) and area of cross section \( A \) (cm\(^2\)). The total conductance may be fully or partially ionic. The ionic conductance may be due to positive or negative ion species and the electronic contribution to the total conductivity can be due to negative electrons and positive electron holes. In general,

\[
\sigma_{\text{tot}} = \sigma_{\text{ion}} + \sigma_{\text{elect}}
\]

The first step in the interpretation of conductivity results is to separate electronic and ionic contributions.

The conductivity measurements using blocking electrode is a powerful method for measuring both ionic and electronic conductivity. The blocking electrode or polarization method used for the measurement of transference number is originally due to Wagner\(^{16}\). The principle is either ionic or electronic transport is suppressed in a mixed conductor by the proper choice of the electrodes allowing the contribution of the non-suppressed species can be determined.

The sample for which the transference number is required is sandwiched between two blocking electrodes and a dc voltage is applied across the electrodes. When the circuit is closed, the instantaneous current \( (i_t) \) gives a measure of the total conductivity (electronic and ionic). The time variation of the current through the sample gives an idea about the polarization at the electrode-electrolyte interface. The final stabilized current is the electronic conductivity \( (i_e) \). The ionic transference number \( (t_{\text{ion}}) \) can be determined using the relation\(^{17}\)

\[
t_{\text{ion}} = (i_t - i_e)/i_t
\]

\[ (1) \]

5.3 Experimental

The compositions of the glass samples used for the study of \( t_{\text{ion}} \) along with sample codes are shown in table 5.1 and 5.2. Glass samples were
prepared as described in section 2 chapter 2 of this thesis. Glass samples of uniform thickness of about 1 mm and diameter about 10 mm were selected for the study of transference number. Both sides of the glass samples were polished and coated with graphite electrodes.

A programmable KEITHLEY 617 electrometer was used for transference number measurements. The sample was held between the sample holders of lab made conductivity cell which can be evacuated. The sample holder was provided with spring - mechanical pressure to ensure good electrical contact. A constant voltage of 0.5V was applied to the sample and the initial current (t =0) was taken as the total current. The instantaneous current through the sample was recorded at an interval of 1 minute. The measurement was performed at room temperature \(30^0\) C and at a pressure of \(10^{-3}\) torr.

In the present study ionic transference number was determined by the Wagner's polarization technique using blocking electrodes. The principle of determination of ionic transference number in Wagner's Polarization Method is shown in figure 5.1.

![Figure 5.1](image)

**Figure 5.1.** The electrical arrangement used for measuring ionic transference number

A material in which the mobile ions are not soluble is used as electrodes. Hence the electrodes acted as blocking electrodes for the ionic movement. Graphite paste was used as the blocking electrodes in the present
study. When the circuit in closed, the initial current gives a measure of the total conductivity \( i_t \) (electronic plus ionic). The time variation of the current through the sample was monitored. The final stabilized current is the total electronic conductivity \( i_e \). The ionic transference number \( t_{ion} \) can be calculated using the relation (1). Three trials were performed on each sample and the average values are given in the table 5.1 and 5.2.

5.4 Results and Discussion

The variations of the dc current versus time for \( 60B_2O_3-(40-x)PbO-xPbCl_2 \) and \( 50B_2O_3-(50-x)PbO-xPbCl_2 \) glasses are shown in Figures 5.2 to 5.7. All the six graphs show the similar variation of current with time. As the dc potential is applied movable ions migrate towards the respective electrodes resulting in an ionic current. The initial total current will be the sum of the contributions from the ionic current and the electronic current. Since graphite electrodes do not supply mobile ions, after some time the ionic current is suppressed and the final stabilized current will be due to the contribution of electrons only.

The least square fitting of the experimental data points was performed and it was found that the current follows the law

\[
i = A + \frac{B}{t} + \frac{C}{t^2}
\]

were \( A, B \) and \( C \) are constants. The time \( t \) is expressed in minutes and current in nA. The constant \( A \) which is the limit of \( I \) when \( t \to \infty \), was assumed to be the steady state electronic current \( (I_e) \), given by the intercept of the asymptotic line on the current axis. In the present study, the graphite electrode acted as a blocking electrode for the motion of ions. First reading at \( t = 0 \) was taken as the total current \( i_t \) due to both the ionic and electronic contribution. As time progressed, the ionic conductivity was suppressed because the graphite electrode do not supply the mobile ions and also the polarization of ions at the
electrode produced a backfield that prevented further ion migration, resulting in a continuous decrease of current. The theoretical curve representing the variation of current with time given by equation (2) is shown as the solid line in the graph.

**Figure 5.2.** Plot of d.c. current vs time of 60B$_2$O$_3$-30PbO-10PbCl$_2$ glass sample.

**Figure 5.3.** Plot of d.c. current vs time of 60B$_2$O$_3$-25PbO-15PbCl$_2$ glass sample.

**Figure 5.4.** Plot of d.c. current vs time of 60B$_2$O$_3$-20PbO-10PbCl$_2$ glass sample.

**Figure 5.5.** Plot of d.c. current vs time of 50B$_2$O$_3$-40PbO-10PbCl$_2$ glass sample.
For all the samples, in the present study the ionic transference number was found to be greater than 0.98 indicating that the samples were ionic conductors.
In general, both cations and anions can move in a solid electrolyte. In alkali halide containing glasses, due to the relatively small ionic radii of alkali metal ions, the electric current is carried more effectively by the cations as compared with the anions. Since the ionic radii of halide ions \( F^-(1.36 \text{Å}), \text{Cl}^- (1.81 \text{Å}), \text{Br}^- (1.95 \text{Å}) \) and \( \text{I}^- (2.16 \text{Å}) \) are relatively higher, the possibility of halide anion conduction in glasses is small, except for the smallest ion \( F^- \). 

Opinions about the type of current carriers in alkali free glasses are contradictory. Schultz and Mizzoni\(^1\) studied glasses of the composition \( 48.5\text{PbO}-29.2\text{PbX}_2-35\text{SiO}_2 \), where \( X \) is \( \text{F}, \text{Cl}, \text{Br} \) or \( \text{I} \). Results of their study revealed that the conductivity of these glasses increased several orders of magnitude when a lead halide was substituted for lead oxide. They also observed a decrease in conductivity with increase in the radius of the halide ion and demonstrated that the glasses were anionic conductors through the use of the Tubandt technique. But from the results of a study of electrical conductivity in \( \text{PbI}_2-\text{PbO}-\text{B}_2\text{O}_3 \) glasses, Schleitweiler and Johnson\(^2\) suggested that the conducting species were \( \text{Pb}^{2+} \) ions. According to Sokolov et al\(^3\), the electrical transport in \( \text{PbO}-\text{SiO}_2 \) is not due to the \( \text{Pb}^{2+} \) ions but due to the protons from the impurity water in the glasses. It is reported that in \( \text{PbF}_2-2\text{PbO} \cdot \text{SiO}_2 \) glasses\(^4\), when the concentration of \( \text{PbF}_2 \) is less than 20 mole percentage, electrical transport occurs through protons and fluorine ions. As the concentration of \( \text{PbF}_2 \) is increased to more than 20 mole percentages, electric charge was carried by the fluorine ions alone. Aono\(^5\) et al estimated the ionic transference number of \( \text{PbX}_2-\text{PbO}-\text{SiO}_2 \) (\( X=\text{Cl}, \text{Br}, \text{I} \)) glasses and established that the sole electrical carriers are \( X^- \) ions.

In the present study for \( 60\text{B}_2\text{O}_3-(40-x)\text{PbO}-x\text{PbCl}_2 \) and \( 50\text{B}_2\text{O}_3-(50-x) \text{PbO}-x\text{PbCl}_2 \) glasses, the ionic transference number was found to be nearly 1. Substitution of \( \text{PbCl}_2 \) for \( \text{PbO} \) in these glasses resulted in an increase in \( \text{Cl}^- \) ion concentration but total lead content remains a constant in the glass structure. The charge carriers in these glasses could be either \( \text{Pb}^{2+} \) ions or \( \text{Cl}^- \) ions. Generally
migration of divalent ion is very difficult as compared to monovalent ions because the coulombic energies involved in hopping of di or trivalent ions would be more than those for monovalent ions. Since Cl\textsuperscript{-} ions are monovalent, the electrical charge carriers are assumed to be anionic.

In order to ascertain the result that the charge carriers are anionic (i.e., Cl\textsuperscript{-} ions), in 60B\textsubscript{2}O\textsubscript{3}-(40-x)PbO-xCdCl\textsubscript{2} and 50B\textsubscript{2}O\textsubscript{3}-(50-x)PbO-xCdCl\textsubscript{2} glass samples, CdCl\textsubscript{2} was substituted for PbO in a similar fashion as PbCl\textsubscript{2} was substituted for PbO in 60B\textsubscript{2}O\textsubscript{3}-(40-x)PbO-xPbCl\textsubscript{2} and 50B\textsubscript{2}O\textsubscript{3}-(50-x)PbO-xPbCl\textsubscript{2} glass samples. The variation of the dc current with time for 60B\textsubscript{2}O\textsubscript{3}-(40-x)PbO-xCdCl\textsubscript{2} and 50B\textsubscript{2}O\textsubscript{3}-(50-x)PbO-xCdCl\textsubscript{2} glass samples are shown in Figures 5.8 to 5.13.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure5.8}
\caption{Plot of dc current vs time of 60B\textsubscript{2}O\textsubscript{3}-30PbO-10CdCl\textsubscript{2} glass sample.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure5.9}
\caption{Plot of dc current vs time of 60B\textsubscript{2}O\textsubscript{3}-25PbO-15CdCl\textsubscript{2} glass sample.}
\end{figure}
Figure 5.10. Plot of d.c. current vs time of 60B₂O₃-20PbO-10CdCl₂ glass sample

Figure 5.11. Plot of d.c. current vs time of 50B₂O₃-40PbO-10CdCl₂ glass sample.

Figure 5.12. Plot of d.c. current vs time of 50B₂O₃-35PbO-15CdCl₂ glass sample

Figure 5.13. Plot of d.c. current vs time of 50B₂O₃-30PbO-20CdCl₂ glass sample.
For a constant concentration of PbCl₂ or CdCl₂ in the glass system, the number of ions per cm³ is assumed to be a constant. But, cadmium ions (ionic radii = 0.97Å) are smaller in size than lead ions (ionic radii = 1.32Å). If the charge carriers are cations, the ionic current in 60B₂O₃-(40-x)PbO-xCdCl₂ and 50B₂O₃-(50-x)PbO-xCdCl₂ glass samples should have decreased at a faster rate than in 60B₂O₃-(40-x)PbO-xPbCl₂ and 50B₂O₃-(50-x)PbO-xPbCl₂ glass samples because smaller ions may diffuse more easily in a glass matrix. Also, the total initial current in CdCl₂ substituted glasses should have greater than PbCl₂ substituted glasses. But the total initial current in CdCl₂ substituted glasses was found to be less than that of PbCl₂ substituted glasses (figures 5.8 to 5.13).

### Table 5.2

Sample code, glass composition and ionic transference number of C₁ to C₆ glass samples

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Glass composition</th>
<th>Ionic transference number (tᵢ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>60B₂O₃-30PbO-10PbCl₂</td>
<td>0.997</td>
</tr>
<tr>
<td>C₂</td>
<td>60B₂O₃-25PbO-15PbCl₂</td>
<td>0.995</td>
</tr>
<tr>
<td>C₃</td>
<td>60B₂O₃-20PbO-20PbCl₂</td>
<td>0.996</td>
</tr>
<tr>
<td>C₄</td>
<td>50B₂O₃-40PbO-10PbCl₂</td>
<td>0.998</td>
</tr>
<tr>
<td>C₅</td>
<td>50B₂O₃-35PbO-15PbCl₂</td>
<td>0.982</td>
</tr>
<tr>
<td>C₆</td>
<td>50B₂O₃-300PbO-20PbCl₂</td>
<td>0.998</td>
</tr>
</tbody>
</table>

The decrease in ionic current with time in both the glass systems (figures 5.8 to 5.13) showed a similar trend and the ionic transference number obtained for 60B₂O₃-(40-x)PbO-xCl₂ and 50B₂O₃-(50-x)PbO-xCdCl₂ glass samples was nearly 1 (table 5.2), similar to that obtained in 60B₂O₃-(40-x) PbO-xPbCl₂ and 50B₂O₃-(50-x)PbO-xPbCl₂ glass samples. This indicated that the sole charge carries were anionic.
5.5 Conclusion

Ionic transference number of glasses of the system $60B_2O_3-(40-x)\ PbO-xPbCl_2$ and $50B_2O_3-(50-x)\ PbO-xPbCl_2$ was investigated for 6 different compositions. The transference number was determined using Wagner's polarization technique. The ionic transference number obtained was nearly unity indicating that the sole charge carriers were ions and electronic contribution to total conductivity was negligible. When $CdCl_2$ was substituted for $PbO$ in $60B_2O_3-(40-x)\ PbO-xCdCl_2$ and $50B_2O_3-(50-x)\ PbO-xCdCl_2$ glass systems, the decrease in ionic current with time showed a similar trend similar to that of $PbCl_2$ substituted glasses and also the ionic transference number obtained was nearly unity indicating that $Cl^-$ were the charge carriers.

References

13. C. Tuband, A org All Chem., 15 (1920) 105