CHAPTER IV

INVESTIGATION ON

\[ x(0.75\text{AgI}:0.25\text{AgCl}): \]

\[ (1-x)(\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3) \]

GLASS SYSTEM
§ 4.1 Introduction

Glasses are recognized by its disordered structure and an enormous amount of effort has been made to produce fast ion (Ag⁺, Na⁺, Li⁺, Cu⁺ etc.) conducting superionic systems by different preparation routes. Such a thorough study of structural, thermal and charge transport properties in these amorphous/glassy systems is desirable to ascertain their suitability for device application. Now-a-days much of the attention has been devoted to the development of new FIC glasses having thermal and mechanical stability, investigation of its physical properties and the effects of compositional variation, from of their potential point of view to use as a power source in various applications e.g. spacecrafts, portable devices, medical equipments & cell phones etc. Details have been mentioned in chapter-I.

The glasses with heavy metal oxides viz. (PbO, Bi₂O₃, Ga₂O₃ etc.) have found their application in sensors, optical and electrical devices, optical switches and reflecting windows etc. Among them, Bi₂O₃ based glasses possess greater chemical stability and excellent optical properties which make them suitable applicant for ultra fast optical switches, infrared transmission components and third order optical non-linear material [525,526]. Bi₂O₃-containing glasses could be formed without other conventional network formers by rapid quenching [527]. Conventional glass forming oxides such as SiO₂, P₂O₅, B₂O₃ etc. can form glasses either alone or with considerable quantities of non-glass-forming oxides [528]. But their less chemical durability makes them unsuitable for practical applications [529]. It was found that bismuth containing glasses possess high chemical and mechanical stability, less hygroscopic [530, 531]. In the present chapter we are aimed to study the transport behavior of silver-bismuth system in the composition: x [0.75AgI:0.25AgCl] : (1-x)[Ag₂O:Bi₂O₃].

§ 4.2 Results and discussion

§ 4.2.1 Complex impedance analysis

Figure-(4.1) shows the real and imaginary parts of impedance (z' & z'') measured for quenched OCC 0.75[0.75AgI:0.25AgCl]:0.25 [Ag₂O:Bi₂O₃], at room temperature. It is obvious from the figure that the plot consists of two suppressed semicircles. The semicircle at high frequencies shows the capacitive effects in the bulk of the electrolyte associated with the kinetics of the charge transport, while the semicircle or a capacitive arc at lower frequency regime indicates the effective polarization at electrode/electrolyte interfacial region. The points were well fitted to a semicircle, the bulk resistance (Rb) of the OCC system was obtained from
Investigation on $x[0.75\text{AgCl}:0.25\text{AgCl}]: (1-x)[\text{Ag}_2\text{O}:\text{B}_2\text{O}_3]$ glass system.

Figure 4.1: ($Z'$-$Z''$) plot for quenched OCC: 0.75[0.75AgCl:0.25AgCl]:0.25[Ag$_2$O:( B$_2$O$_3$)].
the intercept of the higher frequency semicircle on the real (z') axis. Thus, the true bulk a.c. conductivity of the different compositions was calculated at various temperatures from their impedance plots, using the well known relation \( \sigma = U / (\pi R_{db}) \), by knowing the thickness (l) and area (A) of the pellet.

**§ 4.2.2 Compositional variation of conductivity (\( \sigma \)) Studies:**

Figure-(4.2) shows the room temperature conductivity as a function of composition for the systems in the following compositions:

- **System I:** \( x[0.75\text{AgI}:0.25\text{AgCl}] : (1-x)[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3] \)

- **System II:** \( x\text{AgI} : (1-x)[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3] \) for \( 0 \leq x \leq 1 \)

It was observed that both of the plots are analogous, but on comparing the conductivity values of these systems, it can be seen that the conductivity is higher for the new host salt \( [0.75\text{AgI}:0.25 \text{ AgCl}] \)-based system than that of conventional host AgI based system. The conductivity maxima for both the glass systems were found at \( x=0.75 \) and the glass system: \( x[0.75\text{AgI}:0.25\text{AgCl}] : (1-x)[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3] \) exhibited the highest conductivity of the order of \( \approx 2.7 \times 10^{-3} \text{ S/cm} \), and it was referred as optimum conducting composition (OCC).

The reason behind the conductivity enhancement on altering the composition can be well understood by observing the figure-(4.3), which shows the compositional variation of ionic mobility (\( \mu \)) and mobile ion concentration (\( n \)), along with the corresponding conductivities, for the system \( x[0.75\text{AgI}:0.25\text{AgCl}] : (1-x)[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3] \). Thus we can say that the mobility of charge carrier species enhances on increasing the host salt content and exhibits a peak value at \( x=0.75 \), beyond this composition, the decrease in ‘\( \sigma \)’ may be because of space narrowing or blockage of path due to large ion concentration making them immobile. The mobile ion concentration (\( n \)) remained almost unchanged for the whole of the range of ‘\( x \)’. The enhancement in conductivity in the conductivity value was mainly due to increased ionic mobility, which signifies that in OCC there are more open channels/pathways for easy ion migration in the system. Further investigations on this system have been performed to identify its phase and to seek for the valid reason of high ionic conductivity of the present superionic system.

**§ 4.2.3 Structural characterization/phase identification:**

The structural analysis of the OCC was done by XRD and DSC measurements. In order to find the effect of cooling rates, the comparison has been made between the systems (in
Figure 4.2: ‘$\log \sigma$ vs $x$’ plots for quenched bismuth: $x[0.75\text{AgI}:0.25\text{AgCl}]; \ (1-x)[\text{Ag}_2\text{O}: (\text{Bi}_2\text{O}_3)]\ (\Delta)$; and $x [\text{AgI}]; \ (1-x) \ [\text{Ag}_2\text{O}: (\text{Bi}_2\text{O}_3)]\ (\cdot)$ system.

Figure 4.3: ‘$\log \mu$ vs $x$’ ($\Delta$); ‘$\log n$ vs $x$’ ($\cdot$) & ‘$\log \sigma$ vs $x$’ ($\square$) plots for quenched bismuth system: $x [0.75\text{AgI}:0.25\text{AgCl}]; \ (1-x) \ [\text{Ag}_2\text{O}: (\text{Bi}_2\text{O}_3)]$. 

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similar composition) prepared by adopting two different preparation routes, (a) by slow/controlled cooling in the furnace i.e. annealing, and (b) quenching in liquid nitrogen bath.

A. XRD studies: The XRD patterns of the quenched and annealed OCC: 0.75[0.75AgI:0.25AgCl]: 0.25[Ag₂O:Bi₂O₃] along with host salt has been carried out by the X-Ray diffraction method (using Rich.Seifert MZ III) with a typical Cu Kα radiation of wavelength 1.54Å, as shown in the figure-(4.4). It was observed from the figure that annealed system shows some sharp diffraction peaks corresponding to the pattern of the host salt, it also have few broad peaks, which indicates that annealed system have acquired less degree of amorphism.

While in quenched system, broad and diffused peaks along with very small peaks are observed indicating that the system attains amorphous phase with small degree of polycrystallinity due to partial presence of undissolved host salt.

B. DSC studies: The DSC thermograms for quenched and annealed systems: 0.75[0.75AgI:0.25AgCl] : 0.25[Ag₂O:Bi₂O₃] are shown in figure-(4.5) (a) & (b) respectively. The DSC was carried out using MDSC (TA Instrument model 2910 USA). An endothermic peak at about 135°C was marked for both the systems attributed to β→α like phase transition of new host salt. Thus we can say that, (0.75AgI:0.25AgCl) salt has been remained embedded in the glass matrix and as a result a highly disordered mixed phase has been formed. Further, the exothermic peaks (T_c) in both of the curves revealed that the crystallization takes place at ~252°C, for both the systems prepared by two different routes as mentioned above. The quenched system shows an endothermic peak (T_m) at ~287°C which may be corresponding to the softening/melting of the sample. Although, the glass transition peak was not observed in both of the thermograms, hence it is apparent that very less degree of amorphism has been introduced.

§ 4.2.4 Temperature variation studies:

The electrical conductivity has been studied as a function of temperature and frequency to find the valid reason for the fast ion conduction in bismuth glass system. Some other important transport parameters were also evaluated as a function of temperature, which would help to examine the charge transport behavior of the system. The ion conduction mechanism was explained using appropriate conduction model.

A. Temperature dependence of electrical conductivity (σ):

The mechanism dominating the charge transport process in the present system was examined by studying the thermal variation of a.c. conductivity, measured by IS technique at different compositions. Figure-(4.6) shows the log σ vs 1/T plots for the system, with the
Investigation on $x[0.75\text{AgI}:0.25\text{AgCl}]: (1-x)[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3]$ glass system.

Figure 4.4: XRD results for (a) quenched host salt $(0.75\text{AgI}:0.25\text{AgCl})$, (b) Annealed & (c) quenched $0.75[0.75\text{AgI}:0.25\text{AgCl}]:0.25[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3]$ system.

Figure 4.5: DSC thermograms for (a) Quenched & (b) Annealed OCC: $0.75[0.75\text{AgI}:0.25\text{AgCl}]:0.25[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3]$. 

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Figure 4.6: 'Log $\sigma$ vs $1/T$' plot for various compositions of the quenched OCC system: $x[0.75\text{AgI}:0.25\text{AgCl}] : (1-x) [\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3]$. (Inset shows the activation energy (Ea) for different composition of x)
Investigation on $x[0.75\text{AgI}:0.25\text{AgCl}]: (1-x)[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3]$, for $0 \leq x \leq 1$. Initially, the conductivity of all the compositions shows a linear trend, where the conductivity increased slightly following Arrhenius-type behavior up to $\sim$135°C and beyond this temperature, for the compositions $0.7 \leq x \leq 0.9$ shows the phase transition phenomena. This sudden jump in electrical conductivity may be probably due to $\beta \rightarrow \alpha$ like phase transition of the unreacted $[0.75\text{AgI}:0.25\text{AgCl}]$ host salt present in the matrix of systems in compositions $0.7 \leq x \leq 0.9$. The conductivity get increased by several orders of magnitude in the $\alpha$-like phase, which may be due to the modification in the structure of the network. The composition $x = 0.9$ shows the larger jump in conductivity and this transition reduced gradually with decreasing values of ‘$x$’, and lowest transition was marked for the composition $x = 0.7$.

Whereas, no phase transition was observed in the compositions below $x = 0.6$, since these compositions have a small content of host salt, which may get dissolved easily in glass matrix. The activation energies of the different compositions were calculated from the slope of the $\log \sigma$ vs $1/T$ plot below the transition. The inset in the figure-(4.6) shows conductivity activation energies ($E_a$) of all compositions.

As shown in the figure, the highest conductivity at room temperature was found for quenched OCC: 0.75$[0.75\text{AgI}:0.25\text{AgCl}]:0.25$ $[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3]$ in which, the phase transition was marked at $\sim$135°C. It was in accordance with the XRD and DSC studies carried out for OCC. The Arrhenius equation governing the thermally activated processes for the system $x=0.75$ is given as:

$$\sigma_{ac} = 1.37 \times 10^{2} \exp[-0.144/kT]$$  \hspace{1cm} (4.1)

where the activation energy $E_a$=0.144eV, $\sigma_0$ (pre-exponential factor) $\sim 1.37\times10^{-2}$. The OCC possess the lowest activation energy value. This confirms the less temperature dependence of conductivity as well as the relative ease of charge transport in the system.

B. Thermal cycle of conductivity

The heating-cooling cycle of OCC: 0.75$[0.75\text{AgI}:0.25\text{AgCl}]:0.25$ $[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3]$, for (a) quenched and (b) annealed samples are depicted in figure-(4.7). As observed, the quenched system possesses higher conductivity value, as compared to that of annealed sample at room temperature.

In the heating cycle, first, the conductivity increased slightly with temperature and at $\sim$135°C a sharp phase-transition has been noticed for both the systems prepared by two different routes, where, the conductivity increased abruptly. As mentioned earlier, this jump in the conductivity is due to well known $\beta \rightarrow \alpha$-like phase transition of the unstabilized host salt present in the system. This was also confirmed by XRD and DSC results of both the systems.
Figure 4.7: 'Log $\sigma$ vs $1/T$' plot for heating-cooling cycle of the (a) quenched (♦) & (b) Annealed (□) OCC: 0.75[0.75AgI:0.25AgCl]:0.25[Ag$_2$O:Bi$_2$O$_3$].
The jump in conductivity may be due to the rapid enhancement in mobile ion concentration in the system due to breakup of bonds.

In the cooling cycle, the conductivity of quenched sample decreased with rapid initial drop, this is accompanied with the hysteretic effect, this initial decline in conductivity indicates that α-like high conducting phase has been destabilized. The cooling trend for quenched sample almost coincides with that of annealed system.

C. Frequency dependence of conductivity:

In order to shed light on the microscopic nature of conduction process, the frequency dependence of conductivity has been measured in frequency range from 42Hz to 5 MHz using HIOKI LCR Bridge (model 3532-50, Japan). Figure-(4.8) shows the frequency dependence of electrical conductivity of fast ion conducting system for all compositions at room temperature an abrupt decrease in the d.c. conductivity value was seen at lower compositions. The plateau region of the plot gives the d.c. conductivity of the system. The compositional variation of the d.c. conductivity has been plotted in figure-(4.9). \( \log \sigma_{dc} \text{ vs } x \) plot was found to be similar to compositional variation of the a.c. conductivity drawn in figure-(4.2).

Figure-(4.10) shows \( \log \sigma \text{ vs } \log f \) plot for quenched OCC: 0.75[0.75AgI:0.25AgCl]: 0.25 [Ag2O:Bi2O3] at different temperatures. All the plots showed similar trend having three distinct regions:

(i) The lower frequency (f<1 KHz) region: The conductivity increases with increasing frequency which is attributed to the polarization effect at the electrode and electrolyte interface. In this region change in the magnitude of polarization effect was found for different composition.

(ii) The middle frequency (1 KHz<f<1 MHz) region: The conductivity is found to be frequency independent in the middle, and it is equal to true bulk d.c. conductivity of the electrolyte.

(iii) The high frequency (1 MHz < f) region: In this region, the linear increase in conductivity with the frequency is observed. This phenomenon of the conductivity dispersion in the high frequency region could be analyzed using Jonscher’s power law \( \sigma_{dc} = \sigma_{dc} + A\omega^n \); as mentioned in chapter -III (in eq. 3.2) [532].

Where \( \sigma_{dc} \) is conductivity at particular frequency (ω), \( \sigma_{dc} \) is d.c. conductivity of the sample at \( \omega = 0 \), A is a constant for a particular temperature and n is the power law exponent (0 < n <1). In this figure we observe that as the temperature rises, plateau shifts towards the high
Figure 4.8: 'Log $\sigma$ vs $\log f$ plots for quenched x[0.75AgI:0.25AgCl]: (1-x) [Ag$_2$O:Bi$_2$O$_3$], system.

Figure 4.9: 'Log $\sigma_{dc}$ vs x' plots for quenched x [0.75AgI:0.25AgCl]: (1-x) [Ag$_2$O:Bi$_2$O$_3$] system.
Figure 4.10: ‘Log $\sigma$ vs log $f$’ plots for quenched OCC: 0.75[0.75AgI:0.25AgCl]:0.25[Ag$_2$O:Bi$_2$O$_3$] at different temperatures.

Figure 4.11: ‘Log $\sigma_{dc}$ vs $1/T$’ plot for quenched 0.75[0.75AgI:0.25AgCl]:0.25[Ag$_2$O:Bi$_2$O$_3$].
frequency region and the onset almost disappears at higher temperatures; since the jump frequency of the charge carriers increases with temperature.

The composition & temperature dependence of d.c. conductivity (σ_{d.c}) is extracted from plateau region of frequency curve. Furthermore, d.c. conductivity for OCC as a function of temperature has been shown in figure-(4.11). Figure shows a linear increase in conductivity below 135°C and the Arrhenius equation for d.c. conductivity can be expressed as,

$$\sigma_{d.c} = 1.45 \times 10^{-2} \exp(-0.128/kT)$$ (4.2)

where, the activation energy calculated for d.c. conductivity is $E_{a(d.c)} \sim 0.128$eV, which is close to the activation energy of a.c. conductivity [$E_{a(a.c)} \sim 0.144$]. An abrupt jump has been found in the d.c. conductivity at $\sim 135°C$, which is again associated with $\beta \rightarrow \alpha$-like phase transition of the host salt. These outcomes were found to be supporting to the results obtained from the a.c. conductivity studies.

D. Temperature dependence of ionic mobility ($\mu$) and mobile ion concentration ($n$):

The conductivity enhancement in an ionic system may be either due to increase in ionic mobility ($\mu$) and/or mobile ion concentration ($n$). Therefore, the temperature dependence of mobility ($\mu$) was measured using TIC technique and mobile ion concentration ($n$) has been deduced using the well known relation [$\sigma(T) = q \cdot n(T) \cdot \mu(T\cdot T)$] to find out the origin of ion conduction in the OCC. The temperature dependent ionic mobility ($\mu$) and mobile ion concentration ($n$) has been depicted in figure-(4.12). The room temperature mobility for OCC is found to be $\mu_{r} \sim 2.8 \times 10^{-2} \text{cm}^2/\text{V.sec}$. In the $\log \mu$ vs $1/T$ plot, the mobility exhibited a linear decreasing trend with increasing temperature up to $\sim 135°C$, thus the thermally activated processes are governed by the Arrhenius equation, which has been expressed as below:

$$\mu = 2.1 \times 10^{-6} \exp(0.254/kT)$$ (4.3)

where, energy of migration $E_m$=0.254 eV. Beyond 135 °C, there was a sudden decline in mobility, which may be due to $\beta \rightarrow \alpha$ like phase transition. In this region, the mobility remained almost constant up to 200 °C.

While, in the $\log n$ vs $1/T$ plot for OCC, the trend was opposite to that of mobility, but it was almost analogous to the trend observed for ‘$\log \sigma$ vs $1/T$’ as shown in figure-(4.6) the room temperature mobile ions concentration for OCC is $n_r = 6.03 \times 10^{17} \text{cm}^{-3}$ i.e. the mobile ion concentration increased with temperature linearly up to $\sim 135 °C$, and the slope of this linear region was evaluated by Arrhenius equation given as,

$$n = 3.28 \times 10^{22} \exp(-0.391/kT)$$ (4.4)
Figure 4.12: 'log μ vs 1/T' and 'log n vs 1/T' plots for quenched OCC: 0.75[0.75AgI:0.25AgCl]:
0.25[Ag₂O:Bi₂O₃].
where, energy of formation $E_f \approx 0.391$ eV. After 135 °C the ion concentration did not remain in the linear trend, but it jumped to higher values corresponding to $\beta \rightarrow \alpha$ type phase transition.

Both the plots showed linear change within the temperature range 25°C-135°C, where, the energies involved in expressions of mobility and mobile ion concentration are responsible for various thermally activated processes, theoretically the relation between these energies is given by $E_a = \pm E_m \pm E_f$ ; where, the -ve & +ve signs in the above expression corresponds to the increasing or decreasing trend of the parameters with increase in temperature respectively. This relation was found to be in good agreement with the results obtained from present studies.

The abrupt jump of mobile ion concentration pointed towards the breaking up the covalent bonds, thus a large number of immobile Ag$^+$ (attached with the network,) ions has been converted into mobile ions and contribute to electricity conduction [533,534]. At the same time, the rapid decrease in mobility during the phase transition may be due to the interruption in the ion migration because a large number of mobile ions have been introduced into the bulk.

The weak electrolyte model could also explain the ion conduction mechanism in the present system. According to the weak electrolyte model, whole of the ions do not contribute to the charge transport process at the room temperature and the system behaves like a weak electrolyte. Moreover on increasing the temperature, the more ions become free to move in the network, which occurs due to the dissociation of silver containing compounds, liberating more equi-energetic Ag$^+$ ions, thus ‘n’ shows an increasing trend with temperature, while the decrease in ionic mobility is accompanied with the obstacles presented by other mobile ions, as with increasing temperature, the no. of mobile ions increases, which have a tendency to block the pathway of other ions i.e. space narrowing effect. Thus as the concentration increases, the mobility becomes depleted.

**E. Temperature dependence of ionic transference number (t_{ion}) and drift velocity (v_d):**

The ionic transference number (t_{ion}) and ionic drift velocity (v_d) provide support for the results obtained from earlier studies as well as deliver some additional information such as the kind of mobile species and the extent of ionic contribution in the system. Both of these parameters have been measured for the quenched OCC system, as a function of temperature.

Figure-(4.13) shows current vs time plots for quenched OCC: 0.75[0.75AgI: 0.25AgCl]: 0.25[Ag$_2$O:B$_2$O$_3$] at different temperatures. One can note from the figure that:

(i) All the plots are similar except that the $I_T$ and time were changing in a regular increasing fashion. The value of $I_T$ substantially increases with the rising temperature, which is due to

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Figure 4.13: $I_T$ vs. time plots for quenched 0.75[0.75AgI:0.25AgCl]:0.25[Ag$_2$O:Bi$_2$O$_3$] at different temperatures.
increasing conductivity at higher temperatures, accompanied with the increase in number of mobile ion, in accordance with the expression \( I_T = A n q v_d \).

(ii) The current finally approaches to zero, and thus the transport number \( (t_{on}) \) for the system is close to unity.

(iii) The time taken by ions for complete polarization has increased at higher temperatures: this is because of the thermal agitations that caused obstruction the relaxation of ions.

(iv) The inset in the figure-(4.13) displays \( t_{on} \) against temperature, which shows that \( t_{on} \) remained unaltered for the whole of the temperature range, which means that the system is purely ionic even at higher temperatures.

Figure-(4.14) shows \( \log v_d \) vs \( 1/T \) plot for the OCC, which was evaluated by TIC technique using the relation: (eq. 2.9.a: \( v_d = I_T / A n q \)), where \( I_T \) is the total transient current, \( q \) is the charge on mobile ion and \( A \) is the cross sectional area of sample. The Arrhenius equation governing the variation of \( \log v_d \) vs \( 1/T \) plot in the temperature range 25°C-135°C can be expressed as:

\[
v_d = 2.1 \times 10^8 \exp\left\{0.241/kT\right\}
\]

(4.5)

where \( E_d \approx 0.241\text{eV} \) is the activation energy involved in the thermally activated process. Theoretically also ionic drift velocity \( (v_d) \) is directly proportional to the ionic mobility \( (\mu) \) at a constant d.c. field, in accordance with the expression (eq. 2.9.b, \( V_d = \mu E \)).

The mobility at unit field strength gives the drift velocity of the system. Thus, the thermal variation of \( v_d \) must be analogous to that of \( \mu \), which is evident by comparing the figures (4.12) and (4.14). Moreover the activation energy \( E_d \), involved in the Arrhenius relation for '\( v_d \)' should be equal to energy of migration \( (E_m) \). The energy involved in thermally activated process for drift velocity \( (E_d \approx 0.241\text{eV}) \) was found to be in good agreement with \( (E_m \approx 0.254\text{eV}) \) for the present studies.

In deriving the equation \([2.9.a, v_d = I_T / A n q]\) it has been supposed that the initial current is directly proportional to the applied d.c. potential which implies that the \( I-V \) variations should be linear [507], but the applied d.c. field may cause a polarization to build up instantly right in the beginning of the measurement. Current vs voltage studies has been performed by varying d.c. potential below the decomposition potential (i.e. 0.687V), which is shown in figure-(4.15), for the OCC. A linear trend has been clearly seen in the figure indicating the fact that the effect of instantaneous rising up of polarization charges due the applied d.c. voltage was negligibly small during the study.

The d.c. conductivity value was also computed by calculating the resistance from the slope of \( I \text{ vs } V \) curve. Table 4.1 shows the value of room temperature ionic drift velocity and
Figure 4.14: ‘log \( v_d \) vs \( 1/T \)’ plot for quenched \( 0.75[0.75\text{AgI}:0.25\text{AgCl}]:0.25[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3] \).

Figure 4.15: Voltage vs Current plot for quenched \( 0.75[0.75\text{AgI}:0.25\text{AgCl}]:0.25[\text{Ag}_2\text{O}:\text{Bi}_2\text{O}_3] \).

Table 4.1: Comparative results for the parameters measured by different ways:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Drift velocity (cm/sec)</th>
<th>d.c. conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_d = I_d / A.n.q )</td>
<td>3.5x10^-1</td>
<td>From conductivity spectra; 3.4x10^-1</td>
</tr>
<tr>
<td>( V_d = V.n.\mu )</td>
<td>1.4x10^-2</td>
<td>From V - I plot</td>
</tr>
</tbody>
</table>

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d.c. conductivity ($\sigma_{dc}$) for the system. As given in table 4.1, the values obtained earlier from IS technique, one can notice that the present values of d.c. conductivity is much lesser, which is due to the reason that the values of the initial current $I_T$ obtained in the present measurements (i.e. with the help of x-y-t recorder) are much lower than the actual values. The value of drift velocity determined using equation (2.9.a) was found to be close to the value evaluated by equation (2.9.b), which are given in table-4.1. The low measured values of $I_T$ would also lead to the decrease in the values of drift velocity ($v_d = I_T/\eta q A$). However some inconsistency was found in the values. This inconsistency can be eliminated if we measure initial current values accurately at $t = 0$ sec, then the difference in the values of $v_d$ and $\sigma_{dc}$ can be reduced.

§ 4.3 Conclusions

The overall studies of the silver-bismuth system shows that the newly synthesized system: 0.75[0.75AgI:0.25AgCl]: 0.25 [Ag$_2$O:Bi$_2$O$_3$] may prove to be a fast ion conducting solid electrolyte that can support to the fabrication of solid state batteries. Various transport parameters have been measured and following conclusions are drawn:

1. The optimum conducting composition (OCC): 0.75[0.75AgI:0.25AgCl]: 0.25 [Ag$_2$O:Bi$_2$O$_3$] exhibited the highest conductivity of the order of $2.7 \times 10^{-3}$ S/cm at room temperature.

2. XRD pattern of the OCC indicates the small degree of glassy phase along with partial presence of unreacted polycrystalline host salt. The characteristic $\beta \rightarrow \alpha$-like phase transition at about 135°C was observed in DSC thermogram of the system indicating the presence of the host salt. Glass transition ($T_g$) was not observed in the system.

3. The temperature variation of conductivity studies have been carried out on the OCC and the activation energy (Ea=0.144 eV) was found to be minimum.

4. Temperature dependence studies of $\log \mu$ vs $1/T$ and $\log n$ vs $1/T$ shows that room temperature mobility ($\mu$) and mobile ion concentration ($n$) of OCC were found to be $\mu_n \sim 2.8 \times 10^{-2}$ cm$^2$/V/sec and $n_n \approx 6.03 \times 10^{17}$ cm$^{-3}$ respectively. Further as temperature rises, $\mu$ decreases and subsequently $n$ increases, giving overall increase in conductivity below phase transition ~135°C. The conduction mechanism in this system is explained by weak electrolyte and cluster bypass model.

5. Ionic transference number ($\text{trans}$) and current vs time plot study confirmed that the system remains purely ionic.

Hence we concluded that the system possesses the main characters of superionic solids, and hence can be employed to fabricate the electrochemical devices. All important transport parameters for the OCC are listed in the table-5.2 given in the chapter-V.