CHAPTER I

FAST IONIC CONDUCTING SOLIDS

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CHAPTER - I

FAST IONIC CONDUCTING SOLIDS

1.1 GENERAL INTRODUCTION

Superionic Conductors (SICs) (or) Fast Ionic Conductors (FICs) (or) Solid Electrolytes (SEs) are the class of materials which exhibit high ionic conductivity comparable to liquid electrolytes. These materials are characterised by, (a) the electrical conductivity as high as $10^{-6}$ S cm$^{-1}$ to 1 S cm$^{-1}$, (b) the principal charge carriers are ions with negligible electronic conductivity, (c) the low activation energy for ion migration and (d) the conduction pathways across intergranular and interparticle boundaries for ion migration [1-5]. The study of FIC materials have been receiving more and more importance owing to their potential applications in advanced solid state ionic devices. The applications include Solid State Batteries, Fuel Cells, High Energy Density Batteries for Vehicular Traction, Gas Sensors, Electrochemical Capacitors, Electrochromic Displays, Analog Memory Devices, Miniature Cells, etc. [1-10]. Different types of FICs are being synthesised to meet the practical requirements. Understanding of ion conduction mechanism in FICs is another interesting area.
of active research on the theoretical side. Excellent reviews of the earlier works and recent trends are found in literature [1-27].

1.2 ION CONDUCTING SOLIDS

1.2.1 Normal Ionic Conductors (NICs)

It is well known that common ionic solids such as KCl, NaCl, CaCl2, etc. have ionic conductivity of the order of $10^{-14}$ to $10^{-12}$ S cm$^{-1}$ at room temperature. The thermally generated imperfections, in the periodic arrangement of their lattice structure, of these materials lead to the migration of ions [1]. Other halides like, silver, copper, etc. have also been found to exhibit low ionic conductivity [1]. These materials are classified as Normal Ionic Conductors (NICs).

1.2.2 Fast Ionic Conductors (FICs)

The temperature dependence of conductivity in AgI shows an unusual behavior at 147$^\circ$C and the conductivity increases abruptly by several orders, leading to an high ionic conducting phase [28]. Similar phase transitions are also found in other silver and copper halides [1]. Materials having very high ionic conductivity at room temperature and at higher temperature have also been synthesised. These
materials are called Fast Ionic Conductors (FICs). The temperature dependence of conductivity for a few ionic and superionic conducting solids are shown Figure 1.1.

1.2.3 Comparison between NICs and FICs

(1) Normal Ionic Conductors have low ionic and may have appreciable electronic conductivity. FICs have very high ionic and negligible electronic conductivity.

(2) NICs have high ionic conductivity at temperatures just below melting point while, FICs show high ionic conductivity even well below melting point.

(3) Number of charge carriers in NICs are very low as $10^{16}$ to $10^{18} \text{ cm}^{-3}$ and are strongly temperature dependent. In FICs, mobile charge carriers are very high, about $10^{22} \text{ cm}^{-3}$, and are almost temperature independent.

(4) The activation energy for ion migration in FICs is very low (eg. 0.1 eV for RbAg4Ir5) whereas in NICs, the activation energy for ion migration is high (eg. 1-2 eV for NaCl) [29].

(5) In NICs, conduction is due to thermally generated defects and the activation process involves both energy of defect formation ($H_f$) as well as migration ($h_m$). The conductivity is expressed as

$$\sigma = \infty / T \exp(-H_f/2kT) \exp(-h_m/kT) \quad (1.1)$$

whereas in FICs, the carrier concentration is very high and
Fig. 1.1 Conductivity versus temperature plots for some ionic and superionic solids.
the enthalpy of formation is almost zero hence, the conductivity expression is written as

$$\sigma = \alpha_0/T \exp(-h_m/kT)$$

(1.2)

The activation energy $h_m$ is only due to ion migration. The pre-exponential factor $\alpha_0$ is given by

$$\alpha_0 = (e^2 \nu_0 \cdot f \cdot \lambda^2 N X) / k$$

(1.3)

where, $e$ the charge, $\nu_0$ the jump or attempt frequency, $f$ the correlation factor, $\lambda$ jump distance, $X$ fraction of mobile charge carriers and $N$ the charge carrier density.

1.2.4 Development of FICs

The earliest known ion conductor is silver sulfide (Ag$_2$S) reported by Faraday in 1830's [30]. The oxygen ion conductivity at high temperature was then found in Yttria stabilised zirconia (85% Y$_2$O$_3$ - 15% ZrO$_2$) in 1899 by Nernst [31]. In 1913, Tubant and Lorenz reported the superionic phase in $\alpha$-AgI [28], this discovery stimulated the great interest in the ion conducting properties of solids. Later, in 1932, Tubant reported high ionic conduction at high temperature in Ag$_2$Se and Ag$_2$Te [32]. Till 1960, only stabilised zirconia and silver iodide (above 147°C) were known to have very high ionic conductivities. Later, in the year 1966, Ag$_2$SI was found to exhibit high silver ion
conductivity at room temperature [33]. In 1967, sodium β-alumina was proposed as a high sodium ion conductor [34]. Very high ionic conductivity, of the order of 0.3 S cm⁻¹ at room temperature, was obtained in RbAg₄I₅ by Bradley & Greene [35] and Owens & Argue [36] independently. Since then, various kinds of cation and anion conductors exhibiting high ionic conductivity at ambient conditions and at high temperatures have been synthesised.

Recently, high ionic conductors have been found in glassy or amorphous and polymeric forms [8-10]. High ionic transport is also obtained by dispersing insulating particles in ionic solids, such materials are called Dispersed Solid Electrolytes or Composite SEs [10].

1.3 CLASSIFICATION OF FAST IONIC CONDUCTORS

Wide varieties of fast ion conducting materials are available today and these are classified in different ways. Based on their micro-structure and phase, these materials are classified as

(1) Single / Polycrystalline FICs
(2) Ion Conducting Glasses
(3) Ion Conducting Polymers
(4) Composite Solid Electrolytes
1.3.1 Single / Polycrystalline FICs

Numerous crystalline cationic (Ag\(^+\), Cu\(^+\), Li\(^+\), Na\(^+\), etc.), anionic (O\(^2-\), F\(^-\)) and proton conductors have been reported. An excellent history of the development and list of these materials are available in the text by Chandra [1]. A brief list of these materials are given in the Table 1.1. The temperature dependence of ionic conductivity for some of the crystalline FICs are given in Figure 1.1. Only silver ion conductors are discussed in the next section, since the present thesis work investigates silver ion conducting solids.

Silver Ion Conductors

Monovalent silver ion (Ag\(^+\)) is the charge carrier in this class of materials and they possess the highest conductivity that has been observed so far. The discovery of a phase in AgI is the starting point for the development of silver ion conductors [28]. This transition is represented as

\[
\beta\text{-AgI (Wurtzite)} \quad \longrightarrow \quad \alpha\text{-AgI (Cubic)}
\]

\(\alpha\text{-AgI}\) has body-centred cubic anion (I) arrangement with high cationic structural disorder. The structural evidence of high cationic disorder in \(\alpha\text{-AgI}\) was first reported by Strock
### Table 1.1: Some examples of Single / Polycrystalline Superionic Solids

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (S/cm)</th>
<th>Temp. (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Silver Ion Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-AgI</td>
<td>1</td>
<td>147</td>
<td>28</td>
</tr>
<tr>
<td>RbAg4I5</td>
<td>0.27</td>
<td>25</td>
<td>35, 36</td>
</tr>
<tr>
<td>α-Ag0Si</td>
<td>2</td>
<td>240</td>
<td>33</td>
</tr>
<tr>
<td>2. Copper Ion Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-CuI</td>
<td>$9 \times 10^{-2}$</td>
<td>450</td>
<td>37</td>
</tr>
<tr>
<td>KCu4I5</td>
<td>0.6</td>
<td>280</td>
<td>38</td>
</tr>
<tr>
<td>α-Cu0Se</td>
<td>0.11</td>
<td>150</td>
<td>39</td>
</tr>
<tr>
<td>3. Lithium Ion Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li2SO4</td>
<td>1.0</td>
<td>800</td>
<td>40</td>
</tr>
<tr>
<td>Li4SiO4</td>
<td>$1 \times 10^{-9}$</td>
<td>400</td>
<td>41</td>
</tr>
<tr>
<td>LiTa5O18</td>
<td>$1.5 \times 10^{-2}$</td>
<td>450</td>
<td>42</td>
</tr>
<tr>
<td>4. Sodium Ion Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium β-Alumina</td>
<td>$1.4 \times 10^{-2}$</td>
<td>25</td>
<td>43</td>
</tr>
<tr>
<td>NaTa2O5F</td>
<td>$4 \times 10^{-5}$</td>
<td>25</td>
<td>44</td>
</tr>
<tr>
<td>NaSbO3:1/6 NaF</td>
<td>$5.6 \times 10^{-5}$</td>
<td>300</td>
<td>45</td>
</tr>
<tr>
<td>5. Potassium Ion Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K2O-Ga2O3</td>
<td>$1 \times 10^{-3}$</td>
<td>300</td>
<td>46</td>
</tr>
<tr>
<td>Potassium β-Alumina</td>
<td>$6.5 \times 10^{-5}$</td>
<td>300</td>
<td>47</td>
</tr>
<tr>
<td>K2O-6Fe2O3 (for K⁺ ion alone)</td>
<td>$1.5 \times 10^{-9}$</td>
<td>300</td>
<td>48, 49</td>
</tr>
</tbody>
</table>

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cont...
<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (S/cm)</th>
<th>Temp. (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂ + Y₂O₃</td>
<td>1.2 x 10⁻¹</td>
<td>1000</td>
<td>50</td>
</tr>
<tr>
<td>GeO₂ + SrO</td>
<td>1.1 x 10⁻¹</td>
<td>1000</td>
<td>51</td>
</tr>
<tr>
<td>Bi₂O₃ + WO₃</td>
<td>1 x 10⁻¹</td>
<td>750</td>
<td>52</td>
</tr>
<tr>
<td>6. Oxygen Ion Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Fluorine Ion Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-PbF₂</td>
<td>1</td>
<td>500</td>
<td>53</td>
</tr>
<tr>
<td>CaF₂</td>
<td>4 x 10⁻²</td>
<td>700</td>
<td>54</td>
</tr>
<tr>
<td>LaF₃</td>
<td>1</td>
<td>600</td>
<td>55</td>
</tr>
<tr>
<td>8. Proton Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HUO₂PO₄·4H₂O</td>
<td>4 x 10⁻³</td>
<td>25</td>
<td>56</td>
</tr>
<tr>
<td>Sb₂O₅·4H₂O</td>
<td>3 x 10⁻⁴</td>
<td>25</td>
<td>57</td>
</tr>
<tr>
<td>Polytungstic acid (PWA)</td>
<td>1-7 x 10⁻¹</td>
<td>25</td>
<td>58</td>
</tr>
</tbody>
</table>
and was later confirmed by Hoshino [60]. According to these authors, two silver ions are statistically distributed over 42 sites (6-octahedral, 12-tetrahedral, and 24-trigonal bipyramidal) as shown in Figure 1.2. Buhrer & Halg [61], Wright & Ferder [62] indicated that silver ions are preferentially found in oblong ellipsoidal regions of space centred at the tetrahedral sites and extending in the directions of the neighbouring octahedral sites as shown in Figure 1.3. This extended region of cation site occupancy corresponds to large amplitude of vibrations, which is a general feature of liquid-like structures.

Since the discovery of α-AgI, a large number of silver ion conducting solids have been synthesised. Most of the silver ion conductors are based on AgI, obtained by substituting either cation or anion or both. The best reported room temperature silver ion conductor is RbAg₄I₅, which is obtained by cation substitution RbI + 4AgI [35,36]. Table 1.2 and Figure 1.4 give a few examples of the silver ion conducting solids. Excellent reviews of silver ion conductors are found in literature [5,12].

The AgI based fast ionic conducting solids have the following properties to a greater or lesser extent [12]:

The cations are structurally disordered because, the number of sites (voids) available for them exceeds the
Body-centered cubic anion arrangement with interstices for cation (Ag⁺)

- tetrahedral
- trigonal bipyramidal
- octahedral interstices

Fig. 1.2 Structure of α-AgI.

Fig. 1.3 Silver ion occupancy regions in α-AgI.
Table 1.2: Examples of Silver Ion Conductors

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (S/cm)</th>
<th>Temp. (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-AgI</td>
<td>1</td>
<td>147</td>
<td>28</td>
</tr>
<tr>
<td>Cation substituted systems:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbAg4I5</td>
<td>0.27</td>
<td>25</td>
<td>35, 36</td>
</tr>
<tr>
<td>KAg4I5</td>
<td>0.21</td>
<td>25</td>
<td>63</td>
</tr>
<tr>
<td>NH4Ag4I5</td>
<td>0.19</td>
<td>25</td>
<td>63</td>
</tr>
<tr>
<td>α-Ag2HgI6</td>
<td>1.2 x 10⁻⁹</td>
<td>60</td>
<td>64</td>
</tr>
<tr>
<td>Anion substituted systems:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Ag3SI</td>
<td>2</td>
<td>240</td>
<td>33</td>
</tr>
<tr>
<td>Ag5I2SO4</td>
<td>0.02</td>
<td>20</td>
<td>65</td>
</tr>
<tr>
<td>Ag3I4WO4</td>
<td>0.047</td>
<td>25</td>
<td>65</td>
</tr>
<tr>
<td>Ag4I5P2O7</td>
<td>0.09</td>
<td>25</td>
<td>66</td>
</tr>
<tr>
<td>Anion &amp; Cation substituted:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAg4I4CN</td>
<td>0.14</td>
<td>25</td>
<td>67</td>
</tr>
<tr>
<td>RbAg4I4CN</td>
<td>0.18</td>
<td>25</td>
<td>67</td>
</tr>
<tr>
<td>Others:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver β-Alumina</td>
<td>6.4 x 10⁻³</td>
<td>25</td>
<td>68</td>
</tr>
<tr>
<td>Ag5S+Ag4.7Te+Ag4P2O5</td>
<td>0.16</td>
<td>25</td>
<td>69</td>
</tr>
</tbody>
</table>
Fig. 1.4 Conductivity versus temperature plots for some silver based superionic conductors.
number of cations leading to liquid like cation sublattice (as in the case of pure AgI). The anions are arranged in such a way that the local potentials are flat along certain paths, which interconnect the sites (voids). These lines serve as pathways for cation migration with less activation energy of the order of thermal energy.

Systematic investigations on the preparation methods and transport properties were started, owing to their applications as solid electrolytes in solid state batteries. Silver ion conducting films were also prepared for solid state micro battery applications [70]. Developing new techniques for the preparation, transport studies and applications are still an active area of research.

1.3.2 Ion Conducting Glasses

Silver Iodide was taken as a basic model substance for the search for new silver ion conductors. Several oxy-acid anions (e.g. SeO$_4^{2-}$, WO$_4^{2-}$, etc.) have also been introduced into the silver iodide lattice in an attempt to obtain high silver ion conducting solid electrolytes at room temperature. Most of these systems have a tendency to form glasses when cooled rapidly from their melts. Kunze [71] first reported the ion conduction in glassy phase of the system AgI-Ag$_2$SeO$_4$. Later, silver ion conduction have also
been found in the glassy systems, AgI-Ag₂S-AsS₃, Ag₂S-GeS₂ [72], AgI-Ag₂O-B₂O₃ [73], Ag₂O-B₂O₃-P₂O₅ and others [74,75]. Because of the similarities in the properties of silver and copper ions, high ionic conducting copper glasses have also been synthesised in the same way [76].

Today, wide range of Ag⁺, Cu⁺, Li⁺, Na⁺, F⁻ and O²⁻ ion conducting glasses are available, but only cation conducting glasses are receiving more and more attention. In the order of conductivity value, silver ion conducting glasses dominate the series in the following sequence.

\[ \sigma(\text{Ag}^+) > \sigma(\text{Cu}^+) > \sigma(\text{Li}^+) > \sigma(\text{Na}^+) \& \text{others} \]

where, \( \sigma(M^+) \) \( (M = \text{Ag, Cu, Li, Na}) \) denote the room temperature conductivity of the respective glasses. Though high ionic conductivity is found in copper glasses, they suffer the drawbacks like difficulties in preparation and the formation of Cu²⁺ immobile ion. Some of the examples of fast ion conducting glasses are given in Table 1.3 and in Figure 1.5. The ionic conductivity of these glasses possess 1-2 orders of magnitude higher than that of their polycrystalline forms. These ion conducting glasses possess a number of advantages over their polycrystalline forms, summarised as

(1) High conductivity at room temperature.
(2) Isotropic properties.
Table 1.3: Examples of Superionic Conducting Glasses

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (S/cm)</th>
<th>Temp. (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silver glasses</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60%AgI-30%AgzO-10%BzO5</td>
<td>8.5 x 10^{-3}</td>
<td>25</td>
<td>74</td>
</tr>
<tr>
<td>55%AgzS-45%GeS2</td>
<td>1.4 x 10^{-3}</td>
<td>25</td>
<td>77</td>
</tr>
<tr>
<td>70%AgPO4-30%Ag2SO4</td>
<td>5.0 x 10^{-6}</td>
<td>25</td>
<td>78</td>
</tr>
<tr>
<td><strong>Copper glasses</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuI-Cu2O-P2O5</td>
<td>1.0 x 10^{-2}</td>
<td>25</td>
<td>79</td>
</tr>
<tr>
<td>CuI-Cu2O-MoO3</td>
<td>1.0 x 10^{-2}</td>
<td>25</td>
<td>80</td>
</tr>
<tr>
<td>CuI-Cu2MoO4-Cu3PO4</td>
<td>1.0 x 10^{-2}</td>
<td>25</td>
<td>81</td>
</tr>
<tr>
<td><strong>Lithium Glasses</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li2WzO7</td>
<td>1.17 x 10^{-5}</td>
<td>60</td>
<td>82</td>
</tr>
<tr>
<td>50%Li2S-50%GeS2</td>
<td>4.0 x 10^{-5}</td>
<td>25</td>
<td>83</td>
</tr>
<tr>
<td>45%LiI-18%P2S5-37%Li2S</td>
<td>1.0 x 10^{-8}</td>
<td>25</td>
<td>84</td>
</tr>
<tr>
<td><strong>Sodium Glasses</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na2O-SiO2</td>
<td>2.8 x 10^{-5}</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td>39%Na2O-8%Y2O3-53%SiO2</td>
<td>3.39 x 10^{-3}</td>
<td>300</td>
<td>86</td>
</tr>
<tr>
<td>60%Na2S-40%GeS2</td>
<td>1.5 x 10^{-4}</td>
<td>100</td>
<td>87</td>
</tr>
<tr>
<td><strong>Lead Glasses</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40%Pb(PO3)2-60%PbCl2</td>
<td>7.08 x 10^{-6}</td>
<td>200</td>
<td>88</td>
</tr>
<tr>
<td><strong>Fluoride Glasses</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-Ba-Cs-F</td>
<td>1.0 x 10^{-5}</td>
<td>200</td>
<td>89</td>
</tr>
<tr>
<td>Zr-Th-Ba-Li-F</td>
<td>1.0 x 10^{-4}</td>
<td>200</td>
<td>90</td>
</tr>
</tbody>
</table>
Fig. 1.5 Conductivity versus temperature plots for some ion conducting glasses.
(3) Absence of grain boundaries.
(4) Ease of shaping into various forms.
(5) Ease in preparation of thin films.
(6) Wide selection of glass forming systems.
(7) Wide range of control of properties with change in composition.

More details about silver ion conducting glasses are described in the later section, since the present work is concerned with silver ion conducting glasses.

1.3.3 Ion Conducting Polymers

Polymer solid electrolytes are generally formed by complexes between salts of alkali metals and polymers containing solvating heteroatoms. The common prominent polymer solid electrolyte systems are complexes based on polyethylene oxide and salt, MX:

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{O} & \quad \text{CH}_2\text{CH}_2 \\
M^+ & \quad X^-
\end{align*}
\]

Polymer SEs are classified as, "Solvent free polymer salt complexes", "solvent swollen polymers" and "Polyelectrolytes" [91-93]. Fast ion transport in such complexes are first observed by Fenton et al. [94]. Some of the examples of polymer electrolytes are given in Table 1.4.
### Table 1.4: Examples of Polymer Electrolytes

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (S/cm)</th>
<th>Temp. (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Ion Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PEO)-NaI</td>
<td>10⁻⁵</td>
<td>25</td>
<td>95</td>
</tr>
<tr>
<td>(MEEP)₄-NaCF₃SO₃</td>
<td>10⁻⁵</td>
<td>25</td>
<td>96</td>
</tr>
<tr>
<td>Lithium Ion Conductors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PEO)-LiClO₄</td>
<td>10⁻⁶</td>
<td>25</td>
<td>97</td>
</tr>
<tr>
<td>(PEO)-LiCF₃SO₃</td>
<td>10⁻⁴</td>
<td>100</td>
<td>98</td>
</tr>
<tr>
<td>(PvAc)-LiSCN</td>
<td>10⁻⁹</td>
<td>40</td>
<td>99</td>
</tr>
<tr>
<td>(MEEP/PPO)-(LiClO₄)₉</td>
<td>10⁻⁷</td>
<td>25</td>
<td>100</td>
</tr>
<tr>
<td>Proton Conducting Polymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PVA)-H₃PO₄</td>
<td>10⁻⁵</td>
<td>25</td>
<td>101</td>
</tr>
<tr>
<td>(PEO)-NH₄SCN</td>
<td>10⁻⁸</td>
<td>25</td>
<td>102</td>
</tr>
<tr>
<td>(PEO)-NH₄I</td>
<td>10⁻⁵</td>
<td>30</td>
<td>103</td>
</tr>
<tr>
<td>Other Polymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PEO)-CuI</td>
<td>10⁻⁶</td>
<td>30</td>
<td>104</td>
</tr>
<tr>
<td>(PEO)-KAg₄I₅</td>
<td>2.0 x 10⁻³</td>
<td>25</td>
<td>105</td>
</tr>
</tbody>
</table>
These polymer solid electrolytes have many advantages like, visco elasticity (which favors accommodations of volume change), thin film forming property, stability, etc. The lithium polymer electrolyte systems are of practical interest for the development of high energy batteries [97-100,106]. Proton conducting polymers like PUA-H$_3$PO$_4$, PEO-NH$_4$I, etc. have also been synthesised [101-103]. Copper, Silver and other ion conducting polymers are also available today [104,105].

1.3.4 Composite Solid Electrolytes

Attempts were also initiated to enhance the ionic conductivity of the solids by dispersing an electrically insulating and chemically inert phase in the ionic hosts. C.C.Liang, in 1973 [107], first reported enhancement in the ionic conductivity of lithium ion in the LiI-Al$_2$O$_3$ system. These solid electrolytes are called dispersed or composite SEs or some times generally heterogeneous SEs. Since the discovery of LiI-Al$_2$O$_3$, several composite solid electrolytes have been developed. Table 1.5 illustrates the variety of available composite solid electrolytes. These Composites are classified into four categories as, (a) Crystal - Crystal composites, (b) Crystal - Polymer composites, (c) Crystal - Glass composites and (d) Glass - Polymer composites. Good reviews are available in literature about
Table 1.5: Examples of Composite Solid Electrolytes

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity Enhancement at room temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystal - Crystal</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiI-Al₂O₃</td>
<td>10</td>
<td>108</td>
</tr>
<tr>
<td>AgI-Fly Ash</td>
<td>50</td>
<td>109</td>
</tr>
<tr>
<td>AgI-Al₂O₃</td>
<td>2500</td>
<td>109</td>
</tr>
<tr>
<td>CaF₂-CeO₂</td>
<td>1000</td>
<td>110</td>
</tr>
<tr>
<td>HgI₂-Al₂O₃</td>
<td>1000</td>
<td>111</td>
</tr>
<tr>
<td>LiBr-NaBr</td>
<td>3 (400°C)</td>
<td>112</td>
</tr>
<tr>
<td>Li₂SO₄-Na₂SO₄</td>
<td>100 (400°C)</td>
<td>113</td>
</tr>
<tr>
<td><strong>Crystal - Glass</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-AgI-(Ag₂O+B₂O₃)</td>
<td>3000</td>
<td>114</td>
</tr>
<tr>
<td>α-AgI-(Ag₂O+GeO₂)</td>
<td>3000</td>
<td>114</td>
</tr>
<tr>
<td><strong>Crystal - Polymer</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion</td>
<td>σ = 0.1 S/cm</td>
<td>115</td>
</tr>
<tr>
<td>(PEO)-LiClO₄</td>
<td>σ = 10⁻⁶ S/cm</td>
<td>116</td>
</tr>
<tr>
<td><strong>Glass - Polymer</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LiI-Li₂S-B₂S₃)-PEO</td>
<td>---</td>
<td>115</td>
</tr>
</tbody>
</table>
composite electrolytes [115, 117-119]. Designing composite solid electrolytes with better control of important physical and chemical parameters is an active area of research [120].

1.4 APPLICATIONS OF SOLID ELECTROLYTES

The applications of solid electrolytes have started with the use of oxygen ion conductor in the determination of thermodynamic properties of high temperature materials [121]. High energy density batteries using sodium \( \beta \)-alumina solid electrolyte were developed by Yao and Kummer [34]. These were followed by large number of applications of ion conducting solids and the technology is being referred as "Solid State Ionics", a term parallel to solid state electronics. Solid electrolytes find applications in various fields like,

(1) Measurement of electrochemical and thermodynamic properties.
(2) Gas & Humidity Sensors and Pressure Gauges.
(3) Fuel Cells.
(4) Electrolytic Decomposition.
(5) Oxidation Catalysis.
(6) Solid State Batteries.
(7) Capacitors, Coulometer and Timers.
(8) Electrochromic Displays.
Thermometers.

(10) Thermoelectric Generators

In Table 1.6, application of different class of solid electrolyte systems with specific examples are listed. Solid electrolyte cells based on LiI and RbAgIIs find application in pace makers, etc. [122]. The principle, fabrication, advantages and characteristics of solid state batteries will be discussed in detail in Chapter VI.

1.5 SILVER ION CONDUCTING GLASSES

Silver ion conducting glasses dominate the list because of ease in preparation, high conductivity at room temperature and stability of the glass. Generally, these glasses can be expressed in the form

$$\text{Ag}_X\text{Ag}_2Y\text{F}_M\text{Y}_n$$

where, $X = I, Br, Cl$; $Y = O, Se, Te$; $F = Si, B, P, W$, etc. These systems are called ternary glasses. The compounds $F_M\text{Y}_n$ are generally glass forming oxides like, borates, germates and phosphates, etc. Superionic conducting glasses have also been prepared from compounds, not usually identified as glass formers, like vanadates, arsenates, chromates, selenates, molybdates, tugstates, sulfides, etc. These oxides form a network like skeleton structure, which
Table 1.6: Applications of Solid Electrolytes - Examples

<table>
<thead>
<tr>
<th>Materials</th>
<th>Applications</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline / Polycrystalline Conductors</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbAg$_4$I$_5$</td>
<td>Solid State Batteries, Electrochromic Displays &amp; Timers</td>
<td>122,123</td>
</tr>
<tr>
<td>Sodium $\beta$-Alumina</td>
<td>High Energy Density Sodium-Sulfur Battery</td>
<td>124</td>
</tr>
<tr>
<td>NASICON</td>
<td>SOx &amp; COx sensors</td>
<td>125</td>
</tr>
<tr>
<td>LiI</td>
<td>Lithium Batteries</td>
<td>122</td>
</tr>
<tr>
<td>Proton Conductor(HUP)</td>
<td>Photo-Electrolysis Cell</td>
<td>126</td>
</tr>
<tr>
<td>Proton Conductor(SrCeO$_3$)</td>
<td>Fuel Cells</td>
<td>127</td>
</tr>
<tr>
<td>ZrO$_2$-Y$_2$O$_3$</td>
<td>High Temperature Fuel Cells</td>
<td>128,129</td>
</tr>
<tr>
<td>CaO-ZrO$_2$</td>
<td>Thermometer</td>
<td>130</td>
</tr>
<tr>
<td>Glasses</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag$_4$I$_2$-AgzO-MoO$_3$</td>
<td>Bulk &amp; Micro Batteries Electrochromic Displays</td>
<td>123,131,132</td>
</tr>
<tr>
<td>LiAlF$_4$ &amp; LiNbO$_3$</td>
<td>Smart Windows</td>
<td>133</td>
</tr>
<tr>
<td>Polymers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEEP-PEO-LiCoO$_2$</td>
<td>Bulk and Micro Batteries</td>
<td>134,135</td>
</tr>
<tr>
<td>PEO-LiCF$_3$SO$_4$</td>
<td>Electrochromic Displays</td>
<td>136,137</td>
</tr>
<tr>
<td>PVA-H$_3$PO$_4$</td>
<td>Hydrogen Sensors</td>
<td>91</td>
</tr>
</tbody>
</table>
supports the superionic transport of silver ion and hence, these are called "network formers" or "glass formers". The Ag₂O is known as "modifying oxide", Ag₂O breaks the continuous network and creates more open like structure for the passage of silver ion.

The conductivity of these glasses are found to enhance appreciably by the addition of AgI (or AgBr or AgCl) associated with a reduction in activation energy. The compound AgX, from which the mobile species are doped in to the glass is called "dopant salt". Some examples of silver ion conducting glasses are listed in Table 1.7. More details are available in the literature [143-144]. Generally, these glasses are classified based on the valancy of glass forming cations. The available structural informations for silver ion conducting glasses are discussed briefly in the next section, since these informations are very useful to study conduction mechanism.

1.6 STRUCTURE OF SILVER ION CONDUCTING GLASSES

The glass former has a three-dimensional continues random network structure composed of some basic structural units, like, planar triangular BO₃ units in B₂O₃ glass and tetragonal SiO₄ units in SiO₂ [145-146]. The structural arrangement in glass was put forth by W.H.Zachariasen in
### Table 1.7: Examples of Silver Ion Conducting Glasses

<table>
<thead>
<tr>
<th>Material Description</th>
<th>Conductivity (S/cm)</th>
<th>Temp. (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trivalent Systems</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60%AgI - 30%Ag₂O - 10%B₂O₃</td>
<td>$8.5 \times 10^{-3}$</td>
<td>25</td>
<td>74</td>
</tr>
<tr>
<td>50%AgI - 25%Ag₂O - 25%B₂O₃</td>
<td>$2.7 \times 10^{-3}$</td>
<td>25</td>
<td>74</td>
</tr>
<tr>
<td>40%AgI - 30%Ag₂O - 30%B₂O₃</td>
<td>$6.3 \times 10^{-4}$</td>
<td>25</td>
<td>74</td>
</tr>
<tr>
<td><strong>Tetravalent Systems</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgI - Ag₂O - GeO₂</td>
<td>$1.0 \times 10^{-3}$</td>
<td>25</td>
<td>138</td>
</tr>
<tr>
<td><strong>Pentavalent Systems</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>66.7%AgI - 25%Ag₂O - 8.3%V₂O₅</td>
<td>$2.6 \times 10^{-3}$</td>
<td>30</td>
<td>139</td>
</tr>
<tr>
<td>50%AgI - 25%Ag₂O - 25%P₂O₅</td>
<td>$8.0 \times 10^{-3}$</td>
<td>25</td>
<td>140</td>
</tr>
<tr>
<td>75%AgI - 12.5%Ag₂O - 12.5%As₂O₅</td>
<td>$3.0 \times 10^{-3}$</td>
<td>25</td>
<td>138</td>
</tr>
<tr>
<td><strong>Hexavalent Systems</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75%AgI - 12.5%Ag₂O - 12.5%M₀₂</td>
<td>$1.0 \times 10^{-2}$</td>
<td>25</td>
<td>138, 141</td>
</tr>
<tr>
<td>70%AgI - 15%Ag₂O - 15%SeO₂</td>
<td>$1.0 \times 10^{-2}$</td>
<td>25</td>
<td>138</td>
</tr>
<tr>
<td>66.6%AgI - 16.7%Ag₂O - 16.7%CrO₃</td>
<td>$1.0 \times 10^{-2}$</td>
<td>30</td>
<td>142</td>
</tr>
</tbody>
</table>

References: 74, 138, 139, 140, 138, 141, 138, 142
1932 [147], familiarly known as Zachariasen rules

(1) An oxygen atom is linked, at most, to two other atoms.
(2) The coordination number of all other atoms is small.
(3) The Coordination polyhedra, formed by oxygen atoms around the other atoms, share corners not edges or faces.
(4) The polyhedra link to form a three-dimensional network.

A two-dimensional representation of the structures of BzOs in crystalline and glassy form are shown in Figure 1.6. Structural informations on other glass forming oxides are available in literature [5].

The structure of silver based fast ionic conducting glasses are studied by various techniques like, X-Ray diffraction, Neutron scattering, IR, Laser Raman, NMR, EXAFS and other related techniques [1]. The addition of silver oxide (AgzO) and halide salt (AgI) lead to suitable structural rearrangement of continuous random network of the glass former to support superion transport. The addition of modifying oxide (AgzO) changes the coordination of the basic former unit and breaks the continues random network of former which leads to the formation of Non-Bridging Oxygens (NBOs) [148]. The change in borate coordination (of BOs to BO4 units) and NBO formation in silver borate glass is reported by Dalba et al. [149-151]. The breaking up glass
Fig. 1.6 Two dimensional representation of (a) crystalline and (b) glassy Borate.
network creates more and more open-like structure and helps silver ion migration as shown below.

\[
\text{Si} - \text{O} - \text{Si}^- + \text{Ag}_2\text{O} \rightarrow \text{Si} - \text{O}^- / \text{Ag}^+ / \text{O}^- - \text{Si}^- / \text{Ag}^+
\]

Minami, et al. [138-141], have studied the IR spectrum of various ternary glasses and supported the presence of basic former units like MO$_m$-, in the compound, in the form of macro anions. EXAFS studies on glasses of different dopant salt contents have suggested that the addition of dopant salt AgI does not significantly alter the structure of glass [151]. Thus, the AgI is expected to be dispersed in between the glass network without any long range order [138].

The informations about the coordination of silver ions with glass network and iodine are also available [151-154]. The various structural studies support the presence of two types of silver ions, one bonded to NBO site and the other to iodine atom [151-154]. Dalba, et al. have proposed model for silver ion bonding with borate network based on the EXAFS results [149-151]. The same authors have also estimated Ag-I coordination in these glasses. The RDF measurements have provided a valuable information about various inter-ionic distances [152-154]. The RDF studies
evidenced that the silver ions are bonded to different environments, as initially proposed by Minami [155]. These results are helpful in understanding the conduction mechanism of silver ion and to elucidate model structure of these glasses.

To summarise, the silver ion conducting glasses are essentially composed of

(i) Broken glassy network with NBO sites / discrete former anion units like $\text{MO}^n_\text{II}$.

(ii) The former anion units in most of the glassy systems have tetragonal structure [138,148] and in some cases higher coordination with polyhedral shapes [152,153].

(iii) The $\text{I}^-$ ions are dispersed in between the glass matrix without any long range order.

(iv) The $\text{Ag}^+$ ions are either bonded to NBO sites by partial covalency (or) to $\text{I}^-$ ions by ionic bond.

The possibility of intermediate range of ordering by micro cluster formation in certain silver based glasses were also suggested from the neutron diffraction measurements [156,157].
1.7 PRESENT EXPERIMENTAL WORK

In previous sections, the potentials of solid electrolyte for device applications have been highlighted. From this review, it is clear that the synthesis of SEs for promising device applications is an active field of research. Among various class of SEs, the silver ion conducting glasses have several advantages as described in previous sections. In glassy ionic conductors, recently, it is found that mixing of another different network former oxide to the ternary glass improves the glass forming region and enhances the conductivity, by mixed former effect (158). These four component systems are called quaternary FIC glasses with general formula

\[ \text{AgI - AgzO - (FmOn + F2m'On')} \]

Where, FmOn and F2m'On' are glass formers.

In view of these backgrounds, the present work is aimed at synthesis of high silver ion conducting quarternary glasses. Mixed former effect in the mixtures of hexavalent and pentavalent formers is studied in the following systems

(i) \( \text{AgI-Agz0-}(\text{MoO}3 + \text{VzO}5) - \text{Silver Molybdovanadate (SMV)} \).
(ii) \( \text{AgI-Agz0-}(\text{MoO}3 + \text{AszO}5) - \text{Silver Molybdoarsenate (SMA)} \).
The glasses differing in the composition of glass formers, glass modifiers and doping salt are prepared to select the highest conducting composition of the glassy systems. The highest conducting composition in both the systems has been used as electrolyte in the fabrication of solid state batteries and the battery performance is studied. The conduction mechanism in these glasses is discussed based on the existing models.
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