INTRODUCTION TO SUPERIONIC SOLIDS
1.1 Introduction:

Solid electrolytes are termed as "superionic solids" or "fast ion conductors". These materials have ionic conductivity in solid state. Typically a superionic solid has the following characteristics (Chandra):

(i) Crystal bonding is ionic.
(ii) Electrical conductivity is high ($\sim 10^{-1}$ to $10^{-4}$ ohm$^{-1}$cm$^{-1}$).
(iii) Ionic transference number is nearly one as the main charge carriers are ions.
(iv) The electronic conductivity is small.

Solid electrolytes have been known from time of Faraday. The first systematic report of conductivity in solid electrolyte was given by Tubandt and Lorentz. They found conductivity of AgI at high temperature and molten AgI ($\sim 1$ ohm$^{-1}$cm$^{-1}$). Then the following materials were studied and was found that their conductivity was high.

- Li$_2$SO$_4$ by Benrath and Drekopf
- CuI by Tubandt et al.
- Ag$_2$HgI$_4$ by Ketelaar
- Ag$_2$S-AgI(Ag$_3$SI) by Reuter and Hardel
- Ag$_2$S-AgI(Ag$_3$SI) by Takahashi and Yamamoto

Takahashi and Yamamoto reported that conductivity of Ag$_3$SI was $\sim 10^{-1}$ohm$^{-1}$cm$^{-1}$ at room temperature. Yao and Kumar reported
\( \beta \) alumina which showed high conductivity at moderately high temperature. Bradley and Greene\(^{14} \) and Owens and Arge\(^{15} \) independently reported high conductivity of \( \text{MAg}_4\text{I}_5 \) (where \( M = \text{Rb, K, NH}_4 \) ) at room temperature. Takahashi\(^{16} \) reported copper rubidium chloro iodide which shows still higher conductivity (\(~ 0.34 \text{ ohm}^{-1}\text{cm}^{-1} \) ) at room temperature. Since then many solid electrolytes have been investigated. Now-a-days studies on mixed solid electrolytes are in process (Shahi and Wagner\(^{17} \)).

1.2 Types of Ionic Solids:

From the crystallographic point of view, a perfect crystal of an ionic compound would be an insulator (Lidiard\(^{18} \)). The presence of defect or disorder is a necessity to sustain meaningful ionic transport. Therefore ionic solids are classified according to the types of defect or disorder which are responsible for ionic transport. According to the classification, the ionic solids are of two types:

(i) Point defect type

(ii) Molten sublattice type.

In the point defect type solids, the ionic movement is only through Frenkel or Schottky defect pairs which are thermally generated. In fact, the number of defects is a function of temperature. The activation energy is generally high \(~ \text{1 eV or more} \). The defect concentration can be modified by doping with
foreign ions. This type of solids can be further subdivided according to defect concentration density.

(a) Dilute viz., normal Ag and alkali halides.
(b) Concentrated viz., ZrO₂, CaF₂ etc.

The "molten sublattice type" solids are the superionic solids, with very large number of defects. In these solids generally crystal structure is such that one of the sublattice (mostly cationic) can be considered as completely disordered. Therefore these solids are also called "cation disordered sublattice" type. There are large excess of available sites in sublattice than the number of ions. So these ions can hop like a free ion from one site to another. Since all these ions (cations) are available for transport, the conductivity is large and activation energy is low.

Rice and Roth¹⁹ has classified the ionic solids on the basis of "free ion like theory". According to this scheme, ionic solids are of three types.

**Type 1**: This is the category of "dilute point defect" as mentioned above. Normal insulating ionic solids come in this type. In this case defect concentration is \(10^{18}/\text{cm}^3\) or below.

**Type 2**: This is the case of "concentrated point defect". The ionic solids in which number of mobile defects is \(10^{20}/\text{cm}^3\) are included in this type.
Type 3: This is the case of "liquid like molten sublattice" in which all the ions in the sublattice are available for movement. The defect concentration is $10^{22}/\text{cm}^3$. These are superionic solids which have channelled or layered structure.

1.3 Insulating Ionic Solids:

The solids possessing conductivities less than $10^{-10}\text{ohm}^{-1}\text{cm}^{-1}$ at room temperature can be termed as insulating ionic solids. A large number of ionic solids belong to this class e.g., alkali halides, silver halides etc.

In an ideally perfect ionic crystal the movement of ions under the action of electric field is not possible if we assume that transport of charge could only take place via anion-cation exchange. This process involves a very high energy of order of 15 eV i.e., in one gram molecule; such an event could occur once in $10^{30}$ years. From extensive series of measurements of ionic conductivity as a function of temperature, two facts stand out:

(i) The existence of two main regions in conductivity curve as a function of temperature, and

(ii) In both the regions the log ($\sigma T$) vs. $T^{-1}$ is approximately linear.

The high temperature conductivity above the transition region or 'knee' in general is an intrinsic properties of the
crystal and the measurements in this region are quite reproducible. On the other hand, low temperature conductivity (or extrinsic conductivity) displays a smaller slope in \( \log (\sigma T) \) vs. \( T^{-1} \) curve but it depends upon the purity of the sample. In order to explain the low but finite temperature dependent ionic conductivity, the existence of thermally generated point defect is invoked.

In general electrical conductivity is given by:

\[
\sigma = \sum_i n_i q_i \mu_i
\]

where \( n_i \) is the number of charge carriers, \( q_i \) is the charge and \( \mu_i \) is the mobility of the charge carrier of the \( i \)th species. It is now well recognized that predominant types of charge carriers in ionic solids are either Frenkel defects or Schottky defects.

In case of Frenkel defect, an ion (cation or anion) from a normal lattice site is activated to a nearby interstitial site, creating an interstitial ion and an ion vacancy. If this pair of defect becomes thermally dissociated to beyond the range of their Debye-Hückel charge clouds, they will migrate independently in an electric field, in general, with different mobilities. If the temperature is high enough to assure ion defect equilibrium (and impurity effects be ignored) there will be a fixed and equal concentration of the two types of defects given by the following expression:

\[
n_f = (NN')^{1/2} \exp \left( -q_f / 2kT \right)
\]
where $q_f$ is the energy required to form a thermally dissociated Frenkel defect pair, $N$ is the number of normal lattice sites and $N'$ is the number of interstitial sites per unit volume. Silver bromide and chloride are the classic example of this class.

Schottky defects (cation and anion vacancies) are assumed to be introduced in pairs into the crystals lattice from the surface sites or from vacancy sinks. Fixed and equal concentrations of the two types of vacancies result at each temperature assuming ionic equilibrium and negligible impurity effects. Again associated defects may migrate independently in an electric field. In general Schottky defects occur in crystals with comparable cationic and anionic radii. The number of vacancies ($n_s$) of each type is given by:

$$n_s = N \exp \left( \frac{-q_s}{2kT} \right)$$  \hspace{1cm} (1.3)

where $q_s$ is the amount of energy required to form a Schottky defect pair.

Ionic mobility in such solids occurs as a result of random thermally activated jumps either of an interstitial ion into an adjacent unoccupied interstitial site or of an ion on a normal lattice site into an adjacent vacancy for that type of ion. Another migration mechanism is that in which an interstitial ion replaces a like ion on normal lattice site, pushing it into an unoccupied adjacent interstitial site. The later is known as
"interstitialcy" mechanism. In any event each jump process is assumed to involve an activation energy of \( \Delta E \) such that the jump frequency when no electric field is applied is given by:

\[
W = \omega \exp\left(-\frac{\Delta E}{kT}\right) \quad (1.4)
\]

where \( \omega \) is the vibrational frequency. Suppose an uniform electric field \( E \) acts along one of the axes (say X axis). The applied electric field can be regarded as adding a term \(-eE_x\) in the potential energy of the interstitial. The net effect is that a jump in the direction of field would take place with an increased probability:

\[
W' = \omega \exp\left[-\frac{1}{kT}\left(\Delta E - \frac{1}{2} eaE\right)\right] \quad (1.5)
\]

and a jump in a direction opposite to the applied field takes place with reduced probability:

\[
W'' = \omega \exp\left[-\frac{1}{kT}\left(\Delta E + \frac{1}{2} eaE\right)\right] \quad (1.6)
\]

where \( e \) is the charge on a particular ion participating in conduction mechanism and \( a \) is the nearest anion-cation separation.

If \( eaE \ll kT \), this would result in a current density:

\[
J = \frac{na^2 e^2 E}{kT} \omega \exp\left(-\frac{\Delta E}{kT}\right) \quad (1.7)
\]
The mobility \( \mu_1 \) is given by:

\[
\mu_1 = \frac{J}{neE} = \frac{ea^2}{kT} \exp \left( \frac{-kT}{e} \Delta E \right)
\]

(1.8)

Hence the partial conductivity (from Eqn. 1.1) due to mechanism considered above is:

\[
\sigma = \frac{n e^2 a^2}{kT} \exp \left( \frac{-kT}{e} \Delta E \right)
\]

(1.9)

where \( n \) is given by Eqn. (1.2) or Eqn. (1.3). Hence a plot between \( \log(\sigma T) \) and \( T^{-1} \) would be linear if one type of defect mechanism is responsible for the conductivity.

In actual experiment, broadly speaking, the \( \log(\sigma T) \) Vs. \( T^{-1} \) plot shows two distinct regions. The high temperature conductivity is independent of purity of crystal (if the impurity concentration is not large), but the low temperature conductivity is strongly impurity sensitive. The former is known as intrinsic conductivity and the later as the extrinsic. The intrinsic conductivity is due to thermally generated defects while the extrinsic conductivity is due to vacancies created by impurity doping (allovalent cation or anion). A few more variations in slope can be seen in the conductivity curve due to association and precipitation of impurities. For alkali halides, it is now well established that both the positive and negative ion vacancies are mobile. The transport parameters can be obtained either by following Chandra and Rolfe's 20 procedure (from electrical conductivity measurements...
on pure and divalent cation and anion doped samples) or by the method of Fuller et al. 21 (from diffusion and electrical conductivity measurements on pure and divalent doped samples).

1.4 Important Superionic Materials:

For superionic conductors, the ionic transference number \( t_{\text{ion}} \) should be nearly equal to one and electronic transference number \( t_e \) should be nearly zero or less than \( 10^{-4} \). Both anions and cations can move in a lattice. The ionic radii of cations are smaller than that of anions. For example, Pauling ionic radii of alkali metal ions and halide ions are:

<table>
<thead>
<tr>
<th>Cations</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>F(^-)</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>Cl(^-)</td>
</tr>
<tr>
<td>K(^+)</td>
<td>Br(^-)</td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>I(^-)</td>
</tr>
</tbody>
</table>

The ions having high mobilities are:

- Cations: \( \text{Ag}^+, \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Cu}^+ \)
- Anions: \( \text{F}^-, \text{O}^{2-} \)

The superionic conductors have monovalent ion except oxygen ion conductors. As the coulombic energies involved in jumping of di or trivalent ions would be more than those for monovalent ions, the di and trivalent ions show low mobility.
Table 1.1 lists electrical conductivity and activation energy of some good superionic solids. The Ag⁺ and copper ion conductors have good ionic conductivity. From Table 1.1 we conclude that most of good ionic conductors at low temperatures are cationic conductors while anionic conductors (O²⁻ and F⁻) normally give high ionic conduction at high temperature only.

The structure is probably the most important factor (Wiedersich and Geller 22) responsible for high ionic conduction. Structural principles governing the formation of solids showing fast ion transport have been given by Phillips 23 and Raleigh. 24

Table 1.1

<table>
<thead>
<tr>
<th>Some Superionic Solids with their Electrical Conductivities and Activation Energies.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material</strong></td>
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<tr>
<td>----------------</td>
</tr>
<tr>
<td>Silver Ion conductor</td>
</tr>
<tr>
<td>α-AgI</td>
</tr>
<tr>
<td>Cation substituted AgI based</td>
</tr>
<tr>
<td>NH₄Ag₄I₉</td>
</tr>
<tr>
<td>KAg₄I₉</td>
</tr>
<tr>
<td>RbAg₄I₉</td>
</tr>
<tr>
<td>[(CH₃)₄N]⁺₂Ag₁₃⁻I₁₅</td>
</tr>
</tbody>
</table>
Table 1.1 continued

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (ohm $^{-1}$ cm $^{-1}$)</th>
<th>Temp. ($^\circ$C)</th>
<th>Activation energy (eV)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}_3\text{SI}$</td>
<td>0.01</td>
<td>25</td>
<td>0.21</td>
<td>Reuter and Harel, Hoshino et al. 28</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{I}_4\text{PO}_4$</td>
<td>0.019</td>
<td>25</td>
<td>0.16</td>
<td>Takahashi et al. 30</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{I}_4\text{WO}_4$</td>
<td>0.047</td>
<td>25</td>
<td>0.16</td>
<td>Takahashi et al. 31</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{I}_4\text{AsO}_4$</td>
<td>0.004</td>
<td>25</td>
<td>0.17</td>
<td>Shahi and Chandra. 32</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{I}_4\text{Cr}_2\text{O}_7$</td>
<td>0.017</td>
<td>25</td>
<td>0.15</td>
<td>Scrosati et al. 33</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{I}_3\text{MoO}_4$</td>
<td>0.021</td>
<td>25</td>
<td>–</td>
<td>Lazzari et al. 34</td>
</tr>
<tr>
<td><strong>Cation and Anion substituted AgI based</strong></td>
<td></td>
<td></td>
<td></td>
<td>Kuwano and Kato 35</td>
</tr>
<tr>
<td>$\text{KAg}_4\text{I}_4\text{CN}$</td>
<td>0.14</td>
<td>25</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>$\text{RbAg}_4\text{I}_4\text{CN}$</td>
<td>0.18</td>
<td>25</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>$\text{Ag}<em>{1.85}\text{Hg}</em>{0.4}\text{Te}<em>{0.65}\text{I}</em>{1.35}$</td>
<td>0.094</td>
<td>25</td>
<td>–</td>
<td>Takahashi 37</td>
</tr>
<tr>
<td><strong>Miscellaneous</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{AgGaS}_2$</td>
<td>$\sim \sim 10^{-5}$</td>
<td>25</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>$\text{AgGaS}_3$</td>
<td>$10^{-5}$</td>
<td>25</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>$\text{AgGaSe}_2$</td>
<td>$10^{-4}$</td>
<td>25</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td><strong>Silver $\beta$ alumina</strong></td>
<td>0.006</td>
<td>25</td>
<td>1.7</td>
<td>Kennedy 39</td>
</tr>
<tr>
<td><strong>Copper Ion conductors</strong></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$\text{CuI}$</td>
<td>0.09</td>
<td>450</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>$\text{KCu}_4\text{I}_5$</td>
<td>0.6</td>
<td>280</td>
<td>0.22</td>
<td>Matsui and Wagner 40</td>
</tr>
<tr>
<td>$(\text{C}_5\text{H}_5\text{NH})_2\text{Cu}_3\text{Br}_7$</td>
<td>0.017</td>
<td>292</td>
<td>0.18</td>
<td>Banino and Lazzari 41</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Skarstad and Parker 42</td>
</tr>
<tr>
<td>Material</td>
<td>Conductivity (ohm$^{-1}$cm$^{-1}$)</td>
<td>Temp. (°C)</td>
<td>Activation energy (eV)</td>
<td>References</td>
</tr>
<tr>
<td>----------------------------------------------</td>
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<td>----------------</td>
</tr>
<tr>
<td>C$<em>5$H$</em>{12}$N$_2$.2HBr-CuBr</td>
<td>~ 0.05</td>
<td>20</td>
<td>0.07</td>
<td>Takahashi and Yamamoto 43</td>
</tr>
<tr>
<td>CuTa$_2$O$_6$</td>
<td>~ 10$^{-3}$</td>
<td>300</td>
<td>0.36</td>
<td>Goodenough et al. 44</td>
</tr>
<tr>
<td>α-Cu$_2$Se</td>
<td>0.11</td>
<td>150</td>
<td>0.05</td>
<td>Takahashi et al. 45</td>
</tr>
<tr>
<td>Copper(I)rubidium-chloro iodide</td>
<td>0.34</td>
<td>25</td>
<td>-</td>
<td>Takahashi 15</td>
</tr>
</tbody>
</table>

**Lithium Ion Conductors**

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (ohm$^{-1}$cm$^{-1}$)</th>
<th>Temp. (°C)</th>
<th>Activation energy (eV)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiI (pure)</td>
<td>5.5x10$^{-7}$</td>
<td>30</td>
<td>0.434</td>
<td>Schlaikjer and Liang 46</td>
</tr>
<tr>
<td>LiI + (2% CaF$_2$)</td>
<td>1.0x10$^{-5}$</td>
<td>30</td>
<td>0.434</td>
<td>Liang 47</td>
</tr>
<tr>
<td>LiI + (40% Al$_2$O$_3$)</td>
<td>1.2x10$^{-5}$</td>
<td>25</td>
<td>0.434</td>
<td></td>
</tr>
<tr>
<td>Li$_2$SO$_4$</td>
<td>~ 1</td>
<td>800</td>
<td>0.36</td>
<td>Kvist and Lunden 48</td>
</tr>
<tr>
<td>LiAlSiO$_4$</td>
<td>4.7x10$^{-3}$</td>
<td>25</td>
<td>0.95</td>
<td>Raistrick et al. 50</td>
</tr>
<tr>
<td>LiAlSiO$_4$ (glass)</td>
<td>1.5x10$^{-3}$</td>
<td>400</td>
<td>0.68</td>
<td>Johnson et al. 51</td>
</tr>
<tr>
<td>Li$<em>4$(Si$</em>{0.7}$Ti$_{0.3}$)O$_4$</td>
<td>4x10$^{-3}$</td>
<td>400</td>
<td>0.62</td>
<td>West 52</td>
</tr>
<tr>
<td>Li$_4$SiO$_4$ (40 m/o) + Li$_3$P$_2$O$_5$ (40 m/o)</td>
<td>1x10$^{-4}$</td>
<td>100</td>
<td>0.555</td>
<td>Huggins, 53</td>
</tr>
<tr>
<td>Li$_3$N (pure)</td>
<td>3.7x10$^{-8}$</td>
<td>25</td>
<td>0.61</td>
<td>Mu et al. 54</td>
</tr>
<tr>
<td>Li$_3$N (Li rich)</td>
<td>2x10$^{-4}$</td>
<td>25</td>
<td>0.19</td>
<td>Huggins 53</td>
</tr>
</tbody>
</table>

**Sodium Ion Conductors**

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (ohm$^{-1}$cm$^{-1}$)</th>
<th>Temp. (°C)</th>
<th>Activation energy (eV)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium β alumina</td>
<td>1.4x10$^{-2}$</td>
<td>25</td>
<td>0.16</td>
<td>Kennedy 39</td>
</tr>
<tr>
<td>Material</td>
<td>Conductivity (ohm$^{-1}$ cm$^{-1}$)</td>
<td>Temp. (°C)</td>
<td>Activation energy (eV)</td>
<td>References</td>
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</tr>
<tr>
<td>NaAlCl$_4$</td>
<td>3.5x10$^{-7}$</td>
<td>25</td>
<td>0.44</td>
<td>Huggins 53</td>
</tr>
<tr>
<td>NaAlSiO$_4$</td>
<td>~5.2x10$^{-4}$</td>
<td>300</td>
<td>-</td>
<td>Goodenough et al. 44</td>
</tr>
<tr>
<td>Na$_2$Gallate</td>
<td>3.0x10$^{-2}$</td>
<td>300</td>
<td>0.27</td>
<td>Boilot et al. 55</td>
</tr>
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<td>Foster and Scardfield 57</td>
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<td></td>
<td>Beyeler and Himba 58</td>
</tr>
<tr>
<td>Na$_5$GdSi$<em>4$O$</em>{12}$</td>
<td>6.0x10$^{-2}$</td>
<td>200</td>
<td>0.26</td>
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**Potassium Ion Conductors**

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (ohm$^{-1}$ cm$^{-1}$)</th>
<th>Temp. (°C)</th>
<th>Activation energy (eV)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$Al$_2$O$_4$</td>
<td>6.5x10$^{-5}$</td>
<td>300</td>
<td>0.29</td>
<td>Kennedy 59</td>
</tr>
<tr>
<td>K$_2$Al$_2$O$_4$</td>
<td>5.0x10$^{-5}$</td>
<td>300</td>
<td>-</td>
<td>Goodenough et al. 44</td>
</tr>
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<td></td>
<td></td>
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<td></td>
<td>Schoonman et al. 59</td>
</tr>
</tbody>
</table>

**Anion Conductors**

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (ohm$^{-1}$ cm$^{-1}$)</th>
<th>Temp. (°C)</th>
<th>Activation energy (eV)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbF$_2$</td>
<td>1.0</td>
<td>900</td>
<td>0.6</td>
<td>Bonne and Schoonman 60</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Derrington et al. 61</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>01' keefte 62</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>4.0x10$^{-2}$</td>
<td>700</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>LaF$_3$</td>
<td>0.15</td>
<td>890</td>
<td>-</td>
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</table>

**Oxygen Ion Conductors**

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity (ohm$^{-1}$ cm$^{-1}$)</th>
<th>Temp. (°C)</th>
<th>Activation energy (eV)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$ : 12% CaO</td>
<td>5.5x10$^{-2}$</td>
<td>1000</td>
<td>1.09</td>
<td>Etsell and flengas 53</td>
</tr>
<tr>
<td>ThO$_2$ : 8% Y$_2$O$_3$</td>
<td>4.8x10$^{-3}$</td>
<td>1000</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>CeO$_2$ : 7% SmO</td>
<td>0.11</td>
<td>1000</td>
<td>1.12</td>
<td></td>
</tr>
</tbody>
</table>
A highly "disordered structure" is the common feature in all the materials. The number of sites in cationic sublattice is more than the number of cations in the unit cell. Thus the percentage occupancy of each site is low. A free ion like hopping of these ions from one site to another may take place giving high conduction. The low percentage occupancy is also present in the $\beta$ alumina group of superionic solids.

Ion conduction studies in binary compounds (e.g., AgI, CuCl, CuI etc.) made by Phillips reveals that energies related to covalent and ionic bonds in these compounds may be determined spectroscopically and their values furnish the possibility of determining the free energy difference, $\Delta G$ between the two possible configurations. Four fold and six fold coordinations when displayed in covalent ionic plane, compounds with four fold coordination are separated from six fold coordination by a line at a critical value of ionicity equal to 0.785. The closer is the value of the ionicity $f_1$ of a given compound to this critical value, the lower will be the Gibbs free energy difference $\Delta G$, between the four fold and six fold coordination when a foreign ion is added to AgI (or generally to a $A^N B^S-N^-$ salt with a $\Delta G$ value near zero) and the mixture is brought to a temperature near or above the phase transition (147°C for AgI) where the Ag ions are separated from the I partners, a double salt is formed with 'scaffolded' structure which results as a compromise between the two possible coordination configurations which AgI may assume.
This scaffolded structure may be regarded as formed by a skeletal framework of minority cation complexes (e.g., RbI in RbAg₄I₅) decorated by loosely bound, quasi interstitial majority cations Ag⁺²³. This would account for the relative ease in obtaining double salts from AgI. This structural principle has been deduced on the basis of cation substituted system.

1.5 Silver Ion Superionic Solids

A number of workers Wiedersich and Geller, Takahashi, Funke, Shahi and Chandra studied silver ion superionic solids. The measurement of conductivity in silver halides by Tubandt and Lorenz may be taken as starting point for the present day effort to understand and search for new silver ion conductor. It was reported that conductivity of AgI increases abruptly at 147°C due to conversion of low conductivity β AgI to high conductivity α AgI. Since then a large number of silver ion superionic solids have been discovered.

Most of silver ion superionic solids are based on AgI. These conductive new superionic solids have been obtained by substituting either different cations for Ag⁺ or different anions for I⁻ or both. Bradley and Greene and Owens and Argue independently reported silver ion superionic solids MAg₄I₅ (where M = Rb, K, NH₄) first time. Below disproportionation temperature MAg₄I₅ decompose as:

\[ 2MAg_4I_5 \rightarrow M_2AgI_3 + 7AgI \]
The disproportionation temperature for RbAg₄I₅, KAg₄I₅ and 
NH₄Ag₄I₅ are 28°, 39° and 32°C respectively. The presence of 
water vapour accelerates the rate of disproportionation reaction.

On the basis of ion transport studies of silver ion 
superionic solids by various workers 1,35 the following 
conclusions have been drawn.

(1) The cations are structurally disordered and cation 
sublattice is 'liquid like'. The number of cations is less 
than the number of sites available for them and these sites 
are occupied at random.

(2) The anions are arranged in such a way that the local 
potentials are rather flat along certain lines which inter-
connect neighbouring sites. Along these lines the difference 
in potential energy is of the order of thermal energy. 
According to Geller 70 "the common structural motif in the 
conductive compounds is the existence of passage ways of 
face shared iodide ion polyhedra".

(3) Due to the reasons given in (1) and (2) above, all or a large 
fraction of the cations can move from one site to another site 
with a very low activation energy of the order of thermal 
energy and thus, in general, participating in the cation 
diffusion process. The diffusion path is channel like and 
not exactly liquid like.

(4) The dis ordering process may be first order or second order.
At the first order transition temperature the conductivity changes abruptly and involves a change in lattice symmetry and latent heat. In second order phase transition, there is no abrupt change in conductivity but only a slope changes slightly. There is no or small change in lattice symmetry and is accompanied by a power law divergence in specific heat.

(5) Ion-ion correlation is an important factor in bringing about disorder.

(6) The ion transport is possibly by a jump diffusion process on which an additional cation local motion is superimposed (diffusive and/or overdamped oscillatory local motion).

(7) Number of sites available are more than the number of ions per unit cell giving the ions a free-ion like state.

1.6 Relation of Conductivity to Structure

Many solid electrolytes are formed between AgI and various iodides and silver compounds. These solid electrolytes have certain common structural features. The structure demonstrate that the role of the substituent ions is to stabilize structures in which mainly iodide tetrahedra share faces rather than corners as in \( \gamma \) AgI. This results in bringing adjacent sites closer together than in a corner sharing structure.

A unit cell of \( \gamma \) AgI contains eight tetrahedral and four octahedral sites in a volume of 274 Å\(^3\). A unit cell of \( \alpha \) AgI
contains twelve tetrahedral sites in a volume of $128 \, \text{Å}^3$. Though the volume of octahedron is four times than that of tetrahedron, it is nevertheless true that the site concentration in $\alpha\text{AgI}$ is higher than that of $\gamma\text{AgI}$. In $\text{RbAg}_4\text{I}_5$, the volume attributed to the 56 tetrahedra is $669 \, \text{Å}^3$ \cite{57}. More than half the crystal space is attributable to the four tetrahedra surrounding the $\text{Rb}^+$ ions and unoccupiable intersites. The substituent immobile cations and the parts of the iodide ions that are considered to belong to them occupy half or more of the crystal space (See Table 1.2).

The average coordination of the ions does not change significantly in the solid electrolytes relative to the separate salts, and therefore the volumes occupied are not much different e.g., the volume per RbI in RbI is 98.9 $\text{Å}^3$. The total volume of 4RbI and 16AgI is 1486 $\text{Å}^3$ as opposed to the volume 1420 $\text{Å}^3$ of a unit cell of $\text{RbAg}_4\text{I}_5$. If we take the volume per AgI from AgI at 145°C i.e., 64.2 $\text{Å}^3$, we obtain for the total volume 1422 $\text{Å}^3$ nearly equal to the volume of unit cell of $\text{RbAg}_4\text{I}_5$. It is nevertheless true that we cannot get such agreement from calculations of the volume of the polyhedra. For AgI, the volume of an iodide tetrahedron is 10.7 $\text{Å}^3$ while the volume of an RbI octahedron in RbI is 131.8 $\text{Å}^3$, both much smaller than the respective polyhedra in $\text{RbAg}_4\text{I}_5$. Also in $\text{RbAg}_4\text{I}_5$ there are interstices which cannot be occupied but even if account is taken of their volumes, the total is still low. In $\text{RbAg}_4\text{I}_5$ the volumes of the polyhedra are larger.
than in the separate compounds.

Another example is that of PyAg₅I₅. The volume per PyI \( 0^0 \) is 165.2 \( 0^0 \) \( \text{A}^3 \). The separate formula for unit volumes give a total volume of 1012 \( 0^0 \) \( \text{A}^3 \) or 972 \( 0^0 \) \( \text{A}^3 \) (from AgI) to be compared with 931 \( 0^0 \) \( \text{A}^3 \) for the unit cell of PyAg₅I₅. In this case, the average coordination of both Py⁺ and Ag⁺ ions is increased over the respective coordination in the separate compounds. The face sharing of the polyhedra also tends to reduce the volume relative to corner sharing.

It appears that a reaction of AgI with another compound will be favoured if it results in lower average molar volumes for the components. It has been emphasized that AgI-based solid electrolytes all have networks of passageways formed from the face sharing of the anion polyhedra. This has been discussed in many papers.

The following points are worth emphasizing:

1. The structure in which current carrier sites are crystallographically equivalent, the distribution of the current carriers over the different sites is non-uniform.

2. As long as the crystal structure does not change, the distribution of current carriers over crystallographically non-equivalent sites will remain non-uniform up to the melting point but the distribution does not change with temperature.
### Table 1.2

Some specialized data on AgI based solid electrolytes.

<table>
<thead>
<tr>
<th>Solid Electrolytes</th>
<th>Mobile Ag⁺ ions per unit cell</th>
<th>Ag⁺ ion sites per unit cell</th>
<th>Vol. of Channels Vol.of unit cells</th>
<th>nₐg</th>
<th>nₛ</th>
<th>cm⁻¹ cm⁻¹ 295 K</th>
<th>cm⁻¹ cm⁻¹ 419 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; AgI</td>
<td>2</td>
<td>12</td>
<td>1.0</td>
<td>1.57</td>
<td>9.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbAg₄I₅</td>
<td>15</td>
<td>56</td>
<td>0.471</td>
<td>1.13</td>
<td>3.94</td>
<td>0.27</td>
<td>0.65</td>
</tr>
<tr>
<td>PyAg₃I₅</td>
<td>10</td>
<td>34</td>
<td>0.525</td>
<td>1.07</td>
<td>3.65</td>
<td>0.077</td>
<td>1.1</td>
</tr>
<tr>
<td>[(CH₃)₄N]₂Ag₁₃I₁₅</td>
<td>13</td>
<td>41</td>
<td>0.39</td>
<td>1.04</td>
<td>3.28</td>
<td>0.04</td>
<td>0.26</td>
</tr>
<tr>
<td>Ag₂₆I₁₈(W₄O₁₅)</td>
<td>23.2</td>
<td>90ᵃ + 55ᵇ</td>
<td>0.344ᵃ + 0.221ᵇ</td>
<td>0.78</td>
<td>4.96</td>
<td>0.058</td>
<td>0.31</td>
</tr>
<tr>
<td>Py₅Ag₁₈I₂₃</td>
<td>18</td>
<td>55</td>
<td>0.315</td>
<td>0.89</td>
<td>2.72</td>
<td>0.008</td>
<td>0.05</td>
</tr>
</tbody>
</table>

ᵃ = Pure iodide polyhedra.  
ᵇ = Mixed I - O polyhedra.  

nₐg = Ag ion concentration.  

nₛ = Site concentration.
(3) The conductivity appears to be associated with the nature of the passageways. As the passageways become simpler, the conductivity becomes higher.

(4) Three dimensional networks give higher average conductivities than two dimensional networks.

(5) Higher site concentrations give higher conductivities.

(6) Larger volumes of crystal space occupied by the conduction passageways lead to higher conductivities.

(7) The ratio of an available sites to current carriers must be greater than two for solid electrolytes. From Table 1.2 it can be seen that for AgI the factor is highest and for Pb3Ag18I23 it is lowest.

(8) Interactions between cations on nearest neighbour tetrahedral sites must be strong and repulsive because the intersite distances are so short as to imply that such sites cannot be occupied simultaneously.

(9) The 'squeezing' of Ag+ ions on passing through a shared triangular face from one polyhedron to another probably determines the activation enthalpy of motion. This is cation-anion interaction.

(10) The stability of the Ag+ ions in both 4- and 3-coordination and their monovalency are responsible for their being mobile ion in most of the good solid electrolytes.
1.7 **Superionic Phase Transition**

A large number of ionic solids are found to undergo a transformation from a poorly conducting state at low temperature to a highly conducting state with the activation energy of ionic motion and preexponential factor apparently characteristics of liquids at high temperature. This has been concluded on the basis of electrical conductivity Vs. temperature studies for a large number of ionic solids. The phase transitions have been classified in the following way:

**Class I** : Insulator-electrolyte phase transition :-

This shows the following characteristics.

(i) A discontinuity in conductivity Vs. \( T^{-1} \) curve.
(ii) A change in lattice symmetry.
(iii) Latent heat is typical like first order transition.

**Class II** : Order-disorder phase transition :-

The characteristics of this class is given below.

(i) The conductivity Vs. \( T^{-1} \) curve is continuous with a small change in slope at the transition temperature i.e., there is no abrupt change in conductivity.
(ii) No change in lattice symmetry.
(iii) There is power law divergence in the specific heat.

Class I transition occurs for \( \text{RbAg}_4\text{I}_5 \) and \( \text{AgI} \) at \(-151^\circ\text{C}\) and \(147^\circ\text{C}\) respectively. Class II transition occurs at \(-54^\circ\text{C}\) for \(\text{RbAg}_4\text{I}_5\).
If the characteristics of fast ionic conduction are due to sublattice disorder, the existence of a transformation to a conducting state with temperature means that some structural changes occur with temperature which lead to a phase change. A possible structural change for disorder which increases the conductivity, is a repopulation of conducting ions from their regular sites to other available interstitial sites. Sato and Kikuchi explained this process with two dimensional honeycomb lattice with two equivalent sublattices. Activation energy \( W \) is required to promote an ion from regular one site to other site. The situation is changed due to interactions among ions.

Different theories have been given to explain the phase transition in superionic solids, some of them are given below:

1. **Phenomenological models** — In these models, the thermally generated defects interact in such a way that charge carriers density increases abruptly or discontinuously. This results to an abrupt or discontinuous increase in conductivity. These models were proposed by Huberman, Rice, Strassler and Toomba (R.S.T.) and Welch and Dienes. According to Huberman, Frenkel pair attractive interactions take place between the interstitial ion and the lattice vacancy. Rice and coworkers showed that in their model the defects interacting with the strain field was shown to be responsible for the transition to superionic state. Welch and
Dienes incorporated the above two models and assumed that the activation energy for formation is concentration dependent due to defect interactions. They have given an expression for $F(c)$, concentration ($c$) dependent term for free energy per ion as under:

$$F(c) = E(c) - kT \left[ -2c \ln c - (1-c) \ln (1-c) - (\alpha - c) \ln (\alpha - c) + \alpha \ln \alpha \right] - T S_{vib}(c) \quad \ldots (1.10)$$

where $\alpha$ is the ratio of number of interstitial "cells" to the number of ions, $E(c)$ is the concentration dependent energy required for pushing an atom into an interstitial site, $S_{vib}$ is the vibrational contribution to the entropy.

O'Reilly derived an expression for $F(c)$ including a nearest neighbour interaction energy term and degeneracy of sites available to the mobile ions.

(ii) Another theory to explain superionic phase transition is given by Phillips. He postulated that the microdomains or dual phases are developed when material is cooled. At high temperature no microdomain is in the material. As temperature decreases and when it is equal to temperature of second order transition, microdomain nucleate in the quasi first order transition. If the material is soft the phase transition thus nucleated may be arrested by strain interaction between nuclei. Further reduction of temperature the nuclei grow slowly until temperature becomes equal to temperature of first order transition.
the sample transforms to low temperature phase.

(iii) **Lattice Gas Theory** — In these theories the mobile ions can be considered as a "Lattice gas" hopping from one site to another. The hopping "Lattice gas" particles interact with each other and modify the ion diffusion or transport activation energy. For β alumina, using path probability method Sato and Kikuchi 82 did statistical calculation. Using Monte Carlo method, Murch and Thorn 83 also did these calculations. Both the above calculations could simulate Class II type phase transitions.

1.8 **Dynamics of Ion Transport**

Fast ion transport in superionic solids has been explained by the following three ways.

1. Free ion model.
2. Domain model.
3. Hopping or jump diffusion model.

1. **Free ion model** — In this model Rice and Roth 19 assumed that an ion is thermally excited from a localized state to a state in which the ion moves translationally through the solid to another localized state. They assumed existence of energy gap $E_0$ in superionic conductors. Ions can be thermally excited from localized states to free ion like states with a velocity $V$ and energy ($E = \frac{1}{2}MV^2$). $M$ is the mass of
ion. The excited free ion like states have finite life time $\tau$. With the help of Boltzmann transport equation governing the rate of change of thermal occupation of free ion like states, Rice and Roth $^{19}$ gave the equation for ionic conductivity :

$$\sigma = 2/3 \frac{(Ze)^2}{kT} n_1 \epsilon_0 \tau \epsilon_o e^{-\epsilon_o / kT} \quad (1.11)$$

where $n_1$ is the number of available conducting ions per unit volume and $Ze$ is the charge on each mobile ion. The Eq. (1.11) resembles the Arrhenius type expression for the simple hopping model of ionic conductivity :

$$\sigma = 1/3 \frac{(Ze)^2}{kT} n \cdot a_o^2 \omega_o e^{-E/kT} \quad (1.12)$$

where $a_o$ is the hopping distance, $\omega_o$ is ionic oscillator frequency and $E$ is migration activation energy.

According to Haas, $^{34}$ it is not necessary to invoke "free ion" theory and same results can be obtained by 'hopping models'.

(ii) Domain Model — This model has been given by Van Gool $^{35}$ and Van Gool and Bottlebergs. $^{35}$ We know that conductivity increases with lowering of activation energy in superionic solids. Two important possibilities for low values of activation energy are :

(a) Cooperative jump of a number of ions (Sato and Kikuchi). $^{31,32}$
(b) Movement of walls between domains of ordered configurations
(Van Gool and Bottleberghe). 85

In one domain it is assumed that ions are occupying one
type of position (say BR or aBR site in case of β aluminas)
and in an adjacent domain another set of positions is occupied.
Considering the domain as a "defect", the energy per ion
necessary to create "defect" has been found to be low to explain
the low activation energy.

Kharkats 87 has given thermodynamic theory of domain
formation in superionic crystals. The theory is similar to
phenomenological models as discussed earlier with one important
difference. For defect formation it is assumed that system
processes local electroneutrality at every point of crystal.
This gives homogeneous states of crystal. Kharkats has shown
the possibilities of thermodynamically stable states in crystal
which do not satisfy the conditions of local electroneutrality
(i.e., nonhomogeneous states) but comply "integral electroneutrality"
condition. These nonhomogeneous states corresponding
to the separation of the crystal into domain regions with
increased or lowered concentrations of interstitial cations and
vacancies in relation to their average values. The solution of
the expression for free energy of disordering obtained for the
system obeying "integral electroneutrality" conditions correspond
to the division of the crystal into a set of regions (domains) of
two types. These inhomogeneous integrally electroneutral domain
states may exist only a certain temperature intervals where
the thermodynamic potential of all homogeneous states of the
crystal.

(ii) **Jump Diffusion Model** — Huberman and Sen has given
his theory for jump diffusion. They assumed that mobile ions have two basic degrees of freedom
(a) an oscillatory motion in the harmonic potential provided by
a rigid lattice and (b) a random walk process through which they
can diffuse throughout the crystal. The jump process was assumed
instantaneous and being uncorrelated with the oscillatory motion.
This theory was unable to explain detailed structure but it could
predict the peak in conductivity for $\beta$ alumina. Bruesch et al.,
Fulde et al., and Zeller et al. have investigated the Brownian
motion in periodic lattice including the effects of polarisability
of lattice and correlated jumps of ions relevant to the problem
of superionic conductors.

In the perfect crystals, the diffusion of ions takes place
in the form of hopping. The ions are located mostly in their
specific lattice sites and the attempt frequency $W_0$ should be
the ordinary vibrational frequency of crystal lattices. Due to
sublattice disorder and low activation energy, the potential wells
in which the conducting ions are located are shallow and makes
attempt frequency low. At the same time the amplitude of thermal
motion becomes large as indicated by results of diffraction
experiments.
If ions are making large amplitude motion around many possible interstitial positions and translational motions from one site to another, it should be possible to observe such motions as a high frequency response of the conductivity. Funke et al. concluded that silver ion in AgI might be described as a superposition of translational jump diffusion and a large amplitude local random motion. They analysed the data in terms of dwell time $T_0$ and the mean hopping $T_1$ assuming jump distance, $d$ is of the order of lattice constant. The measurements of Raman spectra for many fast ionic conductors confirmed the existence of liquid like, slow large amplitude motion in these substances. The distribution of the above two degrees of freedom is carried out in terms of the velocity correlation function:

$$Z(T) = \left< v(t) \cdot v(t + T) \right>$$  \hspace{1cm} (1.13)

and Fourier transformation of Eqn. 1.13 is:

$$\tilde{Z}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} Z(T) \exp(-i\omega T) \, dT$$  \hspace{1cm} (1.14)

After solving the above equation we get frequency dependent ionic conductivity.

$$\sigma(\omega) = \frac{\pi n (Z_0)^2}{kT} \tilde{Z}(\omega)$$  \hspace{1cm} (1.15)

Zeller et al. discussed the problem based on memory function formalism. The motion of the particles in the periodic potential is described by Langevin equation:
\[ m\ddot{x} + m\gamma \dot{x} + f(x) = K \]  

(1.16)

where \( m \) is mass of particle, \( \gamma \) the damping, \( f(x) \) the restoring force and \( K \) the stochastic force. At low frequency the Eqn. 1.16 should reduce to a simple diffusion equation while at high frequencies it should represent a damped harmonic oscillator. Zeller et al. solved the Eqn. 1.16 using memory function formalism and got the following expression for frequency dependent conductivity.

\[
\sigma (\omega) = \frac{n(Ze)^2}{m} \frac{1}{-i\omega + \gamma + \frac{\omega_0^2}{-i\omega + \gamma}}
\]  

(1.17)

where \( \omega_0 \) is the resonance frequency.

For solid electrolytes and molten salts \( \sigma(\omega) \) have been determined experimentally. The calculated and experimental values of \( \sigma(\omega) \) for AgI match below \( \sim 20 \text{ cm}^{-1} \).

Cleman and Funke \(^9^4\) has given a jump diffusion model for explaining microwave conductivity. During conductivity measurements, he assumed that applied electric field give (i) start effect, (ii) acceleration effect for jumping of ions. The experimental and calculated results are similar. This confirms that jump diffusion model superimposed by local motion is the good phenomenological description of ion dynamics in superionic conductors.
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