Thesis summary
The thesis entitled “Preparation of Superionic Conductors by Solid State Reactions”, deals with the preparation and studies of electrical properties of pure and substituted superionic conductors.

Superionic conductors are solid compounds in which electric current is carried by charged atoms, i.e. by ions. The passage of current is thus associated with mass transfer. Such ionic conductors are called superionic conductors and sometimes “composites solid electrolytes”, by analogy to liquid electrolyte solutions, and have permitted development of a new scientific discipline, viz. solid state electrochemistry. The associated technology is termed solid-state ionics, in contrast to solid-state electronics.

1. Introduction:

Composite solid electrolytes of the ionic salt–oxide (MX–A) type can be considered a new class of superionic conductors with high ionic conductivity which occurs through interfaces. Composite materials are heterogeneous materials of solid phases. The effect of heterogeneous doping strongly depends on the chemical nature of components and the morphology of the system. This new class of solid electrolytes interfaces called ion conducting electrolytes made up of ionic salt and insulating chemically inert component, affects the properties of composite materials at low and moderate temperatures. Studies concerning electrical properties of TlI, CsI and CdI\textsubscript{2} were performed in this work.

Thallium iodide (TlI) exists in two polymorphs; yellow β-TlI, a double layered orthorhombic structure related to NaCl which transforms to red α-TlI at 172 °C. This phase transition is accompanied by about two orders of jump in conductivity. However, CsI exist in rhombic dodecahedral form and transferred to cubic form at higher temperature. CdI\textsubscript{2} was found to be in hexagonal polymorph
with rhombocentered lattice. Many attempts have been made to stabilize the high conducting phases of these compounds at room temperature, by substituting ionic oxides e.g alumina, titania etc. Hence, the aim is to decrease the temperature of high conducting phase or, in other words, to stabilize the superionic phases at lower temperatures to be suitable for low temperature applications.

In the present work, preparation and studies of electrical properties of pure and substituted superionic conductors of the following types have been studied.

1. Pure TII and TII doped with titania, alumina and vanadia.
2. Pure CsI and CsI doped with titania and alumina.
3. Pure CdI₂ and CdI₂ doped with titania and alumina.

X–ray powder diffraction, DSC, SEM and electrical conductivity measurements were used mainly to confirm the preparation and investigate the properties of these superionic conductors.

**Preparations**

All the superionic compounds were prepared by the usual solid state reaction method from their corresponding raw materials. The required amounts were mixed thoroughly using agate mortar and pestle to produce samples with substitution ratio 0-0.7. The mixtures were then heated in an electrical furnace at 150°C for 3 hrs with intermittent grinding. The following mixtures were prepared:

1. (1-x)TII-xD where, dopant D = TiO₂, Al₂O₃ and V₂O₅.
2. (1-x)CsI-xD where, dopant D = TiO₂ and Al₂O₃.
3. (1-x)CdI₂-xD where, dopant D = TiO₂ and Al₂O₃.

**X–ray powder diffraction and DSC**

The prepared materials were crushed to fine powders and subjected to X–ray powder diffraction and differential scanning calorimetry (DSC). The
compounds were identified by comparing their 2θ values with the standard values of the expected compounds. The sharp phase transitions of the compounds were identified from their corresponding thermal arrests in the DSC curves.

**Scanning electron microscopy**

SEM micrographs were taken for the pelletized samples using the STEREOSCAN 360 MICROSCOPE in order the surface features and particle size of the composites.

**Ionic conductivity measurement**

Impedance spectroscopy at room temperature were performed for circular pellets pressed under pressure of 4 tonnes/cm², with carbon painted on two opposite surfaces of the pellets. The measurements were carried out using HIOKI3532-50 LCR meter in the frequency range 40 Hz-5 MHz.

2. **Electrical conduction in metallic oxide titania, alumina and vanadia doped TII**

The conductivity increases with the titania, alumina and vanadia contents in the materials and passes through a threshold value, thereafter it starts to decrease with further increase in the mole fraction of the dispersoid. The threshold value is found to be $x = 0.5$ in TII-$x\text{TiO}_2$ and TII-$x\text{V}_2\text{O}_5$ systems. However, when the pure thallium iodide is dispersed with different mole percent of $\text{Al}_2\text{O}_3$, conductivity seems to increase as the amount of alumina increases and reaches a maximum at $x=0.4$ mole fraction of alumina, thereafter it decreases. This drop in ionic conductivity after threshold value is due to the blocking of conduction pathways by the dispersoid particles.

Room temperature X-ray diffractograms of the pure TII and its mixtures with $\text{TiO}_2$, $\text{Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5$ were taken. The diffractograms of the mixtures show
two phase nature of these materials with no effect of the second phase on the peak positions of first i.e. TII.

DSC traces showed endothermic peaks in the temperature range of 172°C, depending on the sample composition. These are attributed to the solid state reaction between TII heterogeneously mixed with TiO₂, Al₂O₃ and V₂O₅.

Impedance spectra showed the prominence of electrode–electrolyte interface effect which is explained in terms of the high rate of ion migration. The SEM micrograph shows reasonable homogeneity with the average particle size in the range 200–400 nm.

3. Electrical conduction in alumina and titania doped CsI

Ac impedance spectroscopy has become a powerful tool for the investigating of the ionic conductivity of metallic samples. The introduction of alumina and titania into the lattice of CsI has marginally increased the ionic conductivity at lower concentration of Al₂O₃ and TiO₂ while a further increase in the dispersoid concentration till threshold value, which is x = 0.3 in these cases, leads to a 2-3 fold enhancement of the ionic conductivity beyond that of the pure compound. X-ray Diffractogram of pure CsI and CsI doped with alumina does not show any characteristic peak associated with the alumina, indicating the two phases are completely dispersed due to the cubic phase nature of CsI as well as alumina. However, in CsI doped with titania, a new peak was observed, which is attributed to anatase phase of titania. DSC Curves showed that the pure cesium iodide does not give evidence of any transition and give only its melting peak at 620°C. In case of alumina a small hump appear but on contrary titania does not give any additional peak when its doped with CsI. It has been observed from SEM
images that dispersoid and CsI have different particle size which can leads to a large number of point defects leading to enhancement of ionic conductivity.

4. Electrical conduction in composites electrolyte systems CdI$_2$-TiO$_2$ and CdI$_2$-Al$_2$O$_3$.

   Impedance plots of ionic conductors showing a semicircle at high frequency side and a spike at lower frequency. The threshold value (maxima) is estimated to be $x = 0.5$ for titania and $x = 0.3$ for alumina. The reason behind such high conductivity mainly includes defect formation at the interface region, which is itself a disordered region.

   The X-ray diffractograms of the pure CdI$_2$ and its mixtures with TiO$_2$ and Al$_2$O$_3$ shows the standard pattern corresponding to β–phase of CdI$_2$ stable at room temperature. The single phase of CdI$_2$ has been fitted equally well to the hexagonal polymorph with the rhombocentered lattice. Pure CdI$_2$ shows the expected behavior with a moderate strength peak that appears at 551$^0$C, which corresponds to β–α phase transition of the compound and an intensive peak at 381$^0$C which is attributed to the melting point. In case of alumina doped in CdI$_2$, at higher concentration ($x=0.6$) a small peak appears at 278$^0$C on the lower temperature side of the melting peak.