Solid State Ionics, a rapidly growing interdisciplinary branch of science and technology, mainly deals with physics, chemistry and technological aspects of fast ion conduction in solids. Solid state ionic materials show several technological promises in various solid state electrochemical devices, such as solid state batteries, fuel cells, electrochromic displays, sensors, super capacitors etc. These materials are termed as "Superionic Solids" or "Fast Ion Conductors" or "Solid Electrolytes" or "Hyperionic Solids". Because of their characteristic high conductivity properties, superior to the liquid/aqueous electrolytes, these materials have tremendous industrial as well as academic importance. The devices based on these materials can potentially overcome all the major limitations of aqueous electrolyte based devices. This fact motivated many researchers to develop new materials with high ionic conductivity and a large number of fast ion conductors with various mobile cations like H+, Li+, Na+, K+, Ag+, Cu+ as well as anions like F-, O2- have been investigated and their macroscopic/microscopic transport properties have been extensively studied. On the basis of structure and physical properties these materials have recently been classified broadly into crystalline/polycrystalline, glassy/amorphous, polymers and composite phases. Proton conductors are considered to be belonging to crystalline/polycrystalline phase, however, because of some of their specific physical properties, proton conductors are kept in a separate sub-class. Composite electrolytes mostly involve two phases coexisting separately in the system and are prepared in general by dispersing submicron size particles of an inert and chemically insoluble compound viz. Fe2O3, SiO2, ZrO2, Al2O3, SnO2, fly-ash etc. (referred to as second phase dispersoid) into a moderately conducting ionic solid such as AgI, AgCl, CuCl, Cul etc. (termed as first phase host matrix salt. Enhancement of ~1-3 orders of magnitude in the room temperature conductivity of the host material has been reported in these systems. Amongst the various superionic materials, AgI based silver ion conducting solids have their distinct position, because of their very high ionic conductivity at room temperature and low mobile ion activation energy. AgI is well known for its characteristic β-→α structural phase
transition at \(-147 ^\circ \text{C}\). It undergoes a transition from a low conducting \(\beta - \text{AgI}\) to superionic conducting \(\alpha - \text{AgI}\). Numerous attempts have been made to arrest the \(\alpha - \text{AgI}\) at room temperature and a large number of fast \(\text{Ag}^+\) ion conducting systems in various phases have been discovered. In a recent investigation at the present laboratory, a new compound a "quenched/annealed \(0.75\text{AgI} : 0.25\text{AgCl}\) mixed system/solid solution" has been synthesized which exhibited several transport parameters superior to \(\text{AgI}\) including identical \(\beta -> \alpha\)-like phase transition at a substantially reduced transition temperature \((-135 ^\circ \text{C})\). The new host yielded several 2-phase composite/glassy systems which exhibited superior electrolyte properties as compared to those prepared identically using conventional host salt \(\text{AgI}\). In the present investigation, following two new 2-phase composite electrolyte systems have been synthesized using this new host as a first phase host matrix salt.

(i) \((1-x)[0.75\text{AgI} : 0.25\text{AgCl}] : x\text{SiO}_2\) and

(ii) \((1-x)[0.75\text{AgI} : 0.25\text{AgCl}] : x\text{ZrO}_2\)

Submicron size particle of fumed \(\text{SiO}_2\) and \(\text{ZrO}_2\) were dispersed as second phase dispersoid. An enhancement \((-10^1\)\) in the conductivity at room temperature has been achieved for the compositions : \(0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1\text{SiO}_2\) & \(0.9[0.75\text{AgI} : 0.25\text{AgCl}] : 0.1\text{ZrO}_2\). The room temperature conductivity value for both the systems are much higher than those systems prepared identically using conventional host \(\text{AgI}\).

The work reported in the present thesis includes the synthetization of the above 2-phase composite electrolyte systems adopting various route sequences, identification of optimum conducting compositions (OCCs), materials/transport property characterization and solid state battery studies. The structural, phase identification and the coexistence of two separate phases were done by XRD & DTA/DSC. The various studies on ionic transport parameters \(\text{viz.}\) conductivity \((\sigma)\), mobility \((\mu)\), mobile ion concentration \((n)\), transference number \((t_{\text{ion}})\), drift velocity \((v_d)\) and thermoelectric power \((\theta)\) were carried out employing different experimental techniques. Finally, batteries were fabricated by using the optimum conducting compositions (OCCs) as solid electrolyte and discharge characteristics were studied under different load conditions and with several cathode preparations. An additional, dc polarization/self-depolarization study was also carried out for the first time on some \(\text{Ag}^+\) ion conducting systems including both the hosts. These studies revealed that the mobile \(\text{Ag}^+\) ion of the system played
unique role which led to persistent polarization/electret-type behaviour in these systems. DC
polarization/self-depolarization technique was further extended in a novel way to estimate the
mobile ion concentration 'n' directly in these systems. The work reported in this thesis has been
divided in the seven Chapters and summarized as below:

Chapter 1 presents an overview on this relatively new field, Solid State Ionics, along with the
historical background. Various kinds of high ion conducting materials discovered so far are listed
along with the broad classification of these materials into various phases. The theoretical
models suggested to explain the ion transport mechanism in these materials have been reviewed.
The applications of these solids as electrolytes in various electrochemical devices, has been
described in brief. Since, the basic theme aimed at in the present work mainly concerns the
investigations on Ag⁺ ion conducting superionic solids in composite phase, hence, this phase has
been discussed extensively. Fast Ag⁺ ion conducting systems are normally AgI based solids. AgI
exhibits characteristic superionic α-phase after ~147 °C. In the preparation of fast Ag⁺
conducting glass/composite solids, this unique high conductivity property of AgI is exploited
using AgI as host matrix salt. However, in a recent investigations an alternate compound "a
quenched/annealed [0.75AgI : 0.25AgCl] mixed system/solid solution" has been reported to
exhibit better ionic parameters identical transport characteristics as AgI including β-α-like phase
transition at ~135 °C. In the present investigation two new 2-phase composite electrolyte systems
have been synthesized using this alternate host. The scope of the present thesis is given at the
end of the Chapter.

Chapter 2 reports the methods of preparation of two new fast silver ion conducting 2-phase
composite electrolyte systems : (i) (1-x)[0.75AgI :0.25AgCl]: xSiO₂ and (ii) (1-x)[0.75AgI :
0.25AgCl]: xZrO₂. Various experimental techniques employed to study the material/transport
property in these systems, have been discussed in greater detail. Following usual techniques
have been used:

- XRD and DTA/DSC for phase identification/material characterization;
- Impedance spectroscopy (IS) for electrical conductivity (σ) measurement;
Transient ionic current (TIC) technique for direct determination of ionic mobility ($\mu$), subsequently, mobile ion concentration ($n$) has been measured from 'c' and 'c' data.

Wagner's dc polarization method to measure ionic transference number ($t_{\text{on}}$) and drift velocity ($v_d$)

Differential thermal method for thermolectric power ($\Theta$) studies measurement.

The method of fabrication and discharge characteristic study on various solid state batteries are briefly discussed in the end of the Chapter.

Chapters 3 & 4 report the results obtained from various experimental measurements on the transport properties of the above mentioned two composite electrolyte systems: (i) (1-x)[0.75AgI :0.25AgCl]:xSiO$_2$ and (ii) (1-x)[0.75AgI : 0.25AgCl]:xZrO$_2$ respectively. The compositions: 0.9[0.75AgI : 0.25AgCl]:0.1SiO$_2$ and (ii) 0.9[0.75AgI : 0.25AgCl]:0.1ZrO$_2$, prepared by melt-quenched technique for soaking time ~ 20 & 15 min respectively, exhibited maximum enhancement in the room temperature conductivity and has been referred to as 'optimum conducting compositions (OCC)'. The XRD and DSC analysis demonstrate the coexistency of constituent phases. The temperature variations of conductivity, mobility, mobile ion concentration, ionic transference number and drift velocity on OCC exhibited Arrhenius-type behaviours. The activation energy ($E_a$), energy of formation ($E_f$), energy of migration ($E_m$) and energy $E_d$ have been computed from $\log \sigma$ vs $1/T$, $\log \mu$ vs $1/T$, $\log n$ vs $1/T$ and $\log v_d$ vs $1/T$ plots respectively. These results have been discussed in the light of existing theoretical models suggested for the 2-phase composite electrolyte phases.

Chapter 5 reports the method of solid state battery fabrication and discusses the results of discharge characteristic studies on solid state batteries fabricated using OCCs: 0.9[0.75AgI : 0.25AgCl]:0.1SiO$_2$ and (ii) 0.9[0.75AgI : 0.25AgCl]:0.1ZrO$_2$ as solid electrolytes. The cell performance were studied under different load conditions and with various cathode preparations viz. (C+I$_2$), (C+KI$_3$), [C+(CH$_3$)$_2$NI$_3$] and [C+(C$_2$H$_5$)$_2$NI$_3$]. These studies revealed that the battery fabricated with cathode (C + I$_2$) exhibited better cell performance as compared to those with other cathode materials. From the theoretical and experimental values of Open Circuit...
Voltage (OCV), ionic transference number ($t_{\text{ion}}$) has been measured for the two new composite electrolyte systems $t_{\text{ion}} \sim 1$ has been obtained which is in agreement with the earlier results.

Chapter 6 presents a subsidiary and additional work. A novel technique of polarization/self-depolarization has been proposed to demonstrate the role played by mobile Ag$^+$ ions in the ionic/superionic system. The electret-type/persistent-polarization-type behaviour has been observed in both the conventional and new host salts AgI and a quenched [0.75AgI:0.25AgCl] mixed system/solid solution. Involving another novel idea, dc polarization/self-depolarization technique has also been used to estimate the mobile ion concentration directly from 'current vs depolarization time' profile. The results obtained are found to be very close to those reported earlier using 'TIC' technique.

Finally, Chapter-7 gives the summery of the work done in the present thesis.