PREPARATION OF SOLID ELECTROLYTE USING SOLID STATE REACTIONS

SUMMARY

THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

CHEMISTRY

By

KHALID SIRAJ

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

2004
Summary
This thesis entitled, “Preparation of solid electrolyte using solid state reactions”, deals with the preparation and electrical conductivity measurements of pure and doped solid electrolytes.

Solid electrolytes also called superionic conductors are a class of materials exhibiting ionic conductivity comparable to strong liquid electrolytes, though they are in the solid state. Their history dates back to 1834 when Michael Faraday observed high electrical conductivity of PbF$_2$ at high temperature. In the early part of this century, cation conduction in silver halides has been extensively studied, contributing to the establishment of solid state electrochemistry. Since the sodium sulfur battery employing Na$^+$ conducting β-alumina ceramics was proposed in the 1960s, the practical importance of solid ionic conductors has been widely noticed. Nowadays these materials are indispensable for many kinds of electrochemical devices such as sensors and high – temperature fuel cells, etc.

Solid state ionic is now a thrust area because of ever increasing demand of solid electrolytes and the most widely used method for the preparation of solid electrolytes is the direct reaction in the solid state called solid state reaction. Though solid state reactions were known for a long time, it was only during the last few decades that interest has
been focused both experimentally and theoretically in revealing the secrets of the atomic structures of crystals and their reactivity.

In the present work, preparation and electrical conductivity of pure and doped solid electrolytes of the following types have been studied.

1. CdHgl₄ - Cul mixed system
2. Pure and Na⁺, Ag⁺ doped Cu₂CdI₄.
3. Pure and K⁺ doped Ag₂CdI₄.

X-ray powder diffraction and electrical conductivity method were used mainly to confirm the preparation and properties of these solid electrolytes.

**X-ray powder diffraction**

For the preparation of solid electrolyte reactants were mixed thoroughly in an agate mortar in different molar ratios and heated at 200°C for 48 hours. X-ray powder diffraction pattern of the reaction mixtures were measured and the compounds were identified by calculating their ‘d’ values and intensities, and comparing them with the standard values of the expected compounds.
Electrical conductivity measurement

For measuring the electrical conductivity of a compound sample powders were pressed into pellets of 4.54 cm$^2$ surface area with its thickness of 0.1 cm at a pressure of about 4 tonnes with the help of SPECTRA LAB Press (Model SL-89). The pellets were heated upto 200°C temperature for 12 hours, 2 or 3 times in order to relieve strains and improve their homogeneity before the conductivity measurements were made. It was then placed between two discs of platinum foil. Adequate electrical contact between the platinum and the pellets were ensured by placing the pellets and the platinum discs between two copper plates, to which leads were attached and were held tightly together by placing a fixed weight. This assembly was then placed inside an oven. The temperature was brought to each desired level and maintained for about 15 minutes to ensure that equilibrium has been reached. GenRad 1659 RLC Digibridge was employed for measuring conductivity. Electrical conductivity were measured over the temperature range of 25°C to 200°C.
1. CdHgl₄-CuI mixed system

Cadmium tetraiodomercurate, CdHgl₄, was prepared from CdI₂ and HgI₂ by the conventional solid state reaction. Both the reactant were mixed in requisite composition in an agate mortar and were heated at 200°C for 48 hours with intermittent grinding. The product so formed was confirmed by the X-ray powder diffraction.

Mixed systems of CdHgl₄-CuI were prepared by mixing 10,20,30,40 and 50 mol% CdHgl₄ with CuI and heated at 200°C for 12 hours.

The electrical conductivity of 10:90, 20:80, 30:70, 40:60 and 50:50 molar ratio CdHgl₄-CuI mixed system were measured. The electrical conductivity was found much higher for 10:90 mol% CdHgl₄-CuI mixed system as compared to other concentration. It is found that this mixed system exhibits the highest conductivity of 3.30×10⁻³ Scm⁻¹ at 25°C. In all other concentrations the conductivity of the mixed system is not so high. This increase in conductivity results from the availability of additional vacancies created by addition of 10 mol% CdHgl₄ but above 10 mol% CdHgl₄ the conductivity decreased due to the reduction in the mobility of Cu⁺ ion following vacancy interaction.
2. Pure and Na+, Ag+ doped Cu₂CdI₄

Copper tetraiodocadmiate, Cu₂CdI₄, was prepared by solid state reaction from the mixture of CdI₂ and CuI. Both the reactants were mixed in a requisite composition in an agate mortar and were heated at 400°C for 48 hours with intermittent grinding. The product so formed was confirmed by X-ray powder diffraction.

Cu₂CdI₄ so formed was doped with sodium and silver ions by mixing various mol% of these ions with Cu₂CdI₄ in an agate mortar and heating them at 200°C for 12 hours, before measuring conductivity.

The sample of 20mol% Na⁺ doped Cu₂CdI₄ shows highest conductivity as compared to other concentration of Na⁺ doped Cu₂CdI₄ which suggest that the sample is behaving analogous to compounds referred as NASICON. Whereas, the same compound Cu₂CdI₄, when doped with Ag⁺ ion (40mol%) , the sample shows initial decrease in conductivity. The conductivity increase in both these cases is explained on the basis of increased free volume created by addition of Na⁺ and Ag⁺ ions. At 82°C a sharp rise in conductivity was observed which suggest the formation of Ag₂CdI₄, a solid electrolyte since pure Cu₂CdI₄ does not show any phase transition.
3. Pure and K\(^+\) doped Ag\(_2\)CdI\(_4\).

Silver tetraiodocadmiate, Ag\(_2\)CdI\(_4\), was prepared from AgI and CdI\(_2\) by the solid state reaction method. AgI and CdI\(_2\) were mixed in the requisite composition in an agate mortar and were heated at 400°C for 48 hours with intermittent grinding. Ag\(_2\)CdI\(_4\) doped with different mol\% of K\(^+\) ion was heated at 200°C for 12 hours before measuring conductivity.

The electrical conductivity of 8,9 and 10 mol\% K\(^+\) doped Ag\(_2\)CdI\(_4\) showed slight decrease whereas the phase transition was observed almost at the same temperature as it was reported for pure Ag\(_2\)CdI\(_4\). This decrease in conductivity likely results from decrease in free volume because of the larger K\(^+\) ion (r\(_{K^+}\) = 133 pm and r\(_{Ag^+}\) = 129 pm) entering Ag\(_2\)CdI\(_4\) lattice which is unchanging in size.

The dielectric constant of Ag\(_2\)CdI\(_4\) was found to increase with temperature. This is due to the reason that the molecules cannot orient themselves in dielectrics. As temperature rises, the orientation of dipoles is facilitated and dielectric constant increases.
CERTIFICATE

This is to certify that the thesis entitled "Preparation of Solid Electrolyte Using Solid State Reactions", describes the original work of Mr. Khalid Siraj, carried out under my supervision and is suitable for the submission for Ph.D. degree in Chemistry.

(Rafiuddin)
Dedicated to My Parents
ACKNOWLEDGEMENT

It is my privilege to record a deep sense of gratitude to my guide Dr. Rafiuddin, Reader, Department of Chemistry, Aligarh Muslim University, Aligarh for his persistent inspiration, supervision and suggestions throughout the work.

I am grateful to Prof. Kabiruddin, Chairman, Department of Chemistry, Aligarh Muslim University, Aligarh for extending research facilities.

I am also thankful to Dr. Robert E. Dinnebier, Max-Planck Institute for Solid State Research, Germany and Dr. Joseph H. Reibenspies, Texas A & M University U.S.A. for their help in X-ray powder diffraction.

Thanks are due to Prof. M. Nasim Beg and Dr. Suhail Sabir, Department of Chemistry, Aligarh Muslim University, Aligarh for his valuable suggestions from time to time.

I would be failing in my duties if I don't mention the names of my laboratory colleagues Mohd. Sarfaraz Nawaz, Miss. Huma Naseer and Mr. Munish (J.L.A) for their cooperation and generous help, I am also thankful to Mr. Hasan for neat and patient typing of the thesis.

I would wish to put on record the encouragement inspiration and the quality of perseverance I received from my parents and my brother, Mr. Shahab Saqib.

Last but not least all the members of the Department of Chemistry are thankfully acknowledge for their kind help during my research.

(Khalid Siraj)
CONTENTS

Certificate
Acknowledgement

CHAPTER-1
General Introduction 1-51
References 52-61

CHAPTER-2
CdHgl₄-Cul mixed system 62-77
References 78-79

CHAPTER-3
Pure and Na⁺, Ag⁺ doped Cu₂CdI₄ 80-93
References 94-95

CHAPTER-4
Pure and K⁺ doped Ag₂CdI₄ 96-109
References 110-112
CHAPTER - 1

General Introduction
Solid state sciences has exerted larger and broader impact on newer areas of sciences and technology, as evidenced by the rapid growth of this field during the last quarter century. There are many areas of overlap and interest in the solid state sciences, solid state physics, solid state chemistry, materials science, ceramic engineering, mineralogy and metallurgy. Solid state chemistry is most central of the solid state sciences and is concerned with the synthesis, structure, properties and applications of solid materials. Considerable basic work on the theory of solid-solid interaction are reported over the years, particularly in sixties as a result of the emergence of solid state devices. It is the applications that has stimulated interest [1,2] in the studies of solids. Their increasing applications in metallurgy, ceramic technology, laser chemistry, manufacture of artificial gems, geochemical processes in chemistry of polymer and propellants have added new dimensions to their importance. Much of the impetus on research in solid state chemistry have come from the use of solid fast ion conductors, which have become focus of attention in view of their potential use as solid electrolytes in various electrochemical devices.
such as solid state batteries, high temperature fuel cells, chemical sensors and smart devices [3-6].

Solid electrolytes are a class of materials exhibiting high ionic conductivity comparable to those of strong liquid electrolytes. Solid state ionics is now a thrust area because of ever increasing demand of solid electrolytes and probably the most widely used method for the preparation of solid electrolytes is the direct reaction in the solid state called solid state reaction.

In solid state reactions, the reactants have only restricted access to each other as compared to the reactions in fluids where intimate contact between reactant molecules is a natural consequence of kinetic nature of reactants. In solid state reactions, atleast one reactant diffuses into the other in order that reaction may be initiated and propagated.

Evidently, reaction will, therefore occur far easier in liquids and gases than in solids. Usually solid state reactions are diffusion controlled. Tarnishing, decomposition, polymer degradation, polymerization and oxidation reaction involving solids have been studied by many workers [7-15].

The systematic study of reactions between solids goes back to the work of Faraday [16] in 1820 and of Spring [17] in 1885, who claimed to have observed reactions in solid state and that of Sir Robert
Austen [18] on the diffusion of gold in lead at different temperatures. Masing [19] in 1909 found that compressed metal filings reacted at temperature below those of “eutectic” mixtures. In 1910, Cobb [20] described reactions between quartz and alumina with calcium carbonate or calcium sulfate. Hedvall [21,22] in 1912 and in subsequent years demonstrated that reactions in solid state occur frequently and represent indeed an important branch of chemistry. Most of the work [23] on solids has evidently been carried out by scientists among whom Fischback, Huttig, Jander, Jost, Seith, Tammann and Tubandt besides Hedvall may be quoted.

The general problem of solid state reaction is two fold. Firstly, the experimental determination of reaction rate and morphology as a function of all independent variables. Secondly the calculation of the reaction rates and prediction of the morphology under a given set of independent variables in terms of known thermodynamic and transport properties of the system under consideration. These require the knowledge of the atomistic mechanism of the fundamental steps such as nucleation, phase boundary reactions, sintering and diffusion. Such studies will provide valuable aid in furthering the practical utilization of reaction in solid state. Lattice imperfections influence all types of elementary steps in a solid state reaction. They often
constitute preferred sites for reaction and nucleation. In addition, lattice imperfection makes solid state diffusion possible and enable the reactants to reach each other. Although it has been found in a number of solid state reaction in ionic systems that the linear rate law is the initial rate determining step, the atomistic reaction mechanisms are not yet understood. This is due to the fact that in contrast to the gas-solid reactions, it is extremely difficult to study the linear reaction rate as a function of the component activities at solid-solid interfaces. But a knowledge of the reaction rate as a function of the independent variables is a pre-requisite for a correct analysis of the atomistic reaction steps of a phase boundary reaction.

The fact that solid substances and in particular crystalline compounds, can act as ionic conductors has been known since the end of last century. Following early reports of ionic conductivity Nernst in 1899 developed a high temperature cell [24], using mixed oxide solid ionic conductors. A material is said to be solid electrolyte only when it is in a phase that possesses a structure conducive to ionic mobility. Ionic conduction in solids is not new. It goes back to the work of Joffe [25], Frenkel[26] and Schottky and Wagner [27]. Ionic conduction in solids is made possible by disorder in crystal lattice, i.e. deviation from
ideal order. During last twenty years a renewed interest in solid electrolyte began parallel to full cell research.

Research in solid state chemistry is essentially concerned with investigation of structures and properties of solids. The primary motivation being understanding and predicting the properties of solids in terms of their crystal structure, chemical composition and electronic structure [28]. A crucial input in this enterprise is the synthesis of the required material. From the early days, chemists have made significant contribution to the development of solid state sciences by synthesizing novel solids that possess unusual structures and properties [29]. Synthesis of unknown compounds in a structurally related family, in order to extend and extrapolate structure property relations and preparation of known compounds to investigate a specific property, are the challenging and rewarding areas of solid state chemistry. Preparative effort in solid state chemistry become most rewarding when it is coupled with characterization and property evaluation [30]. This aspect of solid state synthesis is being increasingly recognized as evidenced by several articles [31-35] appeared in recent years.

The study of super ionic solids is a new field of materials science and technology. Most of the solid state devices developed in the last
three decades are based on the motion of electrons. Ionic solids have received very little attention in the past because of the non-availability of solids with high ionic conductivity at room temperature. However, in 1967, the situation suddenly changed with the discovery of fast sodium-ion conduction in β-alumina [36] and silver ion conduction in RbAg₄I₅ [37]. Solids having exceptionally high ionic conductivity, are called fast ion conductors, superionic conductors or solid electrolytes. Such materials often have rather special crystal structures in that there are open tunnels or layers through which the mobile ions may move. Conductivity values, e.g. 10⁻³ ohm⁻¹ cm⁻¹ for Na⁺ ion migration in β-alumina at 25°C are comparable to those observed for strong liquid electrolytes. This class of materials is extraordinarily diverse and may include simple inorganic compounds such as PbF₂ and AgI and organic polymers such as poly ethylene oxide (PEO) doped with metals salts [38]. There is currently great interest in studying the properties of solid electrolytes, developing the new ones and extending their range of applications in solid state electrochemical devices. Even after so many years of discovery of super-ionic conductors, the research in this field continues to arouse the interest of scientists all over the world. A complete understanding of the phenomena, their particular features and the microsocopic mechanism are not yet fully understood. An overview of the field can be obtained
from the several conference proceedings [39-44] and reviews [45,46] that have been published in recent years.

1. SUPER-IONIC CONDUCTORS

The diversity of materials showing fast ionic conductivity makes the classification difficult. The most important classes of superionic conducting solids are as follows:

1.1. Solids with phase transition

Some of the ionic conductors attain high electrical conductivity only above a certain temperature. Those compounds for which the high temperature phase shows fast-ion behaviour are included in this class. The transition may be of first order as in AgI or diffuse (Bredig transition) as in all fluorite structure materials [47]. The transition results in the generation of anion Frenkel disorder and it appears that both vacancies and interstitials are mobile in the superionic phase. More recently, the occurrence of Bredig transition has been clearly demonstrated in UO₂ [48].

1.2. Layer and Tunnel structured compounds

For this class of compounds, ion transport is confined to two or one dimensions, respectively. The β-alumina in which the mobile cations are located in conduction planes between the spinel structured
alumina block is a good example [49]. Despite the fact that β-alumina is probably the most widely studied fast-ion conductors, knowledge of the basic migration mechanism is still uncertain. The stoichiometric material has the composition Na$_2$O$_{11}$Al$_2$O$_3$ and has a structure, in which spinel structured alumina layers, sandwich the conduction planes where the mobile Na$^+$ ions and the bridging oxygen ions are located. The structure of β-alumina is shown in Fig.1. Wang et al. has proposed a widely accepted model of migration mechanism [50]. They suggested that excess Na$^+$ occupies a split interstitial configuration in which two Na$^+$ ions occupy mid-oxygen position. Migration involves saddle point where the migrating ion occupies a normal vacant site. The calculations of Wang et al. gave activation energies for migration that agreed well with experimental data. The widely studied NASICON compounds, which has the composition Na$_3$Zr$_2$PSi$_2$O$_2$ provides an example of a three dimensional tunnel structure [51].

1.3 Heavily doped and massively disordered solids

Fluorite structured compounds can be doped with both low and high valence ions to create high concentrations of mobile defects. Yttrium doped CeO$_2$ is a good examples for low valence ion doping. Here, the mobile defects are oxygen vacancies compensating for the
Fig. 1: The Structure of $\beta$-alumina
Y$^{3+}$ cation substitutionals [52]. The rare earth doping of CaF$_2$ provides an example of the latter where the substitutional rare-earth atom has excess positive charge and is compensated by anion interstitials. Both anion vacancies and interstitials are mobile species in the fluorite structure [53]. But the low-valence doped materials have received greater attention as ionic conductors because of the higher mobility with vacancy activation energies being typically 0.5 eV. The most important factor limiting the magnitude of the conductivity in this class of compounds is the nature of the dopant-defect interactions. In anion excess systems, a fascinating range of cluster structures, have been elucidated [54-56]. A subtly different example is provided by RbBiF$_4$, where the presence of the two types of cations results in the ready creation of anion Frenkel defects [57].

1.4 Proton conductors

Solid proton conductors are of great importance in relation to the development of fuel cells, sensors and electrochromic devices. The materials with high proton mobilities are included in a separate class, owing to their distinctive transport mechanisms. Proton conductors can be usefully classified into hydrated materials and hydroxy oxides. Hydrogen uranyl phosphate (HUO$_2$PO$_4$.4H$_2$O) is one of the best example of the hydrated proton conductors [58]. The structure comprises layers of uranyl and phosphate ions separated by layers of hydrogen bonded water molecules. The structures of
deuteriated samples of this material have been studied in details by Fitch and co-workers [59-61]. They found that the H$_2$O molecules are grouped into square planar arrangements, held together by hydrogen bonding. Water molecules in different layers are also bridged by hydrogen bonds which reveal the presence of H$_5$O$_2^+$. The mechanism proposed by Fitch et al. have been challenged with alternative models being proposed based on H$_3$O$^+$ migration and surface transport [62,63].

One of the examples of the second class of proton conductors is Yb doped SrCeO$_3$ [64], which has a distorted perovskite structure. Yb dissolves into the lattice as a cation substitutional with compensation of oxygen vacancies. Many perovskite structured oxides can not act as proton conductors with appreciable oxygen vacancy concentrations introduced by doping.

1.5 Amorphous and polymer --ion conductors:

Current studies are increasingly focusing on non-crystalline ionic conductors which offer distinct advantages to materials fabrication. Amorphous ionic conductors are not new materials. Ionic conductivity in silicate glasses has been extensively studied for several decades [65]. Recent work on conducting glasses has been concentrated on borate materials like (Li$_2$O)$_x$B$_2$O$_3$ which has high
cation conductivity. In a review by Tuller [66] it has been given a wide range of data on the variation of the conductivity with cation concentration and temperature.

Ion conducting polymers are prepared by dissolving salts of monovalent ion in polyethers. Reasonable conductivity can be achieved as they can be readily prepared as thin films and therefore, have the major advantages in battery applications [67]. The cations are solvated by the oxygen of the polyether and there is association between the solvated cations and the dissolved anions. The anions as well as cations are mobile in these materials, and the high mobility requires an amorphous polymer structure. The evidence of these mechanism has been obtained by EXAFS studies [68].

These classifications are not exhaustive. It includes most of the materials that are currently the subject of active investigation.

2. MECHANISMS OF SUPERIONIC CONDUCTIVITY

There has been a substantial effort to understand the physics and chemistry of ionic compounds which have anomalously high ionic conductivity in the solid state [69,70]. They are interesting from a fundamental point of view as a form of disordered solid whose properties, in certain respect, place them intermediate between normal solids and liquids. Theoretical techniques, such as computational -
lattice and defect simulations, molecular dynamics and Monte-Carlo methods [71], together with the major experimental investigations like ionic conductivity, specific heat, NMR, neutron scattering and light scattering [72], have collectively paved the way to the present understanding of the mechanisms of ion transport in these materials. Some of the different models suggested for the superionic conductivity will be discussed very briefly.

2.1 Conventional transport mechanism

The transport is effected by a conventional hopping process, usually of defects, in a framework structured material. There is no fundamental difference between the nature of these migration mechanisms in fast ion and normal ionic conductors, but the defect may be present in exceptionally high concentrations and may have very low activation energies. A good example is provided by CeO$_2$ doped with Y$^{3+}$ [52]. The conductivity is based on the rapid transport of vacancies, which are, however, migrating by a conventional hopping mechanism. The defect chemistry of these materials is based on the replacement by trivalent ions of the host cations with compensation of oxygen vacancies; the latter have activation energies of about 0.5 eV and they may be present in high concentrations in the fluorite host owing to the high solubility of low valence
substitutionals. The material shows intriguing variations of the conductivity with the dopant concentration. Gerhardt-Anderson and Norwick et al. showed that for dopant concentrations of less than 1 mol%, oxygen transport can be analysed in terms of the equilibrium between clusters and free vacancies [73].

In summary, oxygen transport in these materials takes place by conventional vacancy hopping process. At low concentrations, dopant defect interactions may be described by the formation of simple pair clusters, while at higher concentrations it is better to think of the problem using percolation models.

2.2 Correlated migration mechanism

In this category, the rapid ion transport is affected by several ions moving together in a concerted manner. Simulation methods are having greater values in revealing the details of such mechanisms. Li$_3$N and RbBiF$_4$ are good examples to explain this mechanism.

Li$_3$N is possibly the best known Li$^+$ ion conductor with an appreciable conductivity of $10^{-3}$ohm$^{-1}$cm$^{-1}$ at 50°C [74]. The crystal structure consists of Li$_3$N layers containing hexagonal arrays of Li$^+$ ions which are linked by bridging Li$^+$ ions lying between N$^3-$ ions in adjacent layers. The structure of Li$_3$N is shown in Fig.2. The molecular dynamic simulation techniques [75,76] applied to Li$_3$N produce the following important mechanistic informations;
Fig.2: The structure of Li$_3$N.
(i) Li$^+$ ions can be readily excited thermally from the Li$_3$N layers into the gaps between the layers.

(ii) The vacancies that are thereby created can migrate rapidly through the crystal by highly correlated mechanisms. This high degree of correlation in the Li$^+$ ion motion is a key factor in promoting a high conductivity.

The high conductivity of RbBiF$_4$, the cation disordered fluorite structured materials, was first studied by Reau and Coworkers [77,78]. The material have the fluorite structure with disordered distribution of Rb$^+$ and Bi over the cation sites. The EXAFS studies show that disorder is generated preferentially around the Rb$^+$ ions. The interstitials in the fluorite structure migrate by the interstitialcy mechanism, in which the migrating F$^-$ ion displaces neighbouring lattice ions into interstitial sites. The ions are moved in a correlated manner, the motion of each ion being of the interstitialcy type. As with Li$_3$N, ease of creation of the defects is vital for the high conductivity, but correlated migration mechanisms are again clearly of central importance.
2.3 Liquid-like diffusion mechanism

Here, the mobile sublattice is highly disordered and hence transport cannot be interpreted in terms of hopping between distinct lattice sites. There are very few materials to which this is an accurate model for the ion transport mechanism. There is, however, good structural evidence for very high degree of cation disorder in certain silver chalcogenides like Ag$_2$S [79] at high temperatures. It seems that the cation sublattice is structurally liquid like in these materials. It is, therefore, plausible to suggest that the transport mechanisms have a similar character.

2.4 Intermediate mechanisms

This includes materials where there is a breakage of the lattice-hopping models and those for which there is a transition from hoping to liquid like transport. A good example of the first case is AgI which undergoes a phase transition at 147°C from wurzite structure to a structure based on a body centered cubic (bcc) I$^-$ sublattice, with a disordered distribution of Ag$^+$ over the tetrahedral sites. The high temperature phase shows fast Ag$^+$ ion mobility [80]. Neutron diffraction and quasi-elastic neutron scattering studies by Wuench and co-worker have clearly demonstrated the localization of
the silver ions in the tetrahedral sites of the super ionic conducting phase [81-83].

Li$_2$MgCl$_4$ which has an inverse spinel structure is another interesting material in which Li$^+$ ions are distributed between octahedral and tetrahedral sites [84-86]. NMR and conductivity studies suggest a change in the ion transport mechanism in temperature range 500-700K, which is manifested by a ‘knee’ in the conductivity versus 1/T plots. At low temperature the lithium transport mainly involves the octahedral lithium ions which migrate by a hopping mechanism between the octahedral sites, via tetrahedral sites. At higher temperatures the mobility of the lithium ions on the tetrahedral sites becomes appreciable and a large fraction of the ions are found to move through non-hopping mechanisms [87].

3. PHASE TRANSITIONS IN SUPERIONIC SOLIDS

A variety of solids exhibit transformations from one crystal structure to another on varying temperature. The subject of phase transitions has grown enormously in recent years, with new types of transitions as well as new approaches to explain the phenomena. The high ionic conductivity achieved by most of the superionic conductors is through well defined phase transitions, at particular temperatures. With increasing temperature, the electrical
conductivity sometimes changes gradually (as in β-alumina) [36] or shows an abrupt jump (as in β-AgI, RbAg4I5 etc.) [37]. During a phase transition the free energy of the solid remains continuous but thermodynamic quantities such as entropy, volume and heat capacity exhibit discontinuous changes.

Depending on this discontinuous change of Gibbs free energy $G$ at the transition, Pardee and Mahan [88] classified the phase transition as first or second order. In first order transition where the $G$ (P,T) surface of the parent and product phases intersect sharply, the entropy and the volume shows singular behaviour. This transition, otherwise called as insulator – electrolyte transition, is characterized by a sudden rise in the conductivity ($\sigma$) when plotted against the inverse temperature ($1/T$). It can sometimes be associated with a distinct structural and latent heat change. On the other hand in second – order transitions (ordered-disordered phase transitions) the heat capacity, compressibility or thermal expansivity shows singular behaviour. In this case $\sigma$ versus $1/T$ plot is continuous with a small change in slope at the transition temperature. The electrical conductivity of a few superionic solids exhibiting the above types of phase transition are depicted in Fig.3. The phase transitions at 64°C for RbAg4I5, 50°C for
Fig. 3: Ionic conductivity of some superionic solids showing phase transitions
silver-pyridinium iodide, 190°C for \((\text{CeF}_3)_{0.95} (\text{CaF}_2)_{0.05}\), 1150°C for \(\text{CaF}_2\), represent typical order-disorder transitions while transition at 151°C of \(\text{RbAg}_4\text{l}_5\), 147°C for \(\text{AgI}\), 890°C for \(\text{LuF}_3\) were of the first kind.

Landau introduced the concept of an order parameter, \(\xi\) which is a measure of the order resulting from a phase transition. In a 1st-order transition, the change in \(\xi\) is discontinuous, but in a second order transition the change of state is continuous. He also proposed that \(G\) in a second-order or structural phase transition is not only function of \(P\) and \(T\) but also of \(\xi\) and expanded \(G\) as a series in powers of \(\xi\) around the transition point.

The order parameter vanishes at the critical temperature, \(T_c\) in such variation. Hence due to the developments in this field by Kadanoff [89], Wilson [90], and others, it is now possible to characterize all higher order phase transition in terms of the physical dimensionality of the system, \(d\), and the order parameter, \(n\). It is noteworthy that there can be no phase transitions in one dimension if short range forces operates alone [91].

4. ELECTRICAL CONDUCTIVITY OF IONIC SOLIDS

Electrical conductivity measurements were among the earliest physicochemical measurement made on solids. All ionic materials have an electrical conductivity in the solid state due to the diffusive
motion of the ions. In most such materials, this diffusion is associated
with the motion of point defects created either by thermal excitation or
by doping. The concentration of thermally generated defects in most
ionic materials is extremely low. But in superionic conductors, the
thermal disorder is too large at high temperatures and the
conductivity attains liquid like values [92-96].

Any solid at a given temperature has an equilibrium
concentration of intrinsic defects usually vacancies or interstitials
controlled by Boltzmann factor. Since ionic conduction and diffusion
are generally sensitive to this thermal equilibrium concentration of
intrinsic defects, they are called activated processes.

The situation is quite interesting in the case of fast ion or
superionic conductors. These materials are characterized either by the
availability of a very large number of normally vacant lattice sites (i.e.,
a defect structure) or by an essentially complete disordered mobile
ionic species. These mobile ions are distributed randomly over a large
number of sites, and the magnitude of the conductivity indicates that
nearly all of them must contribute to the conductivity. The activation
energy for ionic motion in the superionic region is usually small (~ 0.1
eV).
Ionic conductivity and diffusion have been studied extensively in a variety of ionic crystals at atmospheric pressure, and in many cases the mechanisms for the transport processes in terms of point defects have been established [97]. Experimental results have generally been successfully interpreted in terms of absolute reaction-rate theory. In this theory the elementary diffusive jump is likened to a transition, in thermal equilibrium, between a ground state corresponding to the equilibrium lattice position of the mobile species and an excited state corresponding to the saddle-point position. The basic assumption underlying the use of this theory in diffusive processes is that there exists a well defined transition (excited) state whose lifetime is sufficiently long compared to lattice thermal relaxation time that make sense to define the thermodynamic properties of the excited state. Although the theory has been criticized on this assumption and on other counts [98], its general success in interpreting experimental results provides strong support for the usefulness and perhaps validity of this equilibrium statistical mechanical treatment of the diffusion process in many systems.

There has been a considerable number of studies of the effect of hydrostatic pressure on ionic conductivity and other related ionic transport processes. Both the formation and the motion of lattice
defects which determine the conductivity normally depend exponentially on pressure. Most of the early pressure work was on NaCl and silver halides, whereas recent work has extended these studies to a broader range of materials that includes fast ion conductors. In all these studies, pressure is found to be a complementary variable to temperature in trying to understand the mechanisms of ionic conduction. In some cases, pressure turns out to be an essential variable. In ionic conductivity and other defect-dominated properties in general, it is important to know the elastic volume relaxation associated with the formation of lattice defects as well as the lattice relaxation accompanying the diffusive motion of these defects. Measurements of the hydrostatic pressure dependence of the ionic conductivity give, in principle, direct information about these volume relaxations and this can in turn be used to understand better the mechanism of ionic transport and to test the validity of proposed models. Pressure studies also provide better understanding of the nature of the energy barriers associated with ionic transport and are, in addition, important to the understanding of the phase transitions observed in many ionic conductors.

The simplest consideration for most important lattice imperfections are vacancies and interstitials. Lattice vacancy known as
a Schottky defect is formed in a perfect crystal by moving an ion from a lattice site in the interior to a lattice site on the surface of the crystal. At any given temperature a certain equilibrium number of lattice vacancies is always present in a crystal because the entropy is increased by the presence of disorder in the lattice. In order to maintain the electrostatic neutrality on a local scale, usually it is energetically favourable in ionic crystals to form roughly equal numbers of separated positive and negative ion vacancies (so called Schottky pairs). It is easy to show that the concentration $n$, of such pairs is given by [73].

$$n = N \exp \left( -\frac{\Delta G_f^\nu}{2kT} \right) \quad (1.1)$$

where $N$ is the number of ions (sites) per unit volume, and $\Delta G_f^\nu$ is the Gibbs free energy of formation of a pair.

Another type of lattice defect is the Frenkel defect. In this case an ion is moved from a lattice sites to an interstitial position, normally an unoccupied lattice position. The concentration of Frenkel defects is again easily shown to be given by

$$n = (NN')^{1/2} \exp \left( \frac{\Delta G_i^f}{2kT} \right) \quad (1.2)$$
where \( N \) is the number of lattice sites, \( N' \) is the number of interstitial sites (both per unit volume), and \( \Delta G'_r \) is the Gibbs free energy for the formation of the interstitial.

Equations (1.1) and (1.2) are obtained in the limit \( n \ll N \) and as such are thus strictly not valid for ionic conductors in the superionic regime where \( n \) approaches \( N \).

The production of Schottky defects lowers the density of the crystal because of increased volume without an increase in mass. The production of Frenkel defects, on the other hand, does not change the volume of the crystal, and thus the density remains nearly unchanged. On this basis pressure can be expected to cause a relatively large suppression of the formation of Schottky defects.

Controlled concentrations of vacancies and interstitials can often be introduced by doping an ionic crystal with aliovalent impurities. For example, doping NaCl with CaCl\(_2\) would cause the Ca\(^{2+}\) ion to go in substitutionally for the Na\(^+\) ion. The requirement of charge neutrality would also cause creation of a Na\(^+\) vacancy. On the other hand, doping NaCl with, e.g. Na\(_2\)S, would cause the S\(^2-\) ion to go in substitutionally for the Cl\(^-\) ion and would result in the formation of a Cl\(^-\) vacancy.
The conductivity of a solid ionic conduction can be given by the relation

\[ \sigma = \sum_j n_j q_j \mu_j \]  

(1.3)

where \( n_j, q_j \) and \( \mu_j \) are the concentration, electrical charge and mobility, respectively, of the \( j^{th} \) mobile charge carrier and the summation is over the different types of charge carriers. The temperature dependence arises from the temperature dependence of \( n \) or \( \mu \) or both. In general the temperature dependence of \( n \) can be quite complicated since it can be influenced by the relative amounts of intrinsic defects and impurities as well by the possible association and/or precipitation [77] of these impurities and defects.

The intrinsic regime \( n \) is determined by the concentration of impurities; however, the concentration of intrinsic defects is given either by Eq. (1.1) or (1.2), which can be rewritten in the form

\[ n = N \exp(\Delta S_f/2k) \exp(-\Delta H_f/2kT) \]  

(1.4)

with similar expression for eq. (1.2). Here \( \Delta S_f \) & \( \Delta H_f \) are entropy and enthalpy, respectively, associated with the formation of the defects.

Not only is the concentration of intrinsic defects and activated process, but so is the motion of defects as well, since work is required to move the defects from its equilibrium position of minimum energy
to the saddle point which separates it from another position of minimum energy. The rate at which a defect traverses a barrier is

\[ \frac{1}{T} = \nu \exp \left( -\frac{\Delta G_m}{kT} \right) \]  

(1.5)

where \( \Delta G_m \) is the free energy required to move the defect across the energy barrier and \( \nu \) is the vibrational frequency of the defect in the direction which carries it over the barrier. \( \nu \) is usually a difficult quantity to estimate since it relates to a defective region of the crystal. A useful approximation is to equate \( \nu \) with the Debye frequency for cases where the diffusing species has a comparable mass to the atoms of the host crystal.

The diffusion coefficient (isotropic case) is given by

\[ D = Ar^2r^{-1} \]  

(1.6)

where \( A \) is a dimensionless geometrical factor (of order unity) which depends on the lattice type and transport mechanism, and \( r \) is the jump distance. The mobility \( \mu \) of a given species is related to the diffusion coefficient \( D \) of that species through the Nernst-Einstein relation

\[ D = \frac{\mu kT}{q_r} \]  

(1.7)

where \( q \) is the electric charge of the species. Since \( D \) is given by
D = Aνr² exp (-ΔG_m/kT)  \hspace{1cm} (1.8)

The temperature dependence of \( \mu \) is given by

\[
\mu = (Aq \nu r^2/kT) \exp (-\Delta G_m/kT)
\]

\[
= (Aq \nu r^2/kT) \exp (\Delta S_m/k) \exp (-\Delta \mu_m/kT)
\]  \hspace{1cm} (1.9)

where the subscript \( m \) denotes mobility.

The conductivity in the intrinsic regime where one mobile species dominates can then be written as

\[
\sigma_T = (ANq^2\nu r^2/k) \exp (\Delta S_f/2k + \Delta S_m/k) \exp (-\Delta H_f/2kT - \Delta H_m/kT)
\]  \hspace{1cm} (1.10)

In dealing with experimental data, eq. (1.10) is more commonly written as

\[
\sigma_T = \sigma_o \exp (-E_a/kT)
\]  \hspace{1cm} (1.11)

where it is seen that the pre-exponential factor \( \sigma_o \) is

\[
\sigma_o = (ANq^2\nu r^2/k) \exp (\Delta S_f/2k + \Delta S_m/k)
\]  \hspace{1cm} (1.12)

and the measured activation energy \( E_a \) is

\[
E_a = \frac{1}{2} \Delta H_f + \Delta H_m
\]  \hspace{1cm} (1.13)

In the extrinsic regime, where change in carrier concentration with \( T \) negligible, the measured activation energy is simply associated
with the motion of the mobile species (assuming that the mobility of this species dominates), and

\[ E_a = \Delta H_m \]  

(1.14)

In eq. (1.14), it is assumed that the impurity concentration is sufficiently low so as not to influence the mobility in the lattice.

At this point it is worth emphasizing that Eq. (1.10) is based on the Nernst - Einstein relation (Eq. 1.7) and the absolute reaction rate theory of diffusion. Implicit in the latter theory is the assumption that the diffusive process can be described in terms of equilibrium statistical mechanics. Although there has been criticism of this theory nevertheless it has been very successful in treating diffusion and ionic conductivity data and this success is generally taken as the strongest evidence for its validity.

Reference to eq. (1.11) indicates that a plot of \( \log \sigma T \) versus \( T^{-1} \) should yield a linear response over the appropriate temperature regime. By making measurements on samples with various impurities and over a sufficiently broad temperature range, it is possible to evaluate the various activation energies (or enthalpies) and pre-exponential factors (Eq. 1.12). An idealized response for an ionic crystal showing various conduction regimes of interest are depicted in
Fig. 4. Regime I and II are easiest to understand and are generally of most interest.

In the extrinsic regime (I), the response is determined by the concentration and type of impurity or dopant present in the crystal, whereas in the intrinsic regime (II) the response is determined by the mobility of the more mobile species of these defects. Deviations from regime I and II can be observed at both high and low temperatures. Regime III occurs at high temperature and signals a change in the conduction process. Here, usually the conduction is also intrinsic as in regime II and the transition form regime II to regime III could signify a change, from conduction by vacancy motion to conduction by interstitial motion. At sufficiently low temperatures the so-called association regime is sometimes observed. In this regime $\sigma$ decreases with decreasing temperature at a faster rate than in regime I because the impurity and associated defect become bound (i.e., associate), forming a neutral pair which does not contribute to the conductivity. In this regime the activation energy is $E_a = \Delta H_m + \frac{1}{2} \Delta H_a$, where $\Delta H_a$ is the binding or association enthalpy of the aliovalent impurity and associated defect.
Fig. 4: An idealized representation of $\log \sigma T$ Vs $T^{-1}$ showing the various conduction regimes observed in normal fast ionic conductors.
5. CHARACTERIZATION OF SOLID ELECTROLYTES

Once the solid electrolyte is prepared, the next stage is to determine its structure, if this is not already known. For molecular materials, details of the molecular geometry may be obtained from further spectroscopic measurement. Alternatively, if the substance is crystalline, X-ray crystallography may be used, in which case information is also obtained the way in which the molecules pack together in the crystalline state. For non-molecular substances, however, the word structure takes on a whole new meaning. In order for a solid to be well characterized, one needs to know about:

(a) The form of solids, whether it is single crystal or polycrystalline and, if the latter, what is the number, size, shape and distribution of the crystalline particles.

(b) The crystal structure

(c) The crystal defects that are present, their nature, number and distribution.

(d) The impurities that are present and whether they are distributed at random or concentrated into small regions.

(e) The surface structure, including any compositional inhomogeneities or absorbed surface layers [99].
No single technique is capable of providing a complete characterization of a solid. Rather, a variety of techniques are used in combination. Sometimes, however, one is interested in only one structural aspect, in which case a single technique may provide the required information.

There are three main categories of physical technique which may be used to characterize solids; these are

i. Diffraction

ii. Microscopic, and

iii. Spectroscopic techniques.

In addition, other techniques such as thermal analysis, magnetic measurements and physical property measurements may give valuable information in certain cases. In Table 1, a listing of some of the techniques is given together with the structural information that each is capable of providing.
<table>
<thead>
<tr>
<th>Techniques</th>
<th>Uses for</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray diffraction</td>
<td>Phase identification; Amorphous or crystalline; unit cell, space groups; crystal structure; local structure, CN etc.; Crystal defects; polycrystalline texture; Bond type.</td>
</tr>
<tr>
<td>Electron diffraction and microscopy</td>
<td>Phase identification; Amorphous or crystalline; unit cell, space groups; crystal structure; Crystal defects; polycrystalline texture; Elemental analysis.</td>
</tr>
<tr>
<td>Neutron diffraction</td>
<td>Phase identification; Amorphous or crystalline; unit cell, space groups; crystal structure; Crystal defects.</td>
</tr>
<tr>
<td>Optical microscopy</td>
<td>Phase identification; Amorphous or crystalline; Crystal defects; Surface structure; Polycrystalline texture.</td>
</tr>
<tr>
<td>IR spectroscopy</td>
<td>Phase identification; Surface structure; local structure, CN etc.; Elemental analysis; Bond type.</td>
</tr>
<tr>
<td>UV, Visual spectroscopy</td>
<td>Local structure, CN etc.; Crystal defects; Elemental analysis; Electronic structure; Bond type.</td>
</tr>
<tr>
<td>NMR, ESR spectroscopy</td>
<td>Phase identification; local structure, CN etc.; Crystal defects; Elemental analysis; Electronic structure; Bond type.</td>
</tr>
<tr>
<td>Electron spectroscopy</td>
<td>Local structure, CN etc.; Crystal defects; Surface structure; Elemental analysis; Electronic structure; Bond type.</td>
</tr>
<tr>
<td>ESCA, XPS, UPS, AES, EELS</td>
<td>Local structure, CN etc.; Crystal defects; Surface structure; Elemental analysis; Electronic structure; Bond type.</td>
</tr>
<tr>
<td>X-ray spectroscopy, XRF, AEFS, EXAFS</td>
<td>Local structure, CN etc.; Crystal defects; Surface structure; Elemental analysis; Electronic structure; Bond type.</td>
</tr>
<tr>
<td>Mossbauer spectroscopy</td>
<td>Local structure, CN etc.; Elemental analysis; Bond type.</td>
</tr>
</tbody>
</table>
6. TECHNIQUES AND THEIR APPLICATIONS TO SOLID ELECTROLYTE

6.1 Diffraction Techniques

(a) X-ray powder diffraction

An X-ray powder pattern is a set of lines or peaks, each of different intensity and position (d-spacing or Bragg angle, θ), on either a strip of photographic film or on a length of chart paper (Fig.5). For a given substances the line positions one essentially fixed and are characteristic of that substances. The intensities may vary some what from sample to sample, depending on the method of sample preparation and the instrumental conditions. For identification purposes, principle note is taken of line positions, together with a semi-quantitative consideration of intensities. Some of the applications of X-ray powder diffraction are:

I. Phase identification: Each crystalline substances has its own characteristic powder diffraction pattern which may be used for its identification. Standard patterns are given in the powder diffraction File known as the JCPDS File or, formerly, as the ASTM File.

II. Quantitative phase analysis: The amount of a particular crystalline phase in a mixture may be determined by quantitative
Fig. 5: Schematic X-ray powder diffraction pattern
III. X-ray powder diffraction: The procedure is straightforward but somewhat tedious and prone to errors. It is necessary to add an internal standard, which is a well-crystallized phase such as $\alpha$-Al$_2$O$_3$, to the sample in a closely controlled amount (e.g. 10% by weight). A line in the powder pattern of the phase of interest is selected and its intensity is compared with that of a suitable internal standard line. The amount of the phase present can be determined by interpolation from a previously constructed calibration graph of intensity against composition.

IV. Determination of accurate unit cell parameters: The position (d-spacings) of the lines in a powder pattern are governed by the values of the unit cell parameters ($a, b, c, \alpha, \beta, \gamma$). Unit cell lattice parameters are normally determine by single crystal methods but the values obtained are often accurate to only two or three significant figures.

V. Solid Solution lattice parameters. The lattice parameters of solid solution series often show a small but detectable variation with composition. This provides a useful meaning of characterizing solid solutions and in principle, lattice parameters may be used as an indicator of composition.
VI. **Crystal structure determination:** Crystal structure are solved by analyzing the intensities of diffracted X-ray beams. Normally single crystal samples are used but powders may be used in cases where (a) single crystals are not available and (b) the structure is fairly simple and only a limited number of atomic coordinates must be determined in order to solve the structure.

VII. **Particle size measurement:** X-ray powder diffraction may be used to measure the average crystal size in a powder sample, provided the average diameter is less than about 2000 Å. The lines in a powder diffraction pattern are of finite breadth but if the particles are very small the lines are broader than usual. The broadening increases with decreasing particle size. The limit is reached with particle diameters in the range roughly 20 to 100 Å, then the lines are so broad that they effectively ‘disappear into the background radiation.

VIII. **Short range order in non-crystalline solids:** Crystalline solids give diffraction patterns that have a number of sharp line (Fig.5). Non-crystalline solids-glasses, gels give diffraction patterns that have small number of very broad humps Fig. 6(a). From these humps, information on local structure may be obtained. The results are usually presented as a radial distribution function
(RDF) Fig. 6(b) [100,101]. This shows the probability of finding an atom as a function of distance from a reference atom. Information is thereby obtained on coordination environments and bond distances.

IX. **Crystal defects and disorder:** Certain types of defect and disorder that occur in crystalline solids may be detected by a variety of diffraction effects. The measurements of particle size from X-ray line broadening has already been mentioned. Another possible source of line broadening is strain within the crystals. This may be present in plastically deformed (i.e. work hardened) metals. The technique of small angle X-ray scattering (SAXS) is used for detecting inhomogeneities on the scale of 10 to 1000Å.

(b) **High Temperature X-ray powder diffraction**

Thermal expansion coefficients of, for example, metals is conventionally measured by dilatometry using rod-shaped specimens. An alternative and rather unconventional method is to use high temperature X-ray powder diffraction (HTXR). By this means, the change in unit cell parameters with temperature is measured and from this the thermal expansion coefficients may be calculated. For cubic materials, the result obtained by dilatometry and HTXR should agree
Fig. 6(a): X-ray diffraction pattern of (a) cristobalite and (b) glassy SiO$_2$

Fig. 6(b): X-ray diffraction results for SiO$_2$ glass.
well. Exceptions may arise if the crystal structure changes significantly with temperature and especially if a significant number of atom or ion vacancies is produced at high temperature. In such cases the coefficient determined dilatometry may exceed the X-ray values.

High temperature X-ray powder diffraction is a valuable technique for obtaining structural information on polymorphs and phase that exist only at high temperatures. It is particularly useful for studying high temperature structures that cannot be preserved to room temperature by quenching. An example of a high temperature polymorph that cannot be quenched to room temperature is β-quartz; the stable room temperature polymorph of SiO₂ is α-quartz but this transform to β-quartz on heating above 573°C. When β-quartz is cooled it reverts rapidly to α-quartz. The only way to obtain structural information on β-quartz is by X-ray diffraction at high temperatures.

C. Single Crystal X-ray diffraction

There are several crystal X-ray diffraction techniques. Most use diffraction cameras and the results take the form of pattern of spots on photographic films. Single crystal X-ray diffraction methods have the following applications.

i. Determination of unit cell and space group.
ii. Crystal structure determination.

iii. Electron distribution, atom size and bonding.

iv. Crystal defects and disorder.

(d) Electron Diffraction

For crystal X-ray diffraction studies described above it is necessary to have crystals that are at least 0.05 mm in diameter. Otherwise, the intensities of the diffracted beams are too weak to be detected clearly. This is because the efficiency with which X-rays are diffracted is very low. Often, however, crystals as large as 0.05 mm are simply not available or cannot be prepared. In such cases electron diffraction [102, 103] may be used. This technique makes use of the wave properties of electrons and because the scattering efficiency of electrons is high, small samples may be used. The results take the form of patterns of spots on photographic films. Some applications of electron diffraction are as follows:

i. Unit cell and space group determination –

ii. Phase identification

6.2. Microscopic Technique

Electron microscopy – Electron microscopy [103] is an extremely versatile technique capable of providing structural information over a
wide range of magnification. At one extreme, scanning electron microscopy (SEM) complements optical microscopy for studying the texture, topography and surface features of powders or solid pieces; features up to tens of micrometers in size can be seen and because of the depth of focus of SEM instruments, the resulting pictures have a definite three-dimensional quality. At the other extreme, high resolution electron microscopy, under favour circumstances, is capable of giving information on an atomic scale, by direct lattice imaging. Resolution of ~2 Å has been achieved, which means that it is now becoming increasingly possible to 'see' individual atoms.

Electron microscopes are of either transmission or reflection design. For examination in transmission, samples should usually be thinner than ~2000 Å. This is because electrons interact strongly with matter and are completely absorbed by thick particles. Sample preparation may be difficult, especially if it is not possible to prepare thin foils. Thinning techniques, such as ion bombardment are used, but not always satisfactorily, specially with polycrystalline ceramics. There is also a danger that ion bombardment may lead to structural modification of the solid in question or that different parts of the material may be etched away preferentially in the ion beam. One possible solution is to use higher voltage instruments equal to 1MV.
Thicker samples may then be used since the beam is more penetrating, in addition, the amount of background scatter is reduced and higher resolution may be obtained. Alternatively, if the solid to be examined can be crushed into fine powder then at least some of the resulting particle should be there to be viewed in transmission. Some of the uses of electron microscopy are as given –

(i) Particle size and shape, texture, surface detail.

(ii) Crystal defects

(iii) Precipitation and phase transitions

(iv) Chemical analysis.

6.3 Spectroscopic Techniques

6.3.1 EXAFS (Extended X-ray absorption fine spectroscopy) - The past decade has witnessed significant advances in technology related to X-ray spectroscopic techniques, both as a result of advances in X-ray optics, focusing devices, and detectors and because of greater availability of high-brilliance synchrotron facilities worldwide. The result is that synchrotron based X-ray absorption fine structure spectroscopy (XAFS) has become a mainstream technique in a number of scientific disciplines and is
providing molecular-level information not previously available with other techniques. The XAFS spectrum is typically separated into the X-ray absorption near-edge structure (XANES), also known as the near-edge extended X-ray absorption fine structure (NEXAFS) region, and the extended X-ray absorption fine structure (EXAFS) region. The XANE or NEXAFS spectrum is represented by the energy region just below to ~50eV above the absorption edge and serve as a site-specific probe of local charge state, coordination and magnetic moment of the central absorber. Above this energy, the extended fine structure, characteristic of an EXAFS spectrum, is manifested as oscillation in the absorption cross section arising from constructive and destructive interference of the outgoing photoelectric backscattered from neighboring atoms. The EXAFS spectrum provides information on the number, identity, and distance (±0.02Å) of neighboring atom. The ability to probe matter to determine the chemical state of a system at high spatial resolution with high elemental sensitivity has been important to a number of fields [105].

The EXAFS [106] technique examines the variation of absorption with energy (or wavelength) over a much wider range, extending out
from the absorption edge to higher energies up to ~1keV. The absorption usually shows a ripple, known also as the Kronig fine structure (Fig.7) [107] from which, with suitable data processing, information on local structure and, especially, bond distances may be obtained. For the origin of the ripple suffices it to say that it is related to the wave properties of the electron; the ionized photoelectrons interact with neighbouring atoms in the solids which then act as secondary sources of scattering for the photoelectrons. Interference between adjacent scattered waves may occur and this influences the probability of absorption of an incident X-ray photon occurring. The degree of interference depends on the wavelength of the photoelectron (and hence on the wavelength of the incident X-ray photons) and the local structure including interatomic distances, in the region of the emitting atom EXAFS is therefore a kind of in situ electron diffraction in which the source of the electron is the actual atom which participates in the X-ray absorption event [108].

EXAFS is a technique for determining local structure and is equally suitable for non-crystalline as well as crystalline materials. It is particularly valuable for studying disordered and amorphous materials such as glasses, gels and amorphous metals since structural information on them is generally hard to obtain. For the determination
Fig. 7: EXAFS spectrum of copper metal.
of radial distribution curves in amorphous materials (i.e. graphs showing the probability of finding an atom as a function of distance from a central atom), EXAFS may in future be used in preference to conventional diffraction techniques. This is because EXAFS has one great advantage: by tuning in to the absorption edge of each element present in the material in turn, a partial RDF for each element may be constructed. By contrast, conventional diffraction techniques give only a single averaged RDF for all the elements present.

An example shown in Fig.8 is for the alloy Cu$_{46}$Zr$_{54}$ [108]. The RDFs are Fourier transforms derived from (a) the Zirconium K edge at 18 KeV and (b) the copper k edge at 9 KeV. The positions of the peaks are related but not directly equal to, interatomic distances. From the RDFs, it was shown that each zirconium atom is surrounded by an average of 4.6 Cu atoms at 2.74 Å and 5.1 Zr atoms at 3.14 Å: copper - copper distances are 2.47 Å.

Studies similar to these on metallic glasses enable structural models for the glasses to be tested, for instance (a) whether the dense random packing of spheres is an appropriate model or (b) whether chemical ordering effects occur whereby there is a preference for a certain type of neighbouring atom around a particular atom.
Fig. 8: EXAFS-derived partial RDSs for an amorphous Cu$_{46}$Zr$_{54}$ alloy: (a) Zr K edge, (b) Cu K edge.
Recently researchers like Chadwick [109], Paul M. Bertsch [110], Shin, H. [111], Yun, W. [112], Hayakawa, S [113] and many more are using this technique for characterizing their compounds.
REFERENCES


22. J.A. Hedvall, Ibid., 93, 313 (1915).


89. L.P. Kadanoff, Physics, 2, 263 (1966).


108. S.J. German, EXAFS studies in material science, J. Mat. Sci., 17, 1541 (1982).


CHAPTER - 2

CdHgI₄-CuI mixed system.
CuI is a rather unique material in that both its ordered low temperature γ-phase and disordered high temperature fast ion conducting α-phase have anion face centred cubic (fcc) structures. In the γ-phase Cu⁺ ion sit on a fcc sub-lattice shifted by (\(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\)) from the I⁻ sub-lattice, forming the zine blende structure with space group F\(\bar{4}3m\). In the β-phase, which exists in the narrow temperature range between 642 and 680K, CuI has a hexagonal structure similar to wurtzite, with space group p\(\bar{3}m1\). At 680 K, it transforms back to a fcc I⁻ sub-lattice with Cu⁺ randomly distributed over the (\(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\)) sites, space group Fm\(\bar{3}m\), the α-phase [1-5]. The melting temperature is 873K. In all three crystalline phases Cu⁺ are tetrahedrally coordinated by I⁻. Tracer diffusion experiments [6,7] show a low, yet significant, diffusion constant of order 10⁻⁷ cm²s⁻¹ in the γ-phase, which rises by an order of magnitude to 10⁻⁶ cm²s⁻¹ in the β-phase and then to 3 \times 10⁻⁵ cm²s⁻¹ in the α-phase.

CuI has been regarded as a model system for studying the order-disorder transition in the sense that it involves modification of only the Cu⁺ sublattice (if the intervening β-phase is ignored). Despite a wealth of information on its structure [1-5], lattice dynamics [8, 9] and transport properties [6,7], there are certain
fundamental questions which remain a challenge to our understanding.

To obtain a useful microscope description of such phenomena, especially in the copper halides where anharmonicity is important, molecular dynamics simulation is one of the most powerful methods. However the central problem here is to derive a realistic potential, in the sense that the potential can reproduce the relevant experimentally determined quantities within acceptable limits (which are not always easy to define). The existing potential model for CuI developed by Vashista and Rahman [10] was successful in producing a $\gamma$-$\alpha$ transition but the diffusion constants were much higher in both phases than the experimental values (the $\gamma$-$\beta$ transition is prevented by the fixed simulation volume and shape used in the microcanonical ensemble).

Zheng-Johansson [11] developed two body inter-atomic potentials for molecular dynamics simulations of CuI that satisfactorily reproduce the experimentally determined phonon density of states and diffusion constant in $\gamma$, $\beta$ and $\alpha$ phases, as well as various thermodynamics parameter such as melting point. It is also suggested that the diffusion constants are extremely sensitive to
the exact potential chosen. There is a strong evidence of cooperative diffusion in \(\gamma\) phase.

Villian \textit{et al.} [12] investigated the electrical conduction of copper (I) iodide between 50 and 450°C by measurements at different frequencies and four point d.c. experiments. The resistance and capacitance of the phase boundary copper/copper iodide depend exponentially on temperature. The interfacial resistance is practically negligible in the \(\alpha\) and \(\beta\)-phase, whereas the interfacial capacitance is very high.

Zheng-Johansson \textit{et al.} [11] studied the ionic motion in molecular dynamics simulations of the \(\alpha\), \(\beta\)- and \(\gamma\)-phases of Cul. In the cubic \(\gamma\)-phase the Cu\(^+\) ions have large anharmonic vibrations along \(<111>\) type directions, towards the face centers of tetrahedral edges defined by the neighboring four \(I^-\) ions. However, the diffusion pathway is along \(<100>\) type directions, towards the edges of these cages. The diffusion mechanism involves a correlated motion of “chains” of several Cu\(^+\) ions, which explains the experimental observation of breakdown of the jump diffusion model, with increasing temperature, the number of diffusion “chains” also increases interactions between these chains and then lead to a rapid increase in the diffusion rate and transition to the fast ion conducting
α-phase. In the hexagonal β-phase, Cu⁺ ions exhibit similar behaviour, vibrate towards the cage faces but diffuse in the direction of the cage edges. However, the situation is more complicated because in this structure two cage share a common face. This produces a complex behaviour where the average sites for Cu⁺ ions are in the cage centers over shorter times, but in the shared face centers for longer times.

Keen et al. [13] studied the structural behaviour of CuI between room temperature and its melting point (Tm = 878K) using neutron powder diffraction. Detailed measurements were made in the vicinity of two known structural phase transition γ-β and β-γ, which are observed at 643±2 K and 673±8 K. Within the zinc trend structured γ-phase (space group Fd3m) increasing disorder of the Cu⁺ ion sub-lattice is observed as the temperature approaches the γ-β transition in addition to a non-linear thermal expansion. The hexagonal β-phase (space group P31m) is observed as a single phase in the temperature range 645-668K but on first heating it is found to coexist with a rhombohedral phase. This transient phase observed in isolation for only a short time but this was sufficient to show that its structure was that of CuI-IV (space group P31m), which had only been observed earlier at elevated pressure. The high temperature
phase Cul has Fm$\bar{3}$m symmetry with pressures, with the Cu$^+$ ions distributed randomly over all the tetrahedral sites with the cubic-close I$^-$ sublattice.

Electrical conductivity and structural correlation for MxHgl$_4$ type compounds were studied by Negoiu, et al. [14]. In this study they have explained structural modification of complex compound MxHgl$_4$ by the application of 5.30 Mpa to its powder. These modification were confirmed by X-ray diffraction and by measurement of electrical conductivity.

Diffraction thermal analysis of compound Ag$_2$Hgl$_4$, Cu$_2$Hgl$_4$, Tl$_2$Hgl$_4$, PbHgl$_4$ and CdHgl$_4$ have been compared [15] and the results thus obtained lead to the idea of using DTA and electrical conductivity as methods for accessing the thermochromic transition in these compounds. [MxHgl$_4$, where M = Ag, Cu, Tl, Pb and Cd, x =1, 2].

Earlier workers have studied some mixed systems involving fast ionic conductors and suggested the role of fast conducting ions. Like Rivolta, et al. [16], investigated the system CuI-Ag$_3$AsO$_4$ and observed a high silver ion conductivity. Others like Viswanathan et al. [17], studied the fast ion transport in the mixed system CuI-Ag$_2$MoO$_4$. 
Encouraged by these results we have tried to prepare CdHgI₄, a solid electrolyte using solid state reaction method and measured electrical conductivity of the mixed system involving CdHgI₄ and Cul in various mole percents.

1. EXPERIMENTAL DETAILS

1.1 Preparation of CdHgI₄ and Cul

Cadmium tetraiodomercurate was prepared from CdI₂ and HgI₂ obtained from BDH (India), with stated purity 99.5% and 99.2% respectively, by the conventional solid state reaction. Both CdI₂ and HgI₂ were mixed in the requisite composition in an agate mortar and were heated at 200°C for 48 hours in a silica crucible with intermittent grinding. The product so formed is yellowish in colour and X-ray diffraction of the powder sample has been done and it confirmed formation of the product.

Cul was prepared as a precipitate by gradually adding an aqueous solution of commercially available AnalaR grade chemicals of KI and CuSO₄.5H₂O. Iodine liberated during the process was removed by treating the precipitate with sodium thiosulphate solution. Cul thus obtained was washed several times with distilled water and then dried at 100°C for several hours before use.
Mixed system of CdHgl₄–Cul were prepared by taking 10, 20, 30, 40, and 50 mole% of CdHgl₄ and mixing with powdered Cul in an agate mortar and heating them at 200°C for 24 hours in a silica crucible.

1.2 CONDUCTIVITY MEASUREMENT

In order to measure the electrical conductivity powdered samples were pressed into pellets of 4.54 cm² area with thickness of 0.1 cm at a pressure of about 4 tonnes with the help of a press. Pellets so formed were heated up to 200°C for 12 hours temperature in order to relieve strains and improve homogeneity.

The conductivity measurement were performed by means of two probe method. The pellet was mounted on a stainless steel sample holder assembly between copper leads using two polished platinum electrodes. The electrical conductivity of the samples were measured in the temperature range of 25-200°C using GenRad 1659 RLC Digibridge at a fixed frequency.
2. RESULTS AND DISCUSSION

X-ray diffraction pattern and electrical conductivity measurements (Fig. 1 & 2) of 1:1 molar mixture of \( \text{CdI}_2 \) and \( \text{HgI}_2 \) suggest the formation of tetragonal and fast conducting \( \text{CdHgI}_4 \).

The temperature dependence of ionic conductivity is given by the Arrhenius expression -

\[
\sigma = (ne^2\lambda^2\nu\gamma/kT) \exp\left(-\Delta G^*/kT\right)
\]

\[
= (ne^2\lambda^2\nu\gamma/kT) \exp\left(-\Delta S^*/k - \Delta H^*/kT\right)
\]

where \( n \) is the number of ions per unit volume, \( e \) the ionic charge, \( \lambda \) the distance between two jumps positions, \( \nu \) the jump frequency, \( \gamma \) the intersite geometric constant, \( k \) the Boltzmann constant and \( \Delta G^* \), \( \Delta S^* \) and \( \Delta H^* \) are activation free energy, entropy and enthalpy terms. The equation can be written in a simpler form as

\[
\sigma T = \sigma_0 \exp\left(-E_a/kT\right)
\]

where \( \sigma_0 = ne^2\lambda^2\nu\gamma/k \exp\left(-\Delta S^*/k\right) \) and \( \Delta H^* = E_a \), i.e., the activation enthalpy equals experimental activation energy for ionic motion, which may include a defect formation enthalpy contribution [18].
Fig. 1: X-ray powder diffraction pattern of CdHgI$_4$. 
Fig. 2: Electrical conductivity data of the CdHgl$_4$ with its parent compounds
Fig. 2, show plots of electrical conductivity of pure and mixed CdI	extsubscript{2} and HgI	extsubscript{2}. It can be seen that the conductivity of the 1:1 molar mixture is much higher than pure CdI	extsubscript{2} and HgI	extsubscript{2}. Higher conductivity of the mixture is due to the formation of CdHgI	extsubscript{4} which is a solid fast ion conductor. The formation of product was also suggested by X-ray powder diffraction of the 1:1 molar mixture.

The Arrhenius plots of specific conductivity verses temperature for pure and 10:90, 20:80, 30:70, 40:60 and 50:50 mol\% CdHgI	extsubscript{4}–CuI mixture are given in Fig.3. It can be seen that the electrical conductivity for 10:90 mol\% CdHgI	extsubscript{4}–CuI mixed system is much higher in comparison to other compositions. In all other compositions conductivity decreases with the increasing concentration of CdHgI	extsubscript{4}. Electrical conductivity of the mixed system CdHgI	extsubscript{4}–CuI for different compositions of CdHgI	extsubscript{4} at room temperature is shown in the Fig.4. The maximum conductivity is obtained for 10 mol\% CdHgI	extsubscript{4} in the CdHgI	extsubscript{4}–CuI mixed system.

The activation energy for ionic conductivity is tabulated in Table-1. The lowest activation energy value is obtained for the 10mol\% CdHgI	extsubscript{4} suggesting the highest conductivity for 10:90 mol\% CdHgI	extsubscript{4}–CuI mixed system.

The partial replacement of the monovalent host ion by the divalent guest ion gives rise to additional vacancies in the host lattice
Fig. 3: Variation of $\log \sigma T$ with $(1/T)$ for different compositions in mixed system CdHgl$_4$-Cul.
Fig. 4: Electrical conductivity in the mixed system CdHgl₄-Cul versus compositions of CdHgl₄ at room temperature.
Table 1: Activation energy values of all the compositions of the mixed system CdHgI$_4$–CuI.

<table>
<thead>
<tr>
<th>Composition</th>
<th>CdHgI$_4$–CuI (mol%)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:90</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>20:80</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>30:70</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>40:60</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>50:50</td>
<td>0.43</td>
<td></td>
</tr>
</tbody>
</table>
in accordance with the electroneutrality requirement. It was reported that in the high temperature phase such extrinsic vacancies contribute mainly to the conductivity and ionic size is having insignificant effect following aliovalent dopent substitution in the host lattice [19].

With the availability of additional vacancies created by CdHgI₄ substitution, in the cubic phase of the host lattice CuI, the Cu⁺ ions move through the lattice with a high elementary hopping probability [20]. The increasing vacancy concentrations due to partial replacement of Cu⁺ creates additional migration paths for Cu⁺, which in turn increases the conductivity. Upon further addition of CdHgI₄ over 10mol%, the mobility of the Cu⁺ ion was reduced following vacancy interactions such as cluster formation and also cationic sub-lattice ordering [19].

Another important feature observed in this system is erratic conductivity behaviour above 150°C (Fig.3). This drop in conductivity seems to results from the collapse of the iodide framework [21]. Ionic conductivity is mainly controlled by the valency of the cation. The self-trapping effect of the substituent divalent cation which is negligibly mobile could impede the pathways of Cu⁺. This
will in turn decrease the mobility of Cu\(^+\) and hence, causes an inconsistent behaviour at the higher temperatures.

3. CONCLUSION

The conductivity is very high in 10:90 mol% CdHgI\(_4\)-CuI mixed system as compared to other concentrations. It is found that this mixed system exhibits the highest conductivity of $3.031 \times 10^{-3}$ cm\(^{-1}\) at 25°C. This increase in conductivity is due to the availability of additional vacancies created by addition of CdHgI\(_4\) in CuI, but above 10mol% CdHgI\(_4\) the conductivity of mixed system decreased due to the reduction in the mobility of Cu\(^+\) ion following vacancy interactions.
REFERENCES


CHAPTER - 3

Pure and $\text{Na}^+$, $\text{Ag}^+$ doped $\text{Cu}_2\text{CdI}_4$. 
Solid fast ion conductors, characterized by very high ionic conductivity relative to most ionic solids which in some cases exceeds the ionic conductivity of some strong liquid electrolytes have attracted much attention recently due to their use in various electrochemical devices. Studies of these conductors focus on understanding of the factors directly affecting the mobility of the ions and the mechanism of ion transport with the expectation of incorporating these compounds for use in various electrochemical devices.

A number of ionic solids undergo solid phase transitions to a high temperature phase accompanied by a sharp jump in ionic conductivity. There is a qualitative resemblance of the logarithm conductivity ($\sigma T$) versus $T^{-1}$ plots for these solids, e.g., alkali sulfates $\text{Ag}_2\text{Sb}_4\text{O}_9$, $\text{Ti}_2\text{SO}_4$, $\text{AgI}$, $\text{Li}_2\text{MCl}_4$ spinels, to the site percolation probability function, i.e., the $P(p)$ plot [1, 2], suggesting the percolation model for ion transport. The $P$ versus $p$ curve describes the function $P(p)$, where $P$ is the percolation probability or the fraction of the system taken up by the percolation path and $p$ represents the probability that a site is
unblocked or the probability of intersite connectivity to an activated hopping ion. That is, at the phase transition or the percolation threshold the number of intersite channel connectivities or the percolation probability in the network structure increases sharply, giving rise to the observed sudden jump in ion conductivity. Fast ion conduction in solids is considered a paradigm for a structure-property relation, where the ionic conductivity \( \sigma \) is a composite quantity \( \sigma = nq\mu \) where, \( n \) is the charge carrier concentration, \( q \) the carrier charge and \( \mu \) the mobility of the carriers. The carrier mobility is related to a set of energetically favorable sites that are not normally occupied. The concomitant volume expansion for the sulfates, i.e., \( +\Delta V \) of 3-4.5% with the phase transition implies, *ceteris paribus*, that structure “free” volume was a major contributing factor to conductivity enhancement in these compounds [3-5] and in the lower density glass phase relative to crystal for Na\(^+\), Cu\(^+\) and Li\(^+\) ion conductivity compositions [6-8]. The conductivity jump-free volume correlation is, however, not observed for AgI, TII and CsCl, where the structure factor overrides the volume factor. In AgI and TII the phase transition is accompanied by a volume
decrease where the structure undergoes a change from shared corners and/or edges of coordination polyhedra to shared faces, resulting in a significant increase in the number of accessible/occupancy sites for the mobile ion with lower activation energy. Furthermore, recent studies incorporating quasi-equal radius Rb+ (166 pm) and Tl+ (164 pm) in Ag2SO4 failed to support the conductivity free volume relationship in sulfates [9,10]. Also, the ionic conductivity of Tl2SO4, ~10^3 higher than Rb2SO4, is of the same order of magnitude as that of Ag2SO4 [10] despite the larger mass of Tl+ (factor of 2) and the larger Tl+ radius, viz. rTl+ = 164 pm Vs rAg+=129 pm for CN = 6 [11]. These inconsistencies point to factors other than the geometry of the anion array and structure “free” volume as major contributors to ionic conductivity, such as the bonding characteristics of the mobile cation [12].

Since the chemistry of Tl+ bears some resemblance to that of Ag+ [13] with differences linked to the lone electron pair, Ag+–4d10 versus Tl+–5d106s2, TII was chosen along with RbI for a parallel study with AgI to be compared with Tl2SO4 and Ag2SO4. Yellow TII transforms at
175°C to a red cubic form; i.e., (yellow) β- TII \( \xrightarrow{\text{red}} \) (red) α-TII which is accompanied by 3% reduction in volume paralleling the decrease in volume of 6% for AgI at its phase transition 147°C. Yellow β-TII is a double layered orthorhombic structure related to NaCl. The structure of α-TII is a pm\(3\)m CsCl - type in common with the room temperature stable structure of its analogs TlCl and TlBr. The conductivity study on single crystal TII [14] reported a jump at its transition along with the unusual behavior of higher activation energy for the high temperature α-phase than for the low temperature β-phase. The presence of 20 mol\% Rb\(^+\) in AgI in the form of the compound RbAg\(_4\)I\(_5\) resembles α-AgI by exhibiting high conductivity at room temperature.

Similar work has been carried out on A\(_2\)B\(_{\text{II}}\) type superionic conductors (where, A = Ag, Cu, Tl, In and B = Hg, Cd, Zn). Various workers has reported their work on the fast ion conductors like Ag\(_2\)HgI\(_4\), Cu\(_2\)HgI\(_4\), Tl\(_4\)CdI\(_6\) and Ag\(_2\)CdI\(_4\) and produced good results on the various aspects of these fast ion conductors which is mentioned earlier. Recently, R.B. Beeken et al. [15] has reported ionic conductivity
in Cu-substituted Ag₂CdI₄. Encouraged by the promising results of these compounds we have prepared Cu₂CdI₄, which is a superionic conductor and studied the effect of doping Na⁺ and Ag⁺ ion on the ionic conductivity of Cu₂CdI₄.

1. EXPERIMENTAL

1.1 Materials Preparation

Copper tetraiodocadmiate was prepared by the conventional solid state reaction from the mixture of CdI₂ (BDH, India) with stated purity of 99.5% and CuI which was prepared as a precipitate by gradually adding an aqueous solution of commercially available Analar Grade chemicals of KI and CuSO₄.5H₂O. Iodine liberated during the process was removed by treating the precipitate with sodium thiosulphate solution. CuI thus obtained was washed several times with distilled water and then dried at 100°C for several hours before use. Dried CuI was crushed to fine powder before using in the reaction.

Both the reactants, i.e. CdI₂ and CuI were mixed in a requisite composition in an agate mortar and were heated at 300°C for 48 hours
in a silica crucible with intermittent grinding. The rate of heating was initially kept at 50°C per hour. The product so formed was cooled slowly at room temperature. X-ray diffraction of the reaction mixture was done to ascertain the formation of the product.

Iodocadmiate was doped with sodium and silver ions by mixing various mole percent of these ions with iodocadmiate in an agate mortar and heating them at 200°C for 24 hours in a silica crucible. X-ray diffraction of the doped samples were carried out after the reaction was complete.

1.2 Conductivity Measurement

In order to measure the electrical conductivity of pure and cation doped fast ion conductor Cu₂CdI₄, the sample powders were pressed into pellets of 4.54 cm² surface area with thickness of 0.1 cm at a pressure of about 4 tonnes with the help of SPECTRA LAB Press (Model SL-89). Pellets were found to be of the same colours as the original powders. However, higher pressure were found to cause uneven darkening in the pellets. Samples were heated at 200°C
temperature for 12 hours in order to relieve strains and improve their homogeneity before the conductivity measurements.

It was then placed between two discs of platinum foil. Adequate electrical contact between the platinum and the pellets were ensured by placing of a fixed weight. This assembly was then placed inside an oven. The temperature was brought to each desired level and kept there for about 15 minutes to ensure that equilibrium had been reached. Gen Rad 1659 RLC digibridge was employed for measuring conductivity. Possible impedance contribution from external connection cables and pellet mounting devices were corrected by using its built-in 'short' and 'open' calibration facility. Conductivity of pure and Na⁺, Ag⁺ doped Cu₂CdI₄ pellet were measured over the temperature range of 25°C to 200°C.

2. RESULT AND DISCUSSION

Cu₂CdI₄ is a solid electrolyte whose formation is suggested on the basis of X-ray powder diffraction pattern and electric conductivity of 1:2 molar reaction mixture of CdI₂ and CuI. Fig.1 & 2 shows the
plots of electrical conductivity of pure and mixed CdI$_2$ and Cul. It can be seen that the conductivity of the 1:2 molar mixture is much higher than pure CdI$_2$ and Cul. There is no sharp change in the conductivity of Cu$_2$CdI$_4$ suggesting absence of phase transition in Cu$_2$CdI$_4$.

The temperature dependence of the ionic conductivity is given by the Arrhenius-type expression.

\[ \sigma = \left(\frac{ne^2\lambda^2\gamma}{kT}\right) \exp\left(-\frac{\Delta G}{kT}\right) \]

which reduces to

\[ \sigma = \left(\frac{\sigma_0}{T}\right) \exp\left(-\frac{Q_c}{kT}\right) \]

where \(\sigma_0\) represents the composite constant \(\left(\frac{ne^2\lambda^2\gamma}{k}\right)\) \(n\) the number of ions per unit volume, \(e\) the ionic charge, \(\lambda\) the distance between
Fig. 1: X-ray powder diffraction pattern of Cu$_2$CdI$_4$
Fig. 2: Electrical conductivity data of the Cu$_2$CdI$_4$ with its parent compounds
two jumps position, \( v \) the jump frequency, \( k \) the Boltzmann constant, and \( Q_c \) is the activation energy for ionic motion. Assuming the conductivity to be effectively ionic, the equation is given in simpler form as,

\[
\sigma T = \sigma_0 \exp\left(\frac{Q_c}{RT}\right)
\]

Plots of \( \log \sigma T \) versus \( 1/T \) for pure and doped \( \text{Cu}_2\text{CdI}_4 \) (Figure.3) show high cationic conductivity in \( \text{Na}^+ \) doped \( \text{Cu}_2\text{CdI}_4 \) as predicted on the basis of results of conductivity of cation incorporation in the lattice of related compound [11]. Each addition of a finite quantity of \( \text{Na}^+ \) ion into \( \text{Cu}_2\text{CdI}_4 \) lattice resulted in higher conductivity. The highest conductivity is achieved in the 20 mol\% \( \text{Na}^+ \) doped sample. This can be explained in terms of extra free volume produced by the larger guest ion. The introduction of larger \( \text{Na}^+ \) ion (\( r_{\text{Na}^+} = 116\text{pm} \) and \( r_{\text{Cu}^+} = 91 \text{pm} \) for \( \text{CN} = 6 \)) in the lattice of \( \text{Cu}_2\text{CdI}_4 \) generates additional free volume. This would pursue greater facility of \( \text{Cu}^+ \) ions mobility and therefore enhanced the ionic conductivity. The conductivity data reported in this study show that doped sample.
exhibits very high Na$^+$ ion conductivity analogous to the system of 
compound referred to as NASICON [16].

Electrical conductivity of Ag$^+$ ($r_{Ag^+} = 129$ pm and $r_{Ca^+} = 91$ pm) 
doped Cu$_2$CdI$_4$ in the temperature range 25°C to 200°C are shown in 
Fig.3. The conductivity of 40mol% Ag$^+$ doped Cu$_2$CdI$_4$ exhibits 
decrease in conductivity in the low temperature phase. The sharp rise 
in conductivity at about 82°C seems to be due to the formation of more 
conducting Ag$_2$CdI$_4$. The pure Cu$_2$CdI$_4$ does not show any phase 
transition.

This can be explained on the basis that the partial replacement 
of the host Cu$^+$ ion by the larger guest Ag$^+$ ion gives rise to additional 
free volume in the host lattice. The increase free volume facilitates 
higher mobility of Cu$^+$ ions and hence causing higher conductivity of 
the Ag$^+$ doped sample. This mixed positive cation effect can also be the 
result of an increased number of activated mobile Cu$^+$ ion and possible 
higher $v$ (jump frequency) resulting from the weaker lattice bonding 
forces in mixed cation composition [17].
Fig. 3: Temperature dependence electrical conductivity of pure and doped Cu$_2$CdI$_4$.
3. CONCLUSION

The above studies suggest that in the hexagonal phase, Cu₂CdI₄ is open structure. The conductivity data reported in this study show that the doped sample exhibits very high ion conductivity analogous to compounds referred as NASICON. Ag⁺ ion doped sample show initial decrease in conductivity but at 82°C a sharp increase in conductivity suggest the formation of Ag₂CdI₄. The increase in conductivity behaviour is explained on the basis of increased free volume created by Na⁺ and Ag⁺ ions.
REFERENCES


CHAPTER - 4

Pure and K⁺ doped Ag₂CdI₄.
The compounds like Li₂SO₄, LiNaSO₄ and LiAgSO₄ undergo a first order phase transition with high temperature cubic phase exhibiting very high cationic conductivity. These high temperature phases are described as “Inorganic rotator phases.” On this basis, the cationic mobility could be very much enhanced by the strongly coupled rotational motion of the translationally static SO₄²⁻ ions. The strong coupling of the sulphate ion motion was attributed to the insufficient space for free rotation [1]. This anion-rotation-assisted movement of cations can be referred as the “cogwheel” or “paddle-wheel” mechanism of ion transport [2, 3].

The first note of caution regarding the effective role of the paddle-wheel model of ion transport in A₂BO₄ compounds was recorded by Schoonman and Bottlebergs [4]. Later on efforts by Frech and Cazzanelli [5] and Borjesson et al. [6] failed to provide clear cut experimental evidence to confirm the effectiveness of the rotation-coupled sulphate ions in these so-called rotator phase using Raman spectroscopic analytical techniques. The log σ versus 1/T plots of LiSO₄ [5] could not show any meaningful correlation with regard to the jump in conductivity and the band width breakdown, their respective transition
temperatures or their activation energies over the critical temperature region. Furthermore, an attempt by Borjesson and Torell [6] to separate the component of sulphate ion reorientation from the symmetric A$_1$ sulphate internal mode by comparison of polarized and depolarized spectral band width, lead to a rotational bandwidths versus temperature plot [6], where it was showed that the excess, broadening in the low temperature monoclinic phase joins monotonically to that of the high temperature cubic phase. They also reported a significant disparity in activation energies from the sulphate ion reorientation and conductivity studies.

Using a rigid ion model, Impey et al. [7] tried to established whether the jump diffusion of Li$^+$ ions in Li$_2$SO$_4$ be coupled to the reorientation of the neighbouring SO$_4^{2-}$ groups, by the theoretical analysis. This analysis revealed that in a given simulation, only one unequivocal example of a “knock on”, an insignificant event, was observed.

These facts gave us an inspiration to study the prospect of substitution and other studies in the Al-BI$_2$ system (A=Cu, Ag,In, Tl; B = Hg, Cd, Zn) which forms A$_2$BI$_4$ compounds, that under go phase
transition into superionic state. Structural investigation of superionic materials Ag$_2$Hgl$_4$, Cu$_2$Hgl$_4$ and others show the existence of low temperature $\beta$-phase, as a rule, tetragonal syngony, and high temperature $\alpha$-phase [8,9]. It is considered that during $\beta \rightarrow \alpha$ phase transition iodine sub-lattice remains, while there in $\alpha$ phase $A^+$, $B^{2+}$ ions and stoichiometric vacancies, $V_{Ag^+}$, which are distributed randomly in crystal lattice determine high conductivity of the material.

Ag$_2$CdI$_4$ compounds belong to this type of solid electrolyte and possess smeared phase transitions into the superionic state in the temperature region 330-380K [10, 11]. Sudharsanan et al. [12,13] studied the IR and Raman spectra of this compound.

Yunakova et al. [14], studied the excitation spectrum of Ag$_2$CdI$_4$ at 80-380K. Nair et al. [15] studied the behaviour of Ag$^+$ in Ag$_2$CdI$_4$ by cation substituted smaller Li$^+$ and the larger Tl$^+$ ions. Recently, Beeken et al. [16] tried to determined the effect of Cu-substitution on the conductivity and phase transition temperature of Ag$_2$CdI$_4$. Inspired by the results we have tried to prepare Ag$_2$CdI$_4$ and study the effect of K$^+$ substitution on the conductivity and phase transition temperature of Ag$_2$CdI$_4$. 
The solid fast ion conductor Ag₂CdI₄ exhibits a number of solid state phase transitions upon heating. Room temperature, covalent phase Ag₂CdI₄ crystallizes in a well-defined structure. Ag₂CdI₄ at T<330K belongs predominantly to hexagonal, with space group P₆₃/mmm and unit cell dimensions a = 4.578Å and C = 7.529Å and changes to cubic at T > 380K[10, 17] with space group Pm3m and unit cell dimension a = 5.05 Å.

1. EXPERIMENTAL

1.1 Material Preparation

Silver tetraiodocadmiate (Ag₂CdI₄) was prepared from AgI and CdI₂ obtained from BDH (India), with stated purity 99.2% and 99.6% respectively, by the solid state reaction method. AgI and CdI₂ were mixed in the requisite composition in an agate mortar and were heated at 400°C for 48 hours in a silica crucible with intermittent grinding. X-ray diffraction studies were carried out for the material after the reaction was completed. X-ray diffraction pattern suggest the formation of the product Ag₂CdI₄.
Potassium ion was mixed with Ag₂CdI₄ in requisite amount in an agate mortar by solid state reaction and the powder is kept for 24 hours at 200°C with intermittent grinding so that the reaction takes place properly.

1.2 (a) Electrical Conductivity Measurements

Electrical conductivity was measured by preparing pellet of the compound by pouring its fine powder into a stainless steel die and applying a pressure of about 4 tonnes/cm² with the help of hydraulic press, SPECTRA LAB, model LB-89. The pellet so formed has area of 4.524 cm² and thickness of 0.1 cm. The pellet is annealed at 200°C for 12 hours in order to eliminate any grain boundary effect. The electrical conductivity measurement were performed by means of a two probe method. The pellet was mounted on a stainless steel samples holder assembly between copper leads using two polished platinum electrodes. The copper leads were electrically insulated from the samples holder by Teflon sheets. The electrical conductivity of the samples were measured in the temperature range of 25°C to 200°C by using a GenRad 1659 RLC Digibridge at a fixed frequency.
1.2 (b) Dielectric Measurement

The dielectric constant of Ag$_2$CdI$_4$ was calculated over the frequency range 100Hz to 10 KHz and in the temperature range of 25°C to 200°C using the relation given as,

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}$$

where $\varepsilon_0$ is the constant of permittivity for free space, $C$ is the capacitance which is measured by the RLC Digibridge (mentioned above), $d$ the thickness of the pellet and $A$ is the cross-sectional area of the flat surface of the pellet.

2. RESULT AND DISCUSSION

Electrical conductivity plots of pure and K$^+$ doped Ag$_2$CdI$_4$ are given in Fig. 1 & 2. Arrhenius plot of pure Ag$_2$CdI$_4$ shows gradual increase in conductivity upto 107°C and above this temperature a sharp change in conductivity indicates the occurrence of phase transition at 107°C. Also there is a hysterisis loop in the heating and cooling phase of conductivity in the unannealed sample of Ag$_2$CdI$_4$ which confirm the fact that abrupt change in conductivity is due to the phase transition.
Fig. 1: Temperature dependence electrical conductivity of Ag₂CdI₄.
The conductivity increase observed in the present investigation can be explained on the basis of the space charge model reported by Maier et al. [18]. In thermal equilibrium, the surface and grain boundaries of an ionic crystal may carry an electric charge resulting from the presence of excess ions of one sign. This charge is just compensated by a space charge cloud of the opposite sign adjacent to the boundary. For a pure material, this charge arises if the energies to form anion and cation vacancies or interstitials at the boundary are different. The magnitude and sign of the boundary charge changes if there are aliovalent solutes present in the matrix which alter the concentration of the lattice defects in the crystal. Space charge effects will be predominantly important in very small crystals since the grain boundaries contain a large number of defects compared to the coarser grained polycrystalline materials.

Electrical conductivity measurement were performed on several potassium doped Ag₂CdI₄ sample throughout the temperature range 25-200°C. Arrhenius plots of 8,9 & 10 mol % K⁺-doped Ag₂CdI₄ show slight decrease in conductivity (Fig.2). K⁺ ion was chosen as the dopant with the expectation that it would enhance the conductivity of Ag₂CdI₄.
Fig. 2: Effect of the cation dopant on the conductivity of $\text{Ag}_2\text{CdI}_4$. 
on the basis of lattice expansion due to the larger K\(^+\) radius, (\(r_{K^+} = 133\) pm and \(r_{Ag^+} = 129\) pm). But during the course of reaction the conductivity of \(\text{Ag}_2\text{CdI}_4\) doped with different mol % of \(K^+\) ions was found to decrease. This observed decrease likely results from decrease in free volume which results from the larger potassium ion entering \(\text{Ag}_2\text{CdI}_4\) lattice which is unchanging in size. Another important feature observed in the \(K^+\) doped \(\text{Ag}_2\text{CdI}_4\) is erratic conductivity behaviour in the post transition region of 9 and 10 mol % \(K^+\) doped \(\text{Ag}_2\text{CdI}_4\). After 160°C the conductivity further decreases which is due to the collapse of CdI\(_4\) framework, i.e. CdI\(_4^2\)- sub-lattice, and its subsequently recovered on cooling which implies the restructuring of that sub-lattice [19].

The dielectric constant, \(\varepsilon'\) of \(\text{Ag}_2\text{CdI}_4\) was calculated over the frequency range 100 Hz to 10 KHz and in the temperature range of 25°C to 200°C using the relation given as,

\[
\varepsilon' = \frac{Cd}{\varepsilon_0 A},
\]

where \(\varepsilon_0\) is the constant of permittivity for free space \(C\) is the capacitance, \(d\) the thickness of the pellet and \(A\) is the cross-sectional area of the flat surface of the pellet.
The plot between log $\varepsilon'$ and temperature (Fig. 3), shows almost linear increase in $\varepsilon'$ with temperature. There is a small upward shift in the values of $\varepsilon'$ for all frequencies near the transition temperature of Ag$_2$CdI$_4$, the slope of the graph before and after the transition remains the same (Fig.3).

The dielectric constant of Ag$_2$CdI$_4$ was found to increase with temperature. This is due to the reason that the molecules cannot orient themselves in dielectrics. As temperature rises, the orientation of dipoles is facilitated and $\varepsilon'$ increases [20]. The ionic polarization also increases as temperature increase [21]. Also at higher temperatures, the conductivity due to the hopping of mobile ions becomes important and increased dielectric constant results.

According to Samara [22], the higher the dielectric constant of an ionic crystal, the lower the energy of formation of lattice defects. Since the grain boundary of nanoparticles contain a large density of defects [23, 24], it can be argued that the dielectric constant of nanoparticles should have higher values.
Fig. 3: Temperature dependence dielectric constant of Ag$_2$CdI$_4$ on different frequency
Nanocrystalline materials consists of grain or interphase boundaries. These boundaries contain defects such as dangling bond, vacancies, vacancy clusters etc. [25]. These defects can cause a positive or negative space charge distribution at interfaces. The space charges can move under the application of an external field and when they are trapped by the defects, lots of dipole moments are formed (space charge polarization). Hence the space charge effect will be an important factor which decides the dielectric properties in materials with small particles sizes [19]. In addition, ion jump polarization may also be greater in nano-crystalline materials since there will be a number of position in the grain boundaries for the ions to occupy. Thus the high values of the dielectric constant in Ag2CdI4 may be attributed to the increased ion jump orientation effect and the increased space charge effect exhibited by nanoparticles.

3. CONCLUSION

Electrical conductivity plots of several K+ doped Ag2CdI4 samples show decrease in conductivity. This observed decrease in conductivity was
due to decrease in free volume which results from the larger potassium ion entering $\text{Ag}_2\text{CdI}_4$ lattice. The erratic conductivity behaviour observed in the post transition region of $\text{K}^+$ doped $\text{Ag}_2\text{CdI}_4$ was due to the collapse of CdI$_4$ framework. The dielectric constant of $\text{Ag}_2\text{CdI}_4$ was found to increase with temperature which facilitates the orientation of dipoles in $\text{Ag}_2\text{CdI}_4$. 
REFERENCES


Conclusion
CONCLUSION

In this work solid electrolytes CdHgl₄, Cu₂CdI₄ and Ag₂CdI₄ were prepared by solid state reactions and electrical conductivity of these pure and Cu⁺, Na⁺ Ag⁺ and K⁺ doped forms have been studied.

**Cadmium tetra iodomercurate**, CdHgl₄, prepared from CdI₂ and Hgl₂ by the solid-state reaction was mixed with CuI in different molar ratio making mixed systems of CdHgl₄-CuI. The electrical conductivity of 10:90 mol% CdHgl₄-CuI mixed system was found much higher as compared to other concentrations. This exhibits the highest conductivity of $3.30 \times 10^{-3}$ Scm⁻¹ at 25 °C. It appears that the substitution of divalent cation creates vacancies in the host lattice to maintain the electrical neutrality. The generated cation vacancies can provide larger structure free volume rather than higher numbers of activated mobile ions. Hence the increase in conductivity is due to the availability of additional vacancies created by addition of Cd²⁺. Above 10 mol% the conductivity of mixed systems decreased due to the reduction in the mobility of Cu⁺ ion following vacancies interaction.
Copper tetra iodocadmate, \( \text{Cu}_2\text{CdI}_4 \), prepared by solid state reaction from \( \text{CdI}_2 \) and \( \text{CuI} \) was doped with \( \text{Na}^+ \) and \( \text{Ag}^+ \) ions. 20 mol\% \( \text{Na}^+ \) doped \( \text{Cu}_2\text{CdI}_4 \) shows highest conductivity as compared to other concentrations of \( \text{Na}^+ \) doped \( \text{Cu}_2\text{CdI}_4 \). The highest electrical conductivity of 20 mol\% \( \text{Na}^+ \) can be explained in terms of extra free volume generated by introduction of guest cations \( \text{Na}^+ \) ion (\( r_{\text{Na}^+}=116 \text{ pm} \) and \( r_{\text{Cu}^+}=91\text{ pm} \)). This facilitates the \( \text{Cu}^+ \) ions mobility and therefore enhanced the conductivity. Similarly increase in conductivity of \( \text{Ag}^+ \) doped \( \text{Cu}_2\text{CdI}_4 \) is due to the additional free volume in host lattice generated by addition of larger guest \( \text{Ag}^+ \). At 82 °C a sharp rise in conductivity was observed which suggests the formation of \( \text{Ag}_2\text{CdI}_4 \), a solid electrolyte, since pure \( \text{Cu}_2\text{CdI}_4 \) doesn’t show any phase transition.

Silver tetra iodocadmate, \( \text{Ag}_2\text{CdI}_4 \), prepared from \( \text{AgI} \) and \( \text{CdI}_2 \) was doped with different mol\% of \( \text{K}^+ \) ions. The decrease in conductivity of \( \text{K}^+ \) doped \( \text{Ag}_2\text{CdI}_4 \) was due to decrease in free volume which results from the \( \text{K}^+ \) ion entering \( \text{Ag}_2\text{CdI}_4 \) lattice. The erratic conductivity behavior observed in the post transition region of \( \text{K}^+ \) doped \( \text{Ag}_2\text{CdI}_4 \) was due to the collapse of \( \text{CdI}_4^{2-} \) framework. The dielectric constant of \( \text{Ag}_2\text{CdI}_4 \) was found
to increase with temperature which facilitates the orientation of dipole in 
Ag₂CdI₄.

The above studies show that super ionic conductivity of solid 
electrolytes is affected by the contraction or expansion of the sub lattice 
resulting from the incorporation of wrong size guest cation.