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 temperatures 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 PbF$_2$ 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 microsopic 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 UO$_2$ [48].

1.2. Layer and Tunnel structured compounds

For this class of compounds, ion transport is confined to two or one dimensions, respectively. The $\beta$-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 H₂O 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 H₅O₂⁺. The mechanism proposed by Fitch et al. have been challenged with alternative models being proposed based on H₃O⁺ migration and surface transport [62,63].

One of the examples of the second class of proton conductors is Yb doped SrCeO₃ [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 (Li₂O)ₓB₂O₃ 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 frame work 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 \(\beta\)-alumina) [36] or shows an abrupt jump (as in \(\beta\)-AgI, RbAg\(_4\)I\(_5\) 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 RbAg\(_4\)I\(_5\), 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 \(\text{RbAg}_4\text{I}_5\), 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 variables 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].

$$n = N \exp \left( -\frac{\Delta G^{v}}{2kT} \right)$$

(1.1)

where $N$ is the number of ions (sites) per unit volume, and $\Delta G^{v}$ 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

$$n = (NN')^{1/2} \exp \left( \frac{\Delta G^{i}}{2kT} \right)$$

(1.2)
where \( N \) is the number of lattice sites, \( N' \) is the number of interstitial sites (both per unit volume), and \( \Delta G'_i \) 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 \( \text{NaCl} \) with \( \text{CaCl}_2 \) would cause the \( \text{Ca}^{2+} \) ion to go in substitutionally for the \( \text{Na}^+ \) ion. The requirement of charge neutrality would also cause creation of a \( \text{Na}^+ \) vacancy. On the other hand, doping \( \text{NaCl} \) with, e.g. \( \text{Na}_2\text{S} \), would cause the \( \text{S}^{2-} \) ion to go in substitutionally for the \( \text{Cl}^- \) ion and would result in the formation of a \( \text{Cl}^- \) vacancy.
The conductivity of a solid ionic conduction can be given by the relation

$$\sigma = \sum_{i} n_i q_i \mu_i$$  \hspace{1cm} (1.3)

where $n_i$, $q_i$, and $\mu_i$ 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

$$n = N \exp(\Delta S_i/2k) \exp(-\Delta H_i/2kT)$$  \hspace{1cm} (1.4)

with similar expression for eq. (1.2). Here $\Delta S_i$ & $\Delta H_i$ 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

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

(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

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

(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

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

(1.7)

where \( q \) is the electric charge of the species. Since \( D \) is given by
D = Avr^2 \exp (-\Delta G_m/kT) \hfill (1.8)

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

\[
\mu = (Aq vr^2/kT) \exp (-\Delta G_m/kT)
= (Aqvr^2/kT) \exp (\Delta S_m/k) \exp (-\Delta \mu_m/kT) \hfill (1.9)
\]

where the subscript \( m \) denotes mobility.

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

\[
\sigma_T = (ANq^2vr^2/k) \exp (\Delta S_i/2k + \Delta S_m/k) \exp (-\Delta H_f/2kT -\Delta H_m/kT)
\]

(1.10)

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

\[
\sigma_T = \sigma_0 \exp (-E_a/kT) \hfill (1.11)
\]

where it is seen that the pre-exponential factor \( \sigma_0 \) is

\[
\sigma_0 = (ANq^2vr^2/k) \exp (\Delta S_i/2k + \Delta S_m/k) \hfill (1.12)
\]

and the measured activation energy \( E_a \) is

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

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
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 from 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, LELS</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>
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</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, \( \theta \)), on either a strip of photographic film or on a length of chart paper (Fig.5). For a given substance, the line positions are essentially fixed and are characteristic of that substance. The intensities may vary somewhat 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 substance 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 determined 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 100Å, 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) in used for detecting inhomogeneties 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 SiO₂.

Fig. 6(b): X-ray diffraction results for SiO₂ 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 by 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 disiplines 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).


