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CHAPTER - II

THEORETICAL ASPECTS

2.1 INTRODUCTION

Much of the increased activities in superionic solids are due to their potential applications in solid state ionic devices. In addition, they are also fascinating for Physicists in understanding the conduction process. The fundamental problem of basic research is to establish relationships between ionic transport and local atomic structure. Different classes of fast ionic conductors have different structural arrangements and many theoretical models have been proposed to explain their transport properties. It is necessary to check the validity of these models in respective systems. Computer simulation techniques are now a standard tool to study the structural properties and transport mechanisms in solid state materials. Several excellent reviews have been published outlining the theoretical treatment of solid electrolytes [1-12]. The present chapter gives a brief review of various theoretical models proposed and recent developments for each class of superionic solids.
2.2 DEFECT TRANSPORT THEORY OF NORMAL IONIC CONDUCTORS

Ionic crystals contain thermally generated defects like Schottky / Frenkel. During ionic conduction, the ion movement is mediated through the defects by some transport mechanisms, as shown in Figure 2.1. The ionic conductivity ($\sigma$) in these types of conductors can be written as

$$\sigma = \sigma_0/T \exp(-E_a/kT)$$  \hspace{1cm} (2.1)

$$\sigma_0 = n\lambda q^2\nu/k$$  \hspace{1cm} (2.2)

where, $E_a$ the energy barrier between the ion sites, $n$ the mobile ion concentration, $\lambda$ the jump distance, $q$ the charge, $\nu$ the attempt frequency, $k$ the Boltzmann constant and $T$ the temperature.

The diffusion constant ($D$) and the conductivity are related by the Nernst-Einstein relation,

$$\sigma/D = nq^2/kT$$  \hspace{1cm} (2.3)

The defect mechanism explains the transport properties of conventional ionic solids. If an ionic solid is doped with aliovalent impurities, like CaCl2 in NaCl, additional vacancies are created to compensate the charge difference and mole fraction of the impurity, which decides the defect concentration. The coulombic interactions between the ions
Fig. 2.1 Some possible ion transport mechanism in ionic solids (a) Vacancy mechanism, (b) Interstitial mechanism and (c) Interstitialcy mechanism.
is considered by Lidiard in 1957 [13] using the modified Debye-Huckel theory. The coulombic interaction has been found to change the defect concentration and mobility of the ions.

2.3 THEORIES FOR SINGLE / POLYCRYSTALLINE FICs

Theories have been proposed to describe high ionic motion in superionic solids with cationic disordered phases, phase transitions in SICs, β-aluminas, oxygen ion conductors, etc. A brief review has been presented here.

2.3.1 Defect Transport Theory to FICs

The defect transport theory developed for normal ion conductors can also be extended to superionic solids like fluoride ion conductors (α-PbF2) and some oxygen ion conductors. Bonne and Schoonman, in 1971 [14], successfully explained ion transport in PbF2 using defect theory and similarly Etsell and Flenges applied it to ZrO2-Y2O3 [15].

2.3.2 FICs with Phase Transition

Most of the cationic and some fluoride ion conductors have phase transition characterised by an abrupt increase in conductivity. Huberman [16] has showed that Frenkel pair attractive interaction is responsible for such superionic
phase transition. Whereas, Rice et al. [17] proposed that
the superionic phase transition is due to the interstitial
defects interacting with the strain field they induce.
Welch and Dienes [18,19] gave a generalised model combining
both the above models. They suggested that thermally
generated defect concentration modified the free energy of
ionic crystal resulting in phase transition.

2.3.3 FICs with Second Order Phase Transition

Superionic solids with second order phase transition
like, CaF$_3$, LaF$_3$-SrF$_3$, etc. are typical examples of this
type. The conductivity changes in this type of FICs is
dealt by "Lattice Gas Theories". In lattice gas models ions
are considered as "Lattice Gas" hopping from one lattice
point to another. These theories interpret phase transition
behavior in terms of the change in enthalpy of motion due to
various ion interactions. The first extensive treatment was
given by Sato and Kukuchi, in 1971 [20,21], using 'path
probability method' to explain the ionic transport in
$\beta$"-alumina and $\beta$-alumina. Later, ionic polaron theory was
developed analogous to the antiferromagnetic ising model
[4]. Leaderman et al. in 1976 have developed a model to
couple order parameter with static strain and explained the
phase transition in RbAg$_4$I$_5$ [22].
2.4 MICROSCOPIC MODELS

Various microscopic theories have also been developed. Rice and Roth [23] developed 'Free Ion Model' in 1972 and they assumed that a mobile ion can be excited from localised states to free ion like states, in which ion propagates throughout the solid. 'The Domain Model', described by Vangool and Bottleberghs [24], explains low value of activation energy as due to the movement of walls between the domains of ordered configuration. Later, 'Jump Diffusion Models' of ions in a periodic lattice, including the effect of polarizability and correlated jumps, have been developed [25]. These microscopic models are the foundations of current theoretical developments.

2.5 RECENT DEVELOPMENTS IN THE THEORY OF ORDERED FICS

Much progress has been made in the recent past in the understanding of various properties of superionic conductors. These developments include; advancements in lattice gas theories, liquid like models, dynamical properties, universal ac-response of conductivity and computer simulation method to study ion transport.

2.5.1 Lattice Gas Models and Other Theories

The Lattice Gas Model, developed by Sato and Kukuchi,
takes into account only the nearest neighbour interactions \([20,21]\). Bunde et al. \([26]\) have developed the theory for the conductivity of a lattice gas by taking into account of the long range coulombic interactions. They have shown that the conductivity is thermally activated and the activation energy is proportional to strength of coulombic interactions. The many particle hopping in coulombic lattice gas was developed by Bunde et al. in 1985 \([27]\). Furthermore, Tanaka et al. \([28]\) have developed the lattice gas theory to the honey comb lattice by taking into account of the second order perturbation of hopping ion. Recently, the phonon interaction was considered by Tomoyose \([29]\).

The AgI type fast ion conductors show fluid like features and these systems can be considered as a liquid embedded in a periodic medium. The properties of these superionic conductors were examined using Langavin dynamics, literature on such model studies are available \([10,30,31]\).

The dynamic conductivity \(\sigma(\omega)\) of ordered and disordered superionic solids generally exhibit a power law in frequency \([32]\)

\[
\sigma(\omega) \sim \begin{cases} 
A(i\omega)^n, & \omega \tau \gg 1 \\
\sigma(0), & \omega \tau \ll 1
\end{cases}
\] (2.4)
where, \( \omega \) the frequency, \( \tau \) the relaxation time, \( n \) the power-law exponent, \( A \) material dependent constant and \( \sigma(0) \) the d.c. conductivity. where, \( \sigma(0) \propto \tau^{-1} \) is thermally activated. The exponent \( n \) tends to increase by lowering the temperature. This phenomenon is generally known as "universal ac-response" [33]. Power-law spectra are also supported from quasi elastic neutron scattering and nuclear spin relaxation studies [34-36].

2.5.2 Computer Simulation Methods

Computer simulation techniques are now a standard tool in the study of solid state ionic materials [37]. Three class of simulation techniques, like, Static Lattice Simulations, Molecular Dynamics and Monte Carlo Methods have been employed to study the superionic solids.

Static Lattice Simulation

In this method, the lowest energy configuration of the crystal structure with certain defect parameters are obtained and the physical properties are evaluated. Methods based on the Mott-Littleton approximation [38] have proved to be particularly effective and for several systems yielded quantitative agreement with experimentally determined defect parameters [37,39,40].
Classical equations of motions of an ensemble of particles are solved by including kinetic energy in the simulation. The dynamic details of the systems are directly available from molecular dynamical simulations [41]. The first molecular dynamical treatments to $\alpha$-AgI was given by Vashishta and Rahman [42, 43]; they calculated the diffusion constant of silver ion in AgI and studied the microscopic details of ion motion. Kobayashi et al. applied the molecular dynamics method to study the silver ion diffusion in Ag-Te [44, 45] and calculated transport parameters of Ag$_2$Te, which are in quite good agreement with experimental results. They have also suggested the possibility of high ionic conduction in new materials like, AgI-Ag$_2$S system [46]. Most recent work includes; structural and dynamical properties of ZrO$_2$-Y$_2$O$_3$ investigated by Shimoojo et al. [47], and Sodium $\beta$-alumina by Zendejas et al. [48, 49].

Monte Carlo Method

This is essentially a technique of statistical mechanics [50, 51]. In this method, the ensemble configuration is generated by a succession of random moves. The same procedure is applied to study ionic transport in solids [51]. Ion hopping models are conceptually simple and are directly
accessible by monte carlo simulations [50]. Tachibana and Okazaki [52,53] have used ion hopping models for caterpillar migration of mobile ions and simulated the Haven's ratio of α-AgI type FICs. Monte carlo simulations in coulombic lattice gas have been studied by Dieterich et al. [54].

2.6 THEORIES FOR COMPOSITE SOLID ELECTROLYTES

Several phenomenologies have been invoked to explain enhancement in the conductivity of Composite Solid Electrolytes. According to Wagner et al.[55], introduction of dispersoid phase in the host lattice produces a space charge region at the host dispersoid interface facilitating ionic motion. The conductivity is expressed as the sum of conductivity from host and that due to space-charge region. Bunde et al. [56,57] have attempted to explain conductivity behaviour in composites using percolation approach, by considering them as a mixture of normally conducting, insulating and highly conducting bonds. Recently, the high ionic conductivities in AgI-glass composites have been explained in the light of 'Micro Domain Model' [58].

2.7 MODELS FOR ION TRANSPORT IN POLYMER ELECTROLYTES

Many models have been proposed to explain the ion transport mechanism in the polymer electrolytes. Cohen and
Turnbull [59] gave Free-Volume theory. In free-volume picture, the ions are considered as hard spheres and are free to move in a volume fraction (voids), called free-volume. They have derived the probability distribution of void volumes in the total volume of the system. Later, following Cohen and Turnbull treatment, Ratner derived expression for diffusion constant based on free-volume theory [60]. The microscopic behaviors are dealt with Dynamic Bond Percolation Model [61,62], in which the segmental mobility has also been included along with the ionic motion. The dynamic bond Percolation model is able to describe very well the properties of dynamically disordered polymer electrolytes systems.

Different transport mechanisms for proton conduction have also been proposed. They include, liquid like transport (in crystals like H-montmorillonite, H-Al montmorillonite), Grotthus mechanism and proton bond model [63,64] applied to some organic systems like isopolyniobic acid and HUP.

2.8 MODELS FOR ION TRANSPORT IN GLASSES

The understanding of ion transport in glassy electrolytes appears to be even less well developed than that in crystalline conductors. This is largely because of lack of the complete structural informations and the relation of
structure to ion transport. Different superionic conducting glasses exhibit different structural motifs and oversimplification of transport mechanism is difficult. Reviews on transport models of fast ionic conducting glasses are available [5,6,65]. The models most frequently encountered in glass literature are outlined below.

2.8.1 Anderson and Stuart Model

Anderson and Stuart [66] considered that carrier ion as intrinsically mobile and the activation energy is the sum of energy required to overcome electrostatic forces and elastic strain component. They gave expression for the two energies and predicted the activation energy for the diffusion of mobile ion in number of silicate glasses. Later, several modifications have been made to the Anderson and Stuart model [67,68]. Anderson and Stuart model provides highly useful semi-quantitative insights into ion transport phenomenon in glasses.

2.8.2 Random Site Model

In Random Site model [69,70], all the ions of the particular type are treated as potential carriers with a Gaussian distribution of activation energy. The ion mobility varies with distribution of activation energy and
thereby with the glass composition. In general, the variation of carrier concentration with glass composition is relatively small and hence the conductivity variation with glass composition is controlled by change in ion mobility. This model was successful in explaining the conductivity dependence on composition in fluorite structured solid solutions [69].

2.8.3 Weak Electrolyte Model

The Weak Electrolyte Model [71,72] postulated the existence of two distinct carrier populations; 'mobile' and 'immobile' carriers. In this model, carrier mobility is regarded as independent of glass composition and hence structure. The dissociated concentration of ions are mobile and undissociated are immobile. Correlations between the ionic conductivity and the thermodynamic activity is the basis for the weak electrolyte model [73,74]. The dependence of ionic conductivity on the thermodynamic activity 'a' of the glass is given by

$$\sigma = K [a]^{1/2}$$  \hspace{1cm} (2.5)

$K$ being the constant. Ravaine and Souquet [71,72] have correlated ionic conductivity with activity in silica based glasses and Tomozawa, et al. [75] to germinate glasses. Later, Minami [76] reported that mobility may depend on the
glass composition, which is inconsistent with weak electrolyte model.

2.8.4 Diffusion Path Model

The dependence of mobility and carrier concentration on glass composition and the distribution of conducting species in different anionic environment are the basis of Diffusion Path Model [77]. Minami has proposed this model by postulating the existence of two distinct populations of silver ions: mobile silver ions associated with iodide anions and immobile (or less mobile) silver ions linked with charged oxyanion species in the glass network [78,79]. Minami has suggested that, in these glasses, the partial covalency exists between silver and non-bridging oxygen ions which gives raise to the immobile silver ion population. The silver ions surrounded by the halide ions are mobile and give rise to the carrier concentrations. The increase in silver halide concentration increases the mobile ion population and hence the conductivity. Several other experimental results supports the existence of mobile and immobile silver ions in these type of glasses [80-82]. The nuclear magnetic resonance experiments lead to contradictory conclusions concerning the existence of distinct populations of silver ions [83,84].
2.8.5 Cluster Bypass Model

Ingram, et al. have regarded glass as a congelation of ordered microdomains (or) clusters connected by a connective tissue \([85,86]\). According to cluster bypass model, pathways for ion migration lie within the connective tissue. Ingram, et al. have discussed ion transport in various glasses based on this model \([85-87]\).

2.8.6. Chemical Approach

Sastry and Rao \([88]\) have formulated a quantity designated as Structural Unpinning Number (SUN) determined by the unscreened nuclear charge of the cation, average electronegativity of the anions, molar volume and the total number silver ions present in the glass. The Structural Unpinning Number provides insight to the chemical origin of conductivity. The variation in transport parameters with concentration of silver iodide are discussed in the light of SUN \([88]\).

2.9 RECENT DEVELOPMENTS IN THE THEORY OF GLASSY FICS

There is no satisfactory theory at the present time that comprises all the experimental observations in fast ion conducting glassy materials. Substantial progress has been made in the understanding only the partial aspects of the
problem [8]. Theoretical models are developed based on some general features of the disordered structures. Schirmacher and co-workers have analysed a random walk problem in an irregular lattice by means of effective medium theory [89-90]. They obtain dispersive transport and nuclear spin relaxation rates, which are in good agreement with experiments. Kehr and Braun [91] have studied the diffusivity and mobility of lattice gas in lattices with randomly blocked sites. Monte Carlo simulations of lattice gas have demonstrated the importance of both interactions and structural disorder in explaining relaxational effects [92-93]. But, these studies are helpful in understanding of only the general trends of disordered systems and cannot account for any influence of carrier concentration.

In order to gain further insight into the conduction mechanism in glasses, one should construct models exploiting more specific structural information. Bunde, et al. [94] have used the experimental evidence [85] that alkali ion glasses create their own characteristic environment in mixed alkali systems. They assumed reduced hopping rates between the unlike sites and gave new explanation for the mixed alkali effect in glasses [94-96]. The influence of non-bridging oxygen ions as negative counter ions in dilute systems was considered by Kondler, et al. [97]. They obtain the increase in diffusion constant with ion concentration in
parallel with a reduction of activation energy, which is a typical feature of ion transport in network glasses doped with oxides / halides.

Structure and Dynamics of the glasses can also be studied by Molecular Dynamics methods. The details of glass structure simulations are available in literature [98,99]. Abramo, et al. [100,101] have studied the structure of Ag2O-B2O3 ionic glasses by molecular dynamics. The structural complexity of these glasses restricts the fast development of satisfactory theories.

2.10 PRESENT THEORETICAL WORK

The structural studies of silver ion conducting glasses have provided informations on local structure of constituent ions (these results were already reviewed in Chapter-I section 1.6). Based on the available informations, transport models are constructed to study ion conduction mechanism in glasses. One such example is the treatment of non-bridging oxygen ions and their coulomb potentials by Kondler, et al. [97]. Their results display several typical features of ion transport in network glasses.

Based on the available structural informations, Minami [102] has proposed a structural model for the silver ion conducting glasses. For the present study, a two
dimensional structural model for silver ion conducting glasses in triangular lattice, suitable for simulations, has been formulated. The structure of silver ion conducting glasses of different dopant (AgI) concentrations in the system with general formula

\[ \text{AgI} - \text{AgzO} - \text{MzOs}; \; \text{M = B, etc.} \]

has been simulated. The simulated structure is tested for its feasibility, by comparing some features with experimental results. For example, Radial Distribution Function (RDF), partial pair distribution function, packing density, etc.

The Monte Carlo simulations of ion hopping is carried out by taking into account of the short range repulsive and long range coulombic interactions among mobile and fixed counter ions. The tracer diffusion constant for the glasses with different dopant salt concentrations at different temperatures are studied. The conduction mechanism in these glasses are discussed based on the simulation results and experimental observations.
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