CHAPTER V

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STRUCTURAL MODEL AND MONTE CARLO STUDY OF SILVER ION CONDUCTION

5.1 INTRODUCTION

Computer simulation methods are now standard tools in the study of various branches of physics and they bridge the gap between the experiment and theory [1]. Simulation methods are now being increasingly used to study structural and dynamical properties of SIC materials [2,3]. Three class of simulation techniques, Static Lattice Simulations, Molecular Dynamics Methods and Monte Carlo Methods have been employed in the study of superionic solids. A brief introduction to these simulation techniques were already presented in Chapter II (in Section 2.5.2). In first part of this chapter, the statistical background of the computer simulation methods are briefly described. The Markov Process and Monte Carlo method of computer simulation are also explained briefly.

5.2 COMPUTER SIMULATION METHODS

Computer simulation methods provide direct route from
the microscopic details of a system to macroscopic properties of experimental interest. Further, the computer simulation approach allows one to study even complex systems to gain more insight into their behavior. Excellent texts on computer simulation methods are found in literature [1-10].

Computer simulation methods deal with computational properties of well defined model of a system. The properties (or) observables appear as averages of some sample space of the system. The state of the system is specified by its degrees of freedom $X = (x_1, x_2, \ldots, x_n)$, where, 'n' is the number of degrees of freedom. If the system under consideration has a model Hamiltonian $H$, the observable quantity 'A' is then given by

$$\langle A \rangle = Z^{-1} \int_{\Omega} A(X) f[H(X)] \, dX$$ (5.1)

where, $Z$ is the partition function

$$Z = \int_{\Omega} f[H(X)] \, dX$$ (5.2)

Here, $\langle A \rangle$ denotes the ensemble average.

The ensemble average is not accessible in computer simulations, as it involves evaluation of quantity 'A' for a larger number of systems. Instead, propagate the particles along a trajectory in phase space and evaluate the quantity along the path as
\[ \bar{A}_t = (t-t_0)^{-1} \int_0^t A\{x(\tau)\} \, d\tau \quad (5.3) \]

By 'ergocity theorem' these two averages are related by

\[ \langle A \rangle = \bar{A}_\infty \quad (5.4) \]

Computer simulation cannot follow a path over an infinite time since the observation time \( t \) is limited to finite path length. Hence, one has to connect with an approximation

\[ A_t \simeq \langle A \rangle \quad (5.5) \]

The trajectory (or) propagation of the system in phase space can be done by two methods.

(1) **Deterministic Methods** (Molecular Dynamics methods)

(2) **Stochastic Methods** (Monte Carlo methods)

In deterministic methods (molecular dynamics), the classical equations of motions are integrated with time to get the trajectory in phase space. Stochastic methods (monte carlo) involve only the evaluation of configurational part of the problem and its transition from one configuration to another. Such transitions in stochastic methods are brought about by a probabilistic evaluation.
5.2.1 Interaction Potentials

The Hamiltonian $H(X)$ of the system involves the kinetic energy and potential energy. The kinetic energy is calculated from the set of momentum values. The potential energy $V$ contains the interesting information regarding intermolecular interactions. The potential energy, which is a function of positions of the particles, may be derived into term depending on the co-ordinate of individual atoms, pairs, triplets, etc. as

$$V = \sum V_1(r_i) + \sum \sum V_2(r_i, r_j) + \sum \sum \sum V_3(r_i, r_j, r_k) + \ldots \quad (5.6)$$

The first term represents the effect of external field and the remaining are particle interactions. Several forms of pair potentials are used like, hard sphere potential, Lennard-Jones potentials, etc. [1]. The long range interactions are supplemented by including coulomb interactions, etc. The calculation of potentials are carried out by avoiding unnecessary use of computer time.

5.2.2 Finite Size Effects

The major limitation of the simulated physics is the finite size of the model system under study, but in thermodynamic limit the number of particles go to infinity.
One cannot use larger model systems in computer simulations due to limitations of the machines. On the other hand, the use of small systems lead to finite size effects arise, which are more prominent at the boundaries. For example, the particles at the boundaries interact differently and they experience different forces. The finite size effects are minimised by the following techniques.

5.2.3 Periodic Boundary Conditions

The basic cell under consideration is repeated throughout the space to form a infinite lattice. As the particles move, its periodic image in each of the neighboring replicas also moves in the exactly same way. Thus, if a particle leaves the basic cell its image will enter through the opposite face. This is illustrated in Figure 5.1. Mathematically this is stated as, for any observable $A$ we have

$$A(X) = A(X+nL) \quad (5.7)$$

where, 'n' is an integer and $L$ the size of the basic cell or box. This is known as periodic boundary condition. The periodic boundary condition eliminates the surface effects and creates a quasi-infinite volume to represent a macroscopic system more closely. However, periodic boundary condition creates infinite summation for the calculation of
Fig. 5.1 Movement of particles in basic cell and in its periodic images (A to H).
potential energies and of course, is impossible to calculate in practice. The infinite summation is avoided by the following method.

5.2.4 Minimum Image Convention

The infinite summation for the calculation of potentials is avoided by cutting off the potential at a particular range. As shown in Figure 5.2, consider a molecule-5 at the centre of a region, which has the same size and shapes as the basic simulation box. Molecule-5 interacts with all the molecules whose centers lie within this region, that is, with the closest periodic images of the other N-1 molecules. This is called 'minimum image convention' [1,4]. The molecule-1 interacts with molecules 2, 4E, & 1G. The largest contribution of potentials and forces come from neighbours close to the molecule of interest and for short range forces, one can apply spherical cut-off of typical radius $r_c$.

5.2.5 Ewald Summation

A more realistic potentials can be obtained by including interaction of each particle with all the image particles by Ewald Summation method [1]. By this method, the pair potential energy can be written as
Fig. 5.2 Construction of minimum image while calculating potential of particles-5 in basic cell.
\[ V_{ij} = \sum_i \sum_j f(r_{ij}) \]  

(5.8)

where, \( f(r_{ij}) \) is some function of the distance \( r_{ij} \).

Interactions with all other image particles can be included in the calculation of potential energies and written as

\[ V_{ij} = \sum_n \sum_i \sum_j f(r_{ij} + nl) \]  

(5.9)

The sum over \( n \) cells is the sum over all cells, \( n = (n_xL, n_yL, n_zL) \), where \( n_x, n_y, n_z \) are integers and \( L \) the box length. The unit cells are added in sequence, the first term has \( n=0 \), i.e. \( n = (0,0,0) \); the second term, \( n=1 \), comprised of \( n = (\pm L,0,0), (0,\pm L,0),(0,0,\pm L) \); etc. This is illustrated in Figure 5.3.

5.3 MONTE CARLO METHOD

The monte carlo method is built on concepts developed in probability theory and statistical mechanics. The key element in stochastic simulations is the concept of the Markov process (or) Markov chain [1,4,6-9].

5.3.1 Markov Process

The Markov process or chain is a sequence of trials that satisfies two conditions
Fig. 5.3 Ewald construction. In figure, B is the basic cell and cells 1's, 2's, 3's, etc. are considered for the calculation of potentials for the sum over 'n' cells, n = 1, 2, 3, etc. respectively.
1. The outcome of each trial belongs to a finite set of outcomes \((X_1, X_2, \ldots, X_m, X_n, \ldots)\), called the state space.

2. The outcome of each trial depends only on the outcome of the trial that immediately precedes it.

The states are connected by the transition probabilities

\[
P_{ij} = P(X_j \mid X_i) \quad \text{or} \quad P_{ij} = P(X_i \rightarrow X_j)
\]  \hspace{1cm} (5.10)

For example, for thermal equilibrium we have

\[
P(X_i) \propto \exp(-H/kT).
\]  \hspace{1cm} (5.11)

Details of probability theory and statistical mechanics are given in standard texts [6-9].

In monte carlo method, the solution of a problem is represented as a parameter of a hypothetical population. Using a random sequence of numbers, a sample of the population is constructed and from which the statistical estimate of the parameters are obtained.

There are four ensembles in common use to do computer simulations; the microcanonical ensemble (constant-NVE), the canonical ensemble (constant-NVT), isothermal-isobaric ensemble (constant-NPT) and grand canonical ensemble (constant-\(\mu VT\)) (all symbols have usual meaning). The present calculations are carried out using canonical
ensemble (constant-NVT). The following section explains the monte carlo method by Metropolis algorithm developed for NVT ensemble.

5.3.2 Metropolis Method

In metropolis method, the transition probabilities are calculated from the energy difference between the states $\delta V_{ji} = V_j - V_i$ [1]. If

$$
\delta V_{ji} \leq 0 \quad \text{then} \quad P_j \geq P_i \\
\delta V_{ji} \geq 0 \quad \text{then} \quad P_j \leq P_i.
$$

The move is accepted with a transition probability

$$
P(X_i \rightarrow X_j) = \frac{P(X_i)}{P(X_j)} = \frac{Z^{-1} \exp(-V_i/kT)}{Z^{-1} \exp(-V_j/kT)} = \exp(-\delta V_{ji}/kT).
$$

A random number, $R_n$, is generated uniformly between 0 to 1 and $R_n$ is compared with the transition probability. If the random number is less than the transition probability, the move is accepted, if not, the state remains the same. i.e.,

If, $R_n \leq P(X_i \rightarrow X_j) = \exp(-\delta V_{ji}/kT)$; new state $X_j$ \hspace{1cm} (5.14)

If, $R_n > P(X_i \rightarrow X_j) = \exp(-\delta V_{ji}/kT)$; old state $X_i$
5.4 PRESENT STUDY

Ion conduction process in disordered materials like glasses is a subject of current theoretical interest ([11,12]). The ionic conductivity of these glasses are very sensitive to relative concentration of the constituents of the glasses. The knowledge of local structure is the key to understand the transport phenomena in amorphous systems. Theoretical models to understand the conduction process in these materials are developed based on some general features of disordered structure [13-15]. Transport models applying more specific structural informations will provide better understanding of conduction process. In this direction, recently, Kondler et al. [16] have taken into account the influence of non-bridging oxygen (NBO) ions as a negative counter ions in dilute systems. A more realistic model, exploiting more structural features, will provide further insight into the conduction mechanism.

Recent structural studies on silver ion conducting glasses have revealed some informations about the local structure of the glasses [17-31]. Based on the structural informations, the structure of silver ion conducting glasses were discussed earlier in Chapter-I (in Section 1.6). In the present work, a simplified two-dimensional model of the glass has been formulated in a triangular lattice, taking
into account of the available structural informations. The simulation of glass structure, in this model, has been carried out for various compositions of the glass. The computational details of the structural model are described. Some of the properties (like RDF, densities, etc.) of the simulated structure have been calculated and compared with experimental ones to support the feasibility of the model.

Monte carlo simulations of silver ion hopping has been carried out for various composition of the glass at different temperatures. The procedure for the monte carlo calculation and the programing techniques are described. The results of mean square displacement of silver ions, diffusion constant, etc., are presented. The ion conduction process is discussed based on the simulation results, experimental observations and existing theories.

5.5 MODEL STRUCTURE AND SIMULATION

5.5.1 Structure of the Silver Ion Conducting Glasses

In Chapter I (Section 1.6), the structure of silver ion conducting glasses is described based on the experimental investigations. The silver ion conducting oxide glassy systems have general formula, AgI-Ag2O-MmOn where, MmOn is the glass forming oxides like, MoO3, BaO, V2O5, etc., Ag2O is glass modifying oxide and AgI is the doping salt. The
former has a three dimensional random network structure composed of some basic structural units (ex. planar triangular BO$_3$ units in B$_2$O$_3$ glass, tetragonal SiO$_4$ units in SiO$_2$ glass, etc.) [26,27]. The addition of modifying oxide (Ag$_2$O) changes the coordination of the former unit by breaking the continues random network, which leads to the formation of non-bridging oxygens (NBOs) and discrete former units like MO$_n^{m-}$ [17,28,31]. The structure of the glass is not significantly altered by the addition of doping salt AgI [23] and the AgI is randomly dispersed in between the modified glass network without any long range ordering [17]. To summarise, silver ion conducting glassy systems have structural features, comprised of,

1. A broken glassy network with NBO sites / discrete former anion units like MO$_n^{m-}$ [17-20,28].

2. The former anion units have tetragonal and in some cases triangular structures and even have higher co-ordination with polyhedral structure [21-27].

3. The halide I$^-$ anions are dispersed in between the glass matrix with out any long range order [17].

4. The Ag$^+$ ions are either bonded to NBO sites by partial covalency or to I$^-$ ions by ionic bond [20,24,25,29].

As discussed in the Chapter IV, the negatively charged
NBO site can bind the positively charged silver ion with partial covalency and the potential of such interaction is expected to be higher compared to the silver ion bonded to iodine environment which are interacting through ionic bond. Based on these facts, Minami [30] has proposed the existence of two different types of silver ions in different anionic environment. Incorporating these generalised informations, Minami has proposed a simple structural model for these glasses [31]. In his simplified model, he represented the glass former units as triangular / tetragonal units with Ag$^+$ ions at its NBO sites. The dopant anion I$^-$ is distributed between the glass matrix with Ag$^+$ ion bonded to them, thus, differentiating two different populations of silver ions [32,33]. The present model is drafted on the similar grounds and generated in a simple two-dimensional triangular lattice suitable for simulation studies.

5.5.2 Description of the Model

Consider a two-dimensional triangular lattice of spacing $\alpha$ and size $L \times B$ (i.e. lattice of length $\alpha L$ and breadth $\sqrt{3}/2 \alpha B$). The glass structure is represented in this lattice as follows; Each triangle, if filled, represents a planar triangular MOs former unit of the glass, see Figure 5.4 for illustration. The glass forming triangles are filled by distributing former cation (M) at
Fig. 5.4 Two dimensional model illustrating the structure of silver based glasses. In figure, $\text{Ag}^+(i)$ and $\text{Ag}^+(o)$ are $\text{Ag}^+$ ions bonded to $\text{I}^-$ & $\text{O}^-$ ions respectively.
its center and oxygen ions at its corner following the Zachariasen rule. The number of MOs triangles and its NBO sites are chosen according to the desired composition of the glass former $\text{MmOn}$ and glass modifier $\text{AgzO}$. A site nearest to each NBO is chosen, named NBO-Ag site, and filled with silver ion representing silver ions bonded to NBO site by partial covalency. These silver ions are represented as $\text{Ag}^0$ ions (i.e. silver ions bonded to oxygen ions).

The $\text{I}^-$ ions occupy sites available in between the former units following certain inter ion distance criteria found out by experiments. The iodine ions are distributed by following the rules that I-O and I-I distances are respectively greater than or equal to 4.25 Å and 5.0 Å [21-25]. Finally, the $\text{Ag}^+$ ions (silver ions bonded to $\text{I}^-$ ions) are distributed in sites nearest to $\text{I}^-$ ions. The number of $\text{Ag}^+$ ions are chosen according to the number of $\text{I}^-$ ions distributed. All the remaining unoccupied lattice sites are available for the migration of silver ion. Each $\text{I}^-$ ion has six nearest neighbouring sites and thus six interstitial sites available for silver ion migration. The Ag-I distance found out by earlier studies is chosen as the lattice parameter $\alpha$ [29]. This leads to Ag-O distance equal to that of Ag-I distance, in the triangular lattice (which is not experimentally true). Hence, corrections have been made to all $\text{Ag}^0$ positions, according to the distances found
out by experiment, along all Ag\(^{0}\)-O bonds. In the present work, structural simulations for glasses in the system AgI-Ag\(2\)O-M\(2\)O\(3\) differing in AgI contents are carried out for the lattice size \(L \times B = 20 \times 20\).

5.5.3 Simulation of Glass Structure

The structural simulation for the glasses differing in dopant salt (AgI) contents are carried out according to the formula

\[ Y\% \text{AgI} - M\% \text{Ag}2\text{O} - F\% \text{M}2\text{O}3, \ Y\% = 30\% \text{ to } 70\% \quad (4.15) \]

with modifier to former ratio \(M/F = 2.0\) & with \(M+F = 100-Y\).

The structure is simulated for the lattice of spacing \(a\) and size \(L \times B = 20 \times 20\) (i.e. lattice of length \(aL\) and breadth \((\sqrt{3}/2)aB\)). In this section, the various steps in the simulation of glass is explained as per the description of the model given in the previous section. The program is written in Fortran-77 language and is available with the author in the program JKSM.FOR. The program JKSM.FOR generates all lattice point coordinates and indexes for each lattice point with a code used to identify the occupancy of different ions and vacant lattice sites. The flow chart for the structural simulation is shown in Figure 5.5 and the procedure is described below. The important
Fig. 5.5 Flow chart for structural simulation of glass.
programming steps, from the program JKSM.FOR, of this procedure is described in Appendix-B.

5.5.4 Procedure for Structural Simulation

(a) Lattice coordinates generation

* Generate two dimensional triangular lattice coordinates for the lattice of spacing \( a \) and size \( L \times B = 20 \times 20 \).
* Generate former cation (M) lattice coordinates inside each triangles.
* Index all the lattice sites with a number representing unoccupancy.

(b) Distribution of former cations (Refer Appendix-B)

* Calculate the number of glass former cation to be distributed according to the composition of the glass.
* Calculate the fraction of glass former cation sites to be filled, called former cation fraction.
* Generate a random number between 0 to 1.
* Fill the site with glass former cation by comparing the random number with the glass former cation fraction. If the random number is less than the cation fraction fill the site else skip this trial.
* Check for Zachariasen rule. Skip all trials of edge sharing and allow only corner sharing of glass forming
triangles by checking distance between former cations.

* Check glass former cation distribution for periodicity of the lattice by checking the distribution of the ions at the boundaries.

* Check glass former chain length. Certain restrictions are to be satisfied by the glass former chain length and the number of chains. This is necessary to get the desired number of non-bridging oxygen ion sites according to glass modifier to glass former ratio M/F chosen.

* If the distribution of the glass former cation passes the above three checks, index the site with a number used to identify the glass former cation occupancy, else skip the trial.

* Repeat the procedure till all the glass former cations are distributed.

(c) Distribution of oxygen ions

* Choose a filled glass former cation site and select all its corner sites of the triangles.

* Fill a corner site with oxygen ions (former anion).

* Check oxygen ions distribution for periodicity of the lattice by checking the distribution of the ions at the boundaries. (Refer Appendix-B).

* If the distribution passes the check, index the site
with a number used to identify oxygen ion, else skip the trial.

* Index all the non-bridging oxygen ion site by some number (later this index will be referred for the distribution of silver ions)

* Repeat the procedure till all the oxygen ions are distributed.

(d) Distribution of iodine ions

* Choose an unfilled triangular lattice site.

* Fill the site with iodine ion.

* Check for I-O distance. Skip the trial if I-O distance is less than 4.25 Å, else go to next step.

* Check for I-I distance. Skip the trial if I-I distance is less than 5 Å, else go to next step.

* Check iodine ions distribution for periodicity of the lattice by checking the distribution of the ions at the boundaries.

* If the iodine ion distribution passes all the above three checks, index the site with a number used to identify iodine ion occupancy in the lattice.

* Repeat the procedure till all possible sites are filled with iodine ion.

* Normalise the composition of the glass according to the number of various ions filled.
(e) Distribution of silver ions bonded to oxygen ions

* Pick up a non-bridging oxygen ion site and select all the unfilled nearest neighbour sites.
* Assign a random number between 0 to 1 to each of these sites.
* Select the site with a assigned number greater than that of others.
* Fill this site with silver ion, identified as Ag$^0$ ion (i.e. silver ion bonded to oxygen ion).
* Check silver ion distribution for periodicity of the lattice by checking the distribution of the ions at the boundaries.
* If the iodine ion distribution passes the above check index the site with a number used to identify Ag$^0$ silver ions.
* Repeat the procedure till all the silver ions are distributed near the non-bridging oxygen ion sites.

(f) Distribution of silver ions bonded to iodine ion

* Pick up an iodine ion and select all the unfilled nearest neighbour sites.
* Assign a random number between 0 to 1 to each of these sites.
* Select the site with a assigned number greater than that
of others.

* Fill this site with silver ion, identified as Ag\(^+\) ion (i.e. silver ion bonded to iodine ion).

* Check silver ion distribution for periodicity of the lattice by checking the distribution of the ions at the boundaries.

* Check for non-bridging oxygen ion in Ag\(^+\) nearest neighbour distance, if so, skip this site and try other nearest sites available for silver ion near iodine vicinity. If all these sites fails this test (which may be the case in high Ag\(_2\)O content glasses), accommodate the silver ion even near NBO sites as a final choice.

* If the iodine ion distribution passes the above checks, index the site with a number used to identify silver ion (bonded to iodine ions) occupancy in the lattice.

* Repeat the procedure till all the silver ions are distributed near iodine ion sites.

5.6 PROPERTIES OF THE SIMULATED STRUCTURE

The structure of the silver ion glasses in a matrix of size 20 x 20 have been simulated for various composition of the dopant salt (AgI), according to the formula 5.15, using the procedure described in section 5.5. In Figure 5.6, the sample of a simulated structure for AgI concentration of 60% is shown. As shown in figure, the structures satisfy the
periodicity conditions, which is must for these simulation studies. The number of other properties of the structure like, Radial Distribution Function (RDF), Partial Pair Distribution Function (PDF), Density & Packing Density of the constituent ions have been calculated. These properties are compared with the experimentally observed results of silver ion conducting glasses, to support the feasibility of the present model.

5.6.1 Radial Distribution Function

The complete radial distribution function and three ion pair distribution functions \( g_{I-Ag} \), \( g_{O-Ag} \) and \( g_{Ag-Ag} \) are derived from the following expression \([34,35]\), after thermally stabilising the system.

\[
g_{ij}(r) = \rho_o^{-2} \left< \sum_i \sum_j \delta(r_i - R_i) \delta(r_j - R_j) \right> \quad (5.16)
\]

Where, \( \rho_o \) is the number density of the glass and defined as the ratio of the total number of ions to the volume of the glass. The two-dimensional structure is treated as thin slab of radii \( \sigma_i \) (\( \sigma_i \) radii of iodine ion) for the calculation of \( \rho_o \). \( r \) the absolute value of \( r_i - r_j \), \( R_i \) & \( R_j \) the position of the \( i \) th and \( j \) th ion respectively, (for complete pair distribution function, the suffixes \( i \) & \( j \) runs over lattice points of all ions). The symbol \(< \) mean the
ensemble average and $\delta$ is the Kronecker delta. The calculations are performed for glass of different dopant salt contents.

The radial distribution function for the glass with 60% AgI is shown in Figure 5.7, as discrete vertical lines. In the glass, the atoms have thermal vibrations around their mean positions and the lines will broaden as curves. The lines are transformed into broad Gaussian curves as

$$g(r) = A_n \int_{-\alpha}^{\alpha} \exp \left[ -\frac{(r-r_n)^2}{\xi_n^2} \right] dr$$  \hspace{1cm} (5.17)

$$A_n = \frac{N_n}{(4\pi \xi_n^2) C \rho_o \Delta r_n \gamma_n \xi_n}$$  \hspace{1cm} (5.18)

where, in equation 5.18, $N_n$ is the number of ions found at $r_n$, $\Delta r_n = r_{n+1} - r_n$, $C$ is the fraction of ions under consideration (for full pair distribution function $C = 1$), $\xi_n$ is the constant which takes the value $\xi_n = 0.25$.

The radial distribution curves of glass with 60% of AgI is shown in Figure 5.7. The radial distribution functions of silver based borate and molybdate glasses, obtained from the experimental studies [25,29], are also shown for comparison. The dominant peak around 2.8-2.9 Å due to Ag$^+$-I pair and its shoulder on the left at 2.4 Å due to Ag$^0$-O distance are matching very well with the experimental curves. A small peak at 1.6 Å is due to the M-O direct
Fig. 5.7 Radial distribution function of the glasses for,
(a) Simulated structure of 60.1%AgI-26.6%Ag2O-13.3%
MgO, (b) 66%AgI-17%Ag2O-17%Be2O3 from ref. [29] and
(c) 60%AgI-20%Ag2O-20%MoO3 from ref. [25].
distance in M0s unit. This peak is observed at 1.4 Å for borate glass (M = B) [29], at 2.1 Å for molybdate glass (M = Mo) [25], and at 1.8 Å for vanadate glass (M = V) [24]. Thus, the M-O distance of the simulated structure fits very well within the range of M-O distances quoted for silver glasses. The small shoulder at the right of the Ag\textsuperscript{I}-I peak at 3.3 Å is due to the M-M and Ag\textsuperscript{O}-I distances. The Ag\textsuperscript{O}-I shoulder at 3.3 Å and the overlap of O-O peak with the dominant Ag\textsuperscript{I}-I peak at 2.85 Å are the only minor difficulties in reproducing the micro-structure of the silver based glasses in the present structural model.

The radial distribution function for the glasses of different dopant salt contents is shown in Figure 5.8. The three curves, for AgI\% = 30%, 50% and 70%, are rather similar and display a dominant peak centered around 2.85 Å. The similarity of the curves for wide range of change in dopant salt concentrations is consistent with the experimental results, that is, the structure of the glass is not modified by the addition of dopant salt AgI. The dominant peak at 2.85 Å is ascribed to Ag\textsuperscript{I}-I pairs and has almost same height in all three curves. This is due to the overlap of O-O peaks at the same distance and hence the increase in Ag\textsuperscript{I}-I pairs with the AgI concentration are not pronounced well. The progressive increase in Ag\textsuperscript{I}-I pairs with the addition of dopant salt is clearly seen in 0\textsubscript{I}-Ag.
Fig. 5.8 Radial distribution function for the glasses of different dopant salt content; (a) AgI % = 30.3 %, (b) 50 % and (c) 70.6 %.
partial pair distribution function, which will be dealt with in next section. The shoulder on the left of RDF curves at 2.4 Å indicates Ag$^0$-O distance and the small peak at 1.6 Å to M-O direct distances. The decrease in the heights of these two peaks with the dopant addition indicates the reduction in Ag$^0$-I and M-O pairs, as expected.

5.6.2 Pair Distribution Functions of the Ion Pairs

Three types of pair distribution functions of the ion pairs; $g_{\text{I-Ag}}$, $g_{\text{O-Ag}}$ and $g_{\text{Ag-Ag}}$ are derived using expressions 5.16 to 5.18. These ion pair distribution functions for the glass of 60.0% AgI is shown in Figure 5.9, along with the quoted experimental values [24,25]. The location of the nearest neighbour pair peaks agree well with the experimental ones. The compositional dependence of these pair distribution functions are described in the following sections.

I-Ag Pairs: The $g_{\text{I-Ag}}$ pair distribution function for different AgI contents in the glass is shown in Figure 5.10. The progressive growth of the first nearest I-Ag pair, appearing around 2.8 - 2.9 Å, shows the increase in silver ions bonded to the iodine anions.

O-Ag Pairs: The $g_{\text{O-Ag}}$ pair distribution function for
Fig. 5.9 Pair distribution functions for different glasses. SS - simulated structure, SM - Silver molybdate (ref. [25]) and SV - Silver vanadate (ref. [24]).
Fig. 5.10 $g_{I-Ag}$ pair distribution function for the glasses of different dopant salt content. (a) AgI % = 30.3 %, (b) 50 % and (c) 70.6 %.
different dopant salt contents in the glass is shown in Figure 5.11. The nearest neighbour O-Ag peak appearing at 2.4 Å is due to the silver ions bonded to non-bridging oxygen ions.

Ag-Ag Pairs: The compositional dependence of $g_{\text{Ag-Ag}}$ pair distribution function for different dopant salt contents of the simulated structures is shown in Figure 5.12. The prominent peaks of Ag-Ag pairs appear at 3.2 Å and 4.9 Å, and are due to various inter silver ion distances in the structure. There is no nearest neighbour peaks for Ag-Ag ion pairs, this indicates the absence of Ag-Ag pair formations. Thus Ag-Ag pair distribution is independent of dopant salt variation in the glass.

5.6.3 Density and Packing Density

The density of the glasses is calculated by treating the two-dimensional structure as a thin slab of material of thickness $\sigma_I$. The density and packing density calculations are carried out by treating the glass former cation as boron ion (M=B) and the boron radii and weight are used for these calculations. The structure of the glasses are simulated for different configurational trials and the properties are calculated. The composition and properties of the simulated
Fig. 5.11 $g_{O-Ag}$ pair distribution function for the glasses of different dopant salt content. (a) AgI % = 30.3 %, (b) 50 % and (c) 70.6 %.
Fig. 5.12 $g_{Ag-Ag}$ pair distribution function for the glasses of different dopant salt content. (a) AgI % = 30.3 %, (b) 50 % and (c) 70.6 %.
structure, averaged for five different configurations, are shown in Table 5.1. As shown in table, the density of the glass increases with AgI content [32,33].

The packing density of the constituent ions is calculated using the glass composition, density of the glass and ionic radii of the constituent ions. Figure 5.13 shows the AgI dependence of the packing density. The packing density of the constituent ions in the simulated structure increases linearly with the increase in AgI content (refer also Table 5.1) and agrees well with the experimental observations in these types of glasses [17,32,33]. Hence, the present model also takes into account of the dense packing in matrix, which is necessary for the formation of diffusion paths for ion migration.

Thus, the glassy structure can be represented in a simple two-dimensional triangular lattice, taking into account of the various structural features. Glass structure for the wide range of compositional variations can be easily simulated in the triangular lattice. The present structural model has an excellent compatibility with the structure of the real glass for radial distribution functions and densities. Thus, the model will be very useful to study conduction process by computer simulation methods.
Table 5.1

Composition of the glass, Density ($\rho$), Packing density ($P$), Diffusion constant ($D$), Percentage of contribution to $D$ by Ag$^+$ ions ($D_F$), Activation energy ($E_a/V$) and Pre-exponential factor ($D_0$) of glasses in the system AgI-Ag$_2$O-M$_2$O$_3$ of simulated structure and of silver ion hopping studied by Monte Carlo method. The $\rho$ and $P$ values are quoted for borate glasses i.e. $M = B$ (Boron), by using boron radii and weight.

<table>
<thead>
<tr>
<th>Sl. no.</th>
<th>Glass composition in mol. %</th>
<th>$\rho$</th>
<th>$P$</th>
<th>$D$</th>
<th>$D_F$</th>
<th>$E_a/V$</th>
<th>$D_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AgI</td>
<td>Ag$_2$O</td>
<td>M$_2$O$_3$</td>
<td>(g cm$^{-3}$)</td>
<td>%</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>30.3</td>
<td>46.5</td>
<td>23.2</td>
<td>5.40</td>
<td>58.4</td>
<td>0.130</td>
<td>17.3</td>
</tr>
<tr>
<td>2.</td>
<td>40.0</td>
<td>40.0</td>
<td>20.0</td>
<td>5.57</td>
<td>62.9</td>
<td>0.143</td>
<td>15.1</td>
</tr>
<tr>
<td>3.</td>
<td>50.0</td>
<td>34.7</td>
<td>17.3</td>
<td>5.72</td>
<td>66.7</td>
<td>0.230</td>
<td>8.7</td>
</tr>
<tr>
<td>4.</td>
<td>60.1</td>
<td>26.6</td>
<td>13.3</td>
<td>5.99</td>
<td>72.8</td>
<td>0.269</td>
<td>6.8</td>
</tr>
<tr>
<td>5.</td>
<td>70.6</td>
<td>19.6</td>
<td>9.8</td>
<td>6.18</td>
<td>77.5</td>
<td>0.290</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Fig. 5.13 AgI dependence of packing density of the simulated structure.
5.7 MONTE CARLO STUDY OF SILVER ION CONDUCTION

The migration of Ag⁺ ions in the simulated structure is examined by monte carlo method as described in Section 5.3. The silver ion hopping is considered by using the simplified assumption that the Ag⁺ ion can hop to the one of the six nearest neighbour sites in the triangular lattice. In this section, the procedure used for the study of silver ion conduction by monte carlo method is described and the program used for simulation are explained. The results for mean square displacements of ions, diffusion constants, etc. are presented. The ion migration process in silver ion conducting glasses is discussed based on the simulation results, experimental observations and existing theories.

5.7.1 Silver Ion Hopping

The structure of the highly disordered silver ion conducting glass is simulated in the simple triangular lattice as explained in previous sections. All the unoccupied sites of the triangular lattice are available for the migration of silver ion. Each I⁻ ion has six nearest neighbouring sites and thus, six interstitial sites are available for Ag⁺ ions to hop. The silver ion can hop to one of the six nearest neighbouring sites as shown in Figure 5.4. The silver ion sitting in site ‘S’ has six nearest
neighbouring sites, A to F. The potentials of all the unoccupied nearest neighbour sites are calculated and site with minimum potential energy is chosen. The silver ion hopping is considered by Metropolis algorithm described already in Section 5.3.2.

5.7.2 Interaction Potentials

The long range coulomb interactions and short range repulsive interactions of Ag\(^+\) ion with Ag\(^+\), I\(^-\) & O\(^-\) ions are used for the calculation of site energies, described by

\[
V_{ij} = A_{ij} \left[ \frac{(\sigma_i + \sigma_j)^n}{r_{ij}^n} \right] + \left[ \frac{Z_i Z_j e^2}{r_{ij}} \right]
\]  

(5.19)

where, i & j are the types of ions, in our case i = Ag and j = Ag, I & O; A\(_{ij}\) is the repulsive strength, it is assumed A\(_{ij}\) = A and A = 0.1; \(\sigma_i\) & \(\sigma_j\) are the particle radii, \(\sigma_{Ag} = 0.6\) Å, \(\sigma_I = 2.2\) Å & \(\sigma_O = 1.32\) Å; n = 7 and |Z\(_i\)| = |Z\(_j\)| = 0.6. As discussed in previous Chapter IV (Section-4.9), the iodine and oxygen ions are expected to have wide & shallow and narrow & deep potentials respectively. The wide and narrow nature of the iodine and oxide potentials are taken into account by restricting the Ag-I and Ag-O interactions to distances 2\(\alpha\) and \(\alpha\) respectively. The potential of non-bridging oxygen ions (NBOs) is deep and narrow hence,
NBOs influence only nearest neighbouring particles as proposed by Minami [30]. Thus, the present treatment of oxygen ion potentials is quite different from that of Kondler et al. [16], where they have used long range attractive potential for NBO sites. The long range interaction between the silver ions are considered without any cutoff.

Monte Carlo simulations are carried out for the mean square displacement \( \langle R^2(t) \rangle \) of the \( \text{Ag}^+ \) ion using the procedure described in following section. The calculations are carried out for the simulated structure of silver ion conducting glasses \( \text{Y\%AgI - M\%Ag_2O - F\% M_2O_3} \) differing in AgI contents \( \text{Y\% in the glass, Y\% = 30\% to 70\% with M/F = 2.0 and M+F = 100-Y}. \) The diffusion constant is calculated at different temperature of the glass, characterized by the interaction parameter \( V/k_B T \), where \( V = e^2/\alpha \).

5.7.3 Procedure for Calculation

The program for monte carlo simulation of silver ion hopping, JKMC.FOR, is written in FORTRAN language and the calculations are carried out using PC-AT (386 and 486) IBM compatible machines. The intermediate important programming steps are briefly described in Appendix-C. The calculations are carried out for the matrix of size \( L \times B = 20 \times 20 \). All the ions \( \text{M, O (BOs & NBOs), I, Ag}^0 \) and \( \text{Ag}^1 \) are indexed.
with different indices. All the \( \text{Ag}^+ \) ions in different anionic environment are numbered and indexed and the silver ion hopping is treated by the following procedure:

1. Pick up an \( \text{Ag}^+ \) ion (\( \text{Ag}^0 \) or \( \text{Ag}^I \)), which sits on a site \( S \) (see Figure 5.15).

2. The potential energy \( U \) of the nearest sites (A to F in Figure 5.4) is calculated using equation (4) by the Ewald summation method. The summation is limited to \( n = 3 \) in equation 5.9. The subroutine used to evaluate the potential energy is explained briefly in Appendix-C.

3. The site with minimum potential energy \( U_m \) than those of others is chosen, i.e. if site A has so, \( U_A < U_B, U_C, \ldots U_r \).

4. The potential energy difference between the original site \( S \) and site \( A \) is calculated, \( \Delta U = U_A - U_S \), where \( U_S \) is the potential energy of site \( S \).

5. The probability of hop is obtained from Metropolis algorithm

\[
P = \exp \left( -\frac{\Delta U}{k_B T} \right)
\]

(5.20)

6. A uniform random number, \( R \) between 0 to 1 is generated.

7. The jump is performed, if \( P \geq R \).
(8) If the jump is from the NBO-Ag site to its surroundings or vice versa, the corresponding indices of the silver ions are changed.

(9) If the equation (5) is not satisfied, return to step (1) to pick up the next Ag\(^+\) ion and the procedure (2) to (8) is carried out.

One monte carlo (MC) time passes when this procedure is carried out for all Ag\(^+\) ions and the calculations are performed for 30 MC times.

5.8 RESULTS AND DISCUSSION

The calculations for 30 MC time steps are carried out for different configurations and compositions of the system at different temperatures (characterised by the interaction parameter V/k_B T). The simulations are carried out for five different configurations of the system and averaged. The thermal equilibrium is established after a few MC steps, hence, the calculation of mean square displacement, diffusion constant, etc. are carried out after 5 MC times.

5.8.1 Mean Square Displacement

The mean square displacement of the Ag\(^+\) ion after n MC times \(\langle R_n^2 \rangle\) is calculated by the equation
\[ < R_n^2 > = \langle | r(t_n) - r(0) |^2 \rangle \]  

(5.21)

where, \( r(t_n) \) and \( r(0) \) are the position of Ag\(^+\) ions after \( n \) MC times \( t_n \) and that at MC time zero respectively. The mean square displacements (MSDs), \( < R_n^2 > \), of Ag\(^+\) ions in glasses differing in dopant salt concentrations \( Y_\% \) are shown in Figure 5.14. The \( < R_n^2 > \) of Ag\(^+\) ions in all glasses increases linearly with time. The \( < R_n^2 > \) increases with the dopant salt concentration in the glass. The \( < R_n^2 > \) for the glass with AgI\(_\%\) = 60\% at different interaction parameters (i.e. for different temperature) is shown in Figure 5.15. The mean square displacement of silver ion increases with temperature.

5.8.2 Diffusion Constant

The diffusion constant \( D \) is estimated using the relation

\[ D = \frac{< R_n^2 >}{6t} \]  

(5.22)

if \( t \) is defined. The percentage of contribution to the diffusion coefficient by Ag\(^0\) ions alone are also calculated during the above procedure. The diffusion constant, \( D \), determined by the MSDs is shown as vertical bars in Figure 5.16. The diffusion constant increases with AgI content,
Fig. 5.14 Mean square displacement $\langle R_n^2 \rangle$ versus MC time for different AgI concentrations at $(V/kT) = 4.8$. 
Fig. 5.15 Mean square displacement $\langle R_n^2 \rangle$ versus MC time at different interaction parameters.
Fig. 5.16 Diffusion constant at different AgI contents. The shaded portion represents the percentage of contribution from Ag$^+$ ions.
which is a typical feature of the network glasses. The shaded portion in Figure 5.16 represents the fraction of Ag\textsuperscript{0} ions contribution to the diffusivity, D. As shown, the contribution to D from Ag\textsuperscript{0} ion decreases with AgI content in the glass. Only a negligible fraction of (about 1% to 5%) Ag\textsuperscript{0} ions contribute to D in the AgI dominant glasses. Even for glasses with high Ag\textsubscript{2}O content (or low AgI content), the major contribution to D comes only from Ag\textsuperscript{+} ions. This strongly supports our analysis (described in Chapter IV, Section 4.9.4) and Minami's proposal for the presence of two types of silver ions, mobile and immobile or less mobile, respectively Ag\textsuperscript{i} and Ag\textsuperscript{0} ions. Thus, our calculations clearly proves the presence of mobile and immobile Ag\textsuperscript{+} ions in the glassy matrix.

5.8.3 Silver Ion Concentration

The total silver ion concentration in the simulated structure is the sum of silver ion concentrations of the dopant salt AgI and the glass modifier Ag\textsubscript{2}O. The concentration of Ag\textsuperscript{i}, Ag\textsuperscript{0} ions and the total Ag\textsuperscript{+} ions are estimated, by treating the two-dimensional structure as a thin slab of thickness \(\alpha_i\). The AgI dependence of the silver ion concentration is shown in Figure 5.17. The Ag\textsuperscript{i} concentration due to AgI increases, while Ag\textsuperscript{0} concentration due to Ag\textsubscript{2}O decreases. The total Ag\textsuperscript{+} ion concentration is
Fig. 5.17 Compositional dependence of silver ion concentration. The concentration brought to the glass from AgI is represented as (Δ), Ag2O as (O) and the total as (•).
almost constant in the glass, but, the diffusion coefficient increases with AgI content in the glass. This suggests that only a fraction of Ag⁺ ions are mobile, namely, silver ions bonded to iodine ion (i.e. AgI ions) and the rest are immobile or less mobile. These results are in excellent agreement with our earlier experimental results [32,33] and supports the idea that carrier concentration depends on the concentration of AgI ions.

5.8.4 Temperature Dependence of D

The simulations are carried out at various temperatures, characterized by the interaction parameter \( V/k_B T \). The temperature dependence of diffusion constant \( D \) is shown in Figure 5.18. The linear dependence of Log \( D \) versus \( V/k_B T \) shows an excellent agreement with the Arrhenious law, which is the characteristic feature of the ion conducting glasses. The temperature dependence of \( D \) can be written in the form

\[
D = D_0 \exp(-E_a/kT) \tag{5.23}
\]

where, \( E_a \) is the activation energy and \( D_0 \) is the pre-exponential factor. The activation energies obtained from the least square straight line fitting are shown in Figure 5.19. The activation energy decreases with AgI
Fig. 5.18 Arrhenius plots for diffusion constant for different AgI concentrations in the glass.
Fig. 5.19 AgI dependence of activation energy.
content in the glass, which is a characteristic feature of Ea dependence on AgI concentration in the network glasses.

5.8.5 Pre-Exponential Factor

The pre-exponential factor Do increases with AgI content as listed in Table 5.1 and follows the similar trend observed for the conductivity pre-exponential of other silver ion conducting glasses [32,33].

5.8.6 Conduction Process

The observed results suggest that not all the silver ions are mobile and only a part, namely, the ones bonded to iodine anions. The other population of silver ions, the ones bonded to oxygen anions, are immobile or less mobile. The mobile silver ion concentration depends on the number of silver ions located in iodide potential. The increase in dopant salt content increases mobile silver ion and iodine ion concentration and hence increases the period of shallow iodide potentials. When these shallow potentials are connected for a long period, they form diffusion paths for silver ion migration with less activation energy. Thus, the results of present theoretical study indicates the conduction process quite same as the conduction mechanism discussed for the experimental observations in previous Chapter IV (Section 4.9).
5.9 SUMMARY AND CONCLUSIONS

The highly disordered structure of silver ion conducting network glasses, of general formula AgI-AgzO-MzO3, has been represented in a simple two-dimensional triangular lattice. Structure for different concentration of the constituents can be easily simulated in the present model. The simulated structure excellently reproduces the various experimentally observed structural features pertaining to these materials. The radial distribution functions and densities of the structural model agree well with experimental ones, proving its validity.

The silver ion hopping in the above model is studied by monte carlo technique. The results of mean square displacements and diffusion constants of silver ion show strong dependence to AgI content in the glass. The contributions to the diffusion constants from silver ions in different anionic environments have been obtained from our calculations. The present study strongly support the existence of mobile silver ion and immobile or less mobile silver ion bonded respectively to iodine and oxygen ions. The results also include a decrease in activation energy with dopant salt concentrations. The silver ion migration in the diffusion paths supported by the iodine anions is suggested.
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