CHAPTER 1

INTRODUCTION

Solid State Ionics is an interdisciplinary area of science encompassing physics, solid state chemistry, chemical engineering, electro chemistry, material science etc. This field of science involving the study of the phenomena of ions in solids, especially solids which exhibit high ionic conductivities at fairly low temperature and negligible electronic conductivity which can be used as electrolytes in many electrochemical applications.

In the immediate wake of energy crisis. there was a strong interest in the potential of solid glass electrolytes for electrochemical energy storage as in power sources and load leveling. Initial efforts were, therefore, directed towards the identification of glasses with good conductivity and electrochemical stability. This field will cover topics such as physics and chemistry of defects, ionic transport measurements and theory in solids, relationship between structures and ionic transport in ionic conductors and in ionic and electronic mixed conductors, thermodynamics of ionic materials, ion exchange phenomena, interfacial properties between solid electrolytes and electrodes, solid state electrochemistry and related technologies.

In the early 1960s. the only materials known to exhibit high ionic conduction were stabilized zirconias at high temperatures and silver iodide above 150°C. Stabilized zirconia is non stoichiometric oxide ion conductor found to exhibit high extrinsic vacancy concentration. The high conductivity (1S/cm at 420K) in silver iodide, a stoichiometric compound, is attributed to the presence of channel like diffusion paths created by the face sharing iodide ion polyhedron and also to the large number of Ag^+ ion vacant sites. Middle 1960s witnessed the discovery of non stoichiometric β-alumina which exhibited a high Na^+ ion conductivity possessing a high intrinsic sodium ion vacancy concentration. These solids, exhibiting relatively high ionic conductivities are called high conductivity solid electrolytes or Fast Ion Conductors (FIC) or Super Ion Conductors (SIC).

This super ionic conduction behavior of these electrolytes was not observed in the early discovered normal ionic conductors. The super ionic conductors (SIC) differ from normal ionic conductors (NIC) in various characteristics properties given below.

1. SICs have high ionic conductivities of the order of 10^{-1} -10^{-6} S/cm whereas in NICs have 10^{-8}-10^{-16} S/cm at the same temperature.
2. The conduction mechanism is only due to the migration of ions of one type with low electronic contribution in SICs where as in NICs it may be due to the migration of both ions.
3. SICs consist of a large and constant number of mobile charges where as the number is less and highly temperature dependent in NICs.
4. The activation energy for ion transport is very low in SICs since the enthalpy of formation of defects is zero, where as it is high in NICs due to the presence of both enthalpy of formation and migration of defects.

Also in super ion conductors, the number of the energetically equivalent sites available for the mobile ions is greater than the number of mobile ions.

The search for these solid electrolytes has started as most of the then used liquid electrolytes have many inherent disadvantages in ionic device applications. They are (1) the limited life period of the device due to corrosion reaction occurring between the electrolyte solution and the electrodes (2) non-function of the device below the freezing and above the boiling point of the electrolyte (3) decomposition of the electrolytes in the device at high temperature and (4) leakage of the liquid electrolyte from the device. These problems can be overcomed by using solid electrolytes and attained high research and development priority. Substantial progress occurred in this field, can be reviewed by the publications of many famous researchers [1-10].

The super ionic conductors have first been explored in the crystalline state and later in the non-crystalline state on account of their advantages over the crystalline counter parts. They have the following properties;

1. Higher ionic conductivities and negligible electronic conductivities.
2. Isotropic properties.
3. Ease of thin film formation.
4. Absence of grain boundaries.
5. Ease of shaping into various forms.
6. Wide selection of glass forming systems.
7. Wide range of control of properties with changing chemical compositions.

The higher ionic conductivity in these glassy electrolytes than that in the crystalline conductors has been attributed to the disordered-distribution of mobile ions in the random structure of the glass. A wide range of Ag^+, Li^+, Cu^+, Na^+, F^-, O^{2-} conducting glasses are available. Some examples of super ion conducting systems with such ions are listed, in which the maximum conductivities in each system at 25°C (or specified temperature) with references are shown in Table 1.1 [11-40]. Conductivity versus inverse temperature plots for some well known super ion conductors are given in Fig.1.1.

Table: 1.1

Examples of the super ion conducting materials

Ion species	Glass composition	σ_{RT} (S/cm)	Reference
Ag^+	α-AgI	1.3 (at 147°C)	Tubandt et al (1914)
	Ag_3SI	2.0 (at 240°C)	Reuter et al (1966)
	$RbAg_4I_5$	2.1×10^{-1}	Owens and Argue (1967)
	$C_2H_5NHAg_5I_6$	3.0×10^{-2}	Geller and Owen (1972)
	$Ag_6I_4WO_4$	4.7×10^{-2}	Shahi & Chandra (1975)
	$AgPO_3$-PbX_2 (X=I, Br)	$\sim10^{-2}$	Malugani et al (1986)
	AgI-Ag_2MoO_4	1.4×10^{-2}	Minami et al (1980)
	AgI-$Ag_4P_2O_7$	1.8×10^{-2}	Minami et al (1977)
	AgI-Ag_2O-B_2O_3	8.5×10^{-3}	Minam i et al (1981)
	AgI-Ag_3VO_4	5.3×10^{-3}	Hariharan et al (1985)
	Ag-As-Se-Te	$\sim10^{-4}$	Carcaly et al (1986)
	AgBr-Ag_2O-B_2O_3	2.6×10^{-3}	Minami et al (1982)
	AgCl-Ag_2O-B_2O_3	6.4×10^{-4}	Minami et al (1983)
Li^+	Li_2S-LiI- P_2S_5	1.0×10^{-3}	Malugani & Robert (1980)
	Li_2S-P_2S_5	1.1×10^{-4}	Ribes et al (1979)
	Li_2S-GeS_2	4.0×10^{-5}	Souquet et al (1980)
	Li_2O-Ta_2O_5	5.0×10^{-6}	Nassau et al (1981)
	LiF-KF-$Al(PO_3)_3$	1.3×10^{-3} (at 200°C)	Maiti et al (1983)
	Li_2O-LiCl-Al_2O_3-B_2O_3	1.3×10^{-6}	Takahashi et al (1979)
Cu^+	CuI-Cu_2O-MoO_3	$\sim10^{-2}$	Machida et al (1987)
	CuI-Cu_2O-P_2O_5	$\sim10^{-2}$	Liu and Angell (1984)
	CuI-CuCl-RbCl	$\sim10^{-2}$	Liu et al (1986)
Na^+	NaF-NaCl-Na_2O-B_2O_3	$\sim10^{-6}$ (at 150°C)	Hunter & Ingram (1984)
	Na_2O-ZrO_2-P_2O_5-SiO_2	$\sim10^{-6}$ (at 150°C)	Susman et al (1983)
H^+	$H_3PW_{12}O_{40}.29H_2O$	1.7×10^{-1}	Takahashi (1989)
	$HUO_2PO_4.4H_2O$	4×10^{-3}	Takahashi (1989)
F^-	Zr-Ba-Cs-F	$\sim10^{-5}$ (at 200°C)	Kawamoto et al (1985)
	Zr-Th-Ba-Li-F	$\sim10^{-4}$ (at 200°C)	Sun et al (1985)
	In-Sn-Pb-F	$\sim10^{-3}$ (at 200°C)	Minami (1987)
	PbF_2-MnF_2-$Al(PO_3)_3$	1.1×10^{-4} (at 200°C)	Kulkarni et al (1986)
O^{2-}	ZrO_2-Y_2O_3	1.2×10^{-1}(at 1000°C)	Etsell and Flengas (1970)
	$(Bi_{2-x}Y_x)O_3$	$\sim10^{-2}$ (at 500°C)	Steele (1989)

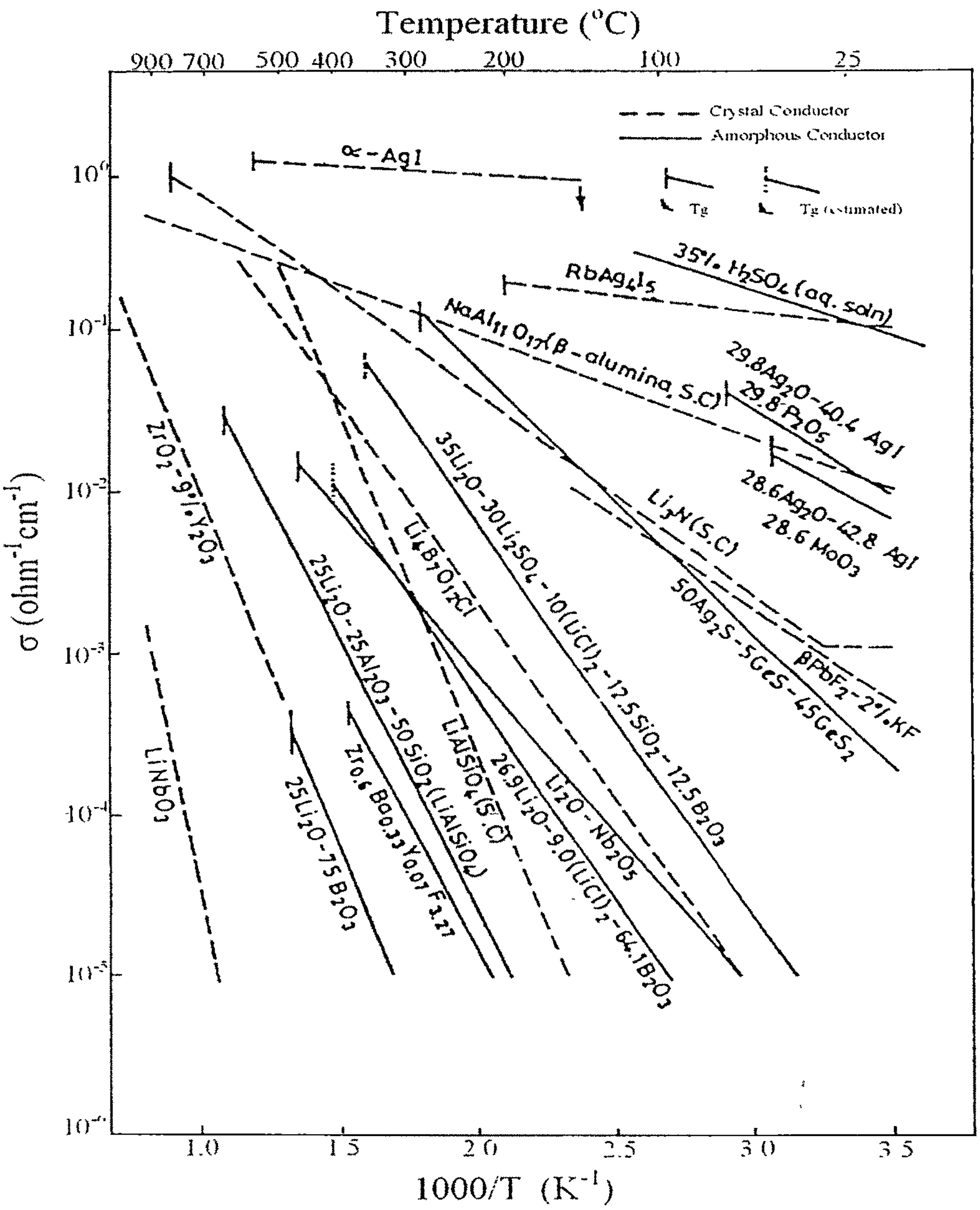


Fig. 1.1 Conductivity versus inverse temperature plots for some well known super ion conductors

1.1 Super Ion conducting materials

Super ion conducting materials can be classified according to the nature of the conducting species. Both cations and anions can move in a solid lattice. The cations are expected to be more conducting compared with anions due to its relatively small ionic radius. The common ions showing high mobility are Li^+, Na^+, K^+, Ag^+, Cu^+, F^-, O^{2-} etc. Apart from oxygen ion conductors, most of the super ionic solids involve a monovalent ion. There is no di and trivalent ions reported showing high mobility, since the coulomb energies involved in jumping/ hopping of these ions would be more than those for monovalent ions [41]. In the following sections a brief description of different cationic and anionic conductors is given.

1.1.1. Oxygen ion conductors

Stabilized zirconias show the oxide ion conductivities based on the oxide ion vacancy mechanism. As stabilizers, CaO. Y_2O_3. Yb_2O_3. Sm_2O_3, Sc_2O_3, Gd_2O_3 and Nd_2O_3 are known [42]. These high temperature solid electrolytes possess a fluorite type structure, which has a large number of octahedral interstitial voids. Thus, this structure is a rather open one and rapid ion diffusion might be expected. Oxide solid electrolytes are used in fuel cells. oxygen pressure gauges. sensors etc.

1.1.2. Fluoride ion conductors

Of halide ion conductors. fluoride ion being the smallest and provides good anionic conduction. There are three types of fluoride ion conductors which have crystal structures of the fluorite. tysonite and YF_3 type. These materials possess fluorite structure and thus provide an open path for high ionic conductivity. Until recently β-PbF_2 was the best available fluoride ion conductor. Much better fluoride ion conductors include alkali and alkaline earth fluorides like $KBiF_4$, $RbBiF_4$. $Pb_{0.75}Bi_{0.25}F_{2.25}$ etc have been studied [42].

1.1.3. Proton conductors

Proton conductors are finding immense value in fuel cell technology with H_2/O_2 cells. Because of the small size and polarizing power of the proton, it is unlikely to conduct in the same way as other ions [43]. Three type of mechanism are indicated for the proton transport like liquid-like-transport of H^+, H_3O^+or NH_4^+ migration and H_3O^+/H_2O jump. High proton conduction was observed in HUP (Hydrated Uranyl Phosphate) $HUO_2PO_4.4H_2O$ and Keggin-type heteropolyanion structures such as $H_3(PMO_{12}O_{40}).nH_2O$ and $H_3(PW_{12}O_{40}).29H_2O$ etc at room temperatures [3]. Proton conduction at high temperatures occurs in certain perovskites such as doped strontium cerate, $SrCe_{0.95}Yb_{0.05}O_{3-x}$.

1.1.4. Lithium ion conductors

A large number of lithium ion conductors are known to date [44-54]. This is primarily because of the small cationic size and high polarizing power of Li^+ ions as compared to other cations. Li is a very promising material for high energy density batteries because of its light weight, high electro chemical potential and ease of handling [55]. The heterogeneous mixture of LiI and Al_2O_3 has been used as the best conducting compound for solid state batteries. Apart from LiI-β-alumina, a large number of Li compounds like silicates, sulphates, tungstates. phosphates. germinates. aluminates, gallates have also been found to show fairly high Li^+ ion conduction at room temperature. The Li^+ion glasses in the system $LiI-Li_2S-P_2S_5$ have been reported to be commercially used as electrolytes in all solid state primary cell of the type Li/glass/ TiS_2.

1.1.5. β-alumina

β- alumina is one of the most extensively studied super ionic solid particularly because of its promise for the development of high energy density batteries and load leveling storage systems. The name β-alumina is used to represent the composition M_2O-xAl_2O_3 (M=Na, K, Rb, NH_4, Tl, Ag and x in between 5-11). Among this Na-β-alumina has a high Na^+ ion conductivity comparable to the aqueous NaCl [43]. The two important members of Na-β-alumina family are hexagonal β-alumina (Na_2O-$11Al_2O_3$) in which interstitialcy mechanism accounts for high conductivity and conduction in rhombohedral β-alumina (Na_2O-$5Al_2O_3$) occurs through the movement of cation vacancies [55]. The glasses in the system Na_2O-ZrO_2-SiO_2-P_2O_5 called NASICON are another class of widely studied Na^+ ion conductors.

1.1.6. Copper ion conductors

The similarities in the properties of silver and copper ions, high conductivity copper ion conductors at room temperature have been synthesized by Takahashi et. al., [43] using the similar method as in the case of silver ion conductors. The replacement of Ag by Cu is of both scientific and practical interest due to its low cost compared with silver. By incorporating Rb^+, K^+, Tl^+, Pb^{2+}, Te^{4+} and various organic substituted ammonium, sulfonium ions in to the lattice of copper halides, high conductivity solid copper ion conductors were obtained. By introducing the Rb^- and I^- ions into the lattice of CuCl simultaneously, $Rb_4Cu_{16}Cl_{13-x}I_{7+x}$ ($0.2 \leq x \leq 0.5$) was obtained which has a Cu^+ ion conductivity of 3.7-2.8×10^{-1} S/cm at room temperature. This conductivity is the highest conductivity ever found at room temperature [40]. Recently, copper ion conducting ternary and quaternary amorphous electrolytes $CuI-Cu_2O-MoO_3$ and $CuI-Cu_2O-P_2O_5-B_2O_3$ etc. have been reported [30].

1.1.7. Silver ion conductors

Silver ion conductors are the most widely studied class of materials with high ionic conductivity at ambient temperature. In the early 1960s, Reuter and Hardel [12], Takahashi and Yamamoto [5] found Ag_3SI which has a silver ion conductivity of 10^{-2} S/cm at 25°C. Since then, stimulated by this discovery of a room temperature high conductivity silver ion conductor being synthesized by combining AgI and foreign ions, many inorganic and organic anions and cations have been introduced in to the lattice of silver iodide to obtain high conductivity silver ion conductors at room temperature in the crystalline as well as in the glassy state [43]. The compounds MAg_4I_5 (with M=Rb, K, NH_4) [55], $Ag_2WO_4.4AgI$ [43], $Ag_3AsO_4.4AgI$ [55] etc. are studied earlier in detail [3]. As the present work deals with silver ion conducting solid electrolytes, the silver ion conductors are discussed in detail in the subsequent sections.

1.2. The Glassy state

Glass is an amorphous solid without long range order or three dimensional periodicity. Glasses do not confirm the rules of stoichiometry and exhibit a characteristic thermal event known as glass transition. Glass is the result of a phase transformation in which nucleation and growth of crystals has been suppressed that is the time allowed for crystallization has been less than the time required by the kinetic factors of atomic rearrangement. These kinetic factors are temperature dependent and devitrifaction temperature is loosely defined as the temperature below which the crystallization time becomes practically infinite. If a glass is formed by cooling of a liquid or vapor, a fast quench is sometimes required to minimize the time at which the glass is below the melting point but above the devitrifiction temperature [56, 57].

The structure of a solid formed by cooling from its liquid state depends on many factors; one important factor is the rate of cooling. The inter-relationship between the liquid, glassy and crystalline state of material can best be brought out in terms of volume- temperature plot as in Fig.1.2. If a liquid of fixed mass is cooled from the original state represented by 'a' in the diagram, its volume decreases steadily. If the rate of cooling is sufficiently low, a discontinuous change occurs at some point 'b' and follows the path 'bc' (temperature T_f) which corresponds to crystallization taking place in the melt. As the temperature is lowered further, the volume decreases but with a slope different from that obtained prior to crystallization .The temperature T_f is usually referred to as the transformation temperature. If the rate of cooling is very fast, crystallization does not take place at T_f and the volume decreases steadily along line 'b' until at a certain temperature 'e' (temperature T_g). The volume-temperature curve undergoes a sharp change in direction and continues almost parallel to the line 'cd'. T_g is usually referred as the Glass-transition temperature and its volume depends on the rate of cooling employed. Thus, for instance T_g would be shifted towards T_f, if the rate is lowered. Between T_g and T_f material is a super cooled liquid and below T_g it is a glass. Since the volume of the material on the glassy state is larger than that in the crystalline state for a particular temperature (lines 'ef' and 'cd' in the figure), it is obvious that thermodynamically glassy state is a metastable one (Jones 1956) [58].

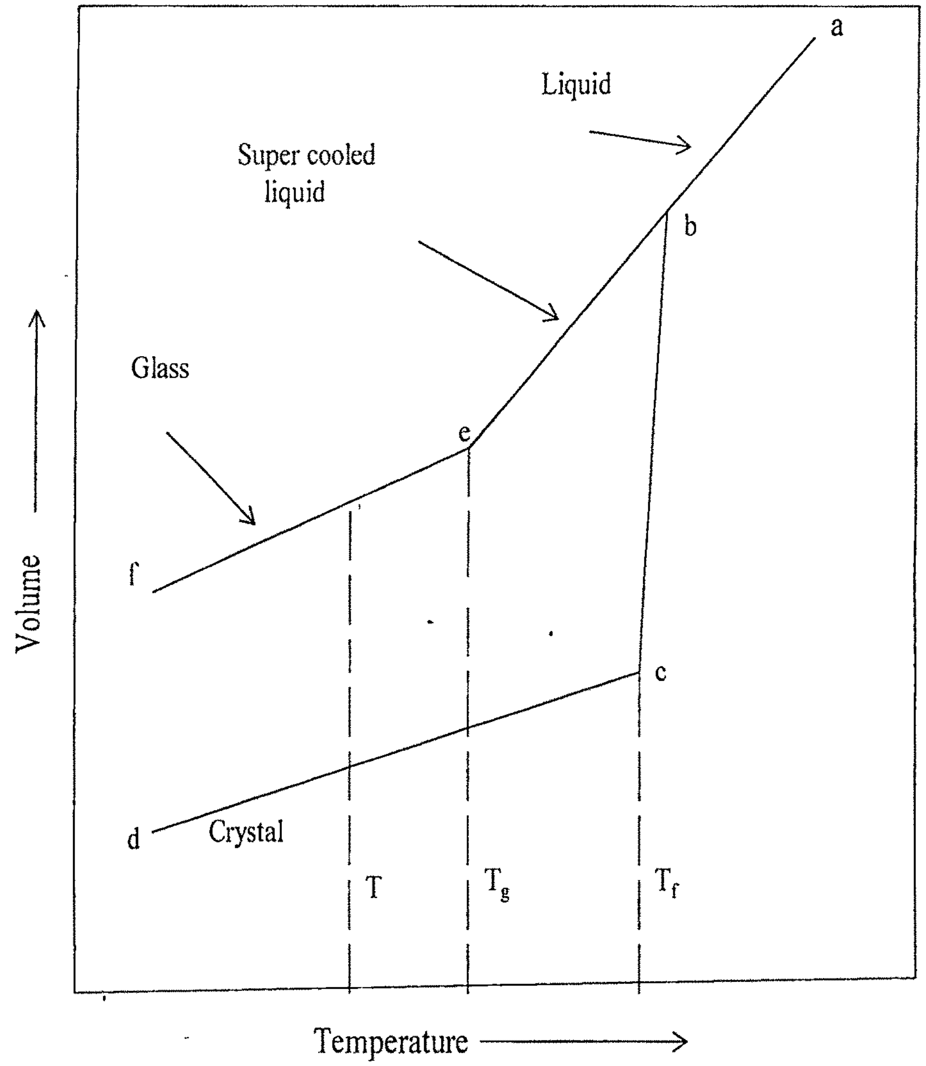


Fig.1.2 Relation between glass, liquid and solid is shown in the volume-temperature plot.

1.2.1. Criteria for glass formation

The earliest effort in understanding glass formation criteria was the structural effort made by Goldschmidt [59], who ascribed the relative size of the cations to be the determining factor for glass formation. Glass formation found to be facile for 0.2< [Rc/Ra] <0.4, where Rc and Ra are the cation and anion radii respectively, have a structure such that each cation is surrounded by four anions. The later being situated at the corner of a tetrahedron. The set of oxides SiO_2, GeO_2, P_2O_5, B_2O_3, V_2O_5 and NbO_2 belong to this category. Later, it has been pointed out that even though the ionic radius ratio of BeO allows the formation of the tetrahedron arrangement of oxygen around Beryllium ion, BeO cannot be obtained in the glassy state. This has been led to examine the characteristics of glass forming oxides further and to develop the random network theory for glass structure.

One of the pioneering contributions made in this area by Zachariasen [60], who postulated that, (1) the inter-atomic forces in glasses and crystals must be similar and the atoms in a glass oscillate about definite equilibrium position, thus maintaining the form of a three dimensional network as in a crystal; (2) the energy content in a glassy state is not greatly different from that of the corresponding crystal network. Thus the coordination number of the cation in M_xO_y must be closely similar to that observed in corresponding crystal. In a crystal, the structural units are built up to give a regular lattice where as in a glass; there is sufficient distortion of bond angles to permit the structural units to be arranged in a non-periodic fashion giving a random network.

Figure 1.3 shows the difference between a regular crystalline lattice and random network of an oxide, SiO_2, where the structural units can be tetrahedral. Thus, glass Possesses a short range order since the oxygens are arranged in fairly rectangular

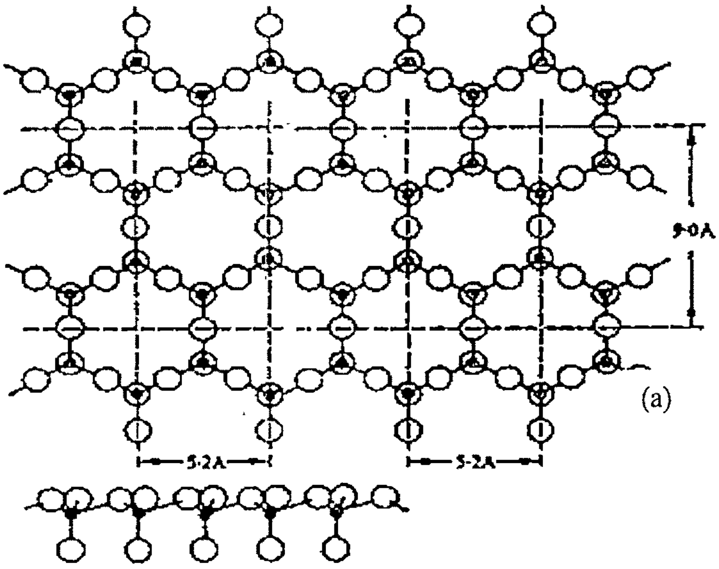


Fig.1.3(a) Regular periodic arrangement of atoms (or ions) in silicate (SiO_2)

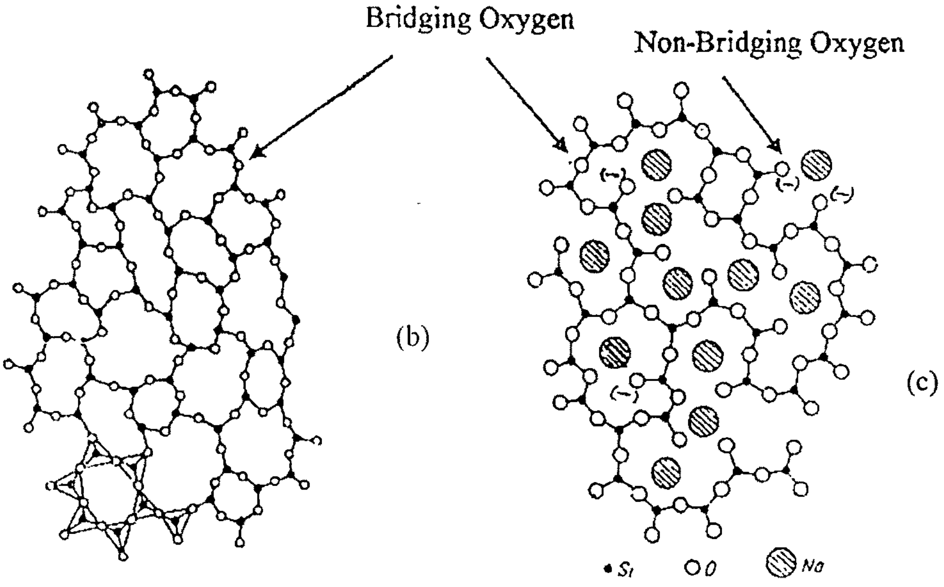


Fig.1.3 (b) Disordered netting of SiO_4 building blocks in SiO_2 glass (c) Arrangement of atoms or ions in sodium silicate glass. When Na_2O is incorporated, the large sodium ions rupture the oxygen bridges and open (modify) the structure.

polyhedra. On the basis of the above postulates, Zachariasen (1932) [60] proposed the following condition of glass formation. For any oxide, M_xO_y to form a glass.

1. An oxygen atom must not be linked to more than two glass forming (M) atoms.
2. The number of oxygen atoms surrounding M atoms should be small.
3. The oxygen polyhedra share corners with each other not edges or faces.
4. At least three corners of each of the oxygen polyhedra must be shared.

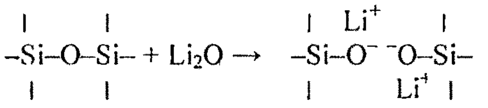
The nature of the bonding between cation and oxygen also plays dominant role. Those oxides that have strong covalent bonds are more likely to act as network former than those in which bonding is predominantly ionic.

1.3. Chemical Composition of ion conducting glasses

Three basic constituents are present in all ionically conducting glasses; network formers, network modifiers and dopant salts in different proportions.

Network formers are compounds of covalent nature such as SiO_2, B_2O_3, V_2O_5, P_2S_5, B_2S_3, GeS_2 etc. They are strongly cross linked by an assembly consisting of tetrahedra (SiO_4, PO_4, BO_4) or triangles (BO_3) which combine to form macromolecular chains by sharing corners or edges. The pure network formers readily form glasses by cooling from the liquid phase and a certain range of bond angles and lengths characterize the disorder existing in the vitreous state. The existence of local order, which is associated with the stability of the tetrahedral or triangular entities is the result of the covalent character of the bonds. The possibility of deforming this local order is the result of the partially ionic character of these same bonds. Stanworth [61] observed in this respect that the former oxides are all characterized by a difference in electro negativity between the oxygen and the former cations.

Network modifiers include oxides or sulphides (Ag_2O, Li_2O. Ag_2S. Li_2S etc) which interact strongly with the structure of network former. A true chemical reaction is involved leading to the breaking of the oxygen or sulphur bridge linking two network former cations. The addition of a modifier introduces two ionic bonds. For instance, the reaction between silica and lithium oxide may be expressed as



$$-\underset{|}{\overset{|}{Si}}-O-\underset{|}{\overset{|}{Si}}- + Li_2O \rightarrow -\underset{|}{\overset{|}{Si}}-\overset{Li^+}{O^-}\ \underset{Li^+}{{}^-O}-\underset{|}{\overset{|}{Si}}- \qquad (1.1)$$

The increasing addition of a modifier to a given former leads to the progressive breaking of all oxygen bridges according to a type (1.1) reaction. As the number of non-bridging oxygen or sulphur atom increases the average length of the macro molecular chain decreases.

Doping salts are halide salts or in some cases sulphates are added to the glassy matrix containing network former and network modifier. Such an addition significantly increases the ionic conductivity. The arrangement of ions from the halide salt with respect to one another in the macromolecular chain is still unknown. Proposed hypothesis range from the formation of salt clusters [62] to a uniform distribution through out the mass of the glass [63].

1.4. General theory of ion transport

The variation in ionic conductivity with temperature, composition and structure is the key to understand the transport phenomena. The total conductivity of a material σ_T is equal to the sum of the contributions of all the charge carrying species σ_i

$$\sigma_T = \Sigma_i \sigma_i = \Sigma_i (t_i \sigma_T) \qquad (1.2)$$

where t_i represents the transference number or the fractional contribution of a particular species of σ_T. For glasses in which the transport by a single type of ion predominates (e.g.. Ag^+, Li^+, F^-) we can simplify equation (1.2) to

$$\sigma_T = \sigma_{ion} \qquad (1.3)$$

The conductivity, σ is given by

$$\sigma = nZe\mu \qquad (1.4)$$

where n is the mobile cation concentration, Ze is the ionic charge and μ is the mobility.

Nernst and Einstein recognized the equivalence of the gradient in particle concentration ∇n which results from the driving force for diffusion

$$F_d = (\frac{kT}{n})\nabla n \qquad (1.5)$$

and the gradient in potential energy $-\nabla\phi$ which results from the application of an external force, F_{ext} and causes particle drift. Equating these forces, $F_e = F_d$ gives

$$F_e = (\frac{kT}{n})\nabla n = -\nabla\phi \qquad (1.6)$$

The requirement of flux balance $D\nabla n = nV_d$ where D is the diffusion constant and V_d is the drift velocity.

$$D = kT(\frac{V_d}{F_e}) \qquad (1.7)$$

In the case of ionic conduction. F_e is related to the electric field E. substituting in equation (1.6). we obtain

$$D = kT(\frac{V_d}{ZeE}) = \left[\frac{kT}{Ze}\right]\mu \qquad (1.8)$$

combining equation (1.4) with the above relation, we get

$$D = \frac{\sigma\, kT}{n(Ze)^2} \qquad (1.9)$$

the Nernst –Einstein relation.

From statistical random walk calculations, the well known expression

$$D = \frac{1}{6}\lambda^2\Gamma \qquad (1.10)$$

where λ is the distance between sites and Γ is the jump frequency. Replacing D in equation (1.9) with this expression and rearranging the terms yield

$$\sigma = \left[\frac{n(Ze)^2\lambda^2}{6kT}\right]\Gamma \qquad (1.11)$$

The jump frequency, Γ is a thermally activated process determined by ΔG_m, the free energy of motion and is given by

$$\Gamma = \upsilon_0 \exp(\frac{-\Delta G_m}{kT}) \qquad (1.12)$$

$$\Gamma = \upsilon_0 \exp(\frac{\Delta S_m}{k})\exp(\frac{-\Delta H_m}{kT}) \qquad (1.13)$$

where ν_0 is the vibrational frequency of an ion in a potential well and ΔS_m and ΔH_m are respectively the entropy and enthalpy of motion. Finally, equation 1.11 can be written as

$$\sigma = \frac{n(Ze)^2\lambda^2\upsilon_0}{6kT}\exp(\frac{\Delta S_m}{k})\exp(\frac{-\Delta H_m}{kT}) \qquad (1.14)$$

$$\sigma = \sigma_0 \exp(\frac{-\Delta H_m}{kT}) \qquad (1.15)$$

$$\sigma = \frac{\sigma_0}{T}\exp(\frac{-E_a}{kT}) \qquad (1.16)$$

where E_a is the activation energy derived from measurement of conductivity versus reciprocal of temperature.

1.5. Structural aspects of AgI

Silver iodide is a prototype super ionic conductor, in which its α-phase is stable between 147 °C and 555 °C at normal pressure, is a typical example of a solid electrolyte [64-69]. AgI exists in the γ- phase at low temperatures possessing a zinc blend structure where iodide forms an fcc lattice and cations are tetrahedrally coordinated to iodide ions. AgI transforms into a β-phase at 410K with a wurtzite structure where iodide forms an hcp lattice and the cations continue to be tetrahedrally coordinated to iodide ions. There exists another structural phase transformation from β to α phase at 420K, where the iodide ions form a bcc lattice and Ag^+ are expected to be mobile in the lattice. The structural evidence of high cationic disorder in α-AgI was first reported by Strock [70] and was confirmed by Hashino [71]. According to these authors, the bcc arrangement of iodide provides a total of 42 available sites for two silver ions in a unit cell. The structure of α-AgI is shown in the Fig. 1.4. The silver ions are in a quasi molten state in the 42 available [12 tetrahedral, 24 trigonal bipyramidal and 6 octahedral] positions. Here the numbers of available sites are very much higher than the number of mobile ions and AgI has a characteristic disordered structure in α-phase with an increase in conductivity by more than three orders of magnitude at 147°C.

Several studies [72-74], performed in order to determine the silver positions in the lattice by neutron scattering data, indicate that the silver ions are preferentially found in oblong ellipsoidal regions of space centered at the tetrahedral sites and extending in the directions of the neighboring octahedral sites. This extended region of cation site occupancy corresponds to large amplitude anharmonics and anisotropic vibrations of the cations. This would give large Debye-Waller factor in diffraction patterns as found for α-AgI. This is more or less general feature of all 'liquid like' super ionic solids. Apart from cation disorder, formation of channel like pathways for moving cations due to face sharing anionic polyhedra is another important structural characteristic. The motion of cations in this path would be affected by the size of the moving cations and the lattice parameter (Geller) [75].

α-AgI is in many ways an ideal electrolyte. It is solid due to the rigid sub lattice of I^- ions. The carrier concentration is high since all of the Ag^+ ions are potentially mobile. It has low activation barrier for migration and high conductivity (~1S/cm) at 147°C. It has the advantage of strong liquid electrolyte level of conductivity with only one mobile species and having mechanical properties of a solid. It is stoichiometric and does not require dopants to achieve high conductivity and insensitive to the presence of dopants. One disadvantage is that it is stable only at high temperatures >147°C [76].

1.6. Model for ion transport in glasses

Many efforts have been directed towards the development of models to provide insight into the fast ion transport in glass. These models were based on the thermal, structural and transport properties of the mobile ions.

1.6.1. Anderson-Stuart model

Anderson and Stuart (A-S) [77] formulated a model called strong electrolyte model for the calculation of activation energy for cationic transport in silicate glasses (Na_2O - SiO_2,

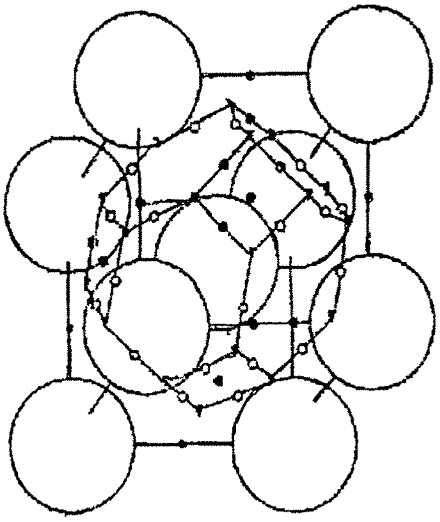


Fig.1.4. Schematic diagram of α-AgI unit cell structure.

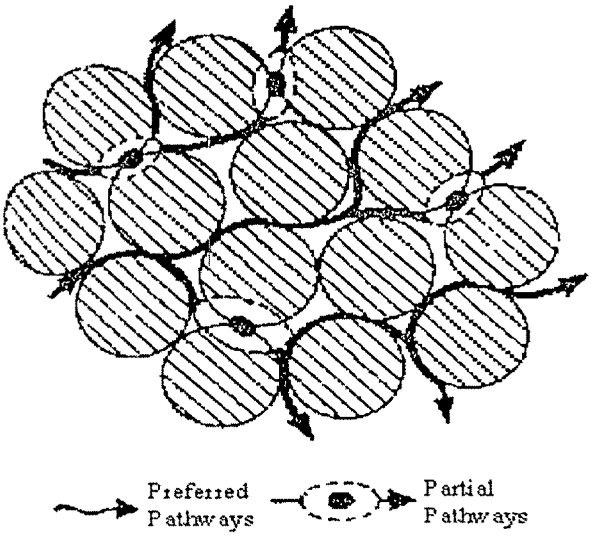


Fig.1.5. Cluster model for the fast ion conducting glasses

PbO-SiO$_2$). They visualized ion motion to be occurring by the jumping of the ion from one site to another through narrow openings present in the walls of the coordinating cage of oxygen ions which constitute constricted doorways. Carrier ions are regarded as intrinsically mobile and E_a, the activation energy, corresponds to energy barrier for cation migration. According to this model, $E_a=E_b+Es$; where E_b represents the electrostatic interactions between the mobile ion and the host network and E_s is the elastic strain component. The carrier concentration *n* is assumed to be independent of glass composition and temperature. The A-S model is not only widely discussed but has also been applied with a reasonable success to Li^+ ion concentration in glasses to study the pressure dependence of conduction and to the investigation of mixed anion effect.

1.6.2. Ravaine- Souquet model

Ravaine and Souquet (R-S) [78, 79] proposed the weak electrolyte model for the ion transport in weak electrolytes and correlated the ionic conductivity and thermodynamic activity. The weak electrolyte theory emphasizes the dissociation of non-bridging oxygen-cations pairs governed by thermodynamic equilibrium and suggests that the mobility is essentially unaltered by the concentration of modifying cations. Thus, the model postulates the existence of two distinct populations of carrier ions, 'mobile and immobile'. The measured activation energy E_a is assumed to be the energy required to promote an immobile ion to a mobile ion population. The mobility of the ion has been regarded as independent of composition and structure of the glass. Weak electrolyte theories derive support from the experimental observation that conductivity varies as the square root of the modifying oxide at low level modification. More recent studies on mixed alkali effect and on conductivity enhancement upon addition of halide salts have provided supportive evidence from R-S model.

1.6.3. Random-Site model

Random-Site model proposed by Glass and Nassau (1980) [80] assumes a large distribution of alkali ion sites in glasses which differ in local free energies and hence a large distribution of activation energies for conduction. This model assumes a Gaussian distribution of activation energies for the mobile Li^+ ions. In this model, all alkali ions are potentially mobile and there is no distinction between the mobile and immobile species as in the case of weak electrolyte model. Glass and Nassau found that the activation energies for several Li^+ ions containing glasses was a linear function of Li content (x) and of the form

$$E_a=E_0 - \rho^2/4kT$$

$$E_a= E_0 - (\rho^2 x)/4kT$$

1.6.4. Cluster –bypass model

Cluster bypass model has been introduced by Ingram et. al., (1988) [81] to explain the mixed mobile ion effect in the glass and non-Arrhenius behavior of conductivity of some ionically conducting glasses. This model recognizes the cluster tissue texture of glasses which has been discussed in the literature. According to this model, glass can be regarded as coagulation of ordered micro domains or clusters (~25-50A° in diameter) embedded in a truly amorphous, low density tissue material (Fig.1.5). The intercluster space is filled by a residual liquid which on cooling below T_g solidifies and forms a residual phase or 'connective tissue'. The central idea of cluster bypass model is that the preferred pathways for ion migration lie within the connective tissue region. This model explains the curvature seen in the Arrhenius plot of certain AgI rich glasses as due to continuous exchange of materials between the cluster and tissue region. Conductivity enhancements in mixed anion glasses as well as the effects of addition of dopant salt have also been explained by this model.

1.6.5. Diffusion Path Model

Diffusion path model was introduced by Minami (1985) [82] by taking into account both mobility and concentration of mobile ions in glasses such as AgI-Ag_2O-M_xO_y (M_xO_y = P_2O_5 B_2O_3, V_2O_5 etc). The fact that all the silver ions in a glass do not contribute to the conduction and the mobility is dependant on the glass composition can probably be explained in terms of a large potential energy difference resulting from the co-existence of two types of anions, iodide and oxide. The schematic diagram of the potential energy is shown in Fig. 1.6. In the figure, three types of combination are shown; (a) shallow-shallow (iodide-iodide), (b) shallow-deep (iodide-oxide) and (c) deep-deep (oxide-oxide).

The wide shallow potential is formed by the interaction of Ag^+ ions with iodide ions, while a narrow deep one is formed for their interaction with oxide ions. The PE difference occurring due to the interaction of iodide ions with oxide ions must be much longer than the width of the random distribution formed by each type of anions. The silver ion trapped in the deep potential well is less mobile than those in the shallow wells.

The carrier concentration depends on how many Ag^+ ions are located in the shallow wells and their mobility depends on how long the shallow wells are connected

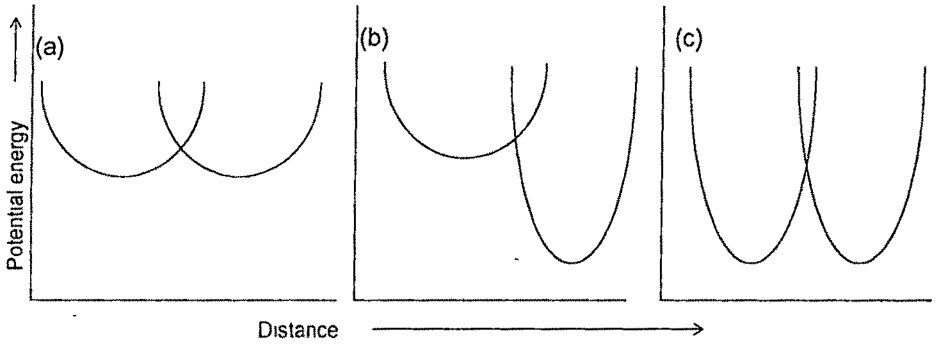


Fig.1.6. Potential energy diagrams explaining the conduction process in super ion conducting glasses

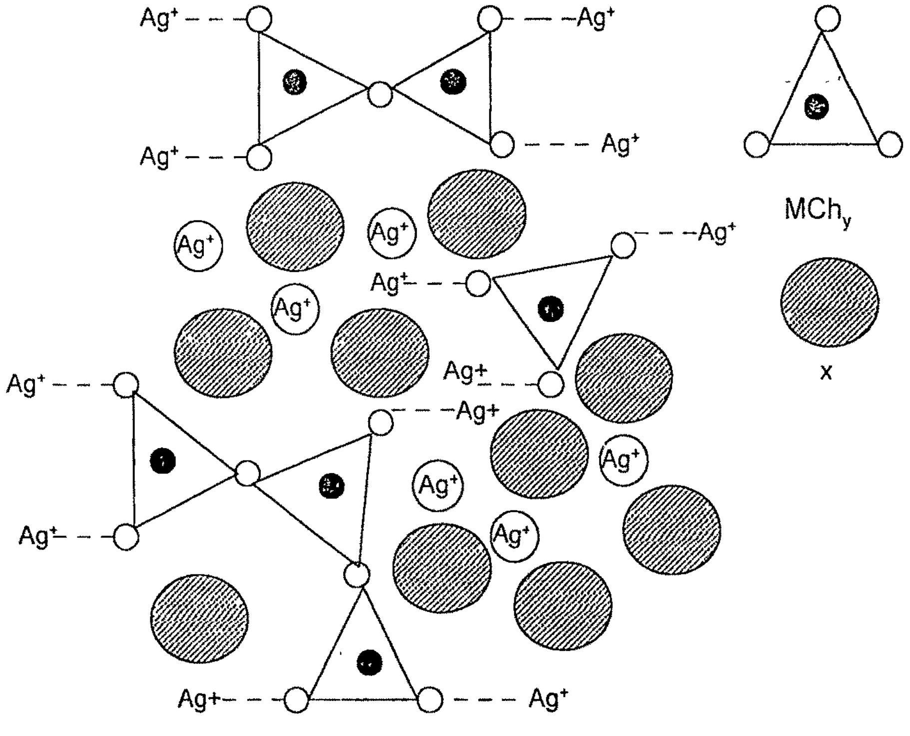


Fig.1.7. A structure model of glasses in the systems AgX-Ag_2Ch-M_xCh_y (X=I,Br,Cl; Ch=O,S,Se; M=various cations in group 3-6.

for a long period, they form a path favorable for ion transport which was referred to as diffusion path. It was also suggested that diffusion path could be found more easily on a random structure than an ordered one, owing to its high configurational freedom. The details of this model with respect to the system in the present investigation are given in chapter 4.

1.6.7. Models for AC conductivity

Frequency dependent conductivity behavior of ionically conducting glasses has been the focus of a large number of studies [83-86] although very limited understanding of this multi-faceted problem has been achieved so far. While there are a large number of theories to interpret the observed dispersion behavior of these glasses, the universal models for ac transport behavior of glasses seem to have been successful. The first approach to develop a universal model to describe ac conductivity in glasses is formulated by Jonscher [84]. The variation of ac conductivity with frequency is represented by the equation $\sigma_{(\omega)}=\sigma_{(0)}+A\omega^{n}$ $(0<n<1)$. The log–log plot of conductivity versus frequency enables to visualize the range of ionic phenomena from long range displacement to resonant vibration. As frequency is increased several power law behavior can be identified from n=0, the dc plateau; to n=0.6 to1, the power law region. According to Funke [87], the dc plateau and the power law region should be considered as a single entity. Both the regions together represent 'successful' and 'unsuccessful' hopping of the mobile ions. In his jump relaxation model, all hops are seen as likely to be unsuccessful, because the ions are predisposed to return to their starting positions. If the back-hope process is delayed, relaxation of the target site occurs and the hop is then successful.

The relaxation process in glasses, in general, is non-Debye like nature. The non–exponential nature shown by these systems can be attributed to the inhomogeneous structure of glasses and to the many body effects on relaxation [88]. The many-body interaction among mobile ions is significant in high ion conducting glasses. The universal theory by Jonscher [83,84], Coupling model [89], Debye-Falkenhagen type theory [90], cluster relaxation theory [91] and diffusion controlled relaxation model [92,93] support this view point. The memory function theory by Kawamura and Shiloh [94, 95] is a phenomenological expression of this view. Extensive measurements of ac conductivity over wide ranges of temperature and frequency have shown that in most cases a single power law is inadequate to describe the dispersion of conductivities. In that case, a double power law of the form $\sigma_{(\omega)}=\sigma_{(0)}+A\omega^{n1}+B\omega^{n2}$ describes the ac conductivity better than a single power law. The behavior of the first region in the double power law equation can be described by the Diffusion Controlled Relaxation model of Elliott [92,93]. The electric field relaxation due to the motion of ions is first descried by Kohlrausch William Watt exponent $\phi(t)=\exp[(-t/\tau_\sigma)^\beta$ $(0<\beta<1)$ [96-98]. The τ_σ and β are the conductivity relaxation time and Kohlrausch constant and $\beta=1$ represents the Debye relaxation. Efforts have been directed towards understanding the physical origin of this behavior. One approach is to treat this stretched exponential behavior as a manifestation of the representative of a distribution of relaxation times [99, 100] and is represented by the β parameter and another is the characteristics of co-operative motion between charge carriers [101,102]. A smaller value of β is attributed to the presence of characteristics of the diverse structural elements present in the system. Attempts have been made to correlate β with a large number of parameters like intercationic distance [103], activation barriers for conduction [97], structural unpinning number [104] etc.

1.7. Silver ion conducting glasses

Silver ion conducting glasses have been developed since 1970s, the ionic conductivity of these glasses is 10^{-1}-10^{-4} S/cm at ambient temperature. Silver has got the highest conductivity among the entire ion conducting species in spite of the fact that silver ions have a large ionic radius and atomic weight. To explain this Minami et al (1989) proposed that the electronic configuration of the ions that is the d^{10} configuration in the outermost orbital as well as ionic radius plays an important role in achieving high conductivities [105]. Silver ion conducting glasses have been found mostly in solids in which the component AgI is dissolved in an oxide glass consisting of Ag_2O with one or mixed glass formers and obtained at ambient temperature by a rapid quenching technique.

Super ionic Ag^+ glasses have been prepared from compounds not usually identified as glass formers including vanadates, arsenates, chromates, selenates, molybdates, tungstates and sulphides as well as from the traditional glass formers, the borates, germinates and phosphates. These diverse glass families share the common characteristics of large ionic conductivity increase associated with the addition of AgI or other silver halides [55]. Modified AgI glasses are obtained by substituting I^- by anions P_2O_7 [106-108], $[VO_4]^{2-}$ [109], $[SO_4]^{2-}$ [110], WO_4 [111], AsO_4 [112], PO_4 [113-114] etc. There are super ionic glasses, where Ag^+ ion is partially substituted by Rb^+ [115], K^+[116], Hg^{2+} [117] etc. Mixed dopant like [AgI-AgCl] [118], [AgI- AgBr] [119], [KI-AgI] [120] etc. based glasses were studied. Binary systems like AgI-$AgPO_3$ [121-127], AgI-Ag_2MoO_4

[128-132], AgI-$Ag_2B_4O_7$ [133], AgI-Ag_2WO_4 [134] etc. and ternary systems like AgI-Ag_2O-B_2O_3 [135-145], AgI-Ag_2O-MoO_3 [146-155], AgI-Ag_2O-V_2O_5 [156-160], AgI-Ag_2O-CrO_3 [161-162], AgI-Ag_2O-P_2O_5 [163-166], AgI-Ag_2O-WO_3 [167-168] etc. have been investigated. Several studies have been made on Ag glasses with mixed glass network formers. Magistris and co-workers [169] exploited this mixed anion effect by manipulating the boron to phosphorous ratio and produced an undoped silver borophosphate glass with room temperature conductivity and thermal stability superior to any prepared with a single glass former. Many ternary mixed former systems have been studied with out dopant like Ag_2O-TeO_2-P_2O_5 [170], Ag_2O-B_2O_3-P_2O_5 [171-173], Ag_2O-WO_3-TeO_2 [174] etc. The enhancement in ionic conductivity and thermal stability is reported for many quaternary glasses like AgI-Ag_2O- MoO_3-V_2O_5 [175,176], AgI-Ag_2O-V_2O_5- P_2O_5 [177-180], AgI-Ag_2O-P_2O_5-MoO_3 [181], AgI-Ag_2O-MoO_3-As_2O_5 [182,183] etc.

A variety of experimental techniques have been employed to investigate the structure of glass. A typical glass model for Ag^+ ion conducting glasses proposed by Minami 1983, is shown in Fig.1.7. In the figure, MChy represents triangles or tetrahedra, where M=B, P, V etc. Ch=O, S, Se. Such polyhedra are present as monomer ions or as condensed macromolecular anions depending on the chemical composition of the glasses. Two types of Ag^+ ions are shown, one is circled and surrounded with halogens and the other is bonded by a dotted line with non-bridging Ch, which denotes the bonding of partial co-valency between Ag and Ch. They proposed this type of structural model on the basis of IR spectra and the IR peak shift accompanying the ion exchange of Ag^+ and K^+ ions [37]. Such evidence of IR spectra gives the information on the structure of MChy and the interaction between Ag-Ch, but not between Ag-X. Raman scattering spectra have been reported to confirm the presence of AgX_4 structural unit as well as Ag-O bonds in AgX-$AgPO_3$ glasses [184]. It has also been reported that the addition of PbX_2, instead of AgX, to $AgPO_3$ causes the formation of AgX_4 and also the high conductivity [185]. EXAFS [186,187] and XANES [188] of Ag and ^{109}Ag NMR [189, 190] also supported the presence of two types of coordination around the Ag^+ ions, Ag-I and Ag-O. The X-ray diffraction study revealed that Ag-I and Ag-O pairs were present but I-I pairs were clearly excluded in these glasses and thus concluded that the formation of AgX_4 units was doubtful [191]. Doreau et al [55] studied $AgPO_3$-NaI and $AgPO_3$-KI systems and explained the increase in conductivity with alkali halide addition in terms of a mechanism, whereby the immobile Ag^+ ions associated with the phosphate chains are exchanged with the alkali cations of the alkali iodide compounds. Interesting results reported for MI_2-$AgPO_3$ [M=Cd, Hg, Pb] system, found the introduction of Ag^+ from AgI, rather than $AgPO_3$ based glasses. They attribute the conductivity rise to the formation of AgI due to the exchange of Cd^{2+}or Pb^{2+} with Ag^+ ions and confirm the presence of AgI_4 tetrahedra (characteristic of the structure of α-AgI) using Raman spectroscopy [184]. The result of ultra sound velocity and attenuation studies in these pseudo binary silver borate systems were also consistent with Minami's model for Ag^+ ions occupying different environments and possessing different mobilities [55].

Electrical conductivities and activation energies for conduction depend on the content of AgX and not on Ag_2O. which lead to a postulation of the presence of mobile and immobile Ag^+ ions at the early stage of research of these glasses [192]. Glass transition temperature [193], optical absorption edges [194], and thermo electric powers

[195] as well as conductivities and activation energies are primarily determined by the AgI content. These results are considered to support the above postulation. Very similar structural models have been proposed by Schiraldi [195] and Malugani et. al., [185]. It is reported from the ^{109}Ag NMR study [190] that at lower temperature, mobile and immobile Ag^+ ions could be detected while at higher temperatures all cations appeared to be mobile. Independent measurement of mobility, carrier concentration and conductivity are needed to reach a persuasive conclusion on the conduction mechanism. Almond et. al., proposed the possibility for determining the concentration term from the analysis of conductivity prefactors [196] and reported that one or two orders of magnitude less than the total Ag^+ ions are mobile and carrier concentration is independent of temperature [197]. It has been demonstrated that the properties of silver glasses are very sensitive to preparation conditions and thermal history.

1.8. Application of solid electrolytes

Since the inception of solid state ionics field, many new materials have been developed and studied in great detail in the hope of promoting their application in a wide range of devices like solid state batteries, fuel cells, sensors, super capacitors and electro chemical devices etc. This section describes some of these applications in which solid electrolytes are effectively used due to their characteristics features.

1.8.1. Solid state batteries

Solid state batteries have many advantages such as miniaturization, long storage life. operation over a wide temperature range, rugged structure, no volatilization and no leakage, because all the components are solids. Their application range from low energy density batteries for pacemaker implants to high energy density batteries used in vehicle traction and load leveling. Low energy density batteries are mainly based on Ag^+, Cu^+, Li^+ ion conductors. Development in the solid state battery field was the discovery of the highly conductive electrolyte material MAg_4I_5 ($M=NH_4$, Rb or K). Sodium ion conducting β or β″ alumina electrolyte, Li^+ ion conducting polymer electrolyte etc have been used for the high energy density batteries, and is explained in Chapter 5.

1.8.2. Solid Oxide Fuel cells

A solid oxide fuel cell is based upon the ability of oxide ions to be conducted through a solid at elevated temperatures. High temperature fuel cells have exclusively been developed by making use of oxide ion conductors such as stabilized zirconias. The electrolyte practically developed is Y_2O_3 stabilized zirconia. The fluorite phase of ZrO_2 is stabilized when it is doped with di or trivalent metal oxides like CaO, Y_2O_3 or Se_2O_3. The select proven material for cathode is $LaMnO_3$ doped with Sr, for anode Ni/ZrO_2 cermet and for interconnector Mg doped $LaCrO_3$. The oxide ion conduction in stabilized zirconia is explained by oxide ion vacancy mechanism. High temperature solid oxide fuel cells can achieve extremely high current densities as high as $1 Acm^{-2}$ because of the high operating temperature of 1000°C.

1.8.3. Solid State Ionic Sensors

Different types of sensors based on solid electrolytes have been developed. These sensors are based on one of the two principles; (a) chemical potential difference across the solid electrolyte (potentiometric sensor) or (b) the charge passed through the electrolyte (amperometric sensor). The most thoroughly developed sensor based on a solid electrolyte is the oxygen sensor using stabilized zirconia electrolyte. This type of sensor is the most successful commercial sensors and is used in combustion control in automobiles and in steel making processes. The following configurations is used in O_2 sensors, Pt. Po_2'/ZrO_2 $(Y_2O_3)/Po_2''$. pt. The protonic conductors such as hydrogen tetra hydrate of uranile phosphate used for the qualitative and quantitative detection of hydrogen in gases have been demonstrated. Sensors have also been developed which are capable of detecting a variety of other gases including H_2, SO_2, CO_2 etc.

1.8.4. Electro chromic Devices

Electrochromism can be defined as a color change induced in a material by an applied electric field or current. Some ions in solid compounds can be reduced or oxidized (redox) electrochromically with a consequent change in color. WO_3 and MoO_3 solid films have been extensively used for this purpose. Most of the developmental work to date has focused upon the use of proton or Li injection into WO_3 using aqueous or organic electrolytes, $RbAg_4I_5$, β-alumina, $HUO_2PO_4.4H_2O$ and polymer electrolytes have been examined as solid electrolytes in an electrochemical device. Green et. al., first developed the ECD with $RbAg_4I_5$ of the type, Ag/ $RbAg_4I_5/WO_3$. ITO. The cell is initially white when viewed from the WO_3 cathode and a blue coloration develops over the region covered by $RbAg_4I_5$ with the application of a dc potential. The film remains colored even after the removal of voltage. These electrolytes are used in electrochromic light transmission modulators, called smart windows for control of temperature and lighting in buildings and automobiles.

1.9. Present Investigation

In the literature, a large number of studies have been reported on the conductivity and structural studies on silver ion conducting binary, ternary and quaternary systems [44].

From the structural studies, it was shown that the addition of dopant is not affecting the glassy matrix and several other experimental results support the theory of mobile and immobile Ag^+ ions. A few other studies have been reported on silver oxysalt system with dopant salt other than AgI like PbI_2-$AgPO_3$ [185], PbI_2-Ag_2O-V_2O_5 [198], CuI-Ag_2MoO_4 [199], KI-$AgPO_3$ [55] etc. These systems exhibited the feasibility of obtaining high silver ion conductivity at ambient temperatures. In view of these facts, an attempt is being made to study whether the silveroxysalt system Ag_2O-V_2O_5-B_2O_3 can serve as a host for the bivalent halide CdI_2 instead of AgI to have a better solid electrolyte system with low cost and appreciably high conductivity.

The present study had planned accordingly:

System Chosen: CdI_2-Ag_2O-V_2O_5-B_2O_3

where CdI_2 - Dopant salt
Ag_2O - Glass modifier
V_2O_5 & B_2O_3 - Glass formers

Preparation: Melt quenching technique

Characterization: X-ray Diffraction
Differential Scanning Calorimetry
Fourier Transform Infra red Spectrometry
Transport Number: emf method &
Wagner's Polarization method
Thermo electric power

Electrical conductivity: Impedance measurements

Solid State Battery: Fabrication & Characterization

The aim of this thesis is to examine the Ag^+ ion conducting glass system, CdI_2-Ag_2O-V_2O_5-B_2O_3 and to correlate structure with the conductivity of these glasses. The three series of the above system were prepared by changing the dopant in the first series, modifier to former ratio in the second series and glass former amount in the third series. Chapter 2 describes the various experimental techniques used for characterization and conductivity measurements. Chapter 3 shows the characterization studies by x-ray diffraction, differential scanning calorimetry, infra red spectroscopy, transport number measurements, thermo electric power studies etc. Chapter 4 describes the results of the ac conductivity measurements on all the three series and is explained in impedance, frequency dependence conductivity, dielectric and modulus methods. Chapter 5 explains the discharge and polarization studies of the cells fabricated out of the prepared samples. Chapter 6 gives the conclusion out of this work.

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