1.1 An Introduction to Solid Electrolytes

The science of solid state electrolytes, that is solids which exhibit appreciably high conductivity for cations or anions but are electronic insulators, developed rapidly in the early 1970s due to increasing demands of alternative energy sources. Solid electrolytes are a class of materials that conduct electricity by means of motion of ions in their solid phase [1-4]. In contrast to solid state electronic conductors such as metals and semiconductors, solid electrolytes conduct electrical current by motion of ions (anions or cations), analogous to liquid electrolytes/electrolytic solutions at ambient temperatures. Solid electrolytes are called fast ionic conductors (FIC), or superionic conductors [5], too. This property connects the electrical conductivity to the change of chemical states and makes these materials suitable for different applications in electrochemical devices such as batteries, super-capacitors, sensors, and smart windows [6-10]. Over the years, a number of materials have been investigated to exhibit super ionic conductivity in solid phase, involving a wide range of materials, including crystalline [11,12], polycrystalline [13], ceramics [14], glasses [15], composites [16], polymers [17], polymer composites [18], etc. A solid electrolyte, in general, should possess following characteristics [19, 20]:

(1). Very high ionic conductivity $\geq 10^{-3}$ S/cm or higher.

(2). Negligible electronic conductivity $\leq 0.01\%$ of ionic conductivity.

(3). Low activation energy ≤ 1 *eV* for easy migration of ions.

(4). A large number of the ions of one species should be mobile and also a large number of empty sites with equivalent activation energy should be available for hopping of ions between them.

(5). The anion framework should be highly polarizable.

(6). Should be physically and chemically compatible with anode and cathode of the desired electrochemical device/application.

Above mentioned criteria suggest that to be functional as a solid electrolyte, a material must possess very high ionic conductivity and its electronic conductivity should be negligible in comparison with ionic conductivity. Moreover, criterion four suggests that the empty as well as occupied sites should have similar potential energies with a low activation energy barrier for hopping between neighboring sites. It is of no use of having large number of interstitial sites if the moving ions cannot get into them [21]. The science and technology of solid state ion conducting materials in general and fast ionic materials in particular is termed as Solid State Ionics (SSI). This interdisciplinary field of materials science, physics, and solid state electrochemistry deals with the preparation and characterization including theoretical aspects concerning ionic motion in the chosen solid electrolytes with its application in solid state electrochemical devices.

Table 1.1: Comparison between Super ionic conductors (SIC) & Normal ionic conductors (NIC)

	Property	**Super ionic conductors (SIC)**	**Normal ionic conductors (NIC)**
1.	Ionic Conductivity	~$10^{-6} – 10^{-1}$ S/cm	~$10^{-8} – 10^{-16}$ S/cm
2.	High Ionic Conductivity	At Ambient temperatures	At and above Melting Point
3.	Conduction mechanism	Due to migration of ions with negligible electronic contribution	Due to migration of one or both types of ions
4.	Mobile charge density	Large and constant no.	Less
5.	Activation Energy	Very low (≤ 1 *eV*)	High (≥ 1 *eV*)

1.2 Classification of Solid Electrolytes

Solid electrolytes, in general, may be classified broadly in two ways as follows.

1. Type of the conducting ionic species e.g. Na^+, Li^+, Ag^+, F^-, O^{-2} etc.
2. Type of the host material, e.g. crystalline/polycrystalline, amorphous/ glassy, polymer, composite, etc.

1.2.1 Classification depending on type of ion conducting species

(a). Li^+ ion conductors: Li^+ Ion conducting systems are one of the most investigated and sought after solid electrolytes due t their applications mainly in primary and secondary batteries which are applicable in many consumer durable goods to various military and life saving medical applications. The polycrystalline lithium compounds such as LiSICON (lithium ion conducting superionic conductor) have a high degree of structural disorder and exhibit significant ionic conductivity as high as 2×10^{-4} S/cm at room temperature [22]. The Thio-LiSICON family introduced by Kanno *et al.* [23, 24] showed conductivity 6.4×10^{-4} S/cm with a moderate activation energy of 0.5-0.6 eV only. This composite electrolyte is found to be one of the high conducting compounds in this class of fast ionic conductors, and has been used in solid state batteries. Numerous lithium ion conducting amorphous systems such as $LiX\text{-}Li_2O\text{-}M_xO_y$ (X = I, Br, Cl; $M_xO_y = P_2O_5, B_2O_3$) [25], $LiI\text{-}Li_2S\text{-}SiS_2\text{-}P_2S_5$ [26] and polymer electrolytes $PEO\text{-}LiCF_3SO_3$, $PEO\text{-}LiPF_6$, $PEO\text{-}LiClO_4$ [27] etc. have also been reported to possess high ionic conductivity enabling them to be used in various solid state ionic devices.

(b). Na^+ ion conductors: Sodium ion conducting solid electrolytes are important for a wide variety of applications ranging from energy storage to industrial process control. Improved energy storage devices are not only needed for mobile applications, such as portable electronics and electric vehicles, but also have become increasingly important for load leveling in the use of renewable energy conversion technologies, such as wind and solar. Concerns over the availability of mineral resources of lithium for lithium ion batteries have increased the level of interest in sodium-based batteries, which also have high energy densities. One promising battery is the sodium–sulfur cell, in which sodium (or sulfur) is contained in sodium ion- conducting ceramic tube and placed into sulfur (or sodium) [28-30]. Recent developments in improving specific energy storage have led to planar designs with chloride (rather than sulfur) cathodes in what is referred to as a ZEBRA cell [31-33]. One widely used sodium ion conducting solid electrolyte is $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, which is commonly referred to as NASICON. The NASICON structure consists of corner-sharing PO_4–SiO_4 tetrahedra and ZrO_6 octahedra that create a 3-D network of channels through which sodium ions can be transported [34].

(c). Ag^+ ion conductors: Silver ion conductors are one of the most studied class of solid electrolytes and most involve an aim to achieve the high ionic conductivity at room temperature of the level of α-AgI exhibited at and above 147˚C. The ionic conductivity demonstrated by α-AgI is so much attractive that many attempts have been made in past to stabilize it at room temperature and the first satisfactory results were reported for $RbAg_4I_5$, which showed room temperature conductivity about the order 0.1 S/cm which is comparable to conductivity of α-AgI at 147˚C. The first superionic solid in glassy phase, a fast Ag^+ ion conducting system of AgI-Ag_2SeO_4 exhibiting very high room temperature conduct ($\sigma \sim 10^{-2}$ S/cm) was synthesized by Kunze in 1973 [35]. Since then other than crystalline routes, amorphous hosts like glasses have been extensively investigated.

(d). **Cu^+ ion conductors**: Copper ion conduction was reported as early as in 1973 by Takahashi [36] and Sammells *et al.* [37] in various cuprous halides like, CuCl, CuBr and CuI. Amongst these, CuI is analogous to AgI, and it also undergoes a phase transition, however at a relatively higher temperature (409˚C).

(e). **H^+ ion conductors:** The need for hydrogen storage and various applications in fuel cells and sensor applications has driven a strong research in the field of proton conducting material systems ranging from stabilized zirconia [38], Ceria based materials [39] , solid solutions like MO_2-In_2O_3-P_2O_5 (M = Ti, Sn, Zr) systems [40] and moreover sulfonated polymers like poly (ether-ether-sulfone)s (PEESs) [41] etc. It seems more likely that protons in solids would be transported with an associated ion such as H_3O^+, OH^-, or NH_4^+ than by themselves. Varieties of proton conducting materials including polymeric membranes have been developed for fuel cell and sensor applications.

(f). **O^{-2} ion conductors:** The O^{2-} ion conducting solid electrolytes find main applications in the field of fuel cells. Fast conduction by oxygen, however, is obtained by doping, which leads to defective fluorite structures. The most important materials of this class are fluorite oxygen-deficient phases obtained by adding either alkaline earth oxides (magnesia or calcia) or sesquioxides (lanthanide, scandium, or yttrium oxides) to ZrO_2, CeO_2, and ThO_2. Typical values of conductivity range from about 0.02 to 0.2 S/cm at l000˚C with an activation energy about 0.7-1.2 eV [42].

(g). **F^- ion conductors:** O^{2-} conductors do conduct only at certain very high temperatures only. In contrast, isostructural fluorides have a significant anionic conduction at relatively low temperatures [43]. This property is obviously a consequence of the higher mobility of F^- as a result of smaller size, but even more of lower electric charge and less covalent bonding. As a consequence, fluorides can be named as the best anionic conductors. Furthermore, these materials are very often electronic insulators, an essential property for their use as electrolytes in electrochemical batteries [44, 45]. These materials possess fluorite structure which provides an open path for fast ionic conduction. However, high ionic conductivity has been realized by generating vacancies through doping of aliovalent cation fluorides. The solid solution of PbF_2 with SnF_2 i.e. $PbSnF_4$, and CaF_2 with rare earth fluorides such as LaF_3 has exhibited conductivity of the order of 10^{-3} S/cm at ambient temperature [46]. These materials have also been introduced as electrode materials for rechargeable lithium batteries due to the high electronegativity value of fluorine and high free energy of formation.

1.2.2 Classification of Solid Electrolytes depending on type of host material

Owing to variability in materials and structures, solid electrolytes are broadly classified into different categories such as crystalline, glassy, polymer, composite electrolytes etc. Let us have a brief look at them.

(1). Framework Crystalline ion conductors:

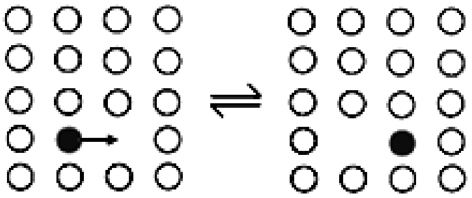
Framework crystalline materials, as the name implies, consist of a crystalline skeleton of more or less rigid and mobile ions. They are further divided into two categories [47, 48] as follows: Soft-framework crystals & Hard framework crystals, their example include AgI, CuI, $RbAg_4I_5$, Ag_2HgI_4 and β alumina, stabilized zirconia, NASICONs, , $LiAlSO_4$, etc. respectively [49]. Ion conduction in crystalline solid electrolytes occurs via the point defects such as Frenkel and Schottky defects.

(a). Soft-framework crystals

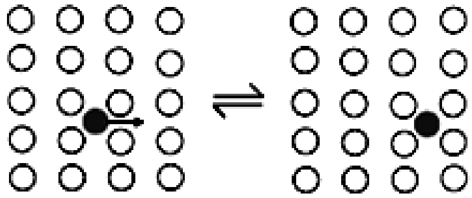
These materials have following characteristic properties: (i) the bonding is mostly ionic; (ii) the mobile ions are generally polarizable and heavy (e.g. Ag^+, Cu^+, etc.); (iii) the Debye temperature is low; (iv) a sharp ionic order–disorder phase transition appears between the low and high conducting phases (e.g. $\beta \rightarrow \alpha$ transition of AgI at 147˚C). Soft crystals– polycrystals are mostly solid solution of double salts (MX:xNY), where NY = AgI, CuCl, CuI, LiI, etc.; M = K, Rb, NH_4 or large ions; X=I, Br, Cl or radicals like S, P_2O_7, etc. The maximum conductivity generally results only for higher value of x [50].

(b). Hard-framework crystals

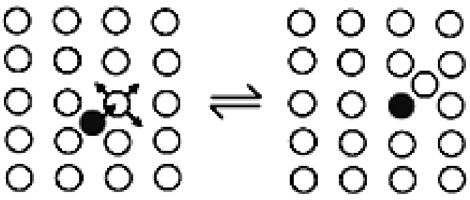
They are generally characterized by: (i) covalent bonds and consequently high frequency for local vibrations; (ii) high Debye temperatures; (iii) low polarizability of mobile ions and (iv) absence of the order–disorder phase transition. These are usually oxides, e.g. β-alumina, stabilized zirconia, NASICONs, $LiAlSO_4$, etc., and are generally referred to as a class of materials having similar structures and compositions.



(a). vacancy mechanism



(b). direct interstitial mechanism



(c). interstitialcy (indirect interstitial) mechanism.

Fig. 1.1. Elementary jump mechanism in crystalline solid electrolytes. (From Ref [51])

Ion transport in crystalline solid electrolytes has been thoroughly investigated by various research groups. It has been established that generally two types of defects facilitate ion transport in the crystalline materials: Schottky and Frenkel defects. In Schottky defects, cations and anions leave their lattice site to create vacancies; while in Frenkel defects a lattice ion (cation or anion) moves to an interstitial position and leaves behind a vacancy. The mobility of one ion species in a stable crystal structure requires point defects that typically move via one of three elementary jump mechanisms: [i] vacancy mechanism: a particle at the regular site hops into a vacancy and leaves behind a vacancy (Fig. 1.1(a)) and two mechanisms involving interstitials: [ii] direct interstitial mechanism: an interstitial defect jumps directly into another interstitial site (Fig. 1.1(b)) and [iii] indirect interstitial mechanism: the interstitial defect pushes a particle at the regular site into an adjacent empty interstitial site (Fig. 1.1(c)).

(2) Glassy/amorphous ionic conductors: Amorphous solids are generally easy to prepare; homogeneous thin films can be produced in different shapes and sizes for device applications. A bulk glass can readily be formed from the melt by relatively slow quenching procedures and near the glass transition temperature the material remains workable over a range of temperatures. Furthermore, the physical properties of bulk glasses are isotropic and homogeneous. And absence of microstructural defects, such as grain boundaries and dislocations, is important for their mechanical behaviors and mechanical engineering applications. Also, amorphous phases can often be formed in mixed-component systems over wide ranges of compositions. This allows their properties to be varied continuously simply by varying the composition. Fig. 1.2 shows a comparison of the temperature dependent conductivities of various crystalline and amorphous solid electrolytes. More details on glassy solid electrolytes have been discussed in Section 1.7.

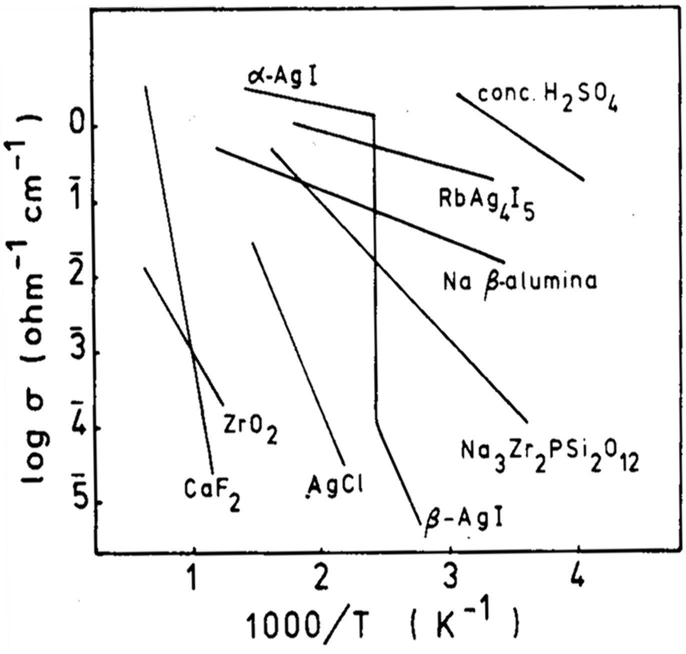


Fig. 1.2. A plot of electrical conductivity versus temperature of some normal-ionic and superionic solids and some good liquid electrolytes. (*from* Ref [52])

(3) Polymer ion conductors: Motion of ions in polymeric matrices in the absence of a solvent is a relatively new phenomenon whose existence and importance have been recognized only in the past decades (Armand [53], Bruce [54], Gray [55], Linford [56], Lipkowski [57], Maccallum & Vincent [58]). Under this concept, the macromolecule itself acts as a solvent for a salt which becomes partially dissociated in the matrix, leading to electrolyte behavior. The term polymer electrolyte has, therefore, come to mean any polymer based structure with significant ionic conductivity. The solid character of polymers is, in general, related to the molecular weight of the polymer. Low molecular weight polymers are often liquids, so the range can be from liquids to very hard and rigid materials. Some polymers can organize at the molecular level in such a fashion as to be crystalline e.g. PEO (Poly Ethylene Oxide). Since conductivity comes about through molecular motion in the structure, crystalline polymers have low conductivity and are not good options for batteries. The 'dry' polymer electrolyte is a single phase, non-crystalline material containing dissolved salt, where the ions of the salt are mobile. Polyethylene oxide (PEO) based polymer electrolytes exhibit moderate ionic conductivity at room temperature, which limits their applicability at lower temperatures, e.g. in car batteries for non-tropical regions.

Many polymer electrolyte materials will exhibit to a greater or lesser extent the following properties: (1) Adequate ionic conductivity for practical purposes, (2) Low electronic conductivity (3) Good mechanical properties, (4) Chemical, electrochemical and photochemical stability and (5) Ease of processing.

In addition to this, their conductivity and transport properties should be sufficiently practical to stimulate their development when compared with other highly conducting solid electrolyte materials. Since 1978, when Armand first introduced polyether–alkali–metal salt complexes to the solid state community as potential materials for electrochemical devices, there has been an enormous amount of research carried out on these (particularly high molecular weight poly (ethylene oxide)–lithium salt) systems, to obtain a better understanding of their fundamental properties and to use this information for the development of new generations of polymer electrolyte materials that are commercially more attractive. Table 1.2 shows ionic conductivities for some selected polymeric solid electrolytes.

Table 1.2: Ionic conductivity (σ_{DC}) and activation energy (E_a) of some solid polymer electrolytes.

Compound	**σ_{DC} (S/cm)**	**E_a (eV)**	**Reference**
$(PEO)_{20}LiClO_4$	1.0×10^{-7} (25°C)	_	[59-61]
$(PEO)_{20}LiBOB$	1.6×10^{-4} (50°C)	_	[62]
$(PEO)_9LiTF$+ 15 wt.% Al_2O_3	7.8×10^{-6} (25°C)	_	[Same As above]
$(PEO)_9LiTF$+ 15 wt.% Al_2O_3 +50 wt.% [75% EC-25% PC]	1.2×10^{-4} (25°C)	_	[Same As above]

$(PEO)_{8.5}LiBETI$	1.8×10^{-4} (25˚C)	0.36–1.15	[63-65]
$(PEO)_{10}$ LiTFSI	3.2×10^{-5} (25˚C)	0.84	[66-68]
$(PEO)_{16}(SN)_{10}LiBETI$	3.2×10^{-4} (20˚C)	0.74	[70]
$PEO\text{-}LiClO_4\text{-}PAA/PMAA/Li_{0.3}$	9.9×10^{-4} (20˚C)	_	[71]

(4) Composite Solid electrolytes: Composite solid electrolytes are a relatively new area of solid electrolyte research, where, higher ionic conductivity is achieved by means of mixing submicron sized inert particles like SiO_2, Al_2O_3, Fe_2O_3, etc. in suitable moderately ion conducting salts, glasses and polymer electrolytes. Research in this are gained interest when Liang [71] reported that ionic conductivity of LiI increases by 50 times when doped with Al_2O_3. Since then, quitted a large number of composite material systems have been investigated to achieve enhancement of ionic conductivity by 1 to 3 orders of magnitude by appropriate composition selection. A thorough and detailed review can be found in reference [72]. Composite solid electrolyte materials can be classified broadly into following classes,

1. Crystal–crystal composites
2. Crystal–glass composites
3. Glass–polymer composites
4. Crystal–polymer composites
5. Ionic liquid - polymer composites

Above discussion on various phases and types of solid state ion conductors suggests that disorders and defects play an important role in the ionic conductivity, and hence it is expected that, more disordered solids, like amorphous ones or glasses may present remarkable ionic conductivity in comparison to their crystalline counterparts.

Non-crystalline/glassy ion conductors posses scores of advantages over their crystalline counterparts; such as absence of grain boundaries, ease of tuning of various chemical mechanical and electrical properties by tuning the chemical/stoichiometric compositions, etc.

Table 1.3: A concise List of various potential ion conducting Solid electrolytes prepared in past and categorized in Crystalline, Glassy, Polymeric or Composite Systems.

Ion conducting species	Type of the System	System	σ_{RT} (S/cm)	Reference
Li^+	Composite	Li_2S-LiI- P_2S_5	1.0×10^{-3}	[73]
	Composite	Li_2S-P_2S_5	1.1×10^{-4}	[74]
	Composite	Li_2S-GeS_2	4.0×10^{-5}	[75]
	Composite	LiF-KF-$Al(PO_3)_3$	1.3×10^{-3} (200°C)	[76]
	Glass	LiI–Li_2O–B_2O_3	3.2×10^{-3} (300°C)	[77]
	Glass	95LiI–37Li_2S–18P_2S_5	1.0×10^{-3} (25°C)	[78]
	Glass	50LiI–20Li_2S–30GeS_2	1.1×10^{-4} (25°C),	[79]
	Glass	50Li_2SO_4–15Li_2O–35P_2O_5	6.8×10^{-3} (350°C)	[80]
Na^+	Glass	NaF-NaCl-Na_2O-B_2O_3	~10^{-6} (150°C)	[81]
	Glass	39.1Na_2O–7.5Y_2O_3–53.4SiO_2	3.4×10^{-3} (300°C)	[82]
		Na_2S–SiS_2	3.1×10^{-4} (100°C)	[83]
	Crystalline	$Na_{3.75}Zr_{1.1}SI_{2.75}P_{0.25}O_{0.2}$	1.9×10^{-3} (300°C)	[84]
	Glass	90$Na_2P_2O_6$–10$Na_2Te_2O_5$	2.4×10^{-6} (150°C)	[85]
	Glass	Na_2O-ZrO_2-P_2O_5-SiO_2	~10^{-6} (150°C)	[86]
Ag^+	Crystalline	α-AgI	1.3 (147°C)	[87]
	Crystalline	Ag_3SI	2.0 (240°C)	[88]
	Crystalline	$RbAg_4I_5$	2.1×10^{-1}	[89]
	Crystalline	$C_2H_5NHAg_5I_6$	3.0×10^{-2}	[90]
	Glass	$AgPO_3$-PbX_2 (X=I, Br)	~10^{-2}	[91]
	Glass	AgBr-Ag_2O-B_2O_3	2.6×10^{-3}	[92]
	Glass	AgCl-Ag_2O-B_2O_3	6.4×10^{-4}	Same as above
	Glass	AgI–Ag_2SeO_4	6.0×10^{-2} (25°C)	[35]
	Glass	AgI–Ag_2MoO_4	6.0×10^{-2} (25°C)	[93]
	Glass	60AgI–30Ag_2O–10B_2O_3	8.5×10^{-3} (25°C)	[94]
	Glass	AgI–Ag_2O–B_2O_3–P_2O_5	5.0×10^{-5} (25°C)	[95]
	Glass	AgI–Ag_2Se–P_2Se_5	~10^{-2} (25°C)	[96]

Cu^+	Glass	CuI-Cu_2O-MoO_3	~10^{-2}	[97]
	Glass	CuI–Cu_2O–P_2O_5	1.0×10^{-2} (25°C)	[98]
	Crystalline	CuI–CuCl–RbCl	1.0×10^{-2} (25°C)	[99]
	Glass	CuI–Cu_2O– P_2O_5–B_2O_3	1.0×10^{-3} (25°C)	[100]
	Glass	CuI–Cu_2MoO_4–Cu_3PO_4	$1.0\times10^{-}2$ (25°C)	[101]
	Glass	30CuI–30Cu_2O–30MoO_3–10WO_3	3.0×10^{-4} (25°C)	[102]
	Glass	CuI–Cu_2WO_4–Cu_3PO_4	10^{-2}–10^{-4} (25°C)	[103]
F^-	Crystalline	PbF_2-MnF_2-$Al(PO_3)_3$	1.1×10^{-4} (200°C)	[104]
	Glass	SiO_2–PbO–PbF_2	2.2×10^{-5} (200°C)	[105]
	Glass	ZrF4–BaF2–CsF	1.4×10^{-5} (200°C)	[106]
	Glass	35InF3–30SnF2–35PbF2	6.3×10^{-4} (150°C)	[107]
O_2^-	Crystalline	ZrO_2-Y_2O_3	1.2×10^{-1}(1000°C)	[108]
	Crystalline	$(BI_{2-x}Y_x)O_3$	~10^{-2} (500°C)	[109]

1.3 Glass as a Solid Electrolyte

To realize the stabilized α-AgI at room temperature several routes were attempted other than crystalline ones. The glasses have been found to be attractive and efficient host materials to stabilize α-AgI.

Usually the ionic conductivity of any undoped glass is very low, e.g. $\leq 10^{-12}$ S/cm or so; when doped with a suitable dopant, it may achieve remarkable ionic conductivity at ambient temperatures. *e.g.* when LiCl or LiBr is doped in Li_2O-P_2O_5 glass [110], an increase in its conductivity as high as 4 to 5 orders of magnitude is observed. Generally, glasses when doped with metal halides in sufficient amounts show enhancement in conductivity, e.g., LiI in Li_2O-B_2O_3 [111], NaI in Na_2O-V_2O_5-B_2O_3 [112], AgI in Ag_2Se–P_2Se_5 [113], and AgI in Ag_2O-MoO_3 host glasses [114] etc. As we know from previous studies that many metal halides such as AgI, NaI, LiI, LiCl, LiBr etc. show remarkable ionic conductivities, when heated to temperatures much higher than room temperature. This unique property can be utilized to fabricate many electrochemical devices to avoid the risks generated by liquid ionic conductors (electrolytes). However, the fast ion conducting phase of the metal halides is stable at higher temperatures, which is generally not suited for their applications at room temperature or even sub-zero temperatures. One may stabilize the superionic phase of metal halides in a suitable glass matrix at room temperature, with somewhat reduced conductivity.

Over the past decades, a great number of fast ion conducting glass systems have been reported. The very first glass system to report ionic conductivity was published as early as in 1973 by Kunze [35] for $AgI-Ag_2SeO_4$ glass, where, AgI is doped as a dopant salt in the host glass Ag_2SeO_4. Since then, a number of ion conducting glasses have been reported to achieve as high as possible ionic conductivity in a variety of glasses systems having Li^+, Ag^+, Na^+, Cu^+, F^- including iodomolybdates, phosphates, arsenets, borates etc. in binary, ternary and quaternary glass systems have been attempted by several research groups across the globe [115]. A detailed review of existing glass materials has been published by Takahashi [116], Funke [117], Ingram [118] and other workers [119-121] in a great detail. Following Table 1.4 shows a brief summary of some important glass systems investigated in past.

Table 1.4: A comprehensive List of various ion conducting glass systems.

Ag^+ ion conducting glasses	σ_{DC} (S/cm)	Reference
$AgI-Ag_2SeO_4$	6.0×10^{-2} (25)	[122]
$AgI-Ag_2MoO_4$	6.0×10^{-2} (25)	[35]
$60AgI-30Ag_2O-10B_2O_3$	8.5×10^{-3} (25)	[123]
$50AgI-33.33Ag_2O-16.67V_2O_5$	2.3×10^{-3} (27)	[124]
$80(Ag_{0.6}Cu_{0.1}I)-20(2Ag_2O-P_2O_5)$	8.6×10^{-3} (25)	[125]
$0.7[0.75\ AgI-0.25\ AgCl]-0.3[Ag_2O-B_2O_3]$	4.4×10^{-3} (27)	[126]
$4AgI - Ag_2Cr_2O_7$	2.2×10^{-2}	[127]

3 AgI - $Ag_4P_2O_7$	4.0×10^{-3}	[128]
3 AgI - Ag_2MoO_4	2.1×10^{-2}	[129]
3 AgI - Ag_2WO_4	3.6×10^{-2}	Same as above
4AgI - $Ag_2Cr_2O_7$	2.2×10^{-2}	[130]
Li^+ ion conducting glasses		
$40Li_2O\text{-}8Al_2O_3\text{-}52B_2O_3$	6.1×10^{-5} (200)	[131]
$50Li_2O–30P_2O_5–20B_2O_3$	$1.8\times10-^{5}$ (110)	[132]
$Li_2O\text{-}SiO_2\text{-}B_2O_3$	2.4×10^{-3} (350)	[133]
$35Li_2O–35P_2O_5–30LiCl$	1.0×10^{-7} (25)	[134]
$37.5SiS_2\text{-}37.5Li_2S\text{-}25LiCl$	1.9×10^{-3} (25)	[135]
$50LiI–20Li_2S–30GeS_2$	1.1×10^{-4} (25)	[136]
Na^+ ion conducting glasses		
$39.1Na_2O\text{-}7.5Y_2O_3\text{-}53.4SiO_2$	3.4×10^{-3} (300)	[137]
$Na_2S\text{-}SiS_2$	3.1×10^{-4} (100)	[138]
38 $Na_2O\text{-}8Y_2O_3\text{-}54SiO_2$	$\sim2.0\times10^{-3}$ (300)	[139]
$Na_2S\text{-}GeS_2$	2.3×10^{-5} (100)	[140]
Cu^+ ion conducting glasses		
$CuI\text{-}Cu_2O\text{-}P_2O_5$	1.0×10^{-2} (25)	[141]
CuI-CuCl-RbCl	1.0×10^{-2} (25)	[142]
$CuI\text{-}Cu_2O\text{-}P_2O_5\text{-}B_2O_3$	1.0×10^{-3} (25)	[143]
$CuI\text{-}Cu_2MoO_4\text{-}Cu_3PO_4$	1.0×10^{-2} (25)	[144]
$30CuI\text{-}30Cu_2O\text{-}30MoO_3\text{-}10WO_3$	3.0×10^{-4} (25)	[145]
$CuI\text{-}Cu_2O\text{-}MoO_3$	1.0×10^{-2} (25)	[146]
F^- ion conducting glasses		
$\beta\text{-}PbF_2$	1.0×10^{1} (500)	[147]
$SiO_2PbO\text{-}PbF_2$	2.2×10^{-5} (200)	[148]
$ZrF_4\text{-}BaF_2\text{-}CsF$	1.4×10^{-5} (200)	[149]
$35InF_3\text{-}30SnF_2\text{-}35PbF_2$	6.3×10^{-4} (150)	[150]
$40ScF_3\text{-}20YF_3\text{-}40BaF_2$	1.3×10^{-5} (200)	[151]
$10PbF_2\text{-}90(Ag_2O\text{-}V2O_5)$	1.3×10^{-5} (28)	[152]

Value in ( ) bracket shows temperature

1.4 α–AgI as a Model Solid Electrolyte

For many years, it has been known that AgI above 147˚C undergoes a $\beta\rightarrow\alpha$ phase transition. Below 147˚C, AgI is stable mainly in two phases: (1) β-AgI which possesses a wurtzite structure with hexagonal close packed I^- ions and Ag^+ ions in tetrahedral sites. (2) γ-AgI which is similar to structure of ZnS (sphaleraite mineral). The β-AgI structure has a moderately low conductivity ~10^{-4} S/cm upto 147˚C. When it undergoes $\beta \rightarrow \alpha$ phase transition, a steep rise in conductivity ~1 S/cm, (147˚C) which is about four orders higher than the room temperature value and is maintained till just before melting; moreover the activation energy for ion conduction is only 0.05 eV. This value is comparable with the electrical conductivity of the melt of this sort, although the phase transition temperature 147˚C is far away from the melting point of 552˚C. The main charge carrier in silver iodide has been shown to be the Ag^+ ion by Tubandt [153].

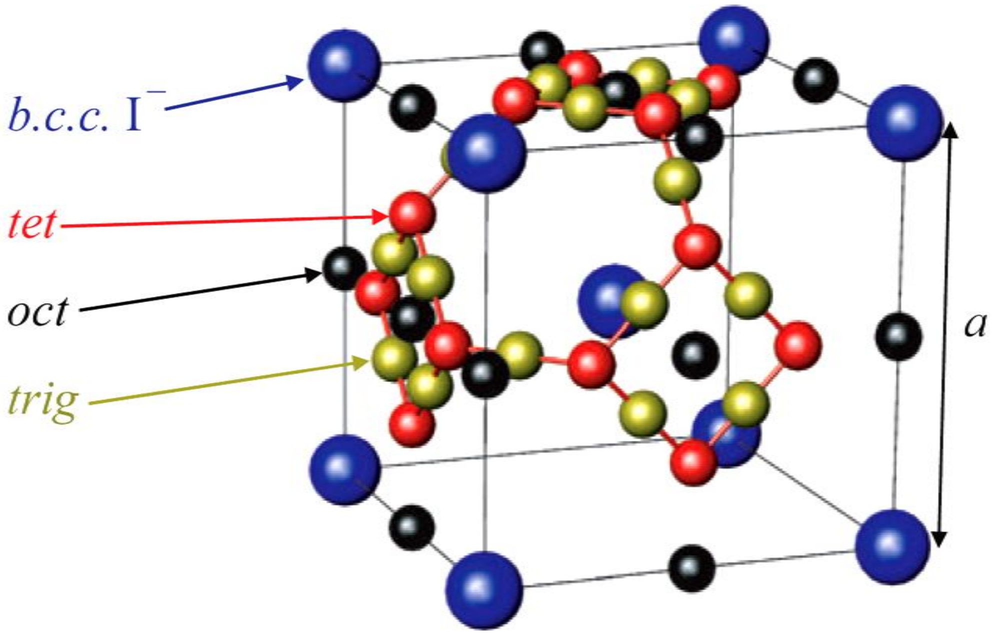


Fig. 1.3. The crystal structure of α-AgI, showing the *bcc* anion sublattice (I^-) and the locations of the octahedral (*oct*), tetrahedral (*tet*) and trigonal (*trig*) interstices. The *tet* sites are predominantly occupied by Ag^+ and diffusion occurs via *trig* sites (Ref. [154]).

To understand the reason of such high ionic conductivity and low activation energy, basic understanding of the crystal structure of α–AgI is essential. The earliest description of the disordered arrangement of ions within superionic α-AgI was provided by powder diffraction studies using x-ray diffraction studies by Strock [155]. As shown in the Fig. 1.3, *α*–AgI has a body centered cubic (*b.c.c.*) structure and iodide ions lie at corner and body center positions and two Ag^+ ions are statistically distributed over 42 sites (i.e., *6b,* 12*d,* and 24*h*) among I^- anions with tetrahedral and trigonal co-ordination. The tetrahedral sites are linked together by sharing faces of and the trigonal sites lie at the centers of the faces of the AgI_4 polyhedra. A study by O'Keefe and Hyde [156] revealed that Ag^+ ions are normally situated at the tetrahedrally coordinated 12*d* sites with a large amplitude anharmonic vibration, tending to move towards the adjacent 12*d* positions via the 24*h* intermediate sites. This highly disordered picture approximates to a uniform distribution of cations over all the free volume not occupied by anions and, coupled with the high values of ionic conductivity [157], and such a structural situation in *α*-AgI encouraged the use of terms such as 'molten sublattice' and 'liquid-like' to describe it and thus *α*-AgI could be considered as a "half-fused" state where only the cation sublattice loses its crystallographic order, it implies that, iodide ions are essentially fixed at their sites; however the Ag^+ ions can readily move from one equivalent site to the next in a liquid like manner, in other words, the silver sublattice is in the disordered, quasi-liquid state in the rigid sub-lattice of the iodide ions. Thus, the disordered nature of the *α*-Agl structure may be regarded as an intermediate between that of a typical ionic solid in which every lattice site is occupied and a typical ionic liquid in which both anions and cations are disordered. The disordered Ag^+ ions arrangement and the easy motion of Ag^+ between sites must be related to the nature of bonding between Ag^+ and I^- ions. Ag^+ is a polarizing cation (*since* its outer 4d electrons are relatively ineffective in shielding its nuclear charge,) while I^- is a large and polarizing anion; and hence covalent bonds readily form between Ag^+ and I^- that are characterized by structures with low co-ordination numbers. While conducting, Ag^+ can move from one tetrahedral site to next via an intermediate, three co-ordinate site; covalent bonding at the intermediate site helps to stabilize it and reduce the activation energy for ion migration [158]. A Neutron-diffraction study on single crystal α-AgI performed by, Cava *et al.* has proved that, indeed, diffusion of Ag^+ ions occurs mainly by jumps between neighboring tetrahedral sites [159].

Some other materials like AgCl and AgBr show reasonably good conductivities at high temperatures, but no such characteristics of a molten sub-lattice kind of structure exists in them.

From application point of view, α–AgI, in many ways, is an *"ideal solid electrolyte".* The carrier concentration is high since all of the Ag^+ ions are potentially mobile due to melting of the silver sublattice. It has a low activation barrier to migration and consequently, the conductivity is high, ~ l S/cm at 147˚C. It, therefore, combines the advantages of a strong liquid-electrolyte level of conductivity with having only one ion species being mobile (unlike liquid electrolytes where everything moves) and having the mechanical properties of a solid owing to the rigid sublattice of I^- ions. An additional advantage arises because α-AgI is stoichiometric; it does not require any dopants to achieve high ionic conductivity and, indeed, is insensitive to the presence of dopants. One major difficulty is that α–AgI is stable only at temperatures above higher 147˚C and hence a need occurred for investigation of new materials to stabilize α–AgI at room temperature. In keeping in view these facts, many a derivatives of AgI were investigated, to achieve high ion conducting solids.

1.5 *α*–AgI based solid electrolytes

Over the years, stabilization of *α*–AgI phase at lower temperatures (room temperature) has been attempted, using various anionic and cation substitutions. The AgI compound was used as a basis in synthesis of the compound MAg_4I_5, where M = Rb, K or NH_4 [160-162], in initial experimental investigations. In many attempts taken so far, special attention has been paid to $RbAg_4I_5$ compound which possesses the highest conductivity (0.25-0.28 S/cm) at room temperature with activation energy of 0.07eV [163]. This compound showed the negligible amount of electronic conductivity ~ 10^{-9} S/cm. In order to prepare $RbAg_4I_5$, a 1:4 molar ratio of RbI and AgI was melted in vacuum and then quenched. The crystal structure of $RbAg_4I_5$ is rather different than *α*–AgI, but a random arrangement of Ag^+ ions over a network of face-sharing tetrahedral sites is present, and also there are many more available sites than actual number of Ag^+ ions to fill them. Rubidium atoms are immobilized in the sites that have a distorted octahedral environment of I^- ions. Studies on many crystalline materials showed clear evidence no other crystalline materials could match the conductivity of *α*–AgI at room temperature. Hence, a research for stabilization of *α*–AgI in non-crystalline forms like polymers and glasses was attempted by researchers from years then to achieve high ionic conductivity like *α*–AgI. A disordered *α*–AgI like structure was stabilized at low temperatures by other cations as well like NH_4^+, and other organic cations as $[(CH_3)_4N]_2Ag_{13}I_{15}$, $PyAg_5I_6$ etc. [50]. A range of anions could be accommodating to partially substitute for I^- ions to form high conducting phases like Ag_3SI, $Ag_7I_4PO_4$, and $Ag_6I_4WO_4$. All compositions mentioned above are crystalline in nature. Hence, in order to stabilize *α*–AgI at room temperature, glasses can also serve as an effective host material to gain high ionic conductivities.

The conventional belief has been that the high degree of local order (crystallinity) is what makes the ionic conductivity too low at ambient temperatures. Therefore, much attention has been devoted to the task of developing the disordered or amorphous conductors. Thus, a systematic investigation was started to stabilize α–AgI in various host glass systems.

1.6 Glass as an effective medium to stabilize α-AgI at room temperature

Glass, in general, is considered electrically insulating in nature and has a conductivity of the order of $\leq 10^{-12}$ S/cm or so. However it can be tailored to achieve high ionic conductivities. Before reviewing the ion conducting glasses and other features, let us have a brief look at glass.

The traditional view is that glass is a solid obtained by supercooling a liquid and that it is X-ray amorphous. Additionally a glass, when heated, should also exhibit a thermal characteristic known as the "glass transition" at a temperature, T_g, glass transition temperature. A more general and precise definition of the term glass and glass transition has been proposed by the U.S. National Research Council as follows: "*Glass is an X-ray amorphous material which exhibits glass transition, this being defined as that phenomenon in which a solid amorphous phase exhibits with changing temperature a more or less sudden change in the derivative thermodynamic properties such as heat capacity and expansion co-efficient, from crystal-like to liquid–like state* [164]". As per this definition, a wide range of materials including polymers, gels, oxide and chalcogenide glasses, etc. can be considered as a glass. However, here only inorganic oxide glasses will be considered.

Glass, as we know, can be formed by conventional quenching method of the molten constituents, as well as some new methods have also been adopted like sol-gel formation, evaporation techniques etc. [165]. Although glasses can be obtained by the any of the methods, no all materials can readily form glasses, or in other words have the glass formation ability. Glass formation occurs in a number of materials including, oxides, sulfides, selenides, tellurides, halides, nitrates, sulfates, carbonates, simple organic compounds etc. [166]. For oxide glasses, the earliest effort to relate glass formation to its structure was undertaken by Goldschmidt [167], who recognized the importance of radius ratio in simple glass forming oxides. He pointed out that in all glass forming oxides (then known), r_c/r_o is 0.2 - 0.4, where r_c and r_o are the ionic radii of the cation and the anion respectively. This value of r_c/r_o is also the ratio found in oxides where the cation is coordinated to four oxygens because the tetrahedral hole has a radius equal to 0.225 times the radius of the surrounding atoms. The observed glass formation in SiO_2 and GeO_2 support Goldschmidt's approach. Although lacking in appreciation of the bonding type and treating all oxides as purely ionic, Goldschmidt's [168] views spurred on further work by Zachariasen [169], who formulated the famous rules for glass formation now bearing his name. He formulated his thoughts as rules for glass formation, which are as follows. In a glass forming oxide of the formula $\mathbf{A_mO_n}$, where A is a metal cation, and **m** & **n** = 1, 2, 3, 4, 5 …

1.) An oxygen atom may be linked to no more than two **A** atoms.
2.) The number of oxygen atoms surrounding **A** atoms must be small.
3.) The oxygen polyhedra share only corners with each other, neither edges nor faces.
4.) At least three corners in each polyhedron must be shared.

The small radius ratio implies low coordination number. The requirement that the structures should be disordered in glasses, suggests that open structures are more likely to give rise to such disorder, because the coordination polyhedra need not share edges and faces. Edge and face sharing induces crystalline order. Further, Zachariasen argued that the energies of the glassy and crystalline states of the glass forming oxides should not be very different since the mechanical properties are similar in the two states. Also if the energy of the glass is very much higher, it may induce crystallization. And hence a thumb of rule kind of criterion for glass formation was given by Zachariasen.

Table 1.5: The main glass components. (From Ref. [170, 171])

Name of the Constituent	**Role of the Constituent & Remarks**	**Example**
Network former	Basic material to form glass, has a general glass forming ability in normal conditions/easily forms glass when quenched from liquid state. Generally forms a continuous random network to form glass.	**Elements:** S, Se, Si, Te, P etc. **Oxides:** B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, etc. **Other compounds:** BeF_2, AlF_2, $ZnCl_2$, $KHSO_4$, sulphides, selenides and tellurides of some elements etc. **Note:** *Each former oxide mentioned above forms a class of glass, called glass family bearing its name, e.g. borate glass (B_2O_3), silicate glass (SiO_2), Fluoride (F^-) glass, etc.*
Network modifier (Property modifier)	Generally a second oxide. Added to tailor chemical durability, network expansion, viscosity, etc. It retains the continuous random network (CRN) of the glass former, but that network gets modified due to the addition of the second oxide.	Ag_2O, CaO, Na_2O, BaO, Li_2O, K_2O etc.
Intermediate / Conditional glass formers	May form glass in specific conditions only. An essential component in tailoring the physical property of host glass by altering its structure	V_2O_5, Fe_2O_3, MoO_3, CrO_3, WO_3, TeO_2, Li_2O, Tio_2 etc.
Dopant salts	Generally metal halides. Used to improve/induce the electrical properties of glass. (details in text)	LiI, LiCl, LiBr, NaI, AgI, AgBr, CuI, CsI, KI, AgCl, ZnF, SnF etc.

There exist a number of both inorganic and organic substances which may form glass when cooled from the liquid state at a rate that does not provide conditions for the formation of a regular lattice structure.

To understand the origin of ionic conductivity observed in fast ion conducting glasses, it is necessary to understand the role played by the basic constituents of these materials. Mainly four basic components are necessary for formation of such glasses; network former, network modifier, intermediates/ conditional glass formers and doping salts, are summarized in Table 1.5 on previous page.

From the Table 1.5 one may infer that a glass former is a must have or the starting material to form the glass. The modifier oxide may alter the desired property/properties of the glass without not much affecting the others.

(a). Network former: There are covalent compounds such as the oxides or chalcogenides of silicon, phosphorous, germanium and arsenic, which form glasses upon cooling from the melt. Their structure in the amorphous state consists of strongly cross-linked macromolecular chains of covalently bonded elementary units such as tetrahedrons and triangles. These units exist in the crystalline state of the material. As an example, Fig. 1.4 shows the difference between well-ordered crystalline quartz and the disordered framework of SiO_2 glasses, shown in 2D for simplicity. The amorphous state, where only local or short range order is maintained, is characterized by a dispersion of the valence angles and bond angles. X-ray and neutron diffraction experiments support the presence of a random network model of glasses formed by these structural units connected randomly in three dimensions. The strongly covalent character of these glass formers in the amorphous state is responsible for the absence of ionic conduction. In certain cases, super structural units (rings or clusters) built from the basic units are present and constitute the essential building blocks of the structures. For example, the boroxol rings in B_2O_3 glasses is one such unit which acts as a basic building block.

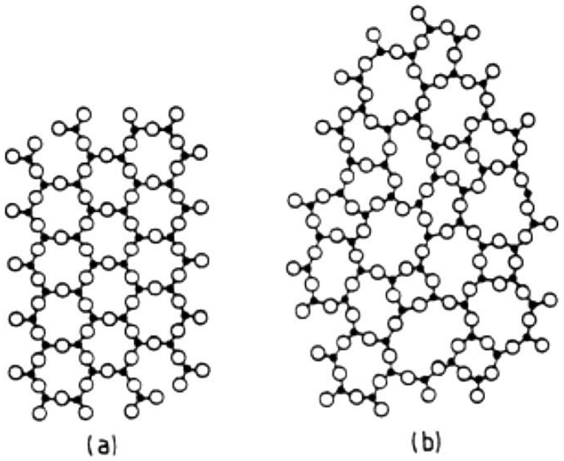


Fig. 1.4. The Difference between (a): well ordered crystalline quartz *and* (b): disordered framework of SiO_2 glass.

(b). Network modifier: These include the oxides and chalcogenides of alkali, alkaline earth or silver cations. They do not normally readily form glasses but do induce structural changes in the networks of the glass formers by introducing ionic bonds between the modifier cations and the covalent chains. The positively charged interstitial cations are accommodated by inclusion of the modifier anions into the polymeric chains. With increasing concentrations of modifier, the distance between two adjacent negative anion sites decreases, causing a corresponding decrease in the depth of the potential well. When such wells become highly interconnected in the glass, they form a favorable path for ionic transport. The ionic conductivity thus generally increases rapidly with the increase of the modifier concentration. The chemical reaction between the former and the modifier changes the network bonding and affects the network rigidity of the glass. The effect of modifier is reflected in the other physical properties also such as density, melting point, glass transition temperature, etc. Consequently, the increase of ionic conductivity must not be considered solely resulting from an increase in the number of free cationic carriers but also due to changes in the network structure leading to changes in the mobility mechanism.

(c). **Intermediates / conditional glass formers:** These compounds are oxides or chalcogenides of e.g. iron, titanium, vanadium, and aluminium etc. They cannot be obtained in glassy form alone. However when combined with a glass former material, however, they behave as former in that they are incorporated in the macro-molecular chains by substitution onto the glass-former site.

(d). **Dopant salts:** In most cases, these additives are halogens, sulphates or phosphates containing the same cation as that of the network modifier. For these salts, the glassy matrix acts as a solvent with evident effects on the network conformation. As shown by spectroscopic measurements, *i.e.* Raman scattering or IR spectroscopy, both cations and anions are generally accommodated into the glass interstitially while the cations contribute substantially to the ionic conductivity. Introduction of dopant salts in the glass network induces changes in the network bonding which are evidenced, in some glassy systems, by density, conductivity and glass transition temperature measurements. Influences on the nature of the anion of the doping salt on structure and transport are reported.

Thus, above mentioned four glass components are necessary to prepare fast ion conducting glasses and electrical properties of the host glass can be tailored to achieve desired electrical properties by means of varying its composition. Any variation in the glass composition mainly affects two factors that contribute towards increases in its conductivity: the first is to the increase the number of mobile cations (or anions in case of anion conducting glasses) while the second comes from creation of a large number of available equivalent energy sites that are essential for ion conduction in the glassy phase.

1.7 A review of AgI based silver ion conducting glass materials

As discussed in previous sections, amorphous or disordered structures are found to possess higher Ag^+ ion conductivity in comparison to their crystalline counterparts. The first successful attempt of stabilizing α-AgI at room temperature was made by Kunze [35] to obtain an anion stabilized α-AgI by melting AgI-Ag_2SeO_4 in different proportions followed by rapid cooling the melt in air/ liquid nitrogen. The 75AgI-25Ag_2SeO_4 composition was found to be highest conducting with $\sigma_{DC} = 3\times10^{-2}$ S/cm at room temperature with an activation energy equal to 0.2 eV only. This marked the beginning of intense studies and synthesis of Ag^+ ion conducting various glass systems including conventional glass formers (B_2O_3, P_2O_5, SiO_2, GeO_2), non-conventional glass formers (MoO_3, WO_3, V_2O_5, As_2O_3, CrO_3), Chalcogenide glass systems (GeS, As_2S, P_2S_3 etc.), halide systems and mixed glass formers (as a contribution of two or more of the glass formers) also.

Thus, according to the type of the glass-former, Ag^+ ion conducting glasses are subdivided into oxide, chalcogenide and halide glasses. This classification may be applied to other cation or anion conducting glasses also. Different Ag^+ ion conducting oxide glasses have been reviewed as follows:

(1) **Phosphate glasses**: Phosphate glasses are one of the most widely used glass formers for synthesis of low melting ion conducting glasses. Table 1.6

summarizes some typical glass characteristics such as glass transition temperature, T_g, DC conductivity, σ_{DC} and activation energy for phosphate glasses. Minami [172] has investigated the glass formation and ionic conductivity in the system $AgI-Ag_2O-P_2O_5$ and has established that glass formation proceeds when the ratio Ag_2O/ P_2O_5 is less than 3. Conductivity as high as 1.8×10^{-2} S/cm has been achieved for 66.7 mol% AgI containing phosphate glasses (see the table).

Table 1.6: Phosphate glasses

	Glass composition	T_g (˚C)	σ_{DC} (S/cm)	E (eV)	Ref
1	$AgI-AgPO_3$ (57.5-42.7)	75	1.5×10^{-2}	0.25	[173]
2	$AgBr-AgPO_3$ (48-52)	92	1.0×10^{-3}	0.31	__
3	$AgCl-AgPO_3$ (40-50)	112	1.0×10^{-4}	0.38	__
4	$AgI-Ag_2O-P_2O_5$ (50 - 25 -25)	64	5.0×10^{-3}	__	[174]
5	$AgI-Ag_4P_2O_7$ (85-15)	__	1.8×10^{-2}	0.23	[175]
6	$AgI-Ag_2O-P_2O_5$ (65-23.3 - 11.7)	49	2.0×10^{-2}	__	[174]
7	$AgI-Ag_2O-P_2O_5$ (66.7-25-8)	50	1.5×10^{-2}	__	[174]
8	$AgI-Ag_3PO_4$ (80-20)	__	1.2×10^{-2}	__	[176]

(2) **Borate glasses**: The second important glass former used is B_2O_3. Table 1.7 shows the characteristics of some of the selected compositions of silver borate glasses. G. Chiodelli [177] and others [178] have used IR, NMR and Raman spectroscopy studies to investigate the glass formation in $AgX-Ag_2O-B_2O_3$ (X= I, Br, Cl) systems as well as ionic conducting and the structure of the glasses obtained with different Ag_2O/B_2O_3 ratios. They have proved the formation of BO_3 ad BO_4 groups and B-O-B bridges as well as additional appearance of BO_3X groups with $Ag_2O/B_2O_3 >1$. Minami [179] has arrived at the important conclusion that all of the Ag^+ ions do not participate in conduction process, instead three kinds of silver ions exist in every Ag^+ ion conducting glass system

(i) Ag^+ which interact with NBOs ; (ii) Ag^+ interacting mainly with halide ion and (iii) Ag^+ interacting with BO_4^- or BO_3X groups.

A study by Kamitsos *et al.* [180] confirms the idea about the existence of Ag^+ ions with different structural positions. IR reflectance spectroscopy studies by them have shown that AgI affects the local and middle order of the main glass matrix and Ag+ ions occupy two different types of positions in oxide and iodide surroundings. In addition to this, mixed oxide-iodide positions exist which lead to formation of AgI rich micro domains with increasing AgI content. Using the ^{109}Ag NMR studies on x AgI-(1-x)(Ag_2O-0.2B_2O_3) glass system, Martin [181]concluded that there should be two kinds of Ag^+ ions at low temperatures: static and mobile whereas at high temperatures all cations are found to be mobile.

Table 1.7: Borate glasses

	Glass composition	T_g **(°C)**	σ_{DC} **(S/cm)**	***E*** **(eV)**	**Ref**
1.	Ag_2O-4B_2O_3	385	9.33×10^{-13}	0.82	[182]
	55AgI - 45(Ag_2O-4B_2O_3)	343	2.50×10^{-5}	0.35	[183]
2.	Ag_2O-3B_2O_3	395	3.79×10^{-10}	0.66	[183]
	60AgI-40(Ag_2O-3B_2O_3)	345	3.33×10^{-4}	0.73	-
	Ag_2O-2B_2O_3	395	8.94×10^{-8}	0.53	[183]
	65AgI-35(Ag_2O-2B_2O_3)	320	2.16×10^{-3}	0.25	-
	AgI-Ag_2O-2B_2O_3	345	2.0×10^{-4}	0.31	-
	AgBr-Ag_2O-2B_2O_3	338	1.5×10^{-4}	0.29	-
	80AgI -20 (Ag_2O-B_2O_3)	220	3.50×10^{-2}	0.20	[183]
	80AgI -20 (Ag_2O-B_2O_3)	210	3.1×10^{-2}	-	[174]
	40AgI - 60 (Ag_2O-B_2O_3)		2.6×10^{-3}	-	[184]
	50 AgBr - 50 (Ag_2O-B_2O_3)		2.7×10^{-3}	-	-
	40 AgCl - 60 (Ag_2O-B_2O_3)		6.3×10^{-4}	-	-
3.	75AgI-25(Ag_2O-0.5B_2O_3)	55	1.90×10^{-3}	0.24	[184]
	60AgI-40(3Ag_2O-B_2O_3)		8.5×10^{-3}	-	[184]
	75AgI- 25 (Ag_3BO_3)	112	3.3×10^{-3}	-	[185]
4.	α-AgI-Ag_2O-B_2O_3		$\sim10^{-1}$	-	[186]

(3) Glasses with non-conventional glass formers: As discussed in Section 1.6, the oxide compound, e.g.; MoO_3, V_2O_5, WO_3, As_2O_5, CrO_3, and TeO_2 are regarded as non-conventional or conditional glass formers. Their main characteristic is that they do not form glasses for low cooling rates (<100˚C /S) alone, but of more complex combinations of components, stable glasses may be obtained.

Kawamura [187], Minami [188], Borino [189] have investigated some compositions in $AgI\text{-}Ag_2O\text{-}MoO_3$ (or quasi-binary $AgI\text{-}Ag_2MoO_4$) glass systems and obtained conductivity of the order of 10^{-2} S/cm at room temperature. The vanadate glasses have been investigated for many years as semiconducting oxide materials and the presence of hopping mechanism of electrons jumping between vanadate ions ($V^{+5} \leftrightarrow V^{+4}$) has been proved [190]. For this reason, they have raised interest usage as cathode materials in lithium batteries [191]. V_2O_5 containing glasses have a chain or layered structure depending on the effect of other components on the formation of vanadium oxygen polyhedral (VO_5 or VO_4 groups) [192], which leads to different effects on transport properties of these glasses. Nishida *et al.* [193] have concluded that the pair of AgI atoms have a high dispersion in the glass matrix and the Ag^+ ions exhibit three types of interactions similar to borate glasses. Other promising groups of amorphous materials are the TeO_2 based glasses. A typical example is the $AgI\text{-}Ag_2O\text{-}TeO_2$ system having a broad glass formation region. It shows conductivity as high as 1.3×10^{-2} S/cm for 53% AgI content, but is also affected by the amount of Ag_2O. Though telluride glasses are mainly used in optical applications, however inclusion of AgI along with Ag_2O has proven it to be useful in electrochemical applications as well. For tungstate glasses, J. Kuwano [194] has recognized the glass formation region in the

AgI-Ag_2O-WO_3 system to be above R = WO_3/Ag_2O >1. The maximum ionic conductivity at 25°C, $\sigma = 3.1\times10^{-2}$ S/cm, is attained with a composition 0.58AgI-0.19Ag_2O-0.23WO_3.

Table 1.8: Glasses with non-conventional glass formers

	Glass composition	Glass former	T_g (°C)	σ_{DC} (S/cm)	E (eV)	Ref.
1.	AgI-Ag_2MoO_4 (75-25)	MoO_3	52	1.1×10^{-2}	0.22	[195]
2.	AgI-Ag_3AsO_4 (80-20)	As_2O_5	65	1.4×10^{-2}	0.20	[185, 196]
3.	AgI-Ag_2CrO_4 (75-25)	CrO_3	52	1.1×10^{-2}	0.22	Same as above
4.	AgI-Ag_2O-V_2O_5 (66.67-22.22-11.11)	V_2O_5		2.4×10^{-2}		Same as above
5.	AgI-Ag_2O-GeO_2 (1/3-1/3-1/3)	GeO_2		1.3×10^{-4}		Same as above
6.	AgI-Ag_2O-WO_3 (58-19-23)	WO_3	130	3.1×10^{-2}		[194]
7.	AgI-Ag_2O-TeO_2 (40-41.96-18.04)	TeO_2		~8×10^{-3}	~0.29	[197]
8.	AgI-Ag_2SeO_4 (75-25)	SeO_3	75	3×10^{-2}	0.20	[198]

(4) Oxide glasses with more than one glass former

The introduction of two network formers increases in many cases the ion conductivity of silver conducting glasses (a mixed anion effect) [199]. Table 1.9 shows the data on the ion conductivity of Ag' conducting glasses with two glass formers.

The mixed anion effect with Ag oxide glasses was recorded for the first time on silver-borophosphate glasses [200]. The ion conductivity is not a linear function of the $B_2O_3/(P_2O_5+B_2O_3)$ ratio. The weak electrolyte model predicts that if more than one anion is present, the conductivity would pass through a maximum with the gradual replacement of one anion by another [201]. Constantini *et al.* [202] have investigated thermal and electrical properties of the system AgI-Ag_2O M_2O_3-P_2O_5 (M = Ga, B). The substitution of Ga_2O_3 by P_2O_3 increases both the glass transition temperature and the electrical conductivity. The dependence on composition of the parameters of the Arrhenius type equation of ion conductivity has been explained on the basis of the AgI-micro-domains in a silver phosphate matrix and of the diffusion path structural model [203]. N. Mashida *et al.* [204, 205] *have* investigated the mixed anion effect in the different sections of the system AgI-MoO_3-P_2O_5. It is found that the mixed anion effect on the conductivity is closely associated with the structural changes in the glasses. Kaushik *et al.* [206] [have studied the transport characteristics of the systems AgI- Ag_2O-V_2O_5 and AgI-Ag_2O-(V_2O_5-B_2O_3) and established that addition of B_2O_3 does not enhance the ion conductivity with respect to V_2O_3 but the conductivity is a nonlinear function of the ratio $y = V_2O_5/(V_2O_5 + B_2O_3)$ and passes through two maxima with y values of 0.2 and 0.8 respectively. Studying the transport and dielectric properties of the glasses AgI-Ag_2O-V_2O_5-P_2O_5, AgI Ag_2O-B_2O_3, As_2O_3 and AgI-Ag_2O-MoO_3-WO_3. Prasad *et al.* [207] have established that the ion conductivity is not a linear function of the content of the Ag_2O. This dependence has been ascribed to the presence of inhomogeneous ion clusters. Govindaraj *et al.* [208] have reported four systems containing AgI, Ag_2O and a combination of two competing network formers: SeO_3+V_2O_5, SeO_3+MoO_3, MoO_3+As_2O_5 and MoO_3+V_2O_5. For all systems the addition of a second glass former enhances the ion conductivity as compared to glasses with one glass former, this effect being different for the different quaternary systems. In the case of the glass formers SeO_3+V_2O_5 the ion conductivity increases about 10 times. Govindaraj *et al.* [209] assumed that the silver ions are localized around Se-O-V bonds, which have been established by Dimitriev *et al.* [210]. According to the data for the complex permeability the distribution of the relaxation time is independent of temperature. That confirms the non-Debye nature of the relaxation process in these glasses.

Table 1.9: Oxide glasses with more than one glass former

	Glass composition	Glass former	σ_{DC} (S/cm)	E (eV)	Ref.
1.	AgI-Ag_2O-B_2O_3-P_2O_5	$B_2O_3 + P_2O_5$	$\sim10^{-2}$	---	[211]
2.	66.67AgI-22.22Ag_2O-11.11(0.8V_2O_5-0.2B_2O_3)	$V_2O_5 + B_2O_3$	3.6×10^{-2}	---	[212]
3.	66.67AgI-22.22Ag_2O-11.11(0.1MoO_3 -0.9V_2O_5)	$MoO_3 + V_2O_5$	2.5×10^{-2}	0.22	[213]
4.	66.67AgI-33.33 Ag_2O-2(MoO_3-WO_3)	$MoO_3 + WO_3$	1.9×10^{-2}	---	[214]
5.	66.67 AgI-21.21Ag_2O-12.12 (0.6V_2O_5 -0.4 As_2O_5)	$V_2O_5 + As_2O_5$	1.6×10^{-2}	0.16	[215]
6.	AgI-Ag_2O-B_2O_3-As_2O_5	$B_2O_3 + As_2O_5$	1.4×10^{-2}	0.20	[216]
7.	60AgI-40(Ag_3AsO_4-$AgPO_3$)	$As_2O_5 + P_2O_5$	3.0×10^{-2}	---	[217]
8.	AgI-Ag_2MoO_4-Ag_3PO_4	$MoO_3 + P_2O_5$	1.8×10^{-2}	---	[218]
9.	60AgI-40 72.3Ag_2O-36.7 (0.4SeO_2 -0.6MoO_3)	$SeO_2 + MoO_3$	3.1×10^{-2}	0.28	[219]
10.	60AgI-26.27Ag_2O-13.33 (0.8SeO_2 -0.2V_2O_5)	$SeO_2 + V_2O_5$	1.6×10^{-2}	0.17	[220]

(5) Mixed cationic glasses: In addition to the above mentioned various glass systems, a small class of new materials have been developed by some groups at different times, not as systematically studied as above cases but rather as a random attempt to achieve higher ionic conductivities. Recent efforts have been made by various research groups to study as they present a challenge as well as opportunity towards developing new potential solid electrolytes by stabilizing α-AgI via and via an indirect route. Thus formed glasses have been found to possess higher ionic conductivity when compared to similar AgI containing glasses. Further discussion is given in section 1.8. Following table 1.10 enlists some mixed cationic glasses prepared in recent past by various research groups.

Table 1.10: Mixed cationic glasses

	Glass composition	σ_{DC} **(S/cm)**	***E* (eV)**	**Ref.**
1	$0.19PbI_2$-$0.81AgPO_3$	$\sim10^{-2}$	--	[221]
2	PbI_2-Ag_2O-Cr_2O3	7.50×10^{-2}	0.27	[222]
3	CsI-$AgPO_3$	--	--	[223]
4	CdI_2-Ag_2O-V_2O_5-B_2O_3	1.3×10^{-3}	0.29	[224]
5	PbI_2-Ag_2O-V_2O_5	$\sim1.29\times10^{-3}$	0.39	[225]

1.8 Applications of Ion conducting glasses

Selection of an appropriate glass material as a solid electrolyte can lead to development of technologically important electrochemical devices and applications. Below is listed a few important applications of them.

A. Solid state batteries

B. Super-capacitors

C. Gas Sensors

D. Electro chromic devices like smart windows

1.9 Motivation

Investigations on most ion conducting glasses emphasizes mainly on two aspects- (1) stabilizing a highly conducting phase like α-AgI at room temperature in a suitable host glass matrix *and* (2) increasing mobility of the mobile cations.

As it has been discussed earlier that α-AgI is a prototype superionic conductor and it has been a center of attraction to stabilize such a highly conducting phase at the room temperature in many host glass systems including binary, ternary and quaternary glass systems [185, 226, 227]. Many interesting results have been obtained regarding the nature of electrical conductivity of these glasses. Instead of directly doping pure AgI in a host glass, some different routes have also been attempted, like using a stoichiometric composition, instead of pure AgI in the host glass [228], or doping with a suitable MI_n type salt in an Ag_2O containing glass and thereby forming AgI as a result of exchange reaction between the two, based on Lewis HSAB (Hard and Soft Acids and Bases) principle [229, 230], where a hard acid ion prefers to co-ordinate to a hard base ion and vice-versa. This approach has led to the usage of various metal halide salts e.g., CuI, CsI, BiI_3 and CdI_2 as dopant, which form AgI in the host glass by an exchange reaction with Ag_2O or $AgPO_3$. According to the HSAB theory, Pb^{+2} ion is a borderline acid and I^- is a soft base while Ag^+ is a soft acid and O^{-2} is a borderline base, hence an exchange reaction between PbI_2 and Ag_2O takes place as per the following equation [225]

$$Pb^{+2}_{[2I^-]} + 2Ag^{+}_{[O^{2-}]} \rightarrow Ag^{+}_{[I^-]} + Pb^{+2}_{[O^{2-}]}$$

From the above reaction we see that for one molecule of PbI_2 and one molecule of Ag_2O, as a result of the exchange reaction, two AgI and one PbO molecules are formed in the glass network. Addition of a network modifier such as Ag_2O introduces ionic bonds, usually associating NBOs (Non-Bridging Oxygen) along with modifying cations. Ag_2O leaves its oxygen and negative charges to the glass network, which becomes rich in charge carriers (Ag^+) and gains the capability to act as a solvent for the metal halide salts. Hence the mobility associated with an iodide environment is considered to be higher and based on the fact that increase in the percentage of AgI in the glass gives rise to higher conductivities. Incorporation of metal halides in the mixed glass formers is considered to be a predominant factor playing the role of enhancing the conductivity of conventional glasses to achieve the values of super ionic conductors. Many reports suggest that the conductivities have been enhanced by mixing of two different glass formers with different coordination polyhedrons. However, such a mixture of glass-formers has a tendency of phase separation at low modifier molar ratio; therefore the complete substitution of one network former by another is always possible.

More recently, the trend of replacing Ag^+ ions with other feasible cations in dopant halide salts like CuI, CdI_2 etc. has been followed to realize new materials exhibiting comparable electrical conductivities and exploiting the favorable character of silver ion to electrical conduction [231, 232]. Moreover, this new route adopted in developing such materials has paved the way for the "mixed cation effect" [233] wherein a second cation is involved in the process of conduction actively or by influencing conductivity via structural alterations. As PbO acts as a glass modifier, it expands the glass network by creating more open and channel type structures, which are helpful for easy movement of Ag^+ ions [233, 234]. The conductivity enhancement in PbI_2-Ag_2O-TeO_2 [236] glasses is more than the conductivity of AgI-Ag2O-TeO_2 [233] glasses and can be correlated with the creation of more open volume induced by PbI_2 than AgI would induce. The effect on conductivity by influencing the network by addition of PbI_2 in the host glass network has been observed in many chalcogenide and chalcohalide glasses, too [235, 236].

1.10 Present work

In light of the discussion done in previous section, the present investigation involves the study: "**Transport properties of PbI_2 doped silver oxysalt based amorphous solid electrolytes**" and their application as solid electrolytes in solid state batteries. In the present work, effect of PbI_2 on electrical properties of Ag_2O-

V_2O_5-B_2O_3 host glass has been investigated. For this purpose, three different glass series in different compositions were prepared as follows,

Series (a): $x\ PbI_2 - (100-x)\ [Ag_2O - 2(0.7V_2O_5 - 0.3B_2O_3)]$
where, $5 \leq x \leq 25$ in steps of 5.

Series (b): $y\ (PbI_2{:}2Ag_2O) - (100-y)\ [0.7V_2O_5 - 0.3B_2O_3]$
where, $30 \leq y \leq 55$ in steps of 5.

Series (c): $z\ (PbI_2{:}Ag_2O) - (90\text{-}z)\ V_2O_5 - 10B_2O_3$
where, $30 \leq z \leq 50$ in steps of 5.

In glass series (a), the amount of PbI_2 has been varied against the host glass Ag_2O - $2(0.7V_2O_5 - 0.3B_2O_3)$. An exchange reaction between PbI_2 and Ag_2O takes place in the glass forming melt and as a result, AgI and PbO are created in the end glass composition. Thus, it is an indirect route of stabilizing highly conducting α-AgI in a host glass and it will provide mobile Ag^+ ions in the glass matrix. PbO acts as a glass modifier/former [237] and may influence the electrical properties of the prepared glass samples. For glass series (b) the ratio of PbI_2 to Ag_2O was fixed at 1:2, so as to l*et al*l PbI_2 molecules to interact with Ag_2O and convert to AgI. The ratios of AgI, Ag_2O and PbO remain in the same proportion for all glass compositions in this glass series. For the third and last glass series, ratio of PbI_2 to Ag_2O was kept 1:1, so that at the end of the exchange reaction, no Ag_2O or PbI_2 is left in the end glass composition and only AgI, PbO and V_2O_5+B_2O_3 constitute the end glass product.

The prepared samples were characterized for their various physical, thermal and structural properties. Transport properties of the prepared glass samples were investigated using impedance spectroscopy and its different formalisms. The optimum conducting compositions from each glass series were selected as solid electrolyte for 'solid state battery' applications.

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