CHAPTER 1

Introduction

1.1 Introduction to Solid Electrolytes:

In the 19th century, Michel Faraday introduced the words 'ION', 'ANODE-ANION', 'CATHODE-CATION' to the world and laid the foundation for Solid State Ionics[1], and made significant contributions to the field of solid-state ionics by introducing important terms such as "ion," "anode," "cathode," "anion," and "cation." These terms laid the foundation for the understanding of ion motion in solid-state materials. Solid-state ionics [1], also known as solid-state electrolytes, is a field of physiochemical science that focuses on the movement of ions as the primary mechanism in solid-state materials. Solid-state electrolytes, or solid-state ion conductors, play a crucial role in solid-state ionics [2]. These materials are characterized by their ability to conduct ions while being electrical insulators. Ion transport is the fundamental phenomenon in solid-state ionics, and solid-state electrolytes enable the conduction of ions, whether they are cations or anions [3]-[6]. Superionic conductors, or superionic solids, are a specific class of solid-state electrolytes that exhibit excellent ion transport properties. These materials have attracted significant attention in the field of solid-state ionics due to their potential applications in various electrochemical devices. Superionic conductors are considered promising candidates for energy storage devices like batteries, fuel cells, and supercapacitors. They also find applications in pacemakers, gas and pollutant sensors, electrochromic and smart memory windows and displays, as well as coulometers and analog potential memory devices [7]-[9]. The study of solid-state ionics and the development of superionic conductors offer vast opportunities for advancing technologies in energy storage, sensing, and other fields that require efficient ion conduction in solid-state materials [10].

The material or system functioning as a solid electrolyte (SE) in solid-state ionics should possess several key features. These features are as follows:

i. The ion conductivity of the material should be on the order of $\geq 10^{-3}\ S/cm$, which is higher than the electronic conductivity (typically around 0.01% of the ionic conductivity). This ensures efficient ion transport within the solid electrolyte.

ii. For easy ion migration, the energy barrier for ion movement should be $< 1\ eV$. The low energy barrier facilitates the mobility of ions within the solid electrolyte.

iii. The material should have physical and chemical compatibility suitable for electrochemical applications. This means that the material should be stable and not react with the surrounding environment, electrodes, or other components of the electrochemical device.

In solid electrolytes, both cations and anions can move within the solid lattice. However, cations typically exhibit higher conductivity compared to anions due to their smaller ionic radius. Most superionic solids involve monovalent ions[2], and high mobility of divalent or trivalent ions is not commonly reported due to the higher coulomb energies involved in their hopping process.

In solid electrolytes, ion migration through hopping depends on several criteria [3],[4]:

1. High polarization ability of the anion framework: The anion framework of the solid electrolyte should have a high tendency to become extremely polarized, facilitating ion migration.
2. Availability of more mobile ion species: The presence of more mobile ion species enhances the hopping process of ion migration within the solid electrolyte.
3. Interconnected ion migration path: The solid electrolyte should have interconnected pathways for ion migration, with accessible vacant sites that possess equivalent activation energy for the hopping process.
4. Modest energy barrier: There should be a modest energy barrier between neighbouring vacant sites to facilitate the hopping process of ion migration.
5. In solid-state ionics, the principle charge carriers are ions, which means that the ionic transference number is almost equal to 1. This implies that ions are the dominant species responsible for electrical conduction within the solid electrolyte.

Solid-state ionics is an interdisciplinary subject that encompasses physics, chemistry, and engineering aspects. It involves theoretical studies, synthesis of materials, physical-thermodynamic-structural characterizations, and exploration of promising applications. The backbone structure of the solid-state ionics system facilitates the transportation of charged matter (ions) over macroscopic distances within the system [1].

1.2 Types of Solid Electrolytes (SE)

Solid electrolytes which exhibit ionic conductivity can be classified based on their nature [3], [4], such as glass (amorphous) electrolytes (GE) [5], polymer electrolyte (PE) [6]/ gel polymer (polycrystalline) electrolytes (GPE) [7], Composites [8], and NASICONs (crystalline /polycrystalline) [9].

(a) Glass Solid Electrolytes (GE/GSE)

The glass structure is the freezed liquid state of the fused organic/ inorganic substances under a rigid condition without crystallization. Glass is an amorphous solid material with absence of long-range order/three-dimensional periodicity and doesn't confirm any stoichiometry rules. The glassy state of substance is obtained by rapid melt quench technique to freeze the molten liquid without getting crystallisation [10]–[12].

In the amorphous solids, glass is one of the solid electrolytes which show advantageous features, like

i. The absence of grain boundary region.
ii. Ease of formation in its desired shape and size.
iii. Isotropic nature of conduction.

These are the supportive properties that have attracted a great deal of attention to make use of 'Glass' as a solid electrolyte in electrochemical devices [13]. The amorphous phase can be formed generally by multi-component systems over a wide range of compositions. This system allows the glass properties to be varied continuously merely by modifying glass composition as listed in Table 1.1. Hence, from a technical point of view, glassy materials are more advantageous than their corresponding crystalline counterparts [14]. The detailed discussion on glassy solid electrolytes is present **in section 1.3.**

(b) Polymer(PE)/ Gel Polymer Electrolytes (GPE)

Polymer electrolytes have been extensively studied, with Polyethylene Oxide (PEO) being one of the most commonly used polymer chains. PEO is a cost-effective and flexible polymer that, when mixed with salts, exhibits moderate ion conductivity at room temperature[14]–[16]. However, it is worth noting that other polymer hosts such as Poly-methylmethacrylate (PAN), Polyvinyl Chloride (PVC), and Poly-vinylidene Fluoride (PVdF) have also been explored in polymer electrolyte research, along with alkali metal salt complexes [17]. In polymer electrolytes, Table 1.2, researchers have observed a relatively new phenomenon where ions can move within a polymer matrix without the presence of a solvent. The polymer matrix contains macromolecules that act as partially dissociated solvents for the salt, resulting in an electrolyte behaviour [15], [18]–[22]. This discovery has opened up new possibilities for polymer electrolyte applications.

Table 1.1: *A comprehensive list of previously prepared ion conducting glass solid electrolytes.*

Glass System	Important feature (literature survey)	Conductivity (S/cm)	Ref.
$(Li, Na)_2O - Li_2X_2 - B_2O_3$	Conductivity variation is due to • The doping of halide ($X = F, Br, Cl$) & Mixed Alkali Effect.	$\sigma_{200} \sim 10^{-9} - 10^{-7}$	[23]
$Li_2O - (B_2O_3 - SiO_2)$	Conductivity variation caused due to • Formation of NBOs, BO_3 and BO_4 units; Mixed Alkali Effect & amount of Li_2O.	$\sigma_{623} = 4.16x10^{-3}$ $\sigma_{298} = 2x10^{-6}$	[24], [25]
$Li_2O - B_2O_3 - P_2O_5$	Enhancement of conductivity is due to • Loosely linked Li^+ to BO_4 units than phosphate units & Mixed Glass Former Effect.	$\sigma_{523} = 1x10^{-6}$	[26], [27]
$LiX: [Li_2O - B_2O_3 - P_2O_5]^*$ $(X = Cl, Br)$	• LiX dissociates more Li^+ (mobile) than oxide modifier & Mixed Glass Former Effect. (**system with LiI couldn't be formed by them).*	$\sigma_{298} \approx 10^{-6}$	[28]
$LiI - Li_2O - B_2O_3 - P_2O_5$	• The addition of LiI shows an impact on conductivity and dielectric study.	$\sigma_{373} \approx 10^{-6}$	[29]
$Li_2O - B_2O_3 - P_2O_5$	• By substituting alumina for phosphate unit, the BO_4 group and conductivity are increased.	$\sigma_{298} = 7.58x10^{-8}$	[30]
$Na_2O: Ag_2O: B_2O_3: P_2O_5: AgI$	• With addition of Na_2O, AgI converts into Ag_2O, reduces $BO_3 \rightarrow BO_4$ unit conversion and eventually the conductivity.	$\sigma_{RT} \approx 10^{-4}$	[31]
$Na_2O - B_2O_3 - SiO_2$	• Improvement in conductivity is observed due to borosilicate glass system.	$\sigma_{573} = 2x10^{-3}$	[32]
$AgI - Ag_2O - B_2O_3 - P_2O_5$	• Because of the weakly coupled silver ion with iodide, ionic glass doped with AgI (even with a small amount) has a shallow potential well.	$\sigma_{303} = 6.24x10^{-5}$	[33], [34]
$AgI - Ag_2O - MoO_3$	• The $\alpha - AgI$ phase helps to expand the grain boundaries and resulting into the diffusion process for conduction with high decoupling index.	$\sigma \approx 10^{-7} - 10^{-3}$	[35], [36]
$AgI - Ag_2O - P_2O_5$	• Conductivity is governed by AgI content due to decrease in the inter nuclear spacing between Ag^+ ion.	$\sigma_{473} = 6.02x10^{-5}$ $\sigma_{298} = 2x10^{-2}$	[37], [38]
$AgI - Ag_2O - TeO_2$	• The network constituting units are deformed due to introduction of iodine ions. • The activation energy is largely influence by cation radius.	$\sigma_{298} \approx 10^{-3}$ to 10^{-1}	[39], [40]

Polymer or polymer gel electrolytes possess several desirable characteristics, including the ability to form thin films, flexibility, elasticity or plasticity, transparency, and the presence of pathways that facilitate ion diffusion and conduction [1]. These properties make polymer electrolytes attractive for various applications.

The conduction mechanism in polymer electrolytes involves two distinct processes: ion hopping and transport phenomenon. The motion of polymer chains facilitates these processes, allowing for the movement of ions within the electrolyte. Ion hopping refers to the movement of individual ions between sites within the polymer matrix, while the transport phenomenon involves the overall transportation of ions through the polymer electrolyte [17].

Practical applications of polymer films in certain contexts face limitations primarily due to two reasons. The first limitation is their ability to sustain high temperatures, while the second limitation is related to their mechanical strength during the device fabrication process [14]. To address these limitations, gel polymer electrolytes (GPEs) have been developed. GPEs are a mixture of solid polymers with liquid electrolytes, designed to combine the mechanical properties of solid electrolytes with the high ionic conductivity of liquid electrolytes [41]. This combination allows for improved performance in terms of both temperature sustainability and mechanical strength.

There are two main approaches to synthesizing polymer gels. The first approach involves the formation of a network structure by simultaneously synthesizing monomers and polymer chains. The second approach involves cross-linking already existing polymer chains to create a gel network. The formation of ion-ion pair aggregates within the gel can play a crucial role in the behaviour of ion-conducting polymer gels. However, it is important to note that the ionic conductivity of polymer electrolytes is often limited by the slow segmental motion of the polymer. This slow motion of polymer segments can hinder the mobility of ions and, consequently, limit the overall ionic conductivity of the electrolyte [7].

The development of gel polymer electrolytes addresses some of the limitations of traditional polymer films and offers improved properties such as enhanced temperature sustainability and mechanical strength. These materials have the potential to find applications in various electrochemical devices and systems where high ionic conductivity and mechanical stability are required.

***Table 1.2**: Previously studied systems of Polymer / Gel polymer Electrolytes, NASICON and composites.*

Framework	**Composition**	**Conductivity (S/cm)**	**Ref.**
Polymer	$MgTf_2/PEO/PC-DEC$	$\sigma_{303} = 3x10^{-5}$	[42]
Polymer	$PEO-PMA-NaCF_3SO_3$	$\sigma_{303} = 2.81x10^{-7}$	[43]
Polymer	$(NaCF_3SO_3)\ (NaTf)\ and\ Sb_2O_3$	$\sigma_{303} = 0.569x10^{-3}$	[44]
Polymer	LiPSTFSI, LiX/PEO (X = PSS, PSTFSI, and PSsTFSI)	$\sigma_{363} = 1.35x10^{-4}$	[45]
Polymer	PEO derivatives	$\sigma_{333-353} \approx 10^{-3}$	[46]
Polymer	$PEO-LiClO_4\ with\ LAPT\ filler$	$\sigma_{293} = 1.7x10^{-4}$	[47]
Polymer	$NaClO_4-EC-PC-SiO_2$	$\sigma_{303} = 3.49x10^{-3}$	[48]
Polymer	$MgTf2/PC-DEC/PEO\ with\ MgO$	$\sigma_{298} = 1.49x10^{-4}$	[42]
Polymer	$PVdF-HFP\ with\ Li\ salt$	$\sigma_{303} = 2x10^{-3}$	[49]
Gel Polymer	$LiClO_4-(PC:DEC)$	$\sigma_{303} = 1.03x10^{-3}$	[50]
Gel Polymer	$PVDF-HFP$	$\sigma_{303} = 0.6x10^{-3}$	[51]
Gel Polymer	$\mathrm{LiMTFS-PEGM-PEGDM-PC}$	$\sigma_{298} \approx 10^{-4}$	[52]
NASICON	$Li-Cr-Ge-Ti-(PO_4)_3$	$\sigma_{303} = 6.6x10^{-5}$	[53]
NASICON	$Li-Al-Y-Ti-(PO_4)_3$	$\sigma_{403} = 5.9x10^{-3}$	[54]
NASICON	$Na-La-Zr_2-Si-O_{12}$	$\sigma_{303} = 3.4x10^{-3}$	[55]
Composite	$Y_2O_3-dopedZrO_2\ (YSZ)\ nanowires$	$\sigma_{303} = 1.07x10^{-5}$	[56]
Composite	$NASICON/PEO$	$\sigma_{303} = 1.4x10^{-4}$	[57]

(c) Composite Electrolyte

Composite solid-state electrolytes (CSSEs) [58] are intentionally created by mixing different ionic conductors, resulting in improved performance compared to single solid-state electrolytes (SSEs). CSSEs typically consist of a host electrolyte (such as a glass, salt, or polymer) in which submicron-sized, inert particles like $SiO_2, Al_2O_3$and Fe_2O_3 are dispersed, as listed in Table 1.2 [4], [59]. The composite solid electrolyte structure is formed by incorporating these inert particles into the ion-conducting host electrolyte. The choice of the host matrix and the inclusion of ultrafine particles of the inert compound play a significant role in determining the properties and characteristics of the two-phase composite solid electrolyte [8]. The composition of the CSSEs can vary depending on the specific ionic salt (MX) and its corresponding oxide (A) framework. Based on the nature of the host matrix and the inert compound, CSSEs can be classified into different categories. The development of composite solid-state electrolytes offers several advantages. By combining different ionic conductors, CSSEs can exhibit enhanced ion conductivity, improved mechanical strength, and increased stability. These materials have the potential to address the limitations of single SSEs and find applications in advanced electrochemical devices and systems.

(i) Crystal-Crystal Composite:

In crystal-crystal composites, the first phase of the host matrix is typically composed of moderate ionic solids such as silver halides (AgX) or copper halides (CuX), where X represents a halogen (e.g., Cl, Br, I). These materials possess moderate ionic conductivity. The second phase of the composite is formed by incorporating either $Ag - Cl, Ag - Br,$ or $Ag - I$ compounds, which act as highly conducting materials. These compounds serve to enhance the overall conductivity of the composite system [8]. Alternatively, smaller-sized inert-insulating particles such as SiO_2 (silicon dioxide), Al_2O_3 (aluminum oxide), ZrO_2 (zirconium dioxide), or fly-ash particles can be added as the second phase. These inert-insulating particles do not contribute directly to the ionic conductivity but may provide benefits such as improved mechanical properties, enhanced stability, or optimized structure of the composite electrolyte. By combining the moderate ionic solids of the first phase with the highly conducting compounds or inert-insulating particles of the second phase, the crystal-crystal composite achieves improved overall ionic conductivity compared to the single-phase host matrix alone. This enhancement in conductivity is a result of the synergistic effect between the two phases in the composite solid-state electrolyte. Crystal-crystal composites offer the advantage of tailoring the properties of the composite electrolyte to meet specific requirements for various applications in electrochemical devices and systems. The combination of different crystal phases allows for improved conductivity while maintaining other desired characteristics of the electrolyte.

(ii) Crystal-Glass Composite:

In a crystal-glass composite electrolyte, the composite structure is prepared by either freezing the crystalline phase of $\alpha - AgI$ or by introducing inert-insulating materials such as Al_2O_3 (aluminium oxide), SiO_2 (silicon dioxide), or SnO_2 (tin dioxide) into an ion-conducting glass system. The presence of $\alpha - AgI$ in the composite structure significantly enhances the ionic conductivity. $\alpha - AgI$ is a highly conducting crystalline phase that facilitates the movement of ions within the composite electrolyte. Its inclusion in the composite structure improves the overall conductivity compared to a pure glass electrolyte. Inert-insulating materials like $Al_2O_3, SiO_2, or\ SnO_2$, on the other hand, do not directly contribute to the ionic conductivity but serve other purposes. They can help improve the mechanical strength, enhance the stability, or optimize the structure of the composite electrolyte.

By combining the highly conducting $\alpha - AgI$ crystal phase with the ion-conducting glass and inert-insulating materials, the crystal-glass composite electrolyte achieves improved ionic conductivity compared to a pure glass electrolyte.

(iii) Glass-Polymer Composite:

In a glass-polymer composite electrolyte, the composite structure is created by dispersing a highly ion-conducting glass within a polymer host matrix. This combination of materials leads to improvements in the electrical and mechanical properties of the composite electrolyte. The highly ion-conducting glass phase is responsible for enhancing the overall ionic conductivity of the composite electrolyte. The glass phase contains mobile ions that facilitate ion transport within the electrolyte, thereby improving its conductivity. The polymer host matrix, on the other hand, provides several benefits to the composite electrolyte. Polymers offer flexibility, mechanical strength, and ease of processing, making them ideal as a host material. By incorporating the ion-conducting glass into the polymer matrix, the composite electrolyte inherits the favourable mechanical properties of the polymer while also benefiting from the enhanced ion conductivity of the glass phase.

(iv) Crystal-Polymer Composite:

In crystal-polymer composite systems, the combination of crystals and polymers offers enhanced mechanical stability and significant improvements in ionic conductivity. Several components can be used in the polymer host matrix to achieve these desired properties. One common approach is to incorporate $PEO - PMMA$ (Polyethylene Oxide-Polymethyl Methacrylate) in the polymer matrix. PEO is known for its high ionic conductivity, while $PMMA$ contributes to the mechanical stability of the composite. This combination allows for improved ion transport within the electrolyte while maintaining structural integrity. Inert-insulating materials such as $SiO_{2,}$ (silicon dioxide) and Al_2O_3 (aluminium oxide) can also be added to the polymer matrix. These materials enhance the mechanical properties of the composite while not directly contributing to the ionic conductivity. They serve to increase the overall stability and strength of the electrolyte. $NASICON$ (Sodium Super Ionic Conductor), $LiAlO_2$ (lithium aluminium oxide), and $LiClO_4$ (lithium perchlorate) are other examples of crystal components that can be incorporated into the polymer matrix. These crystals offer high ionic conductivity and can significantly enhance the overall conductivity of the composite system. By combining these crystal components with the polymer host matrix, the crystal-polymer composite achieves improved ionic conductivity and mechanical stability. This combination is advantageous for applications such as solid-state batteries, fuel cells, and other electrochemical devices where both high ion transport and mechanical integrity are essential.

(d) NASICON

$NASICON$ (Sodium Superionic Conductor) can be described by the general formula $A_nB_2(PO_4)_3$, where A represents an alkali metal ion, such as sodium (Na), and B represents a transition metal (TM) ion or other elements like $Zn, Ge, or\ Sn$. The value of n corresponds to the valency number of the B element. $NASICON$ glasses have a similar composition to crystalline $NASICON$ but in a non-crystalline or glassy state. To prepare $NASICON$ glasses, suitable oxides are selected and melted together with other constituents.

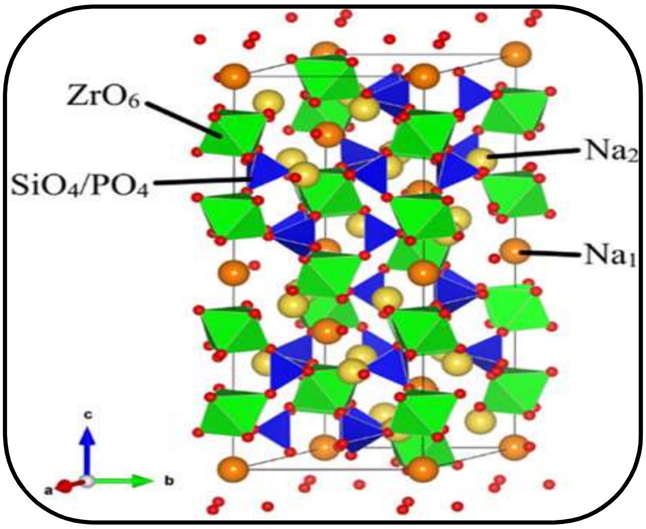


***Figure 1.1**: Crystal structure of NASICON electrolyte.*

The resulting mixture is rapidly quenched or cooled to form the glassy structure, as shown in Fig. 1.1 [60]. Crystalline $NASICON$ materials are known for their high ionic conductivity. However, $NASICON$ glasses face challenges related to their open structure. The open structure can collapse, causing the alkali ions, such as sodium, to quickly become coordinated during this phase. The issue of open structure collapse in $NASICON$ glasses can affect their overall ionic conductivity.

It hampers the free movement of ions and reduces the conductivity compared to crystalline $NASICON$ materials. Researchers continue to explore ways to overcome this issue and improve the ionic conductivity of $NASICON$ glasses for potential applications in solid-state electrolytes and other electrochemical devices.

1.3 The Glass Solid Electrolytes (GSE)

(a) The Basics of Glass

The term "glass" derives from the Old English word "glæs," which means "shiny." The Latin word for glass, "vitreous," also refers to its characteristic shiny appearance. Glass is an x-ray amorphous phase that forms when a molten material cools and solidifies without undergoing crystallization. This occurs when the rate of heat extraction from the molten material is rapid enough to prevent the conventional lattice or motif formation process. In ancient times, glasses were created from inorganic materials such as silica sand (SiO_2), sodium and calcium carbonates ($Na_2CO_3/CaCO_3$), feldspars ($KAlSi_3O_8/NaAlSiO_3/CaAl_2Si_2O_8$), borates ($B_2O_3$), and phosphates ($P_2O_5$). These materials would melt and cool to form solid, transparent materials. Oxides, particularly silica, make up more than 90% of all glasses in use. Silica, which is commonly referred to as "glass is basically sand and ashes," is a prime component. In the modern period, glasses are not limited to silica but can be formed from a wide range of oxides, halides, nitrates, sulphides, chalcogenides, and organic compounds [61], [62]. Different types of glasses have various applications. For example, phosphate and fluoro-phosphate glasses are used as laser hosts, zinc phosphate and lead borate glasses are utilized as solders, and chalcogenide glasses exhibit switching behaviour and are used in memory panels. Glassy selenium (Se) was prominently used in photocopying machines. Halide glasses are being researched as potential replacements for silica fibers in information technology due to their higher transparency. Ionically conducting glasses, particularly those based on lithium (Li), sodium (Na), potassium (K), and silver (Ag), are employed in battery manufacturing. Unlike crystalline materials, glasses do not possess long-range order or periodicity.

Instead, glasses have three levels of structural framework: local or short-range, intermediate range, and long-range structure. Determining the structure of a glass requires multiple diffraction experiments and the use of several spectroscopic and thermal characterization techniques. Diffraction, along with other techniques, is necessary to obtain useful structural information from glasses [63].

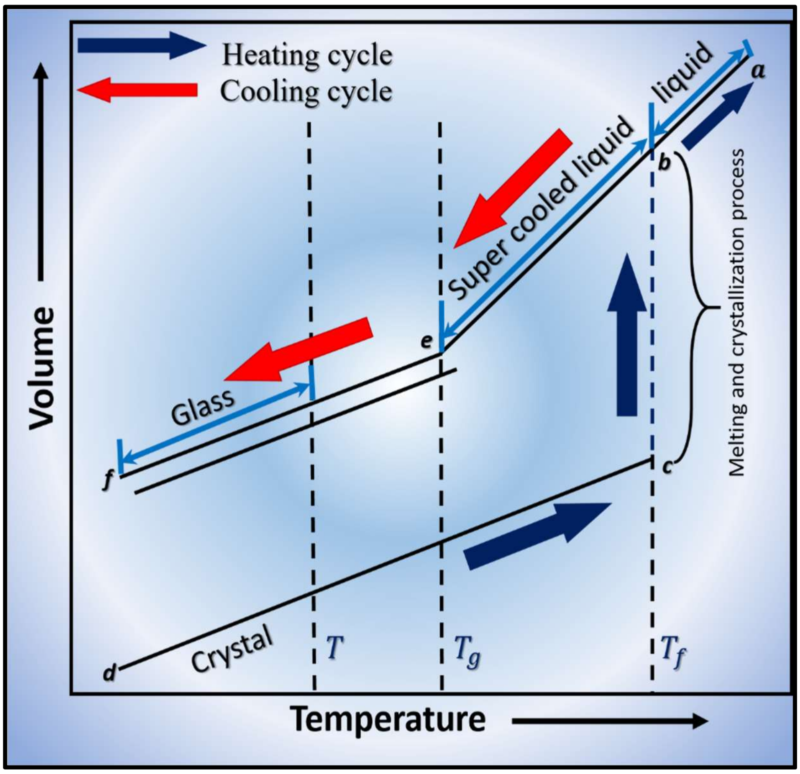


Figure 1.2: A schematic diagram illustrating volume- temp plot to show relation between various phases of the matter.

The volume-temperature curve depicted in Fig. 1.2 shows the relationship between the three phases of a solid-state material. When a fixed-mass liquid is slowly cooled from its initial condition (indicated by 'a' in the diagram), its volume gradually decreases. If the cooling rate is slow enough, a discontinuous change occurs at point 'b' and follows the path 'b-e', indicating the crystallization process occurring in the melt.

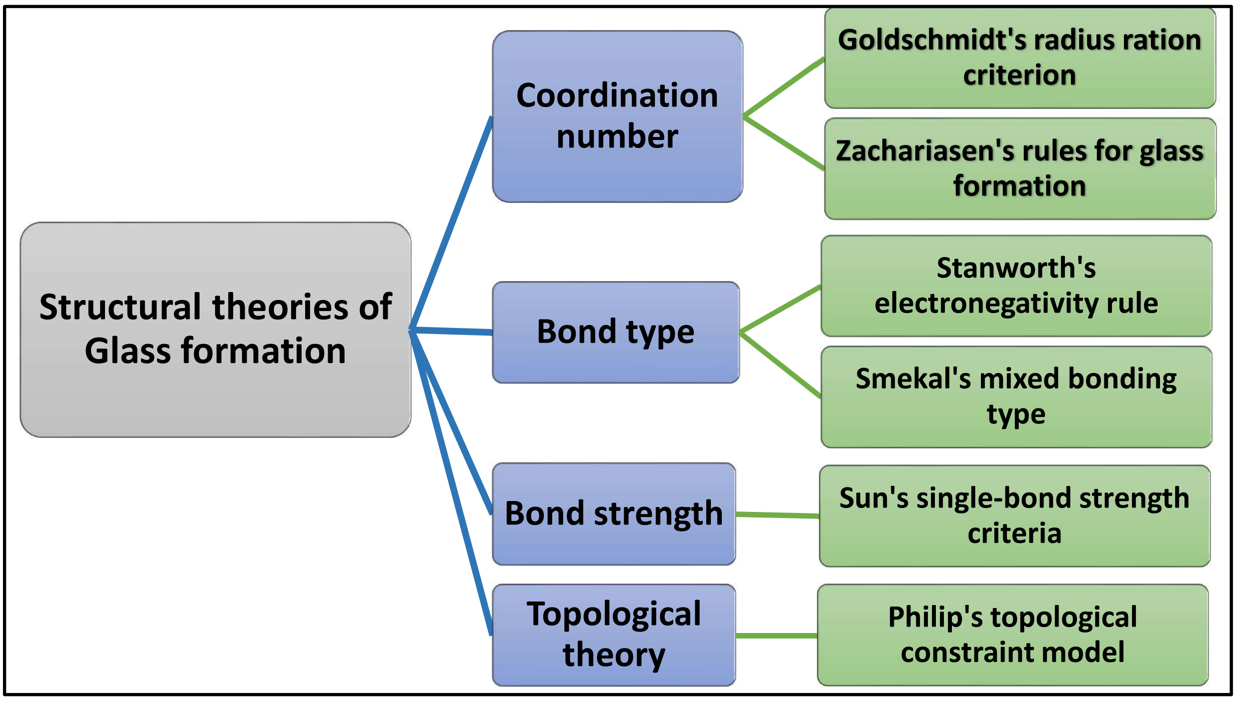
As the temperature drops even further, the volume continues to decrease, but at a different slope compared to before crystallization. If the cooling rate is rapid, such as in a process called rapid quenching, crystallization is bypassed at a transformation temperature T_f, and the volume decreases gradually along line 'b' until it reaches a temperature 'e' at the glass transition temperature (T_g). When the cooling rate is reduced, for example, by slowing down the cooling process, the glass transition temperature (T_g) would be shifted towards T_f. Between T_g and T_f, the substance exists in a supercooled liquid state, and below T_g, it becomes a glassy solid. The glassy phase of the material has a larger volume than its crystallized phase, as indicated by the path lines 'e-f' and 'c-d' in Fig. 1.2. The glassy or amorphous state of the material is the most thermodynamically stable phase [64].

(b) Structural theories of Glass formation / Glass forming chemistry

Glasses, in general, are electrically insulating in nature, with conductivities of the order of $10^{-12} S/cm$ or less. It can, however, be modified to attain high ionic conductivities. Glasses can be obtained by using elements, basic chemical compounds, complex organic molecules, salt combinations, and alloys, with the range of various chemical bond types. Glass can be made using traditional rapid melt quench methods for molten components, as well as newer methods such as sol-gel and evaporation technique. Any of the glass-making procedures can be employed as long as the material has the glass forming potential [65], [66].

There are numerous hypotheses on the structural formation of glass. We will focus mainly on Goldschmidt's radius ratio criterion and Zachariasen's (with Warren) glass formation guidelines. Table 1.3 summarises the classification of fundamental structural hypotheses of the formation of the glassy structure [67], [68].

***Table 1.3**: Classification of structural theories of glass formation based on various chemo-physical parameters*



The criteria for glass formation, particularly for oxide glasses, were first organized by Goldschmidt, emphasizing the importance of the ionic radius ratio in glass-forming oxides. The glass formation was observed to be favourable for $0.2 < \left(\frac{r_C}{r_A}\right) < 0.4$, where r_C and r_A represent the cation and anion radii, respectively. A low cation radius-to-anion radius ratio indicates a low coordination number, resulting in a tetrahedral structure where each cation is surrounded by four anions (O^{2-}) or an octahedral structure with six surrounding anions.

Glass-forming oxides such as $SiO_2, GeO_2, B_2O_3, P_2O_5, V_2O_5, NbO_2, As_2O_5$, and others are classified as glass formers. Zachariasen formulated a set of general guidelines known as Zachariasen's rule for glass formation [69], based on glass-making oxides and the development of the random network theory for glass structure. Zachariasen (1932) proposed the concept of a random structure in oxide glasses, which was later supported by Warren's X-ray experiments [70]. The diffuse nature of the X-ray diffraction (XRD) spectrum of glasses indicates that the unit cell is infinite. According to Zachariasen, the energies of the glassy and crystalline states of glass-forming oxides should not vary significantly since their mechanical characteristics are identical. If the energy of the glassy state is higher, it may promote crystallization [67], [69]. Zachariasen concluded that polyhedron corners must be shared to generate an open and random structure.

For an oxide to be a glass-forming oxide, it must meet Zachariasen's crystallo-chemical postulates, which include the following:

1. Oxygen atoms are bonded to no more than two metal cations (R atoms).
2. R atoms should have a small number of oxygen atoms around them (either 3 or 4).
3. Oxygen polyhedra share only their corners, not their edges or faces.
4. Each oxygen polyhedron in the 3D network must have at least three common corners.

In general, all four requirements must be met for glass formation to occur. Glass formation results in open, low-density polyhedral structures with low coordination numbers and corner-sharing. As a result, glass exhibits short-range order due to the grouping of oxygen atoms in polyhedra. The type of bonding between the cation and oxygen is also important, with oxides that have strong covalent connections being more likely to form glass compared to those with predominantly ionic bonding [69].

(c) Chemical composition of ion conducting glasses

According to the Zachariasen-Warren hypothesis, oxides are classified into two categories: network formers and network modifiers. Network formers, such as SiO_2, B_2O_3, P_2O_5, GeO_2, etc., have the ability to form glasses on their own. They create a network structure by connecting through covalent $Si-O-Si$ or similar bonds. On the other hand, network modifiers, including $Li_2O, Na_2O, Ag_2O,\ K_2O\ and\ CaO, BaO, ZnO$ etc., do not form glasses by themselves but modify the host network structure. They break the $Si-O-Si$ bonds and introduce non-bridging oxygen (NBO) species into the structure. The addition of network modifiers disrupts the $Si-O-Si$ links in the network, as shown in Fig. 1.3 [71].

The Eq. (1.1) represents this process, where $\equiv Si - O - Si \equiv$ represents the network former and M_2O represents the network modifier.

$$\equiv Si - O - Si \equiv + M_2O \rightarrow \equiv Si - O - M + M - O - Si \equiv \quad \text{... (1.1)}$$

The result is the formation of $\equiv Si - O - M$ and $M - O - Si \equiv$ linkages in the glass structure. To understand how ion conduction occurs in a vitreous network, it is important to have knowledge of the different glass-forming elements. Table 1.4 provides a summary of the key components for glass formation, along with relevant examples [72], [73].

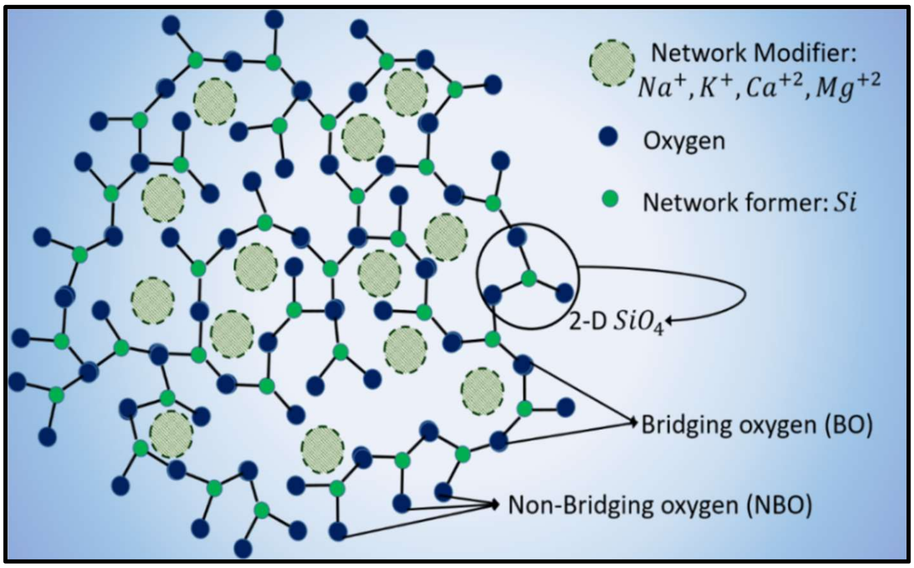


***Figure 1.3**: 2-D schematic illustration of the glass network formation, in which only the covalent links have been depicted.*

The structural model proposed by Zachariasen and the topological aspects discussed by Philip suggest categorizing the different components of a glass as either glass network formers (GNFs) or glass network modifiers (GNMs) based on their role in the glass structure. Network formers create the primary framework, while network modifiers modify the network by introducing NBOs and altering the connectivity of the structure.

(i) Network former:

Network formers, such as boron, silicon, and phosphorus, play a crucial role in the glass structure. They have high valence states, allowing them to form covalent bonds with oxygen. These cations act as the backbone or skeleton of the glass, providing the framework for the overall structure. According to Zachariasen's rules, each class of oxide systems, including SiO_2, GeO_2, B_2O_3, P_2O_5, As_2O_5 and V_2O_5, forms cation-centered polyhedra as local rigid structural units. The connectivity between these structural units occurs through oxygen atoms, which are referred to as "Bridging Oxygen" (BO). The BO atoms serve as bridges, linking the cation-centered polyhedra together and contributing to the overall stability of the glass structure. By varying the composition of the network former, the properties of the glass can be significantly altered. Different network formers have different bonding characteristics and structural arrangements, leading to variations in properties such as thermal stability, mechanical strength, chemical resistance, and optical behaviour in the resulting glass material.

(ii) Network modifier:

Glass network modifiers, such as alkali oxides ($Li_2O, Na_2O, K_2O, Ag_2O$) and alkaline earth oxides (MgO, SrO, CaO, BaO), do not participate in the formation of the glass framework. They have larger cation sizes compared to the network formers and their primary function is to modify the existing glass structure rather than contribute to its formation. When added to the glass composition, the modifier cations mix with the network formers and disrupt the structure by breaking the existing bonds. This leads to the formation of non-bridging oxygen (NBO) sites, where oxygen atoms are not bonded to two network formers. The presence of NBOs reduces the network connectivity and increases the expansion of the glass, resulting in a decrease in viscosity. The main difference between the network formers and modifiers lies in the strength of their cation-oxygen bonds. Network formers have stronger bonding with oxygen and tend to form rigid polyhedra, which contribute to the overall structure and stability of the glass. On the other hand, network modifiers have weaker bonding and readily release their oxygen, occupying interstitial sites within the network formers. The addition of network modifiers alters the properties of the glass, such as its thermal expansion behaviour, viscosity, and chemical reactivity. By varying the type and amount of network modifiers, the properties of the glass can be adjusted to meet specific requirements for different applications.

(iii) Network intermediates:

It is correct that there are cases where certain oxides can act as both glass formers and modifiers, making them intermediates or conditional glass formers. The behaviour of these oxides depends on their oxidation states and their ability to participate in the glass network. For example, iron oxide (Fe_2O_3) in the oxidation state III (Fe^{3+}) can act as a network former, contributing to the formation of the glass structure. However, FeO with iron in the oxidation state II (Fe^{2+}) is more likely to act as a network modifier, disrupting the structure by breaking bonds and creating non-bridging oxygen sites. In chalcogenide glasses, which are glasses composed of chalcogen elements (S, Se, Te) and elements from groups 14-15 (Ge, As, Sb), the chalcogen elements act as the network formers.

They provide a strong covalent foundation for the glass network. In most cases, chalcogenide glasses do not incorporate network modifiers, as the chalcogen elements themselves are sufficient to form the glass structure. It's important to note that the classification of an oxide as a network former or modifier can depend on various factors, including its oxidation state, bonding characteristics, and its interaction with other elements in the glass composition. The role of a specific oxide in a glass system can also vary depending on the overall composition and conditions of glass formation.

(iv) Dopant halide salt:

The Lewis acid-base theory is a concept in chemistry that describes the interaction between acids and bases based on electron pair donation and acceptance. In the context of glass systems, the integration of metal halides (MX) into the glass matrix can lead to the release of cations from their covalent bonds. This can be understood in terms of Lewis acid-base interactions, where the metal halide acts as a Lewis acid, accepting electron pairs from the glass matrix (Lewis base). The Hard and Soft Acid and Base (HSAB) principle is an extension of the Lewis acid-base theory that categorizes acids and bases as "hard" or "soft" based on their chemical properties.

According to the HSAB principle, hard acids prefer to interact with hard bases, while soft acids prefer to interact with soft bases. In the context of glass systems, the HSAB principle suggests that the ion conductivity of the glass can be improved by incorporating metal halides as soft acids, as they can easily release cations for conduction in the glass. By adjusting the proportions of key components in the glass composition, it is possible to tailor the electrical properties of the glass. This includes controlling the number of decoupled ions (either cations or anions) from the host glass matrix and providing them with corresponding energy sites. Increasing the availability of decoupled ions and energy sites is important for enhancing ion conduction in the glassy state.

***Table 1.4**: The key components for glass matrix formation* [63], [67], [71], [74].

Role	Description	Example
Glass Network Former (GNF)	- Comply with all Zachariasen glass forming criteria, - commonly referred to as "Fundamental Glass Formers". - It potentially forms glass on its own. - It easily forms glass when a liquid melt is immediately quenched. - It creates a Continuous Random Network (CRN).	**Element**: S, Se, Si, Te, P **Oxides**: $B_2O_3 - group\ 13\ oxide$ $A_2O_3, SiO_2, GeO_2 - group\ 14\ oxide$ $AO_2, P_2O_5, As_2O_5 - group\ 15\ oxide$ $A_2O_5, Sb_2O_3, In_2O_3, Tl_2O_3, SnO_2, PbO_2, SeO_2$
Glass Network Modifier (GNM)	- As a glass modifier, secondary oxides are used. - Chemical durability and viscosity can be customised. - It is retained in the CRN of the glass former and attributed to the expansion of the host glass framework. - Due to this, Non-Bridging Oxygen (NBOs) are formed.	**Metal oxides**: $Alkali\ oxides$: $Li_2O, Na_2O, K_2O, Ag_2O$ $Alkaline\ earth\ oxide$: MgO, SrO, CaO, BaO
Conditional Glass Former (CGF)	- It complies with Zachariasen's glass forming rules 1,3 and 4, with the exception ofrule2. - Although it does not form glass on its own, it can be melted with other oxides such as P_2O_5 or some basic oxides, to form glass. - It has the potential to form a glassy structure if the other component/network modifier stabilises the charge. It is vital to use it in order to modify the physical properties of the host glass matrix.	$MoO_3, WO_3, Fe_2O_3, Al_2O_3, V_2O_5, TiO_2, TeO_2$
Dopant Salt	- Generally metal halides (MX) are used to improve electrical properties of the host glass. - When the cation linked with halide is disengaged, it aids in ion transport phenomena.	**Fluoride**: ZnF, SnF **Chloride**: $LiCl, AgCl$ **Bromide**: $LiBr, AgBr$ **Iodide**: $LiI, NaI, AgI, CuI, KI, CsI$

1.4 Types of ion conducting glass

Increase in ionic conductivity is the consequence of rigorous glass composition optimization. We can classify them according to the number and type of formers that form the backbone structure of ionic glasses. The following distinctions are made according to the presence of binary, ternary, or quaternary glass systems.

(a) Glasses with single glass former (Binary oxide)

(i) Silica glass (SiO_2)

Amorphous silica, represented by SiO_2, is a common inorganic glass with a relatively simple structure compared to other types of glasses. It can be described as a three-dimensional network of tetrahedra, where each silicon atom is bonded to four oxygen atoms and each oxygen atom is shared by two silicon atoms [67]. This arrangement forms a continuous random network (CRN) model according to Zachariasen's concept. The basic building block of silica glass is the SiO_4 tetrahedron, which is interconnected through bridging oxygen atoms (BOs) located at the corners of the tetrahedra. This network structure provides the rigidity and stability characteristic of silica glass. However, when alkali oxides are added as glass modifiers, they disrupt the CRN by converting some of the BOs into non-bridging oxygen atoms (NBOs) [14], [67] while preserving the SiO_4 tetrahedra as the host matrix.

The introduction of alkali oxides leads to network degradation, which is directly proportional to the amount of alkali oxide present. This degradation results in an increase in the number of NBOs within the glass structure. The addition of alkali oxide also lowers the viscosity of the glass melt and decreases the glass transition temperature. Moreover, the density, refractive index, and thermal expansion coefficient of modified silicate glasses tend to increase with higher concentrations of alkali oxide [65], [75].

The ionic conductivity of alkali silicate glasses exhibits a linear relationship with increasing concentrations of alkali oxides. This is attributed to the diffusion of alkali ions within the glass structure. As the concentration of alkali oxide increases, the activation energy for ion diffusion decreases logarithmically [76]–[78]. These changes in properties are primarily a result of the formation of NBOs, which reduce the network connectivity and increase the openness of the glass structure. The strong directionality of the $Si-O$ bonds in silica contributes to the overall strength and stability of the glass network.

(ii) Borate Glass (B_2O_3)

In B_2O_3 glass, the primary structural unit is the BO_3 triangle, where each boron atom (B^{3+}) is coordinated with three oxygen atoms. The oxygen atoms bridge between adjacent triangles, and the boron atom is slightly raised above the plane formed by the three oxygen ions [63], [67]. This arrangement follows the continuous random network (CRN) model, with the triangular BO_3 units connected at the corners. When an oxide ion is present in the glass composition, boron can acquire two additional electrons through a coordinating bond, resulting in the formation of tetrahedral BO_4 units [63].

The addition of a network modifier to B_2O_3 glass initially increases the coordination number of boron atoms from three to four, rather than converting the BO_3 triangles into BO_4 tetrahedra. The fraction of four-coordinated boron atoms is an important structural parameter. When ionic oxides, such as alkali or alkaline earth oxides, are added to the borate network, they can alter the planarity of boroxyl rings [14], [63], [67]. Alkali oxides modify borate glasses to form several distinct structural units, including BO_3, BO_4, boroxol (B_3O_6) and its modified ring structure, triborate (B_3O_7), and diborate. In alkali oxide glasses, the initial coordination of O^{2-} through two trigonal boron atoms leads to the formation of tetrahedral boron BO_4 units [63].

The addition of alkali oxide, such as Na_2O $(or\ Li_2O\ or\ K_2O)$, to B_2O_3 glass transforms the BO_3 units into BO_4 units, thereby strengthening the network. This is because the $B-O$ bond in borate glasses has a higher covalent potential than the $Si-O$ [63] bond in silica glasses. The effect of alkali oxide in borate glass differs from that of SiO_2 up to a certain concentration [71]. However, as the concentration of the modifier increases, a phenomenon known as the "boron anomaly" is observed. The BO_4 units start to deplete rapidly, leading to the reconversion of BO_4 back to BO_3. This depletion of tetrahedral boron units with increasing modifier content is a characteristic feature of borate glasses.

(iii) Phosphate glass (P_2O_5)

Phosphate glass is composed of a three-dimensional network of vitreous P_2O_5 tetrahedra units, where each phosphorus (P) atom is surrounded by four oxygen (O) atoms [79]. These tetrahedral units serve as the basic building blocks of the glass structure. When alkali oxides, as network modifiers, are added to the phosphate glass matrix, non-bridging oxygens (NBOs) are formed at the expense of bridging oxygens (BOs). The alkali oxide M_2O depolymerizes the phosphate network in the host matrix. The specific structure that emerges depends on the ratio of M_2O to P_2O_5 and the size of the alkali oxide ion (M). With the addition of alkali and alkaline earth oxides, the ultra-phosphate tetrahedral units in the glass transform into a polymer-like linear chain of meta-phosphate units, followed by pyro-phosphate units, and finally to ortho-phosphate units [63], [67], [79], [80]. This transformation occurs based on the M_2O/P_2O_5 ratio and the size of the network modifier ion. The increase in ionic conductivity observed in alkali oxide-modified phosphate glasses is attributed to the formation of more NBOs as the alkali oxide content increases. The presence of NBOs reduces the network connectivity of the glass, allowing for easier movement of cations within the glass structure, thereby enhancing ionic conductivity.

(b) Glasses with Mixed Glass Former (MGF)

When trivalent (e.g., aluminium, boron) and pentavalent (e.g., phosphorus, vanadium) glass formers are combined, it can lead to the development of a competitive network in the glass. This means that the different glass formers compete for bonding with oxygen atoms in the glass structure.

In some cases, when a tetravalent oxide (e.g., silica, SiO_2) is combined with a trivalent or pentavalent oxide, phase separation can occur [81]. This means that the two types of oxides tend to segregate into distinct regions within the glass, forming separate phases.

By combining multiple glass formers in a glass composition, a phenomenon called the "mixed glass former" or "mixed anion effect" [26], [81]–[84] can be observed. This process can alter the characteristics of the glass. For example, in mixed alkali glasses, which contain different alkali metal ions (e.g., sodium and potassium), a decrease in ionic conductivity is often observed. On the other hand, when different glass formers are combined, such as a mixture of boron and phosphorus oxides, an increase in ionic conductivity and improved chemical durability compared to individual glass formers can be achieved.

The mixed glass former effect is attributed to the competition and interaction between the different glass formers, which can lead to changes in the glass structure, connectivity, and ion transport properties. This phenomenon is of interest in glass research as it offers a way to tailor the properties of glasses for specific applications by manipulating the composition and interactions between glass formers.

(i) Boro-Phosphate glass ($B_2O_3 - P_2O_5$)

Pure phosphate glasses are commonly used in various applications, but they have a drawback of being highly hygroscopic, which means they readily absorb moisture from the environment, making them less stable [85]. On the other hand, borate glasses have a highly covalent $B - O$ bond, which results in the formation of a rigid glass structure [33], [63]. When a phosphate network is mixed as a second glass former with B_2O_3, it can enhance the thermal and mechanical stability, improve chemical durability, and enhance electrical properties of the glass. Borophosphate glasses, which combine both phosphate and borate networks, exhibit distinct properties different from pure phosphate or borate glasses [85]. The addition of B_2O_3 to the phosphate network or the substitution of P_2O_5 with B_2O_3 can increase the chemical endurance of the glass. This modification changes the structure of the glass from a linear-chain structure found in metaphosphate glasses to a three-dimensional structure observed in borophosphate glasses [86]. In pure amorphous phosphate glasses, the basic units are composed of PO_4 units connected through covalent bridging oxygens. In contrast, in pure amorphous borate glasses, the basic units are trigonal BO_3 groups, which share a negative charge provided by the oxide modifiers [66]. By combining phosphate and borate networks, borophosphate glasses can exhibit a unique combination of properties, making them suitable for specific applications that require improved stability, durability, and electrical behaviour. The addition of a modifier oxide to borate and phosphate networks has different effects on the glass structure. In the case of borate glasses, the modifier oxide increases the degree of polymerization, meaning that the boron coordination changes from trigonal to tetrahedral. This results in a change in the basic units from BO_3 to BO_4. The addition of the modifier oxide enhances the connectivity of the borate network. On the other hand, in phosphate glasses, the modifier oxide has a depolymerizing effect. The oxygen atoms of the modifier oxide leave the phosphate network, creating negative non-bridging oxygen sites. These sites are compensated by the positive charge of the modifier cations. This depolymerization weakens the connectivity of the phosphate network. Borophosphate glasses, which combine both borate and phosphate networks, offer the advantage of having a changeable structure and properties by varying the amount and composition of the modifier. These changes can be made in either the anionic network (e.g., altering the degree of polymerization) or the cationic network (e.g., modifying the charge compensation and distribution of cations). This flexibility allows for tailoring the properties of borophosphate glasses to meet specific requirements, making them useful in a wide range of applications, including fast ion conductors in solid-state batteries and hermetic sealing materials. The primary objective of studying the borophosphate system is to investigate the formation of homogeneous borophosphate glass and understand how the tetrahedra of boron and phosphorous are interconnected within the glass network. Borophosphate glasses are known to contain $P-O-B$ linkages in their structures, which are formed by replacing $P-O-P$ bonds with $B-O-B$ bonds. This substitution leads to the formation of highly cross-linked $P-O-B$ linkages. The addition of $Li_2O-P_2O_5$ to borophosphate glasses has been reported to result in the creation of BPO_4 units and an increase in thermal and chemical stability. This observation was made by Mohan et al. [87]. Furthermore, the mixed glass network effect (MGFE) has been demonstrated in borophosphate glass systems containing sodium ions ($Na_2O-B_2O_3-P_2O_5-GeO_2$). The MGFE leads to a significant improvement in electrical conductivity [99]. Electrical studies have also been conducted on mixed glass former systems, such as $AgI-Ag_2O-B_2O_3-P_2O_5$ [33]. In these systems, the presence of lithium borophosphate glasses has shown enhanced conductivity compared to binary phosphate and borate glasses [88]. Munoz et al,; [89] confirmed that the formation of BPO_4 units, rather than BO_3 units, plays a significant role in enhancing conductivity. They also suggested that reducing the average $Li-Li$ distance further enhances the mobility of Li^+ ions in the glass structure. Overall, the research on borophosphate glasses aims to understand their structural properties, investigate the effects of different additives, and explore their potential applications in areas such as thermal stability, chemical resistance, and electrical conductivity.

(c) Theory of halide salt (MI : $Metal\ iodide$)

Cation mobility is the key factor determining the electrical ionic conductivity of superionic conductors. This mobility is more pronounced in the glass phase of solids compared to the crystalline phase. In these conductors, cations are partially surrounded by oxide anions and partially by anions from the doped salt [102]. The role of the dopant salt in ionic conductivity has long been a subject of debate, beyond its function of providing additional charge carriers. Salt doping has been shown by numerous research groups to enhance conductivity and expand the network structure [24], [28], [30], [31], [33], [32], [90]–[92].

Halide and sulphate-based dopant salts are commonly used. It is widely acknowledged that adding metal halide salts to binary oxide glasses has minimal impact on the connectivity of the host glass matrix. When dopant salts are introduced into the glass, they tend to dissolve into the structure, filling the interstices without significantly altering the glass network [93]–[97].

The presence of heavier halide species disrupts cation-anion bonding and reduces the energy of the conduction band. Mixing halides with alkali and silver-containing borate glasses has been reported to result in a significant increase in ionic conductivity by several orders of magnitude [98]. Adding AgX salts such as $Cl, Br,$ or I does not appear to alter the network units, but it facilitates the conversion of bridging oxygens to non-bridging oxygens (NBOs) [99]. The primary focus of the present research is the investigation of metal halide (dopant) salts, specifically $AgI, NaI,$ and $LiI,$ in order to understand the process of cation ion conduction in the metal oxide modified borophosphate glass system.

According to the Hard-Soft Acid-Base (HSAB) theory, hard acids tend to preferentially bind with hard bases, often through ionic bonds, while soft acids favour soft bases and form strong covalent connections with them [100]. Table 1.3 provides the physio-chemical characteristics of the halide salts of interest, including $LiI, NaI,$ and $AgI.$ Iodide (I^-), a soft base frequently used in our glass systems, tends to bind with metal cations $(Li^+, Na^+, and\ Ag^+)$ following the HSAB principle. For example, the cation Li^+ and the anion I^- are classified as a hard acid and a soft base, respectively. When combined, they form the compound LiI, which partially neutralizes its charges and forms a covalent bond. In the case of NaI, which consists of Na^+ (also a hard acid) and I^- (a soft base), the electron cloud around iodine becomes "looser," allowing it to exhibit some "covalent" behavior as it deforms toward the Na^+ ion. The high conductivity of AgI can be attributed to the disorder in the Ag^+ tetrahedral sites.

Additionally, based on the HSAB theory, the presence of a soft acid and a soft base compound with an enlarged ionic radius due to the iodide anion explains the high polarizability of silver ions in silver borophosphate glasses doped with AgI, leading to very high Ag^+ ion conductivities of the order of $10^{-2}\ S\,cm^{-1}$. It is believed that the presence of $\alpha - AgI$ structures in the glass is responsible for this high conductivity. Furthermore, Ag^+ ions are known to rotate around I^- ions, facilitating a continuous transfer from one I^- ion to another (Magistris et al., 1983) [101]. Table 1.5 clearly indicates that AgI differs from sodium iodide (NaI) and lithium iodide (LiI) in terms of its composition and properties. AgI is a combination of a soft acid and a soft base, exhibiting a higher degree of ionic character and greater polarizability compared to NaI and LiI, which are mixtures of a hard acid and a soft base.

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***Table 1.5**: The physio-chemical properties of studied metal iodide salts.*

Dopant salt	Metal cation Li^+, Na^+, Ag^+ r_c (pm)- size Soft/Hard acid	Halide Anion (I^-) r_a (pm) - size Soft/Hard base	Bond character	Polarizability	Inter nuclear distance (Å)	Dipole moment (μ in C m) (calculated)	Dipole moment (μ in D) (calculated)	r_c/r_a
LiI	76-small Hard acid	220- largest Soft base	Most covalent, less ionic	Less stable and reactive	2.13	3.82E-29	11.47	0.34
NaI	102-intermediate Hard acid		less covalent, intermediate	Less stable and reactive	2.71	4.33E-29	13.00	0.46
AgI	115-large Soft acid		least covalent, more ionic	Highly polarizable	2.87	4.59E-29	13.76	0.52

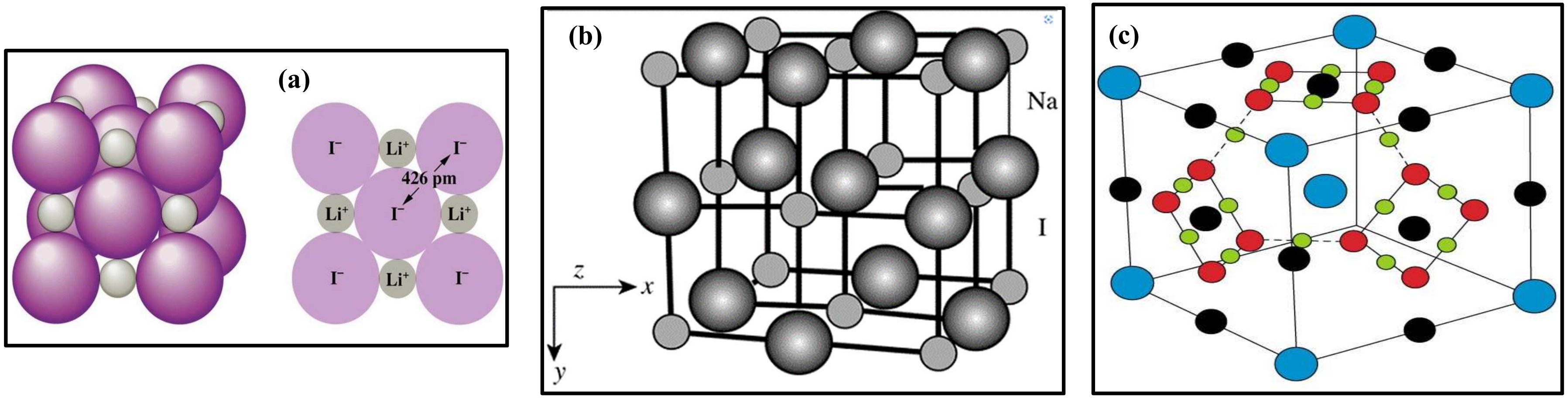

***Figure 1.4**: Lewis structure of (a) LiI- strong covalent bond (b) NaI- less covalent, and (c) α − AgI-ionic bond with **I⁻**, **tetrahedral**, **trigonal** and **octahedral interstitial sites** present in the structure [62], [102].*

Additionally, AgI possesses larger values for internuclear distance, dipole moment, and cation-to-anion radius ratio. As a result, the likelihood of a cation, such as Ag^+, dissociating from an AgI compound is high, while the probability of Na^+ separating from NaI is relatively low, and the lowest probability is associated with the liberation of Li^+ from the LiI compound.

1.5 Application of ion conducting glass materials

Since the inception of the solid-state ionic field, numerous novel materials have been developed and extensively investigated with the aim of enabling their utilization in a wide array of devices. These materials hold promise as electrolytes in electrochemical devices such as solid-state batteries, fuel cells, and electrolyzers. They also find applications in auto exhaust gas sensors, supercapacitors, and electrochromic devices like smart windows. Furthermore, these materials can be employed in electron beam recording. Recently, there has been growing interest in utilizing similar materials in a memory device called the "memristor." These memristors exhibit rapid operation speeds of less than 10 nanoseconds and are believed to be controlled by the electro-migration of cations or anions.

1.6 Motivation and objective of present work

The metal oxide-modified borophosphate glass series was prepared by incorporating three different metal oxide compositions into the borophosphate matrix. These metal oxides were selected based on their potential to modify the electrical and physical properties of the glass. Additionally, the metal iodide (MI) dopant salt was introduced to further enhance these properties.

The choice of borophosphate glass as the base framework is significant because it offers a versatile platform for studying ion conduction mechanisms. Borophosphate glasses are known for their unique structural characteristics and high ionic conductivity, making them suitable for investigating ion transport in glassy electrolytes. To investigate the relationships between composition, structure, and conductivity, impedance spectroscopy was employed. Impedance spectroscopy is a powerful technique used to analyze the electrical response of materials and provides valuable insights into their conduction mechanisms. By systematically varying the metal oxide compositions and incorporating the MI dopant salt, the research aimed to gain a thorough understanding of the ion conduction mechanism in the mixed glass former network. This understanding would then be applied to maximize the physical properties of the materials.

Overall, the objective of the research was to study and optimize the ion transport mechanism in glassy electrolytes by exploring the role of various metal halides as dopant salts in a mixed glass former framework. The borophosphate glass series, modified with metal oxides and MI dopant salt, served as the experimental system to achieve these research goals.

General formulation for the ternary borophosphate glass system is followed here.

$$\boldsymbol{x(MI) - (100 - x)[M_2O{:}\,(B_2O_3 + P_2O_5)];\, where\ M = Li, Na, Ag}$$

The compositional borophosphate glass series are as follows,

Series (a): $x(LiI){:}\,\{(100 - x)[60\, Li_2O{:}\,(8\, B_2O_3 + 32\, P_2O_5)]\}$, known as LBP

$where, 0 \leq x \leq 25\ wt.\%, with\ interval\ of\ 5\ unit$

Series (b): $x(NaI){:}\,\{(100 - x)[30Na_2O{:}\,(56\, B_2O_3 + 14\, P_2O_5)]\}$, known as NBP

$where, x = 1, 2.5, 4, 5, 10, 15, 20\ wt.\%$

Series (c):$x(AgI){:}\,\{(100 - x)[30\, Ag_2O{:}\,(56B_2O_3 - 14\, P_2O_5)]\}$, known as ABP

$where, x = 0, 1, 3, 5, 7\ wt.\%$

To investigate the influence of metal iodide (MI) salt added to above glass series, with the glass compositions (MI) : $(\, M_2O - B_2O_3 - P_2O_5)$ has been selected for investigation.

As for glass series (a), a composition ranging from pure lithium borophosphate to lithium iodide doped $(up\ to\ x\ =\ 25\, wt.\%)$ lithium borophosphate glass was chosen. Lithium oxide (Li_2O) functions as a glass modifier in the boro-phosphate host glass matrix with the glass forming ability by maintaining an F/M ratio of 0.66. Lithium iodide(LiI) dopant liberates the majority of its lithium ions (Li^+) according to the HSAB theory. These liberated lithium ions influence the electrical characteristics and ion dynamics. Eventually, the ion transport takes place as a function of the LiI concentration in the glass framework. In the present study, the glass former to modifier ratio of 2.33 was selected for both the sodium borophosphate glass series (b) and the silver borophosphate glass series (c). This ratio was chosen based on considerations of the glass forming conditions. For the sodium borophosphate glass series, sodium iodide (NaI) additions ranged from $x = 1\ to\ 25\, wt.\%$ in order to investigate the influence of different concentrations of NaI on the glass properties. On the other hand, the silver borophosphate glass series encompassed compositions ranging from zero to $25\, wt.\%\ AgI$ content, exploring the impact of varying silver iodide concentrations. To understand the structural characteristics of the halide-doped phosphate and borophosphate glasses, several techniques were employed. X-ray diffractometer (XRD) was used to analyze the crystallographic structure, while field-emission scanning electron microscopy (FE-SEM) provided information on the surface morphology. Fourier transform infrared (FT-IR) spectroscopy was utilized to investigate the molecular vibrations and bonding in the glass samples. The deconvolution of FT-IR spectra technique specifically focused on the borophosphate glass system to determine the influence of iodide compounds and mixed glass formers on the structure and conductivity of the glass. The glass transition temperature (T_g) of the glasses was determined using Thermo-Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA), which allowed for the identification of the temperature range in which the glass transitions from a super cooled liquid to a solid.

In order to gain a better understanding of the mechanism of metal cation (M: $Li^+/ Na^+/ Ag^+$) transport, relaxation behavior, and ion dynamics in the MI: (M_2O: B_2O_3: P_2O_3) glass systems, frequency-dependent impedance spectroscopy was employed. Impedance spectroscopy was conducted at different temperatures and utilized various formalisms to investigate the electrical conductivity, dielectric properties, and ion transport phenomena in the glass samples. By employing these techniques and conducting the aforementioned investigations, the research aimed to comprehensively understand the structural, physical, and electrical properties of the halide-doped borophosphate glass systems, with a particular focus on the role of metal cations in the ion dynamics and conductivity of the glasses.

During the investigation, several studies were conducted to achieve a comprehensive understanding of the ion transport mechanism in the metal halide-doped borophosphate glass system.

The following is a list of the main studies carried out:

1. X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM) techniques were employed to determine the structural characteristics of the halide-doped phosphate and borophosphate glasses. Glass transition temperatures were determined using Differential Thermal Analysis (DTA), and bulk density was measured using Archimedes' principle.
2. Impedance spectroscopy was utilized to study and analyze the electrical conductivity, dielectric parameters, and electric modulus formalism of the prepared glass series samples. This technique provided insights into the ion transport behaviour and allowed for the investigation of conductive pathways.

3. The characteristics of cation transport dynamics were identified and understood, including factors such as molar volume, oxygen packing density, and Fermi energy level. These parameters were studied to gain insights into the mechanisms of metal cation $Li^+/Na^+/\ Ag^+$ transport in the glass system.
4. The influence of the mixed glass former effect, the role of network modifiers, and the concentration of metal halide dopants were investigated. A comparative analysis was conducted to better understand the distinct ion transport behaviour in the borophosphate glass system.
5. Various theoretical models developed by researchers were explored to gain a deeper understanding of the ion transport mechanism in the investigated samples. These models helped in interpreting the experimental results and establishing theoretical frameworks.
6. Several conductivity and modulus formalisms were investigated to gain insights into the relaxation phenomenon and its Time-Temperature Superposition behaviour. These formalisms provided a better understanding of the dynamic behaviour of ions in the glass system.

By conducting these studies, the research aimed to achieve a comprehensive understanding of the ion conduction mechanism in metal halide-doped borophosphate glasses, with the ultimate goal of optimizing the physical properties of these materials.

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