Alkali Ionic Conductivity in Inorganic Glassy Electrolytes

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Abstract

Glassy electrolytes could be a potential candidate for all-solid-state batteries that are considered new-generation energy storage devices. As glasses are one of the potential fast ion-conducting electrolytes, progressive advances in glassy electrolytes have been undergoing to get commercial attention. However, the challenges offered by ionic conductivity at room temperature (10^{-5} - 10^{-3} S·cm^{-1}) in comparison to those of organic liquid electrolytes (10^{-2} S·cm^{-1}) hindered the applicability of such electrolytes. To enhance the research development on ionic conductivity, the overall picture of the ionic conductivity of glassy electrolytes is reviewed in this article with a focus on alkali oxide and sulfide glasses. We portray here the techniques applied for alkali ion conductivity enhancement, such as methods of glass preparation, host optimization, doping, and salt addition for enhancing alkali ionic conductivity in the glasses.
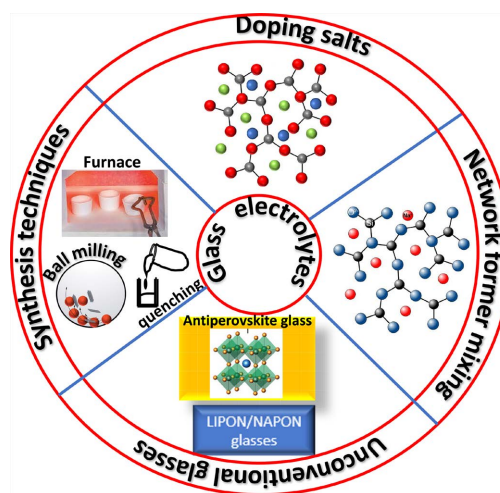
Keywords

Glass Electrolyte, Solid State, Ionic Glass, Battery, Charge, Antiperovskite, Ionic Conductivity

1. Introduction

Since the first commercialization of Li-ion batteries in 1991 [1], many attempts have been made for the revolutionary improvement in safety, efficiency, and durability of batteries that have powered today's essential mobile electronic devices, such as laptops, mobile phones, and electric vehicles all over the world. As the demand for high-performance energy storage and conversion technologies for portable electronic equipment, electric vehicles, and large-scale energy consumption increases, a new type of battery is needed to be developed [2]. Though the Li-ion technology plays a key role in the transport sector, it could not fulfill the demand for the stationary storage sector because of its limited source of availability related to high cost [2]. As an alternative, Sodium-ion battery technology has recently been under study because it is relatively more environmentally friendly and more abundant on the planet [2]. Commercially, available all these batteries consist of two electrodes connected by a liquid electrolyte. The performance of a battery is basically rooted in the efficiency of its electrodes and electrolyte [3]. Most sodium and lithium-based batteries currently in use still depend on liquid-organic electrolytes, which pose restrictions on cyclability due to electrode corrosion, high flammability, and highly resistive solid electrolyte interphase (SEI) formation at the electrodes leading to capacity loss, and risk of leakage [4]. Extensive research works are being conducted for developing solid electrolytes that can be potential candidates to replace liquid electrolytes [5]. All-solid-state batteries (ASSBs), where the electrolyte is also solid, are the safest batteries with no leakage, no volatilization, or no flammability. Generally, solid-state electrolytes can be categorized into inorganic glass/ceramic electrolytes, organic polymer electrolytes, and ceramic-polymer composite electrolytes. The inorganic electrolyte is essential for rigid battery design for its good thermal/chemical stability, wide electrochemical window, high ionic conductivity and low electronic conductivity [6]. Toyota Motor Corp, Japan, for the first time, revealed the prototype of its ASSB on 18 November 2010, in Japan. The battery used a sulfide solid electrolyte of the system Li_2S-P_2S [7]. The same company presented a new prototype of ASSB with five times higher output density after two years. The main improvement in the battery was focused on sulfide-based solid electrolyte, $Li_{10}GeP_2S_{12}$ which showed an ionic conductivity of lithium (Li) ions as high as 1×10^{-2} S·cm^{-1} [7]. Thus, inorganic solid-state electrolytes drew much attention in research. Inorganic solid electrolytes can be crystalline, glassy and glass ceramic electrolytes [5]. Glassy electrolytes are one of the promising candidates as inorganic solid electrolytes, applicable to all-solid-state battery sys-

tems. Such systems offer enhanced safety, simplified cell design and environmental sustainability.

Glasses are amorphous solids that can be distinguished by their unique property known as glass transition temperature. Glasses exhibit variations of thermal expansivity, heat capacity, entropy, viscosity, and entropy. Glassy electrolytes are more attractive compared to their crystalline counterparts in electrochemical applications because they are cheaper, without grain boundaries, easy to fabricate into complex shapes and resistant to environmental effects [8] [9]. They have a wide range of compositional adjustment and isotropic conductivity [8]. Glass electrolytes are considered to exhibit higher ionic conductivity than that corresponding crystalline ones [10] [11] [12]. Depending on the type of ions taking part in conduction and chemical composition, the glasses are classified as shown in the following flow chart (**Figure 1**) [9].

Ionic glasses are generally formed by mixing network modifier, network former and dopant salt in different proportions [13]. Sometimes, intermediates (Al_2O_3, Ge_2O_3, etc.) are also used. Usually, glass network formers are oxide/sulfide materials of covalent nature (e.g. SiO_2, B_2O_3, P_2O_5, SiS_2, P_2S_5, etc.). These oxides and sulfides, when quenched, facilitate glass formation by forming cross-linked macromolecular chains. In general, alkali metal oxides or sulfides (e.g. Li_2O, Na_2O, K_2O, etc.) are used as a modifier, which is ionic in nature [14]. The modifier interacts strongly with the structural units of the network formers leading to the progressive breaking of oxygen or sulfur bridges to result in the maximum number of non-bridging oxygen or sulfur atoms. It reduces the average length of the macro-molecular chain, as shown in **Figure 2**. This lacks long-range order and creates more disorder in the material leading to the formation of interconnected "open channels" or sites, which act as conduction pathways for the charge carriers in the glass matrix [14] [15]. For example, when Li_2O or Na_2O is added as network modifiers to vitreous silica, it results in the chain breaking of the network. It transforms bridging oxygen atoms into non-bridging oxygens, but the silicon atoms remain tetrahedrally coordinated.
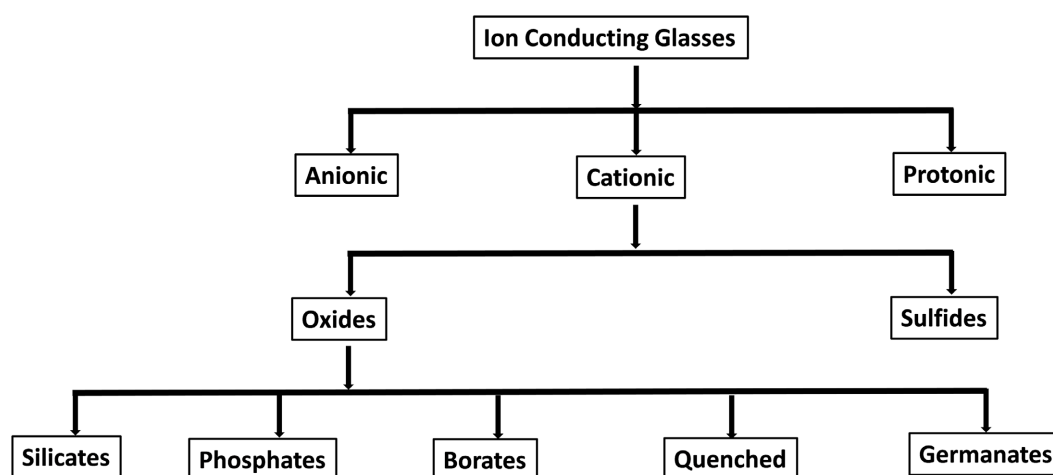

Figure 1. Flow chart for alkali ion conducting oxide and sulfide glasses.

The positive cations are situated near the anionic sites of the non-bridging oxygens for providing local charge neutrality (see **Figure 2**). Non-bridging oxygen sites offer the hopping site for ionic conduction in an oxide glass network. Cations such as Li^+ jump into or out of these hopping sites easily due to relatively weak bonding or shallow energy well [16] [17] (see **Figure 3**). The formation of non-bridging oxygen also contributes to the open network structure with increased free volume for ion conduction [16]. Thus, the increase in alkali-ion (such as Li^+) mobility is due to the formation of the non-bridging oxygens or broken bonds within the glass network. In principle, the positively charged cations are localized in interstitial sites by insertion of the modifier anions into the network chains. It develops ionic bonds between the modifier cations and network anions. With the increase in modifier concentration, adjacent negative anion sites come closer decreasing the depth of the potential well in the energy profile. The ionic transport path becomes favorable when such wells are densely interconnected in the glass. Thus, increasing modifier concentration enhances the ionic conductivity of glasses [18]. However, increasing modifier concentration may cause the glass less stable and with low glass transition temperature. Some
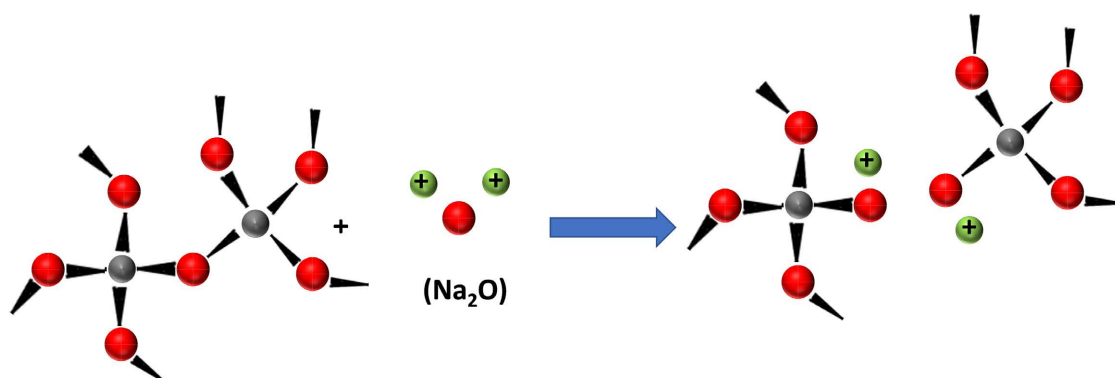

Figure 2. Silicate network cleaved by Na_2O (former) to form nonbonding oxygens (brown, red and green spheres represent Si, O and Na atoms, respectively).

(a)   **(b)**
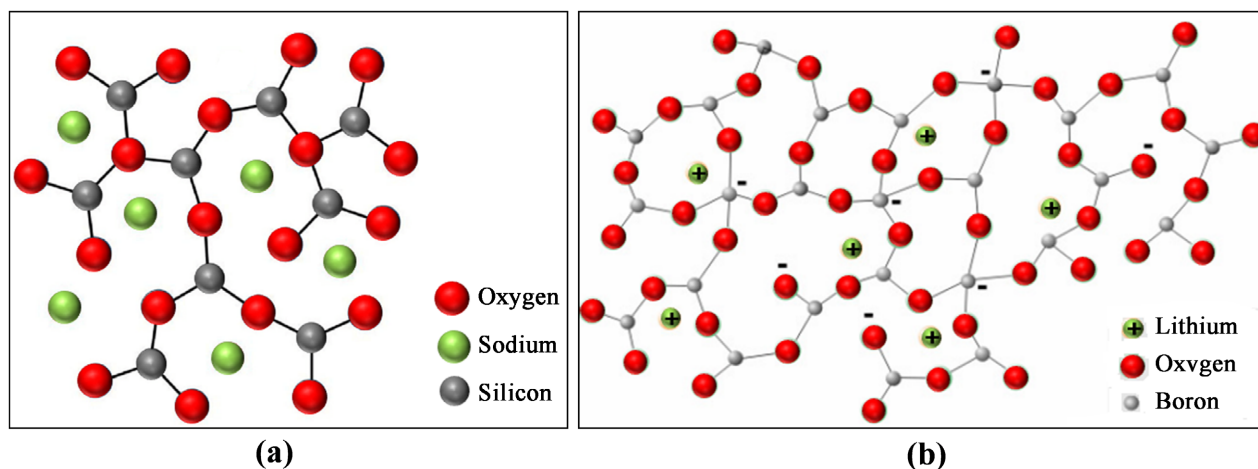
Figure 3. Schematic two dimensional representations of (a) tetrahedrally coordinated silica glass and (b) tetrahedrally and trigonally coordinated borate glass.

examples can be discussed here for the effect of modifier addition on glass networks. In borate glasses, alkali oxides addition to B_2O_3 limits the glass network for a certain boron atoms concentration. In such a case, the added alkali oxide molecules form four-coordinated boron atoms. They form tetrahedral BO_4 units that provide anionic sites for the alkali ions with relatively small binding energy [19]. BO_4 tetrahedra have larger molecular diameters and its oxygens provide relatively weaker ionic field strength to alkali ions (such as Li^+) compared to the field offered by nonbridging oxygen in a 3-coordinated boron structure. The 3-coordinated non-bridging oxygens (negative sites) have binding energies different from those of localized BO_4 units [18]. Thioborate glasses xLi_2S-$(1 - x)B_2S_3$ have also been reported to change four-coordinated boron atoms to three-coordinated with the rise of modifier concentration. Here also, the formation of non-bridging sulfur atoms causes the depolymerization in the thioborate matrix [18] [20].

Ionic salts or dopant salts can be added to a glassy matrix because the addition can significantly enhance the ionic conductivity by several orders of magnitude compared to the one without the salts. In most cases, these additives are halides, phosphates or sulfates which contain the common cation of the network modifier. For these salts, the glass matrix acts as a solvent. When salt is added to the glass matrix, it affects the bonding network between the network former and the glass modifier influencing the network rigidity of the glassy material which leads to reduced activation energy and enhanced conductivity. When lithium salts LiX (X = F. CI. Br or I) were added to lithium borate glasses B_2O_3-Li_2O, the local structural modifications were found which were attributed to interactions between the network and the anions of the doping salt [18] [21]. Though the cations play a dominant role in ionic conductivity, both cations and anions are adjusted interstitially into the glass [22] [23]. Spectroscopic studies revealed that halogenide ions, Cl^- and Br^-, when doped in borate glasses distribute in interstitial positions in the glass matrix [24] but sulfate tetrahedra are incorporated in macromolecular chains [25]. Li_2SO_4 addition forms six-membered rings with BO_4 tetrahedra. However, sulfate anions are completely dispersed in the B-O network for high Li_2O-containing ternary glasses, and increase the concentration of non-bridging oxygen atoms [26]. There is evidence of spectroscopic study for the accumulation of sulfate in the glass network without changing the structure of the B-O matrix by the addition of Li_2SO_4 [27] [28]. Li_2SO_4 can also be added like Li_2O in borate glasses. When Li_2SO_4 is added to lithium borate glass, it can create defects through the modification of the macro-molecular chain as shown below in **Figure 4** [9] [25].

Here, the conduction in glass is considered to take place through a defect type of mechanism [9]. A report mentions that the dopants (salts) do not react with the network former but their dissolution is only due to electrostatic interactions. The addition of ionic salts also rises the amount of charge carriers [14]. Thus, two contributions assist in the increase in ionic conductivity: high mobile cations concentration and redistribution of the sites suitable for ionic motion [18].
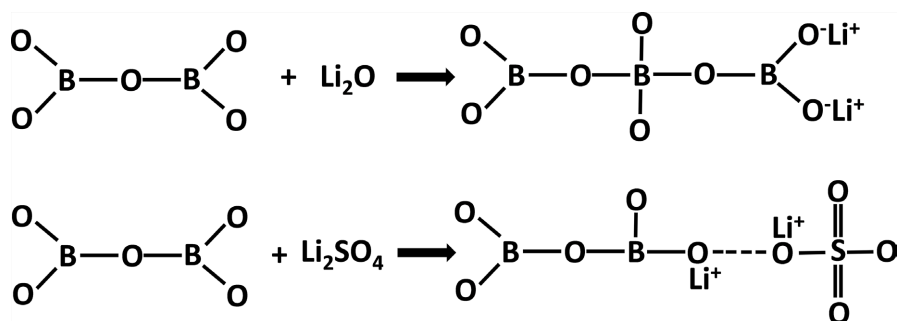
Figure 4. Schematic reaction for Li$^+$ ion arrangement in borate glass. Defect is created around the second B when Li$_2$SO$_4$ is added.

It is believed that binding energies and migration energy barriers control the magnitude of the glass conductivity as will be discussed below. Binding energy is associated with the degree of the mobile ions at their equilibrium (metastable) sites while the migration energy barrier is associated with the volume requirements for their movement [29]. However, a recently published theoretical study reports a new possible mechanism, the paddle wheel mechanism, for cation mobility in glasses with complex anions. The glasses with complex anions and short-range covalent networks are expected to accelerate cation mobility at low temperatures due to paddlewheel dynamics [30].

The glassy solid electrolyte system, AgIAg$_2$SeO$_4$, had conductivities of approximately 10^{-2} S·cm^{-1} at room temperature [31]. Though the first study of a glassy solid electrolyte system, AgIAg$_2$SeO$_4$, had been reported by *Kunze* in 1973, Oxide-based materials, in lithium silicate, borate, phosphate or germanate glasses, such as Li$_2$O-SiO$_2$-Al$_2$O$_3$ [32] had already been studied. We discuss the practice of improving room temperature conductivity of alkali ion conductivity in oxide and sulfide glasses based on the following 4 methods [29]:

1) By adding alkali halide or alkali oxysalt;
2) By adding other glass networks former (mixed glass former effect);
3) By anion mixing effect;
4) By synthesis technique.

These methods are believed to follow the following conduction behaviors in glasses.

1.1. The Strong-Electrolyte Model

According to this model, the effective carrier density is independent of temperature and ion concentration. All ions are mobile while the strain (mobility) energy dominates the direct current (DC) conductivity. This model, also called the *Anderson-Stuart model*, is based on a thermally activated charge hopping process for DC conductivity in the glass. This involves the activation energy required for the migration of cations as studied in alkali silicate glasses. According to this model, a cation hops from an occupied site close to a negatively charged counter ion (such as a non-bridging oxygen (NBO) site in an oxide glass) to a vacancy near another NBO site. To accomplish the hopping, the ion needs to

pass through a *gateway* formed by bridging oxygen (BO) atoms (**Figure 5**) [33]. Here, activation energy (E_σ) is related to an electrostatic binding energy (E_b) required to remove a cation from an NBO site and a strain energy (E_s) of long-range mobility or gate-passing.

$$E_\sigma = E_b + E_s \tag{1}$$

where E_σ is the difference between the maxima of the energy where the cation is located halfway between neighboring sites and the bottom of the energy well, where the cation normally resides without conduction activity.

1.2. The Weak-Electrolyte Model

This approach relates to correlations between thermodynamic activity and ionic conductivity of fast ion-conducting glasses. According to this model, mobility is independent of temperature and ion concentration while the coulomb energy is dominant in the DC conductivity. This approach is widely used to describe the conductivity in silica-based glass. The large increases in conductivity in Na_2O-SiO_2 glasses are associated with large increases in Na_2O activity.

2. Common Characterization Techniques

Some common characterization techniques are mentioned here for general information. Glasses pose relatively more challenges to structural elucidation than crystalline solids do. Diffraction techniques can only be used to identify the
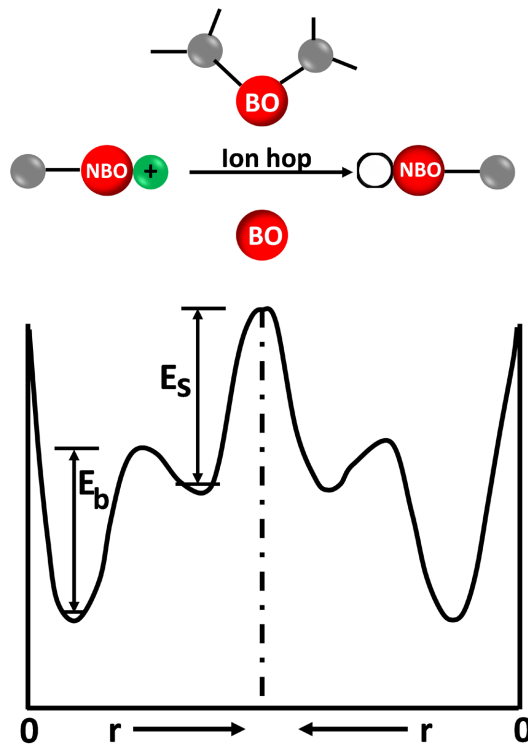

Figure 5. Energy diagram for ion hopping from one site to other in *Anderson-Stuart model*. Red, green and brown spheres represent oxygen (negatively charged), Lithium (or sodium) and silicon (or boron) atoms, respectively.

formation of the glassy state but not to resolve structural details of the glassy state owing to the absence of long-range periodicity. Generally, the structural analysis of glassy state emerges from the joint interpretation of numerous complementary spectroscopic experiments. Some of the widely used common techniques for ion conductive glass characterization are:

1) XRD;
2) DSC;
3) FTIR;
4) Raman spectra;
5) Solid state NMR.

2.1. XRD

X-ray diffraction (XRD) is the chief tool generally used for the identification of glassy/amorphous phase formation for a solid-state material. The molecules or the ions in glass or amorphous solids are arranged in disordered manner lacking 3-D periodicity. Due to the absence of long range ordered arrangements in glasses or amorphous solids, their X-ray diffraction patterns normally contain diffused broad peaks or do not show any peaks in contrast to those of polycrystalline solids which show well-defined sharp diffraction peaks [34] due to the existence of 3-D regular periodic lattice and long-range ordered structural arrangements. Since pure glassy/amorphous solids contain only a few broad/diffused patterns, the presence of broad-diffused peak in the XRD pattern confirms the formation of the glassy/amorphous phase. If a material contains mixed glassy/amorphous solids, XRD pattern contains sharp peaks along with the broad diffused peaks [35] [36] [37] [38]. **Figure 6** shows the distinction between the X-ray diffraction patterns of glassy or amorphous state and crystalline solid.

2.2. DSC

Glasses show transition from hard brittle to softer rubbery state over a narrow temperature range referred to as a glass transition temperature (T_g). The
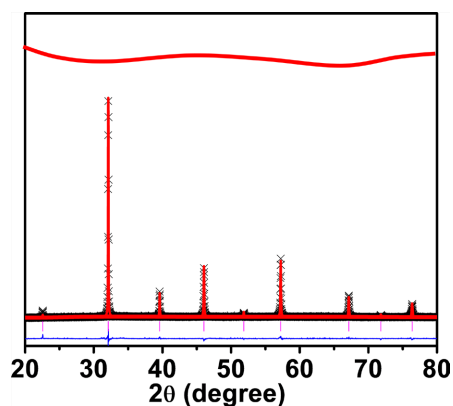

Figure 6. X-ray diffraction for a) diffused peak (upper) representing the formation of glass or amorphous phase and b) sharp peaks (lower, rietveld refined) representing the formation of the crystalline phase.

temperature (T_g) is a characteristic of a glass or amorphous material. Differential scanning calorimetry (DSC) is generally used to characterize the T_g of a glass. T_g can be differentiated from the other two thermal transition temperatures: melting temperature T_m and crystallization temperature (T_c) of a glass or amorphous material in DSC plot. During the T_g measurement in DSC, we may get different curves as shown in **Figure 7**; a dip for melting temperature T_m where a material absorbs heat and melts, a peak for crystallization (T_c) where a material releases heat and crystallizes. For glass transition, there is neither a dip nor a peak, but a slow slope as shown in **Figure 7**. T_g is specific to a particular glass for a particular composition. Sometimes, differential thermal analysis (DTA) is used instead of DSC.

2.3. FTIR and Raman Spectroscopy

Infrared spectroscopy (IR) is used to study the structure and dynamics of amorphous materials [39] [40]. Since glasses lack long range order, the vibrational spectroscopy has strong impact on their structural studies than that of crystalline solids which have long range order and for which diffraction method is probably more informative.

Glass structure can also be studied by Raman spectroscopy [40] [41]. It is also used to study the structural changes like crystallization during the fabrication of glass ceramic materials. This technique involves the comparison of peaks (*Raman shift*) to probe the vibrational levels of specific groups of atoms or ions.

2.4. Solid State NMR

NMR has been used for structural investigation of glassy solids [41] [42]. For example, it has been applied to figure out the relative concentration of three- and four-coordinate boron atoms in alkali borate glasses [43]. Many factors are
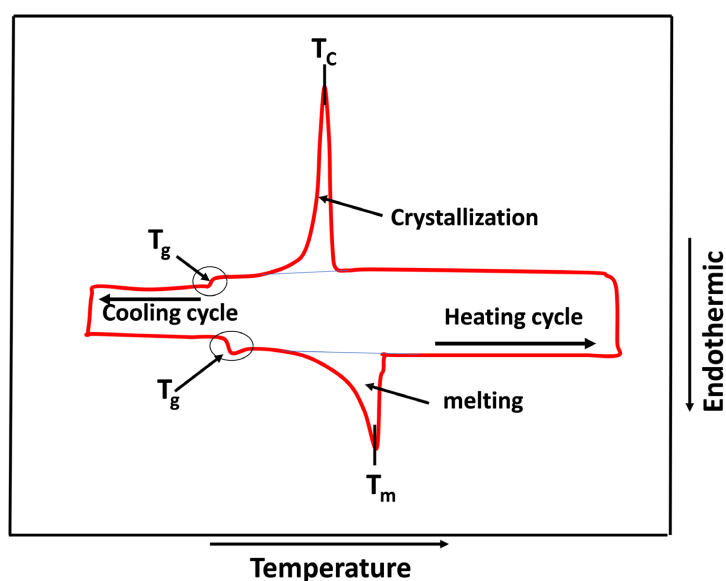

Figure 7. Representative DSC plot of a glassy material.

to be considered during the NMR spectra analysis. In general, the range of chemical shift for different coordination numbers of most commonly studied nuclei are defined based on the comparison with the NMR peaks of known crystalline compounds.

3. Oxide Glasses

3.1. Binary Oxide Glasses

As mentioned above, alkali ion conducting oxide glasses may be prepared from silicate, borate, phosphate and germanate. There are studies of other oxide glass systems as well. Nassau and Grasso in 1979 studied the binary glass system in $Li_2O-Al_2O_3$ and $Li_2O-Ga_2O_3$ [44]. The ionic conductivity is different for different glasses and it is dependent on different factors. Steve W, Martin, 1991 collected some data from previous reports to review the composition dependence of the conductivity and activation energy for binary oxide glasses such as $Li_2O + P_2O_5$ [45] [46], $Li_2O + B_2O_3$ [47] and Li_2O+SiO_2 [13]. For the same amount of Li_2O composition, the conductivity was found to increase from $Li_2O-P_2O_5$ to $Li_2O-B_2O_3$ to Li_2O-SiO_2 [13] [29] [45]. The reason behind the conductivity trend was attributed to the fraction of Li^+ cation to oxygen with full negative charge (0.5 for $SiO_2 > 0.33$ for $B_2O_3 > 0.25$ for P_2O_5) [13] [45]. R. F. Bartholomew [48] reported the ionic conductivity of phosphate groups in $xNa_2O + (1 − x) P_2O_5$ systems. It was reported that the energy barrier to ion migration in the $Na_2O-P_2O_5$ glass (18.8 kcal/mole) is higher than that for the Na_2O-SiO_2 glass, (13 - 14 kcal/mole) [48]. At room temperature, Na_2O-SiO_2 glass has resistivity of 3.5×10^7 Ω/cm which is two order less than that of the $Na_2O-P_2O_5$ glass (7.7×10^9 Ω/cm) [48]. Li-based phosphate series were discussed for $xLi_2O + (1 − x) P_2O_5$ series [29] [45]. Some research groups have also studied lithium germanate glasses $xLi_2O-(1 − x)GeO_2$ [$x = 0.002 - 0.25$] [49] [50]. In the case of Li-borate glass, M.R.S. Abouzari, in 2007 (Thesis) [51], reported that the conductivity of lithium borate thin films of composition 0.20 $Li_2O-0.80$ B_2O_3 depended strongly on the film thickness [51]. **Table 1** shows the highest ionic conductivities of Li and Na-based

Table 1. Ionic conductivities of $Li_2O-P_2O_5$ to $Li_2O-B_2O_3$ to Li_2O-SiO_2 glass systems at 25˚C.

Glass systems	σ at 25˚C (S·cm^{-1})	References
62Li$_2$O-38SiO$_2$ and Li$_2$S-SiO$_2$ (thin film)	~10^{-5}	A. Chandra *et al.* [52] Radhakrishna [53]
0.35Li$_2$O-0.75B$_2$O$_3$ (film)	2.5×10^{-6}	M.R.S. Abouzari [51]
50Li$_2$O-50P$_2$O$_5$	2.8×10^{-9}	M. Ganguli *et al.* [54]
0.3Li$_2$O + 0.7GeO$_2$	4.3×10^{-7} at 200˚C	K. Radhakrishnan *et al.* [55]
Na$_2$O-GeO$_2$	2.3×10^{-5}	D. Ravaine [15]
Na$_2$O-SiO$_2$	2.0×10^{-7} at 30˚C	D. Ravaine [15]
Na$_2$O-B$_2$O$_3$	~10^{-9}	R. Christensen *et al.* [56]
Na$_2$O-P$_2$O$_5$	5.6×10^{-11}	D. Ravaine [15]

binary glasses.

The pseudo binary system, ortho-oxo salt compositions were found to contain high Li ion concentration and exhibit high conductivities. Some research groups studied a series of lithium ortho-oxo salt such as Li_4SiO_4-Li_3BO_3 and Li_3BO_3-Li_2SO_4 glasses for Li ion conduction [57] [58] [59]. The conductivity for different (mol%) compositions of x = 0, 5, 10, 15, 25, 50, 60 in glassy samples of $(100 - x)Li_3BO_3$-xLi_2SO_4 was reported. The conductivity was nearly 10^{-6} S·cm^{-1} at room temperature for x =10 [57] [58]. The increase of conductivity is observed with the addition of small amounts of Li_2SO_4. This is considered to be due to the so-called anion mixing of the glasses and/or the improvement of packing density of the pellet after cold press [57]. Some researchers reported in 1977 that large amounts of LiX, (X = I-, Br-, and CI-) were dissolved into $LiPO_3$ glass [60] [61]. The conductivity increases in the order from I > Br > Cl addition in $LiPO_3$ as shown in **Figure 8**. Martin and Angell compared the effect of addition of Li_2O and LiI to $LiPO_3$ and reported that LiI increases the conductivity and decreases the activation energy than when Li_2O is added. It is also suggested that substituting the larger I^- ion for O^{2-} produces a wide range of compositional effect on the conductivity as in the case with other halides [29] [45]. J.P. Malugani *et al.* suggested that when Li^+ cation is associated with a larger singly charged anion and an oxygen anion, the dissociation energy of the Li^+ cation from halide anion would be less than that from oxygen anion. Hence, the LiX-doped glasses are found with much higher conductivities (see **Figure 8**). They prepared glasses in the Li_2SO_4 + $LiPO_3$ series and reported that addition of Li_2SO_4 in place of LiX (X = Cl, Br, I) and Li_2O increased conductivity [62]. A report suggested that the electrical conductivity in glasses of the Li_2SO_4-$LiPO_3$ system increases upon introduction of lithium sulfate into lithium metaphosphate due to the change in the mechanism of charge carrier migration. It reported that S ions are incorporated into polyphosphate structural fragments as terminal groups (**Figure 9(a)**), while in lithium metaphosphates, the lithium ions are found migrating through the interstitial mechanism. Li_2SO_4 addition increased charge carrier concentration that was reported to migrate through vacancy mechanism leading to enhancement in conductivity [63]. Another report suggests that the higher
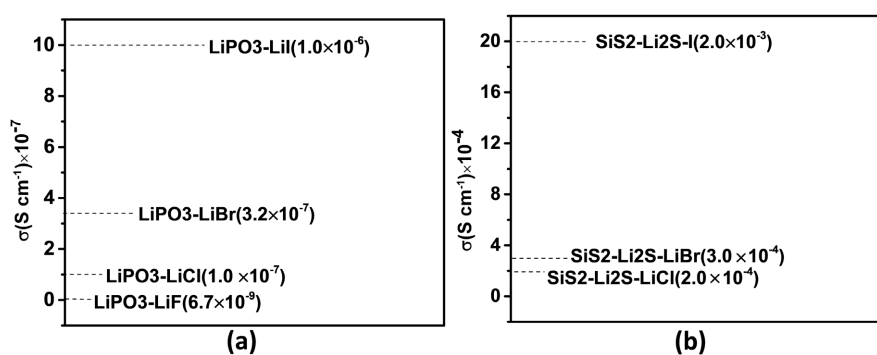

Figure 8. Order of conductivity as an effect of LiX (X = F, Cl, Br and I) addition to (a) $LiPO_3$ and (b) Li_2S-SiS_2 glass systems.
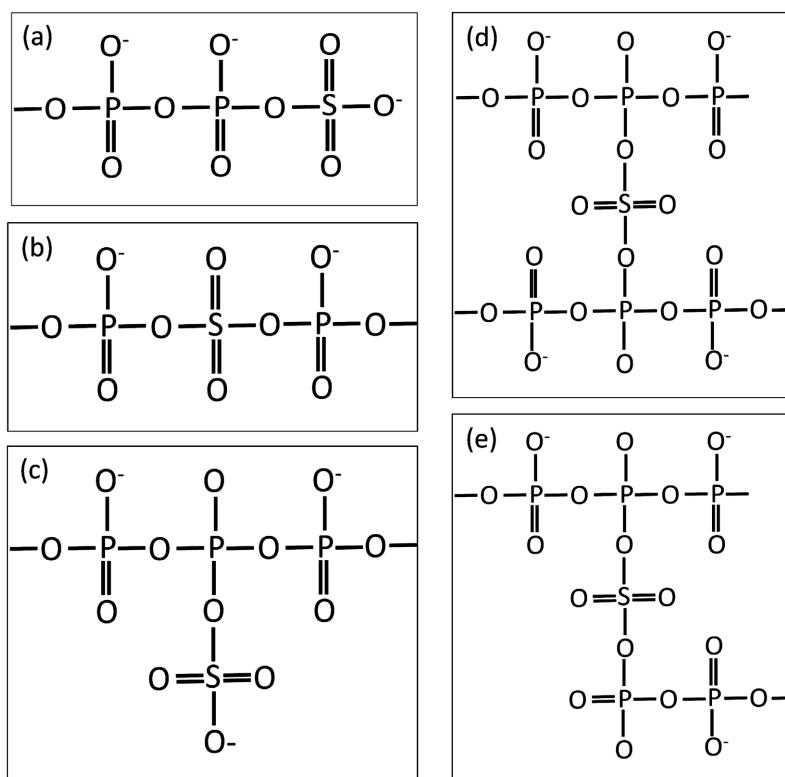
Figure 9. Five different possible structural positions of sulfate in sulfate–polyphosphate chains.

conductivity after Li_2SO_4 introduction is due to the relative weaker columbic force of oxygen in SO_4^{2-} (−0.5 partial formal charge of oxygen) to Li ion compared to that of the oxygen of P-O⁻ entities on the phosphate chains (single negative charge on oxygen) [54]. Different structural arrangements of PO_4^{3-} and SO_4^{2-} groups have been discussed such as SO_4^{2-} group attached terminally to the PO_4^{3-} chains [63] [64], inserted in between PO_4^{3-} groups forming long chain of PO_4^{3-} and SO_4^{2-} groups [65] or sulfate groups are not incorporated into phosphorus–oxygen chains of the initial glass but form an independent sulfur–oxygen network [66]. Even it is hypothesized that sulfur can occupy five different structural positions in sulfate-polyphosphate chains [67] (**Figure 9**). It is also reported that the ortho-oxosalt compositions contain high Li ion concentration and exhibit high conductivities. Thus, the ortho-oxosalt compositions can show improved conductivities. Since, it is difficult to synthesize ortho-oxosalt compositions by melt quenching technique, Hayashi *et al.* studied the systems $Li_2O\text{-}M_xO_y$ (M = B, Si, P, Ge or Al), by mechanical milling which exhibited the glass forming region wider than that by rapid quenching [59]. Similarly, Glasses of Li_3BO_3 and Li_4SiO_4 compositions were also reported for the fabrication by mechanical milling [57].

Compared to Li-glasses, fewer studies can be found for ionic conductivity of binary system of sodium-based glass. Sodium ion conductivity was reported for binary system in $Na_2O\text{-}B_2O_3$ which was prepared by melting borax at tempera-

tures sufficiently high for dehydration without significant volatilization. The resistivity at 300°C was reported to be ~ 6×10^4 Ω/cm [68]. A report mentions the conductivity of ~10^{-9} S·cm⁻¹ for Na_2O-B_2O_3 glass [69]. Na_2O-GeO_2, Na_2O-SiO_2 and Na_2O-P_2O_5 glasses were reported to exhibit the conductivity of 2.3×10^{-5}, 2.0×10^{-7} and 5.6×10^{-11} S·cm⁻¹, respectively [15]. Sodium-based Ortho-oxo salts were also studied, on $(100 - x)Na_3BO_3$-xNa_2SO_4 ($0 \leq x$ (mol%) ≤ 50). The glasses were fabricated by mechanical milling [10]. $50Na_3BO_3 \cdot 50Na_2SO_4$ glass were reported for the highest conductivity of 5.9×10^{-8} S·cm⁻¹ at 25°C.

3.2. Ternary and Quaternary Oxide Glasses

In the attempts to improve the ionic conductivity of glassy electrolytes, the studies were not limited to binary systems. Ternary or quaternary glass systems were also studied and were found to improve ionic conductivity. The conductivity of Li-glass can be improved by increasing the amount of Li^+ ions [44]. The Li ion can be increased by incorporating more Li ion into oxide glasses in the form of LiX (X = Cl, Br, I). A number of studies have been reported on such systems [70]. The conductivity increases with the increase of ionic size of the added halide as shown in Table 2. However, the introduction of LiF has the opposite effect (decrease of Li ion conductivity). This effect was considered to be due to the hindrance of Li^+ ion motion due to formation of local columbic traps of F⁻ ions [54] [71] [72]. Li-salt addition increased the Li^+ ion conductivity in Li_2O-P_2O_5, Li_2O-B_2O_3 and Li_2O-SiO_2 glass systems. The conductivity order after Li-ion addition was found to be Li_2O-$P_2O_5 < Li_2O$-$B_2O_3 < Li_2O$-SiO_2 similar to the pure binary systems [47] [70].

Glasses were synthesized with variety of compositions in the systems Li_2O-SiO_2-B_2O_3, Li_2O-B_2O_3-P_2O_5, and Li_2O-P_2O_5-SiO_2 following a rapid quenching technique [74]. Here, network formers are mixed. The widest glass-forming region among these three systems is observed in the system Li_2O-SiO_2-B_2O_3. The two glass-forming oxides SiO_2 and B_2O_3 form glasses easily and give the glasses with high amount of Li_2O. However, for the other glass formers during mixing, the glass-forming window is relatively narrow [71]. In the system Li_2O-P_2O_5-SiO_2, the mixing of two glass formers is difficult because the mixing of P_2O_5 and SiO_2 tends to raise the liquidus temperature [74] [75]. Study on phosphosilicate glass, xLi_2O-yP_2O_5-$(1 - x - y)SiO_2$ [76] [77] reported larger activation barriers compared to even the binary glasses [78]. The mixed silicate–phosphate system

Table 2. Effect of LiX (X = F, Cl, Br) on the conductivity of B_2O_6-$0.56Li_2O$-$0.08LiX$ [73].

X	σ at 300°C (S·cm⁻¹)
F	6.3×10^{-4}
Cl	1.0×10^{-3}
Br	1.3×10^{-3}
I	3.2×10^{-3}

$36Li_2O$-$63SiO_2$-$1P_2O_5$ was reported to exhibit the activation energy of 0.23 eV [79]. S. Chatterjee *et al.* in 2018 fabricated the nanocomposites of silicophosphate glasses found the electrical conductivity of ~3×10^{-4} S·cm^{-1} at near room temperature with 35 mole % Li_2O. The activation energy for Li$^+$ ion migration was reported as 0.078 eV [80]. The mixed former effect is seen in the case of borophosphate glasses as well. A report mentioned the effect of B_2O_3 addition in the $50Li_2O$-xB_2O_3-$(50 - x)P_2O_5$ glasses. The room temperature conductivity of the glasses was found to increase with boron addition up to 20 mol % B_2O_3 [81]. Another research group prepared, by melt quench technique, the xLi_2O-$(1 - x)(yB_2O_3$-$(1 - y)P_2O_5)$ glasses with wide range of composition, *i.e.* $x = 0.35$ - 0.5 and $y = 0.17$ - 0.67. The ionic conductivity of the electrolyte at room temperature was found to increase with x and y. The maximum conductivity of the glass system was reported as 1.6×10^{-7} Ω^{-1}·cm^{-1} for $0.45Li_2O$-$0.275B_2O_3$-$0.275P_2O_5$ at room temperature [82]. The conductivity of borophosphate glass has been reported of 1×10^{-6} (ohm·cm)$^{-1}$ at 30°C corresponding to a Li/P ratio of unity [83]. Similar conductivity was reported by other group for the glass prepared by twin roller quenching technique [84]. Spectroscopic studies reveal that the glass matrix consisting of B_2O_3 and P_2O_5 undergoes structural modification with the formation of borophosphate structural units during the mixed former effect [16] [85] [86] [87]. The BPO_4 was found to be formed in tri- and pyrophosphate, but not in orthophosphate. The formation of BPO_4 makes the glass heterogeneous and could produce a weak binding area around the strong structure of BPO_4, where a conduction path of electricity is formed [85] [86] [88]. The enhancement of conductivity to 1.8×10^{-5} S·cm^{-1} in the glass composition $50Li_2O$: $30P_2O_5$:$20B_2O_3$, from 8.4×10^{-7} S·cm^{-1} of $50Li_2O$: $50P_2O_5$ at 110°C also shows the evidence of the effect of BPO_4 formation [85]. In this report, ball milling technique shows better conductivity than melt quench technique. Table 3 shows the highest conductivities for ternary mixed former oxide glasses.

SO_4^{2-} anion has also been used for ternary and quaternary systems such as Li_2SO_4-Li_2O-P_2O_5 [54]. For a glass system, xLi_2SO_4-$(100 - x)(0.5Li_2O$-$0.5P_2O_5)$, the conductivity of ~10^{-6} Ω^{-1}·cm^{-1} at 100°C has been reported for $x = 60$. The ionic conductivity is found to increase with the addition of Li_2SO_4 content [90]. The conductivity enhancement is reported in borate glass also. The conductivity increases at 200°C from 5.3×10^{-6} S·cm^{-1} for Li_2O-B_2O_3 to 2.66×10^{-3} S·cm^{-1} $15Li_2SO_4$-$42.5Li_2O$-$42.5B_2O_3$ [25]. Spectroscopic studies show that SO_4^{2-} ions occupy interstitial positions and interact ionically with surrounding in the glass network. Increasing Li_2SO_4 content induces small structural changes to the

Table 3. Highest conductivities for mixed former effect in the oxide glasses.

Glass system	σ (S·cm^{-1})	References
Li_2O-SiO_2-P_2O_5	3.0×10^{-4}	S. Chatterjee *et al.* [80]
Li_2O-P_2O_5-B_2O_3	1.8×10^{-5}	B.K. Money *et al.* [85]
Li_2O-B_2O_3-SiO_2	3.6×10^{-6}	S.S. Gundale *et al.* [89]

depolymerized pyroborate glasses but has a larger effect on the structure of metaborate network where small addition of Li_2SO_4 induces the transformation of metaborate triangles into their isomeric tetrahedra [91]. Similarly, the effect of Li_2SO_4 addition in ionic conductivity was studied in Li_2O-B_2O_3-P_2O_5-Li_2SO_4. The high ionic conductivity was found at the composition of 20 and 35 mol% Li_2SO_4 containing glasses (such as $30Li_2O$-$25B_2O_3$-$25P_2O_5$-$20Li_2SO_4$ and $30Li_2O$-17.5 B_2O_3-17.5 P_2O_5-$35Li_2SO_4$). The conductivities were 9.78×10^{-4} and 1.65×10^{-3} S·cm^{-1} respectively at 473 K [92]. S.S. Gundale *et al.* reported the conductivity of 4.08×10^{-4} S·cm^{-1} at 523 K for Li_2O-B_2O_3-SiO_2-Li_2SO_4 [89]. The report states that the glass transition temperature and density decrease with the addition of Li_2SO_4 indicating weakening of the glass structure and expansion of the network, leading to increase in conductivity [89]. NMR and spectroscopic results revealed the retainment of boron atoms four-coordinated more in sulfate-containing glasses than in pure lithium borate glasses. Some sulfoborate-type units were also reported [93]. P. Kluvanek, R. Klement and M. Karáčoň [71] reported the correlation of oxides ratio (network former) with the properties of the glasses $(Li_2O)_{0.4}(B_2O_3)_{0.6x}(Si_2O_4)_{0.6(1-x)}$ [75]. Generally, the mixed glass former effect increases the conductivity. However, the mixed glass-former effect (positive) was not observed on some samples studied (see **Figure 10**). For example, the conductivity of lithium borosilicate system $(Li_2O)_{0.4}(B_2O_3)_{0.6x}(Si_2O_4)_{0.6(1-x)})$ with $x =$ 0, 0.2, 0.3, 0.4, 0.6, and 0.8 was investigated. The conductivity of the investigated glass samples was found to increase from silica rich ($x = 0$) to the boron rich ($x =$ 0.8) samples. Activation energy of 0.65 eV was reported for high conducting sample and 0.8 eV for low conducting sample, respectively [71].

The ionic conductivity of a glass improves with the increase of network modifier concentration such as Li_2O and Na_2O [13]. The effect of Li_2O concentration was reported in ternary systems such as in Li_2O-$(1 - x)(yB_2O_3$-$(1 - y)P_2O_5)$ glass system [74]. C.E. Kim *et al.* [94] reported study of the electrical conductivity of Li_2O-B_2O_3-SiO_2 glasses with the lithium ion concentration range of 35 - 50 mol%. They reported influence of the variation of SiO_2-B_2O_3 ratio in the range of 0.1 - 0.2 on the lithium ionic conductivity [75]. Lithium ion conducting glasses in xLi_2O-$(1 - x)(0.75B_2O_3$-$0.25SiO_2)$ system were also reported with the x range from 50 to 67.5 mol%. The highest conductivity at room temperature was 3.6×10^{-6} S/cm for the glass containing 65.0 mol% of lithium oxide [75]. M. Neyret *et al.* [95] reported the effect of the alkali cation on the structure and the transport properties of R_2O-SiO_2-B_2O_3 glasses, (R = Li, Na, K or Cs). They reported that larger alkali cation causes the expansion of glass network leading to weaker binding forces between non-bridging oxygen and alkali cations [75]. The volume of the ion diffusion pathway correlates with reduced activation energy and enhanced ionic conductivity [5] [96]. The effect of the alkali ion size in the ionic conductivity has been reported for sulfide glasses as well, which we will discuss below.

The effect of glass former mixing has been studied on Na-based ternary

glasses as well. For example, the ionic conductivity of $0.35Na_2O + 0.65 [xB_2O_3 + (1 - x)P_2O_5]$ glasses changes with varying compositions [56]. The highest conductivity was reported in the order of 10^{-9} S·cm^{-1}. 1) Anderson-Stuart model was used to explain the composition dependence of the activation energy in these ternary glasses. According to this, the strain energy is smaller than the columbic binding energy [56]. Two extreme assumptions have been made for glass conduction theory; Anderson-Stuart model that assumes the independent nature of carrier density with temperature but mobile nature of all ions while the strain (mobility) energy dominates the d.c. conductivity [52] [56] [97] [98]. 2) The weak-electrolyte nature which assumes that mobility is independent of ion concentration or temperature while the Coulomb energy dominates the d.c. conductivity [52] [56] [97] [98]. Bruce *et al.* studied the conductivity in Na_2O-based borosilicate glasses and explained the conductivity on the basis of weak electrolyte theory. The conductivities of two different compositions are shown in **Table 4** [99].

Christensen *et al.* explains the sodium borophosphate $0.35Na_2O + 0.65 [xB_2O_3 + (1 - x)P_2O_5]$ glass, where $0.0 \leq x \leq 1.0$, and sodium borosilicate glass $0.2Na_2O + 0.8 [xB_2O_3 + (1 - x)SiO_2]$, where $0.0 \leq x \leq 1.0$. They reported an ionic conductivity of 10^{-8} S/cm [69] [100] [101]. The "mixed network former effect", was also studied on the sodium borophosphate glass system $(Na_2O)_{0.4} [(B_2O_3)_x(P_2O_5)_{1-x}]_{0.6}$ $(0.0 \leq x \leq 1.0)$ which reported high conductivity and low E_a at a range of compositions $0.4 \leq x \leq 0.9$ [102]. Another report was on the influence of partial replacement of phosphate by borate in $50Na_2O-50 [xB_2O_3-(1 - x)P_2O_5]$ glasses. There was conductivity variation with composition change. When $x = 0$, $\sigma_{200} = 2.38 \times 10^{-6}$ S·cm^{-1} and Ea = 0.79 eV but for $x = 0.6$, $\sigma_{200} = 1.6 \times 10^{-5}$ S·cm^{-1} and Ea = 0.68 eV [103].

4. Sulfide Glasses

In the decade, 1970s, it was demonstrated that improvement in ionic conductivity in glasses could be achieved by replacing oxygen by larger, more polarizable and glass forming S^{2-} ion [15]. The study of ion conducting sulfide glass system can be found to start with simple binary systems such as Li_2S-SiS_2 [104], $Li_2S-P_2S_5$ [105], $Li_2S-B_2S_3$ [106] and Li_2S-GeS_2 glass systems [107] [108]. The most studied sulfide system in the ion conductive glasses is $Li_2S-P_2S_5$. In the early 1980s, R. Mercier *et al.* initiated research on the binary system $Li_2S-P_2S_5$ [105]. Later, A. Hayashi *et al.* followed the study on the $Li_2S-P_2S_5$ system [109] [110]. The sulfide electrolytes in the simple $Li_2S-P_2S_5$ binary system (LPS system) are interesting as they possess high conductivities without the addition of any extra element (e.g. Si, Ge, Al) [111]. The highest conductivity reported at room temperature

Table 4. Conductivity comparision [99].

Glass composition	σ (S·cm^{-1})
$40Na_2O-10B_2O_3-50SiO_2$	2.69×10^{-5}
$25Na_2O-5B_2O_3-70SiO_2$	8.91×10^{-7}

for $Li_2S-P_2S_5$ binary system is 0.160 mS·cm^{-1} with activation energy of 0.40 eV [112] [113]. Several crystalline and amorphous materials in the LPS family were reported using different synthesis methods [114]. In 1999, *Morimoto et al.* used the mechanical milling technique instead of the traditional synthesis based on the melt quenching [115] [116]. The new technique is found to give good conductivity. For example, the new technique used the reactants Li_2S, SiS_2 and Li_4SiO_4 and the mixture was placed in an alumina container with alumina balls in a high-energy ball-mill for 10 hours. The glass formed by this technique exhibited the same conductivity as a glass obtained by quenching from a melt. The conductivity of a mechanochemically prepared sample $60Li_2S-40SiS_2$ (mol%) after a milling for 20 h was around 10^{-4} S·cm^{-1} at room temperature [115]. Like in oxide glasses, increasing the amount of charge carriers and their mobility lead to higher ion conductivity in sulfide glasses [117]. By using mechanical milling techniques [115] as well as twin-roller rapid quenching [104], glasses with higher Li ion concentrations could be obtained compared to the process of traditional melt quenching as it is easy to crystallization during cooling process. The $Li_2S-P_2S_5$ glasses can be prepared by quenching method. The optimization of the synthesis of the $Li_2S-P_2S_5$ glass obtained by mechanochemical milling gave a conductivity of 10^{-4} S·cm^{-1} for the composition $75Li_2S-25P_2S_5$ (wt%) [110] [107]. The compound $0:66Li_2S-0:33P_2S_5$ (in wt%), obtained by melting and quenching in a silica tube, exhibited a conductivity of 10^{-4} S·cm^{-1} at 298 K [118]. The similar conductivity ($\sigma_{25} = 10^{-4}$ S·cm^{-1})) has been reported for another composition of the $60Li_2S-40PS_{2.5}$ (mol%) glass prepared by mechanical milling [113]. In all the systems, the conductivities at 25 ºC values increase with an increase in Li_2S content [113]. Baba and Kawamura reported a study of modeling the glass structures in *ab initio* fashion. They created the structures of $xLi_2S-(100 - x)P_2S_5$ ($x = 67, 70, 75,$ and 80) with the compositions of Li^+, PS_4^{3-}, $P_2S_7^{4-}$ and S^{2-}. They used DFT-MD calculations. They reported the ionic conductivity of 10^{-5} S/cm [119]. The ionic conductivity $x = 75$ was the highest [119]. Si and Ge-based binary sulfide glasses were also reported for high conductivity. A report mentioned the conductivity of $\sigma_{25} = 10^{-4}$ S·cm^{-1} for the $60Li_2S-40SiS_2$ glass [113]. The glass was prepared by mechanical milling. Other synthetic methods have also been reported to obtain better conductivity. For example, glasses with the composition $xLi_2S-(1 - x)SiS_2$ ($x \leq 0.6$) were prepared by twin roller quenching [104]. The highest conductivity reported was 5×10^{-4} S·cm^{-1} at 25˚C [104]. By dissolving a halide salt (LiI) in the matrix, this value was improved to 8.2×10^{-4} S·cm^{-1} [104]. K. Mori *et al.* followed computing/modeling the three-dimensional atomic configurations and conduction pathways for Li ions in $(Li_2S)_x-(SiS_2)_{100-x}$ glasses [120]. They found that $(Li_2S)_x-(SiS_2)_{100-x}$ glass frameworks facilitate high mobility of Li ion conduction relative to those of $(Li_2S)_x-(GeS_2)_{100-x}$ glasses and $(Li_2S)_x-(P_2S_5)_{100-x}$ glasses [120]. M. Ribes *et al.* reported good conductivity of the GeS_2-based glass, $0.5Li_2S-0.5GeS_2$, at 25˚C which was 4×10^{-5} S·cm^{-1} [107].

Comparative study of P_2O_5 and GeS_2-based glasses was also accomplished.

$x\text{Li}_2\text{O}(1 - x)\text{P}_2\text{O}_5$ and $x\text{Li}_2\text{S}(1 - x)\text{GeS}_2$ glasses were prepared in a twin roller apparatus [121]. The effect of cooling rate on the electrical properties of glasses was studied for rapidly quenched and conventional glasses. The results were found to be different for oxide and sulfide glasses. Rapid quenching did not affect ionic conductivity of oxide glasses much whereas pre-exponential factors and activation energies of sulfide glasses [121]. Compositional adjustment exhibited the good conductivity of 4×10^{-5} S·cm^{-1} at 20°C for $0.5\text{Li}_2\text{S}\text{-}0.5\text{GeS}_2$ glass [107]. Replacement of the oxygen atom by a sulfur atom improved the ionic conductivity of glasses noticeably. This may be due to the great polarizability of sulfur. The conductivity can be enhanced by changing the composition to $0.63\text{Li}_2\text{S}\text{-}0.37\text{GeS}_2$ which gives the conductivity of 1.5×10^{-4} S·cm^{-1} at room temperature.

A study on $(1 - x)\text{B}_2\text{S}_3\text{-}x\text{Li}_2\text{S}$ ($0.5 < x < 0.75$) glasses containing B_2S_3 as a part of glass reports the composition dependence of ionic conductivity where the result shows the conductivity in contrast to the expectation. The conductivity decreases with the increase of Li_2S composition. Generally, conductivity increases with higher concentration of glass modifier. However, the maximum conductivity was reported for $0.31\text{B}_2\text{S}_3\text{-}0.69\text{Li}_2\text{S}$ glass among all of the studied compositions. The materials were made by melt quenching method [122]. Glasses obtained in the $\text{B}_2\text{S}_3\text{-}\text{Li}_2\text{S}$ binary system was reported to have a conductivity of about 10^{-4} S·cm^{-1} at 25°C [106] [122].

Sodium-based sulfide glasses were also studied but to a less extent compared to Li-based sulfide glasses. Steve Martin (ISU, MSE) has reported vast majority of Na-based glasses. The very first investigations are related with the $\text{Na}_2\text{S}\text{-}\text{GeS}_2$, $\text{Na}_2\text{S}\text{-}\text{XS}_2$ (X = Si, Ge), $\text{Na}_2\text{S}\text{-}\text{P}_2\text{S}_5$ [123]. Na_2S forms stable glasses with GeS_2, SiS_2 and P_2S_5 to form $\text{Na}_2\text{S}\text{-}\text{XS}_2$ (X = Si, Ge), $\text{Na}_2\text{S}\text{-}\text{P}_2\text{S}_5$ and $\text{Na}_2\text{S}\text{-}\text{GeS}_2$ with a large range of composition [107] [124]. The comparative trend of conductivity at room temperature revealed that $0.5\text{Na}_2\text{S}\text{-}0.5\text{SiS}_2$ (1.2×10^{-5} S·cm^{-1}) > $0.5\text{Na}_2\text{S}\text{-}0.5\text{P}_2\text{S}_5$ (3.9×10^{-6} S·cm^{-1}) > $0.5\text{Na}_2\text{S}\text{-}0.5\text{GeS}_2$ (1×10^{-6} S·cm^{-1}) [107]. The electrical conductivities of these glasses were measured over a range of compositions and temperature (−20°C, 150°C). They reported the effect of electronegativity on the ionic conductivity. The ionic conductivity was found to enhance with decreasing electronegativity of the network forming sulfide [107]. *Ab initio* molecular dynamics (MD) simulations study was performed for sodium thiophosphates [$x\text{Na}_2\text{S}\text{-}(100 - x)\text{P}_2\text{S}_5$] for potential glassy solid electrolytes (GSEs). The highest Na$^+$ ion conductivity of ~10^{-5} S·cm^{-1} was reported for the $x = 75$ composition [125]. Mechanochemical synthetic method was used to prepare $x\text{Na}_2\text{S}\text{-}(100 - x)\text{P}_2\text{S}_5$ (mol%; x = 67, 70, 75 and 80) glasses. Composition dependence of electrical conductivity study demonstrated the higher ionic conductivity with more Na_2S content reaching the highest for $x = 80$ composition. The highest conductivity is 1×10^{-5} S·cm^{-1} [126]. A comparative study of conductivities of GeS_2-based stable glasses with Li_2S and Na_2S in a large range of composition (from 1 - 0.5 in molar ratio of GeS_2) over a wide range of temperature (−20°C - 150°C) exhibited a higher ionic conductivity 10^{-5} (Ω·cm)$^{-1}$ for Li glasses than 10^{-6} (Ω·cm)$^{-1}$ for Na

glasses at high alkali sulfide concentration [127]. There are studies on Na_2S-B_2S_3 system as well. For example, wide compositions and temperature range conductivity measurements have been reported on the fast ion conducting glass series, $xNa_2S + (1 - x)B_2S_3$. Among the reports between $x = 0$ and 0.15, the conductivity was reported highest for the composition $x = 0.005$ [128]. Some high ionic conductivity of binary oxide glasses are given below in Table 5.

Ternary and Quaternary Sulfide Glasses

As in oxide glass systems, sulfide glasses also show improved ionic conductivity in ternary and quaternary systems. Here we first discuss the ternary systems with improved conductivity. Different approaches have been proposed for improving the conductivity of glassy electrolytes, one of them is the addition of Li halide salts. The addition of a lithium halide salt (e.g. LiI or LiCl) can increase the lithium concentration and it increases the ionic conductivities of the glasses. R. Mercier *et al.* (1981) demonstrated that the lithium ion conductivity of $67Li_2S$-$33P_2S_5$ glass increased from 10^{-4} S·cm^{-1} to 10^{-3} S·cm^{-1} when 45 mol% of LiI were added [105]. J.P. Malugani *et al.* (1983) also mentioned LiI doping in Li_2S-P_2S_5 system which improved ionic conductivity to 10^{-3} S·cm^{-1} at room temperature [132]. Studies on glass formation, structure and electrical conductivity in the Li_2S-P_2S_5-LiI system with the ratio $Li_2S/P_2S_5 = 2$ revealed that the addition of LiI did not break the $P_2S_7^{-4}$ units [105]. Table 6 shows the effect of LiI addition on some sulfide glasses.

The studies of addition of Li halide salt to the glass systems with SiS_2, B_2S_3 and GeS_2 can also be found. In the 1980s, Ménétrier *et al.* studied the system Li_2S-B_2S_3-LiI, which exhibited a conductivity equal to 10^{-3} S·cm^{-1} at 298 K [106] [133], while Ribes and Pradel worked on the system Li_2S-(Ge,Si)S_2-LiI [107] [133] with a conductivity a little bit less, around 8×10^{-4} S·cm^{-1}. The conductivities of some glasses, $30Li_2S$-$26B_2S_3$-44LiI (Wada *et al.*, 1983), and $63Li_2S$-$36SiS_2$-Li_3PO_4 (Aotani *et al.*, 1994), have been reported to be as high as 1.7×10^{-3} S/cm, an order of magnitude increase from the Li_2S–B_2S_3 system (10^{-4} S·cm^{-1}) [106] [134]. Another report discussed the system Li_2S-SiS_2-LiX (X = Br, Cl, or I) [133]

Table 5. Ionic conductivity of binary sulfide glasses.

Glass systems	σ (S·cm^{-1})	References
$0.60Li_2S$-$0.40SiS_2$	5.0×10^{-4}	V.K. Deshpande *et al.* [129]
$0.7Li_2S$-$0.3P_2S_5$	1.6×10^{-4}	Z. Zhang *et al.* [112]
$0.7Li_2S$-$0.3B_2S_3$	9.5×10^{-5}	Z. Zhang *et al.* [112]
$0.5Li_2S + 0.5GeS_2$	4.26×10^{-5}	Y. Kim *et al.* [130]
Na_2S-SiS_2	1.1×10^{-5}	D. Ravaine [15]
Na_2S-P_2S_5	3.9×10^{-6}	J.L. Souquet [131]
Na_2S-GeS_2	2.9×10^{-7}	D. Ravaine [15]
Na_2S-B_2S_3	1.0×10^{-7}	H.K. Patel *et al.* [128]

[135] [136] [137]. The SiS$_2$-Li$_2$S-LiI glasses reach room temperature conductivities of nearly 1.8×10^{-3} S·cm^{-1}. This high temperature synthesis can lead to an oxidation of iodide by SiS$_2$ [135] [138]. So, the systems of the SiS$_2$-Li$_2$S-LiBr and SiS$_2$-Li$_2$S-LiCl were also studied [139]. Ionically, conductive glasses have been synthesized using a 1:1 SiS$_2$-Li$_2$S base glass and doping with lithium halides. Conductivity of the glass system SiS$_2$-Li$_2$S-LiCl was 1.2×10^{-4} S·cm^{-1} at 25°C [139] and with the glass system SiS$_2$-Li$_2$S-LiBr, the highest conductivity was reported as 3.2×10^{-4} S·cm^{-1} at 25°C [137]. The conductivity trend in SiS$_2$-Li$_2$S-LiX system is SiS$_2$-Li$_2$S-LiI > SiS$_2$-Li$_2$S-LiBr > SiS$_2$-Li$_2$S-LiCl (see **Table 7**). The conductivity of SiS$_2$-Li$_2$S-LiI glass system is further increased, though slightly, when B$_2$S$_3$ is added to form the composition of 30Li$_2$S-25B$_2$S$_3$-45LiI-25SiO$_2$. It gives the conductivity of 2.1×10^{-3} S·cm^{-1} [8].

The mixed glass former effect (MGFE) has also been investigated for ionic conductivity in different glass systems, such as Li$_2$S-P$_2$S$_5$-SiS$_2$ [140], Li$_2$S-SiS$_2$-GeS$_2$ [129] or Li$_2$S-P$_2$S$_5$-B$_2$S$_3$ [112] [133]. The activation energy for Li$_2$S-P$_2$S$_5$-SiS$_2$ is reported 0.37 eV [140]. A glass processing method using a carbon-coated quartz container was employed for the investigation of B$_2$S$_3$ containing glasses such as $(1 - x)$B$_2$S$_3-x$Li$_2$S and 0.33 $[(1 - y)$B$_2$S$_3$-yP$_2$S$_5]$-0.67Li$_2$S. This technique expanded the glass forming region from $0.66 \leq x \leq 0.68$ for $(1 - x)$P$_2$S$_5$-xLi$_2$S to $0.5 \leq x \leq 0.7$ for $(1 - x)$B$_2$S$_3$-xLi$_2$S. Higher Li$^+$ ionic conductivity was found for the conformer sulfide glasses of the 0.33 $[(1 - y)$B$_2$S$_3$-yP$_2$S$_5]$-0.67Li$_2$S system than for single sulfide network former glasses. The room temperature conductivity of

Table 6. Enhancement of room temperature ionic conductivities by LiI substitution on binary sulfide glasses.

Glass systems	σ (S·cm^{-1})	References
B$_2$S$_3$-Li$_2$S	1×10^{-4}	J.H. Kennedy [108]
B$_2$S$_3$-Li$_2$S-LiI	1.7×10^{-3}	J.H. Kennedy [108]
P$_2$S$_5$-Li$_2$S	1×10^{-4}	J.H. Kennedy [108]
P$_2$S$_5$-Li$_2$S-LiI	1×10^{-3}	J.H. Kennedy [108]
GeS$_2$-Li$_2$S	1×10^{-4}	J.H. Kennedy [108]
GeS$_2$-Li$_2$S-LiI	10^{-3}	S.S. Gundale *et al.* [89]
SiS$_2$-Li$_2$S	5×10^{-4}	J.H. Kennedy [108]
Si$_2$-Li$_2$S-LiI	2×10^{-3}	J.H. Kennedy [108]

Table 7. Comparative room temperature conductivities of LiX substitution on binary sulfide glasses.

Glass systems	σ (S·cm^{-1})	References
SiS$_2$-Li$_2$S-LiCl	2×10^{-4}	J.H. Kennedy [108]
SiS$_2$-Li$_2$S-LiBr	3×10^{-4}	J.H. Kennedy [108]
SiS$_2$-Li$_2$S-LiI	2×10^{-3}	J.H. Kennedy [108]

the glass was 0.141 mS/cm [112]. Glasses belonging to the 0.33 [(1 − x)P$_2$S$_5$-xAl$_2$S$_3$]-0.67Li$_2$S system for $0 \leq x \leq 0.5$ prepared by classical quenching techniques showed improved conductivity (0.267 mS·cm^{-1}) [141]. The system Li$_2$S-GeS$_2$-P$_2$S$_5$ prepared by a high-energy ball-milling process showed the lithium-ion conductivity of 4.0×10^{-4} S·cm^{-1} [142]. This conductivity was higher than that of the Li$_2$S-P$_2$S$_5$ system prepared by the same method. The enhancement of conductivity was attributed to the mixed former effect by mixing two kinds of network-forming sulfides GeS$_2$ and P$_2$S$_5$. The region of glass formation by the ball-milling process was found wider than a method by a conventional melt-quenching [142].

Glasses with GeS$_2$ such as 0.3Li$_2$S-0.7[(1 − x)SiS$_2$-xGeS$_2$] were prepared by the twin roller quenching technique. Here, the composition range is $0 \leq x \geq 1$. A large enhancement of ionic conductivity of about 2 orders of magnitude was reported for glasses at around $x = 6.5$ which was attributed to the mixed glass former effect. The conductivity was in the order of 10^{-4} S·cm^{-1} for 0.3Li$_2$S-0.7 [(1 − x)SiS$_2$-xGeS$_2$] [129] [143] [144] but the conductivities of binary systems were 1.5×10^{-6} and 9.3×10^{-7} S·cm^{-1} for 30Li$_2$S-70SiS$_2$ and 30Li$_2$S-70GeS$_2$, respectively [129] [144]. However, 60Li$_2$S-40SiS$_2$ and 63Li$_2$S-37GeS$_2$ glass compositions were reported to have conductivity of 10^{-4} S·cm^{-1} [129]. The enhancement of conductivity by adding GeS$_2$ is the mixed former effect [144]. The electrical conductivity of 30Li$_2$S-(70 − x)SiS$_2$-xGeS$_2$ $(0 < x < 70)$ glasses has also been studied. The conductivity and activation energy for 30:25:45 for Li$_2$S:SiS$_2$:GeS$_2$ were reported as 1.7×10^{-3} S·cm^{-1} and 0.33 eV, respectively. The enhancement in the conductivity has been attributed to mixed glass former effect [129]. Generally, LiX addition to a binary system increases the conductivity. The addition of LiI in Li$_2$S-GeS$_2$ glass composition did not exhibit difference. The conductivity of 0.24 Li$_2$S-0.36 GeS$_2$-0.40 LiI is 1.2×10^{-4} S·cm^{-1}. Sometimes, quaternary systems also work for ionic conductivity enhancement. LiBr addition to the ternary system gives higher ionic conductivity of 2×10^{-4} S·cm^{-1} at the composition of 0.24Li$_2$S-0.36GeS$_2$-0.36LiI-0.04LiBr [145]. Ionic conductivity of GeS$_2$-Ga$_2$S$_3$-Li$_2$S-LiI glass powders prepared by ball milling is 9.0×10^{-4} S·cm^{-1} at the composition of 0.4LiI-0.24GeS$_2$-0.06Ga$_2$S$_3$-0.3Li$_2$S [146]. Similarly, Ga$_2$S$_3$ addition to the ternary system shows better enhancement in the conductivity. The 0.225Li$_2$S-0.225GeS$_2$-0.5LiI-0.05Ga$_2$S$_3$ glass system gives the conductivity of 1.7×10^{-3} S·cm^{-1} at room temperature [147]. When SiS$_2$ is added instead of LiI, the conductivity becomes 1.7×10^{-4} S·cm^{-1} for the composition, 0.3Li$_2$S-0.45GeS$_2$-0.25SiS$_2$. When Li$_3$PO$_4$ is added instead of LiI or SiS$_2$, the conductivity increases to 3.0×10^{-4} S·cm^{-1} for the composition, 0.58Li$_2$S-0.39GeS$_2$-0.03Li$_3$PO$_4$ [148]. Li$_2$SiO$_4$ addition seems the best for the conductivity enhancement in the glass system. The conductivity is 3.4×10^{-4} S·cm^{-1} for the composition 0.48Li$_2$S-0.48GeS$_2$-0.04Li$_4$SiO$_4$ [130] [149].

Sometimes, the ionic conductivity can be increased by mixing different types of glass formers (sulfide and oxide) [150]. For example, GeO$_2$ was added to Li$_2$S-GeS$_2$ system to get the glass of the composition GeO$_2$ was added to Li$_2$S-GeS$_2$ system to get the glass of the composition 0.5Li$_2$S − 0.5 [(1 − x)GeS$_2$-xGeO$_2$], and the io-

nic conductivity increased from 4.5×10^{-5} $(\Omega\ cm)^{-1}$ to 1.5×10^{-4} $(\Omega\ cm)^{-1}$ and the activation energy was lowered from 0.385 eV to 0.358 eV by the addition of 5 mole % of GeO_2 [130]. When the composition was changed as $x Li_2 S$-$(1 - x)$ $[0.6 GeS_2$-$0.4 GeO_2]$, at $x = 0.7$ the conductivity was improved to 4.36×10^{-4} $S \cdot cm^{-1}$ [151].

For Na-based ternary glasses, a study for the composition dependence of room temperature ionic conductivity of $[Na_2 S]_{2/3}$-$[(B_2 S_3)_x$-$(P_2 S_5)_{1-x}]_{1/3}$ glasses showed the highest conductivity at $x = 0.5$ with $\sigma = 10^{-5}$ $S \cdot cm^{-1}$ [152]. There are reports of other glass compositions such as $0.5 Na_2 O$-0.5 $[x B_2 O_3$-$(1 - x) P_2 O_5]$, $0.5 Na_2 S$-0.5 $[x GeS_2$-$(1 - x) P_2 S_5]$ and $0.67 Na_2 S$-0.33 $[x B_2 S_3$-$(1 - x) P_2 S_5]$. The ionic conductivities of the $0.67 Na_2 S$-0.33 $[x SiS_2$-$(1 - x) P_2 S_5]$ was reported for 30°C. The $x = 0.0$ glass has a conductivity of 3.55×10^{-6} $S \cdot cm^{-1}$. The highest conductivity was reported for $x = 0.6$ as 2.08×10^{-5} $S \cdot cm^{-1}$ [100]. **Figure 10** shows the highest conductivities of the ternary glass systems with MGFE.

The strongest positive effects were observed in alkali borosphosphate glasses [56] [83] [84] [88] [103]. Positive MGFE effect shows the enhanced or higher conductivity than the parent binary glass system and negative MGFE shows opposite results. Phosphogermanate [153], thiogermanosilicate [129] and thioborophosphate glasses [112] [152] were also reported for positive effect. Systems with strongly positive MGFE effects, such as the alkali borosphosphate glasses were found to exhibit non-linear co-relation of composition with physical properties such as glass transition temperatures (Tg), and densities suggesting the effect of structural organization on ionic mobility [102] [154] [155] [156]. The study of negative NFM effects are also reported which are not important for
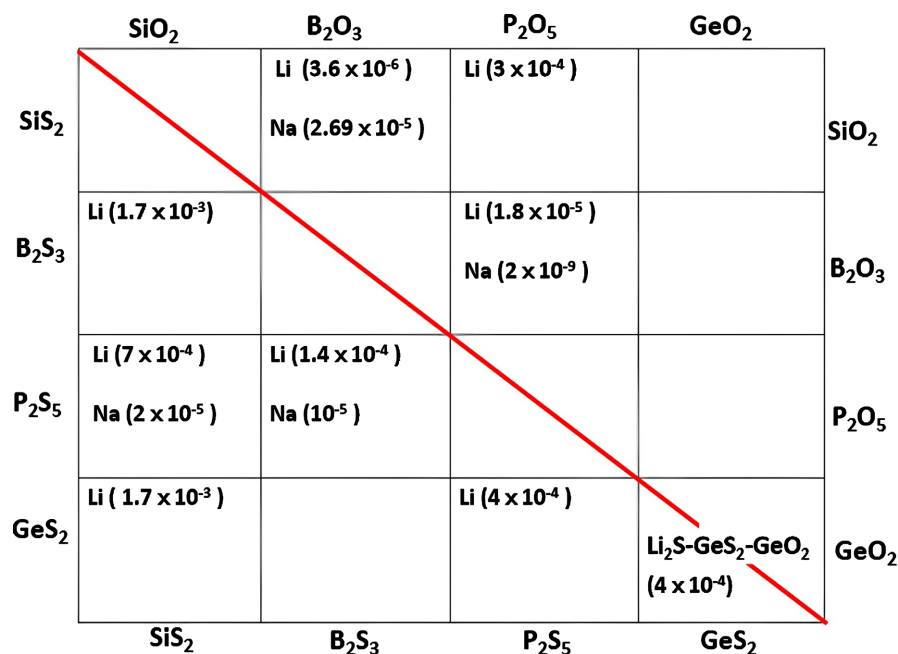

Figure 10. The highest conductivities (in $S \cdot cm^{-1}$) of Li and Na ternary glasses. The glass systems above red line (diagonal) are the oxide systems with $Li_2 O$ or $Na_2 O$ and below the red line are the sulfide glass systems with $Li_2 S$ or $Na_2 S$.

application but can help understand the structure-property correlation. The sodium thio-germanophosphate glass, $0.5Na_2S-0.5$ [xGeS$_2$-(1 − x)P$_2$S$_5$], was reported with a negative MGFE in the ionic conductivity with a minimum of 5×10^{-7} S/cm at x = 0.5 [157].

It is also important to learn the effect of alkali ion size on the ionic conductivity of the glasses. In one study, alkali sulfides, M_2S (M = Li, Na, K, Cs) were systematically mixed with the $0.1Ga_2S_3-0.9GeS_2$ base glass-forming system [158]. Wide range of compositions were formed in $xM_2S-(1 − x)(0.1Ga_2S_3 + 0.9GeS_2)$ system. The addition of Li_2S and Na_2S enhanced the conductivity. When the same concentration of alkali sulfide (M_2S) was added, the conductivities of the glasses were found to decrease with the increasing alkali metal size. The K_2S and Cs_2S compositions showed limited range of glass formation compared to Li_2S and Na_2S compositions. K_2S and Cs_2S glasses exhibited poor conductivity [158].

Glassy electrolytes were also prepared by mixing two different anion species, so called "mixed anion effect" [159]. It is also a kind of mixed former effect. One example is the pseudobinary system of $Li_3BO_3-Li_2SO_4$. The system was prepared by cold press method. The ionic conductivity at room temperature for the cold-pressed $Li_3BO_3-Li_2SO_4$ glass systems ranges from 10^{-7} to 10^{-6} S·cm^{-1}. The conductivity increased with the addition of small amounts of Li_2SO_4 which was considered to be due to the anion mixing in the glasses [58]. The other example is $Li_4SiO_4-Li_3BO_3$ glasses [58] [159]. M. Tatsumisago *et al.* showed the highest conductivity of 5.4×10^{-2} Sm^{-1} at 400 K for the composition 6:4 for $Li_4SiO_4:Li_3BO_3$ while the conductivity reported for individual salts Li_4SiO_4 and Li_3BO_3 were 1.9×10^{-2} and 2.4×10^{-3} Sm^{-1} [159]. Mixed anion effect is studied in thiosulfate systems as well. Here, one report discusses the conductivity in mechanochemically prepared Na_3PS_4-NaI glass system. The conductivity was found to rise with increasing NaI concentration where the highest conductivity of 1.4×10^{-5} S·cm^{-1} was found for $71Na_3PS_4-29NaI$ glass [160]. $(100 − x)Na_3PS_4-xNa_4GeS_4$ glass electrolytes were prepared by mechanical-milling. The glasses exhibit conductivities of $\sim10^{-5}$ S·cm^{-1} at room temperature [161]. Na-based borate and sulfate containing glasses such as $(100 − x)Na_3BO_3-xNa_2SO_4$ ($0 \leq x$ (mol%) ≤ 50) were fabricated by mechanical milling. In this glass system, the conductivity was found to rise with increasing Na_2SO_4 concentration. The highest conductivity of 5.9×10^{-8} S·cm^{-1} at 25°C was found for $50Na_3BO_3 \cdot 50Na_2SO_4$ composirion [10].

The addition of ortho-oxosalts to binary sulfide glasses enhances conductivity. For example, doping small amounts of lithium oxy salts, Li_xMO_y (where Li_xMO_y = Li_3PO_4, Li_4SiO_4, Li_3BO_3, and Li_4GeO_4), into the Li_2S-SiS_2 glass system increased the conductivity [130] [162]. The $(100 − x)(0.6Li_2S-0.4SiS_2)-xLi_xMO_y$ (Li_xMO_y = Li_4SiO_4, Li_3PO_4, Li_4GeO_4 and Li_3BO_3) system demonstrates a maximum ionic conductivity of 10^{-3} S·cm^{-1} at 5mol% Li_xMO_y [123] [162] [163]. The glass-forming regions of each system were $0 <$ mol% $Li_4GeO_4 <15.0 <$ mol% $Li_4SiO_4 < 20.0 <$ mol% $Li_3BO_3 < 25$ and $0 <$ mol% $Li_3PO_4 < 40$ [163]. This is also attributed to the "mixed-anion effect" [164]. The $Li_3PO_4-Li_2S-SiS_2$ and $Li_2SO_4-Li_2S-SiS_2$ glassy sys-

tems present a conductivity somewhat lower than that of their homologs with LiI [134] [165]. The sample $(100 - y)(0.6Li_2S\text{-}0.4SiS_2)\text{-}yLi_4SiO_4$ ($y = 3$) obtained by mechanical milling treatment for 20 h exhibits conductivity of 1.5×10^{-4} S·cm^{-1}, at room temperature. The oxysulfide system $Li_2S\text{-}SiS_2\text{-}Li_4SiO_4$ was obtained by mechanical milling of crystalline starting materials in a dry N_2 atmosphere at room temperature [116]. The glasses $(1 - y)[0.6Li_2S\text{-}0.4SiS_2]\text{-}yLi_4SiO_4$ which were synthesized by a liquid nitrogen quenching method showed glass forming region of $0 \leq y \leq 0.075$. The maximum ionic conductivity was obtained at $y = 0.03$ with 1.5×10^{-3} S·cm^{-1} at 298 K [166]. New Li$^+$ ion-conductive glasses $Li_2S\text{-}B_2S_3\text{-}Li_4SiO_4$ were prepared by rapid quenching. The heat treatment enhanced the ionic conductivities for Li_4SiO_4-doped glasses leading to the highest ionic conductivity of 1.0×10^{-3} S·cm^{-1} at room temperature [167]. Another series of glasses, $40Li_2O\text{-}(40 - x)B_2O_3\text{-}20SiO_2\text{-}xLi_2SO_4$ have also been studied and the highest conductivity of 1.46×10^{-2} S/cm at 523 K was found for the composition of $40Li_2O\text{-}32.5B_2O_3\text{-}20SiO_2\text{-}7.5Li_2SO_4$. The glasses were prepared by melt quench technique technique [168]. When the $Li_3PO_4\text{-}Li_2S\text{-}SiS_2$ glass system with the composition of $0.03Li_3PO_4\text{-}0.59Li_2S\text{-}0.38SiS_2$ was prepared at ambient pressure by quenching in liquid nitrogen, its conductivity was 6.9×10^{-4} S·cm^{-1} at room temperature [165]. The stability of the glass towards electrochemical reduction was dramatically improved when compared with $SiS_2\text{-}Li_2S\text{-}LiI$ glass. The glass synthesized with Li_2SO_4 instead of Li_3PO_4 also indicated good conductivity and stability against electrochemical reduction [165]. But when another synthesis method called twin roller technique was employed instead of liquid nitrogen quenching, the glass forming region expands and conductivity increases up to 1.4 or 1.5×10^{-3} S/cm for $Li_3PO_4\text{-}Li_2S\text{-}SiS_2$ glass system [134] [169]. After composition optimization, structural analysis on the glass revealed that Li_3PO_4 doping changes the glass structure of $Li_2S\text{-}SiS_2$, thereby enhancing the electrical conductivity [134]. In 2012, LiBH$_4$ was also added to the binary system to enhance the conductivity. The $(100 - x)(0.75Li_2S\text{-}0.25P_2S_5)\text{-}xLiBH_4$ ($0 \leq x$ (mol%) ≤ 33) glass electrolytes were synthesized by a mechanical milling [170]. The conductivity was found to rise with increasing LiBH$_4$ concentration. The glass at the composition of $x = 33$ showed the highest lithium-ion conductivity of 1.6×10^{-3} S·cm^{-1} at room temperature [170]. **Figure 11** shows the highest conductivities of different glass systems and **Table 8** reflects the highly ion conducting glasses.

5. Alumina-Based Glasses

The impact of Al_2O_3 addition on ionic conductivity improvement has also been studied. Al_2O_3 and Ga_2O_3 are considered as intermediates for glass formation. Li-containing aluminosilicate glasses are fast ion conductors [171] [172]. The glasses of the $Li_2O\text{-}Al_2O_3\text{-}SiO_2$ system, where Lithium is the only mobile particle, can be polymerized and depolymerized. Polymerized (compositional join LiAl-SiO$_4$-LiAlSi$_4$O$_{10}$) aluminosilicates are faster lithium ion conductors than depolymerized because polymerized glasses have a wider distribution of lithium
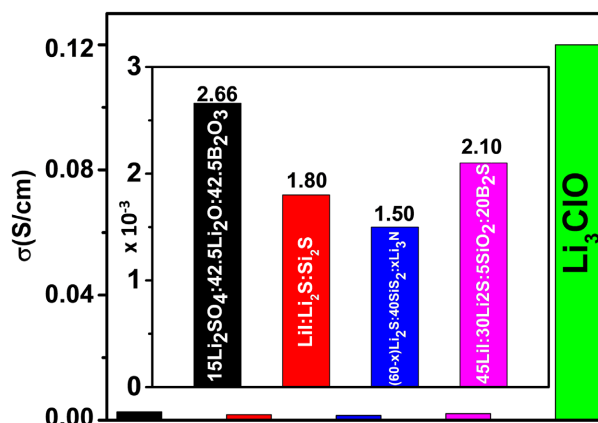
Figure 11. The highest conductivities of different glass systems.

Table 8. Highly ion conductive glasses.

Glass systems	σ (S·cm^{-1}) at 25°C	References
30LiI-41Li$_2$O-29P$_2$O$_5$	3.0×10^{-6}	A. Chandra *et al.* [52]
0.2LiBr-0.48Li$_2$O-0.32P$_2$O$_5$	2.72×10^{-6}	T. Thieu Duc *et al.* [189]
30LiCl-35Li$_2$O-35P$_2$O$_5$	1.0×10^{-7}	J.P. Maligani *et al.* [190]
12.3LiCl-31.8Li$_2$O-59.9B$_2$O$_3$	3.2×10^{-6}	A.R. Kulkarni *et al.* [191]
Li$_{3.3}$PO$_{3.8}$N$_{0.22}$	3.3×10^{-6}	X.H. Yu *et al.* [181]
0.24Li2S-0.36GeS2-0.36LiI-0.04LiBr	2.0×10^{-4}	B. Carret *et al.* [145]
0.36GeS$_2$-0.24Li$_2$S-0.40LiI	1.2×10^{-4}	T. Minami *et al.* [149]
45LiI-37Li$_2$S-18P$_2$S$_5$	1.0×10^{-3}	J.P. Malugani *et al.* [192]
63Li$_2$S-36SiS$_2$-Li$_3$PO$_4$	1.5×10^{-3}	N. Aotani *et al.* [134]
50Li$_2$S-17P$_2$S$_5$-33LiBH$_4$	1.6×10^{-3}	A. Yamauchi *et al.* [170]
30Li$_2$S-26B$_2$S$_3$-44LiI	1.7×10^{-3}	H. Wada *et al.* [106]
0.57Li$_2$S-0.38SiS$_2$-0.05Li$_4$SiO$_4$	2.0×10^{-3}	K. Hirai *et al.* [193]
0.24Li$_2$S-0.36GeS$_2$-0.40LiI	1.2×10^{-4}	Y. Kim *et al.* [130]
0.526Li$_2$S-0.211GeS$_2$-0.25SiS$_2$	1.7×10^{-4}	M. Yamashita *et al.* [194]
0.48Li$_2$S-0.48GeS$_2$-0.04Li$_4$SiO$_4$	3.4×10^{-4}	T. Minami *et al.* [149]
0.58Li$_2$S-0.39GeS$_2$-0.03Li$_3$PO$_4$	3.0×10^{-4}	Y. Yamamura *et al.* [148]
(60-3x/2)Li$_2$S-40SiS$_2$-xLi$_3$N ($x = 3$)	1.5×10^{-3}	R. Sakamoto *et al.* [183]
Li$_3$OCl	1.2×10^{-1}	M.H. Braga *et al.* [186]

percolation paths [173]. J.O. Isard in 1959 studied the composition dependence of activation energy for conductivity in Na$_2$O-xAl$_2$O$_3$-2(4 − x)SiO$_2$ glass system [174]. The effect of alkaline-earth ions on Na transport in aluminosilicate glasses was studied by measuring ionic conductivity for a systematic compositional series of Na$_2$O-RO-Al$_2$O$_3$-SiO$_2$ [175] where R is Mg, Ca, Sr or Ba.

For aluminophosphate glasses, the conductivity was investigated in wide range

of compositions, $(20 + x)Li_2O$-$(20 - x)Al_2O_3$-$60P_2O_5$ ($x = 0, 4, 8, 12,$ and 16, in mol%). The glasses were prepared by the melt quenching technique. The highest conductivity was observed for the glass containing 28 mol% of Li_2O ($x = 8$), ($\sigma = 1.23\ 9 \times 10^{-7}$ S/cm, at 403 K) [176]. Aluminoborate glasses exhibit higher conductivities than aluminophosphate glasses. The ionic conductivity in the glass system with composition, xNa_2O-$(1 - x)(0.87B_2O_3$-$0.13Al_2O_3)$ was studied and the highest conductivity was 10^{-5} S·cm^{-1} for $x = 0.70$ [177]. In a comparative study of sodium-based silicate glasses, borate addition exhibited higher ionic conductivity than alumina addition. The highest conductivity observed for borate glass was with the composition of $40Na_2O$-$10B_2O_3$-$50SiO_2$ and it was 2.69×10^{-5} S·cm^{-1} while for aluminate glass, the best composition was $25Na_2O$-$5Al_2O_3$-$70SiO_2$ and the conductivity was 8.91×10^{-7} S·cm^{-1} [99]. In some borate glass compositions prepared by melt quenching method, the addition of Al_2O_3 has found negative effect on ionic conductivity. Ion conducting glasses $30Li_2O$-$(70 - x)B_2O_3$-xAl_2O_3 have been prepared over wide range of compositions ($x = 0, 5, 10, 15$ and 20 mole %). The addition of Al_2O_3 in the series of lithium borate glasses decreases ionic conductivity. The room temperature conductivity is 6.44×10^{-6} S·cm^{-1} for $x = 0$ [178]. The addition of aluminum oxide influenced positively on the electrical conductivity of $27.5Li_2O$-$(72.5 - x)B_2O_3$–xAl_2O_3 glasses. The conductivity of Li_2O-B_2O_3 system increases with addition of Al_2O_3 up to 2.5 mol% and is 8×10^{-4} S/cm [179].

6. Unconventional Glasses

6.1. Nitrogen Doped Glasses

Oxynitride phosphate glasses of xLi_2O-$(1 - x)P_2O_5$ ($x = 0.5, 0.55, 0.575$) glasses exhibited the conductivity of 10^{-8} S·cm^{-1} [180]. However, LIPON exhibited an average conductivity of 2.3×10^{-6} S/cm at 25°C and an average activation energy of Ea = 0.55 eV [181]. Metaphosphate glasses such as $LiPO_3$ and $NaPO_3$ prepared by the reaction: $(Li/Na)PO_3 + xNH_3 \rightarrow (Li/Na)PO_{3-(3x/2)}N_x + (3x/2)H_2O$, reported partial replacement of two-coordinated oxygen with two- and three-coordinated nitrogen. Ionic conductivity of the glasses improved after nitridation. Conventional melting and casting methods can be used to synthesize $LiPO_3$ and $NaPO_3$ glasses. These glasses are used as base glasses for the ammonolysis procedure to introduce nitrogen in the glasses. The nitridation processes were performed by remelting the base glasses under NH_3 environment at 780°C [182]. Fast lithium ion conducting glasses such as Li_2S-SiS_2-Li_3N were synthesized by a melt-quenching with compositions of $(60-3x/2)Li_2S$-$40SiS_2$-xLi_3N ($x = 0, 3, 5$). The highest room temperature conductivity and activation energy were reported as 1.5×10^{-3} S/cm for $x = 3$ and 27 kJ/mo, respectively. The conductivity at the maximum $x = 5$ is 9.6×10^{-4} S/cm [183]. Boron containing nitride glass was also studied for alkali ionic conductivity. Li_3BN_2 glass was prepared from Li_3N and BN *by* planetary ball milling. Li_3BN_2 glass showed conductivity higher than that of oxide-based glass electrolytes such as Li_3BO_3 glass and LiPON thin films [184]. The re-

ported conductivity was 1.3×10^{-5} S·cm^{-1} at 25 ˚C. Na ion conductivity was studied in NASICON-based NCAP glasses. Na$^+$ ion conductivity was different when boron and gallium substitutes phosphorus in NASICON-based NCAP glass (Na$_{2.8}$Ca$_{0.1}$Al$_2$P$_3$O$_{12}$) to get (NCABP: Na$_{2.8}$Ca$_{0.1}$Al$_2$B$_{0.5}$P$_{2.7}$O$_{12}$) and (NCAGP: Na$_{2.8}$Ca$_{0.1}$Al$_2$Ga$_{0.5}$P$_{2.7}$O$_{12}$), respectively. The dc conductivity were reported as ($\sim 3.13 \times 10^{-8}$ S·cm^{-1}) for NCAP glass, ($\sim 2.27 \times 10^{-8}$ S·cm^{-1}) for NCAGP and ($\sim 1.46 \times 10^{-8}$ S·cm^{-1}) for NCABP. High lithium ion conducting Li$_2$S-P$_2$S$_5$-Li$_3$N glasses were reported with the composition of $(75 - 1.5x)$Li$_2$S-25P$_2$S$_5$-xLi$_3$N (mol%) where $0 \leq x \leq 20$. The glass conductivity increased with more Li$_3$N concentration. The highest conductivity was reported as 5.8×10^{-4} S·cm^{-1} for 20 mol% of Li$_3$N at room temperature [185].

6.2. Antiperovskite-Based Glasses

For the first time, M.H. Braga *et al.*, in 2014, developed a novel type of glasses based on antiperovskite with super ionic conduction [186]. They were inspired from Li$_3$ClO antiperovskite crystals for formation of these glasses. The glass preparation technique is different from conventional melt-quenching, twin roller quenching or mechanical milling techniques. They synthesized the glasses with the composition of Li$_{3-2x}$M$_x$HalO where Hal = halides like Cl$^-$ or I$^-$ or a mixture and $x = 0$ for Li3ClO, $x = 0.002, 0.005, 0.007$ and 0.01 for M = Mg and Ca and $x = 0.005$ For M = Ba). They prepared the glasses from LiCl and hydroxides of Li, Ca, Mg and Ba by paste formation with deionized water. The process used Teflon reactor, heat up to 240 C for several days and cold. The samples needed to be dried at certain temperature for certain duration. Glassy samples could not be obtained if the drying of the powders were too long. They claim that Li$_{2.99}$Ba$_{0.005}$ClO and Li$_{2.99}$Ba$_{0.005}$Cl$_{0.5}$I$_{0.5}$O exhibit conductivities of 25 and 121 mS·cm^{-1} at 25˚C, respectively in the glassy or supercooled liquid state establishing the highest ionic conductivity ever reported in glassy electrolytes. Two years later, *Braga et al.* published another paper stating that dry, glass/amorphous solid electrolytes can be obtained from A$_3$OCl (A = Li or Na) by the addition of water where a small amount of Ba(OH)$_2$ or another oxide or hydroxide may or may not be added [187]. The activation energy of the Li$^+$ or Na$^+$ ionic conductivities were reported as 0.1 eV with the room-temperature conductivity comparable to that of the best organic liquid electrolytes.

Recently, H.H. Hennen *et al.* in 2019 published a theoretical report on the ionic conductivity of antiperovskite-based glass produced from Li$_3$ClO by density functional theory-based on energies, forces, and stresses [188]. In the study, the theoretical Li$_3$OCl glass was created by conventional melt-quench procedures. The study also found high ionic conductivity for the material in the agreement with the Braga's experiment but Cl$^-$ ion mobility was also found in the material showing that the Li$_3$OCl glass is not a single-ion conductor. However, the Li$^+$ ion conduction is dominant with transference number t$^+ \approx 0.84$. The study also did not see the evidence for the dipole alignment in the bulk of the glass in simula-

tions even in the presence of electric fields comparable to those present in a battery as suggested by Braga *et al.*

7. Prospective of K⁺ Ion Conductive Glass

Potassium ion battery has recently attracted much attention for its development because of low reduction potential and low cost of abundant resources for potassium [195]. As the potassium ion has larger mass than those of Na⁺ and Li⁺ ions, it can provide high-density charge storage capacity [195]. Not only the study of K⁺ ion battery, but also the study of K-O2 battery has been reported. Since the interest in these batteries is increasing recently, the demand for the development of their highly conductive and stable solid-state electrolytes lied importance on the research of K⁺ ion conducting glassy electrolytes as in the case of Li⁺ and Na⁺-based batteries. However, less attention has been found on the study for K⁺ ion conducting glassy electrolytes unlike for Li⁺ and Na⁺ ion conducting glassy electrolytes.

The above discussion on the Li⁺ and Na⁺ ion conductivity in glassy electrolytes has shed light on high probability of K⁺ ion conductivity in glassy electrolytes. Since K⁺ ion is larger in size than those of Li⁺ and Na⁺ ions, the transport pathways for K⁺ ion should be wider for its mobility. There are some reports of mixed ion conductivity for K⁺ ions with other cations [196]. As in the Li⁺ and Na⁺ ion conducting glassy electrolytes, K⁺ ion conducting glassy electrolytes may be prepared from oxides, sulfides and phosphates [156] [158] [196] [197]. The introduction of antiperovskite-based glassy electrolyte [186] with unexpectedly high ionic conductivity raised a hope for the invention of new types of alkali ion conductive glasses which throws the message that we should not stick to the synthesis by only traditional methods such as use of only network formers and modifiers and by melt quench technique or mechanical milling. Sol-gel techniques are also used for the preparation of glasses/amorphous solid electrolytes [38] [198].

8. Summary

The conductivities of oxides and sulfides-based glassy electrolytes can be enhanced by increasing the concentration of glass modifiers. The conductivity can be enhanced by the addition of an alkali halide, MX, where M is an alkali and X is a halide (X = Cl, Br, I) or an alkali oxy salt such as M_2SO_4 to the glass matrix and mixing different salts (anions) such as Na_3BO_3-Na_2SO_4. When ionic salts are added, the ionic conductivity increases because of high mobile cation concentration and the re-establishment of the sites suitable for ionic motion. Mixed glass former effect (MGFE) can also be applied for conductivity enhancement. For example, M_2O-P_2O_5-B_2O_3 (M = Li, Na) glasses exhibit conductivities higher than either the pure phosphate or borate binary glasses with similar alkali content. MGFE is believed to originate from microstructural and topological alterations at the short-range level. The conductivities of sulfide-based glasses show better

conductivities than those of oxide-based glasses due to their relatively more polar nature and larger ionic size of the S^{2-} ion. The introduction of alumina and nitrogen has been attempted to improve the conductivity, but there is no significant effect of their introduction to the glass. Finally, a new type of glass that is different from the conventional glasses without a glass modifier and network mixture has been reported to exhibit the highest conductivity ever reported. The new type of glass is antiperovskite-based and is prepared in different ways.

As a conclusion, the traditional synthesis method and compositional method can be reconstructed to get better ionic conductivity. K^+ ion conducting glasses can be developed from oxides, sulfides, phosphates and antiperovskites.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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