CHAPTER 7

Comparison of Li^+, Na^+ & Ag^+ Glass systems

7.1 Introduction:

Ion-conductive glasses offer several key advantages when utilized in electrochemical devices, including high density, chemical resistance, the ability to form thin films, and unique properties compared to crystalline ionic conductors such as a non-grain boundary microstructure and isotropic properties [1]- [3]. Gaining a microscopic understanding of ion dynamics in glasses holds significant scientific and technological importance. Conductivity spectroscopy and its various derivatives, covering a wide range of frequencies and temperatures, provide valuable insights into the dynamic processes occurring in glasses. The linear response theory is commonly employed to comprehend the spectra of conductivity [4], [5]. Building upon this theoretical foundation, previous chapters have focused on three distinct glass series: LiI-doped lithium borophosphate glass, NaI-doped sodium borophosphate glass, and silver borophosphate glass with AgI doping in Chapters 4, 5 & 6 respectively.

In the investigation, the focus is on studying the correlation between the type of metal cation (Li^+, Na^+, and Ag^+) in metal halide dopants (LiI, NaI, and AgI) and the network transformation that facilitates ion transport in metal oxide-modified borophosphate glasses. The goal is to understand how these metal cations influence the structural, thermal, physical, and electrochemical properties of the glasses.

The observations suggested that the size of the metal ion, as well as its interaction with the glass network, play significant roles in determining the charge transport properties of borophosphate glasses. The smaller $Li^+$and Na^+ ions experience stronger Coulombic interactions and are more restricted in their movement, resulting in lower conductivity. Conversely, the larger Ag^+ ion experiences weaker bonding and has more freedom to move, leading to higher conductivity.

Correlations are observed in the ion dynamics of different glassy materials, originating from the structural disorder and interactions between the mobile charge carriers and the network [6]. Over the past few decades, considerable attention has been devoted to enhancing the conductivity of ionically conducting glasses. Numerous experiments involving a significant number of mobile species have been conducted at various temperatures, aiming to improve the transport properties of these glasses. Therefore, it is intriguing to investigate the behavioral transformation resulting from the response of each glass component, including the type of metal cation species, at varying concentrations within the borophosphate glass skeleton across a temperature range from room temperature to higher levels.

The electrochemical impedance spectra of all three glass series under investigation are observed to be influenced by the type, nature, and relative population of the metal iodide (MI) molecules used as dopants. This study aims to examine various properties of MI doped borophosphate glasses, including the glass transition temperature, density, activation energy for dc ionic conductivity, as well as dielectric and conductivity isotherms in relation to frequency.

To ensure a fair comparative analysis of their behaviors, the glasses underwent the same experimental procedures and environmental conditions, with the only variation being the temperature based on the type of metal iodide dopant used during sample preparation. This approach eliminates any potential influence of the preparation method on the comparative analysis. Ionic conductivity measurements have been performed over a broad spectrum of temperature and frequency, spanning from $303\,K$ to $373\,K$ and $1\,Hz$ to $32\,MHz$, respectively.

Motivation:

The motivation behind this study is to investigate the relationship between different metal cations (Li^+, Na^+, and Ag^+) present in metal halides and the underlying network structure of borophosphate glasses. The researchers aim to understand how the presence of these metal cations affects the network transformation and ion transport in metal oxide-modified borophosphate glasses.

To achieve this, the study involves a comparative analysis of various properties of borophosphate glasses doped with LiI, NaI, and AgI in the host matrix. The properties being studied include the structural, thermal, physical, and electrochemical characteristics of the glasses. By comparing these properties among the different doped glasses, the researchers aim to identify any potential correlations between the type of metal cation and the transformation of the glass network.

One significant finding of the study is related to the glass-forming ability of the sodium iodide (NaI) doped glass. The researchers discovered that the glass-forming ability of NaI −doped glass can be achieved by modifying the ratio of the glass former to the modifier. This finding contrasts with the glass series doped with LiI and AgI, which have a similar former-to-modifier ratio. The study emphasizes the importance of the former-to-modifier ratio in achieving the desired glass-forming ability when sodium iodide is used as the dopant. It's important to note that this study focuses on qualitative analysis, providing a comparative overview of the investigated data. The emphasis is on understanding the differences and similarities among the three glass series doped with $LiI, NaI,$ and AgI. By analyzing these differences and similarities, the study aims to shed light on the relationship between the metal cation type and the network transformation that facilitates ion transport in borophosphate glasses.

The findings of this study contribute to the understanding of how metal halides influence the properties and behavior of borophosphate glasses, particularly in terms of ion transport. This understanding has implications for various applications, including solid-state electrolytes, optoelectronic devices, and sensors, where the properties of these glasses play a crucial role.

7.2 Result and Discussion:

In this section, the features of metal iodides, specifically lithium iodide (LiI), sodium iodide (NaI), and silver iodide (AgI), are discussed for the purpose of comparison. These features are important in understanding the differences in the behavior of these metal iodides and their influence on the properties of borophosphate glasses.

One notable characteristic is the gradual weakening of the covalent bond strength as we move from LiI to NaI and then to AgI ($Li^+ < Na^+ < Ag^+$). Fajan's rule explains that the close proximity of Li^+ and I^- ions results in a strong bond-forming interaction, leading to the formation of a covalent bond and a covalent compound. As the cationic radius decreases ($Li^+ < Na^+ < Ag^+$) and the anionic radius increases (for the ubiquitous I^-), the degree of covalent character in the ionic bond increases proportionally. The relationship between polarizability and anion size is also discussed. The polarizability of an anion increases as its size increases, and conversely, decreases as its size decreases. Since the iodide ion (I^-) is the largest among the considered ions, it exhibits the highest degree of polarizability. According to the Hard Acid Soft Base (HASB) principle, LiI is composed of a hard acid (Li^+) and a soft base (I^-). Similarly, NaI is formed by the bond between a hard acid (Na^+) and a soft base (I^-). On the other hand, AgI is a compound of a soft acid (Ag^+) and a soft base (I^-). This principle suggests that LiI exhibits lower stability and higher reactivity compared to NaI. AgI, on the other hand, is a highly polarized compound with a greater degree of ionic bond character.

Table 7.1 provides a comprehensive overview of the bond chemistry associated with the metal iodide compounds discussed. This information is crucial for conducting an in-depth investigation of the transport behavior of cations within the borophosphate glass system. By understanding the characteristics and differences among LiI, NaI, and AgI, researchers can better interpret the results and correlations observed in the borophosphate glasses doped with these metal iodides.

Table 7.1: *Data sheet of the metal iodide compounds under investigation.*

Series code	**MI dopant**	**Metal Iodide (MI) (HASB theory)**	**Bond type**	**Inter-nuclear distance (Å)**	**Dipole moment (μ in Debye)**	**r_c/r_a**
LBP	LiI	Hard base-soft base	Most covalent	2.87	11.4731	0.3454
NBP	NaI	Hard acid-soft base	Less covalent	2.71	13.0061	0.4636
ABP	AgI	Soft acid-soft base	Most ionic	2.39	13.7664	0.5227

In the investigated metal iodide compounds, the bonding characteristics between the metal cations and iodide anions play a significant role in the ion transport mechanism within the borophosphate glass systems. The class-A Lewis acid, lithium cation (Li^+), forms a relatively strong covalent bond with the iodide anion (I^-). This results in a higher degree of covalent bond character between Li^+ and I^-, indicating a preference for binding with hard (non-polarizable) bases. On the other hand, the class-B Lewis acid, sodium cation (Na^+), forms a bond with the iodine anion (I^-) with an intermediate covalent character. The NaI compound exhibits a lower degree of covalent bond character compared to LiI, indicating a preference for binding with soft (polarizable) bases. The compound AgI, which consists of silver cations (Ag^+) and iodine anions (I^-), exhibits an ionic bond character resulting from the interaction between a soft acid (Ag^+) and a highly polarizable soft base anion (I^-). The borophosphate glasses under study are composed of three main components: a polymer-like network consisting of PO_4 tetrahedral structures and trigonal borate units, metal oxides as network modifiers, and metal cations (Li^+, Na^+, and Ag^+) present in the LiI, NaI, and AgI dopant salts, respectively. The presence of network modifiers modifies the structure of the glass, leading to changes in its physical and chemical properties. These modifiers can influence the mobility of ions within the glass network and affect the ion transport mechanism.

The metal cations (Li^+, Na^+, and Ag^+) in the metal iodide dopant salts dissociate within the glass and interact with the host network. The movement of these ions through the glass network is influenced by their interactions with the network and can contribute to the overall ion transport mechanism. By studying the behavior of these metal iodide compounds and their interactions with the borophosphate glass system, valuable insights can be gained into the ion transport mechanism and the influence of different dopants on the physical and chemical properties of glass.

7.2.1 Thermal study

According to Fig. 7.1(a), the glass transition temperatures of the LBP, NBP, and ABP glass series show a decreasing trend as the size of the metal ion in the metal iodide salt increases. This observation can be explained by the inverse relationship between the size of the metal ion and the loosening of the vitreous glassy network.

When larger metal ions are incorporated into the glass structure, they can disrupt the network structure to a greater extent. This disruption leads to a more flexible and less densely packed network, which in turn results in a lower glass transition temperature. The increased size of the metal ions allows for more freedom of movement and reduces the rigidity of the glassy matrix. In terms of cohesive energy, it is observed that the total cohesive energies of the ABP glasses are comparatively lower than those of the NBP and LBP glasses. This can be attributed to the fact that the cohesive energy of Li_2O (from LiI dopant) exceeds that of Na_2O (from NaI dopant) and Ag_2O (from AgI dopant).

The higher cohesive energy of Li_2O indicates stronger bonding interactions within the glass network, resulting in a more compact and tightly bonded structure. In contrast, Na_2O and Ag_2O contribute to weaker bonding interactions, leading to a more relaxed and less densely packed network structure in the NBP and ABP glasses [7].

Consequently, it is reasonable to expect that the ABP glass compositions will exhibit reduced melting and glass transition temperatures compared to the other two glass systems. The lower cohesive energy and the larger size of the metal ions in the ABP glasses contribute to the weakened network structure and increased mobility, resulting in a lower glass transition temperature.

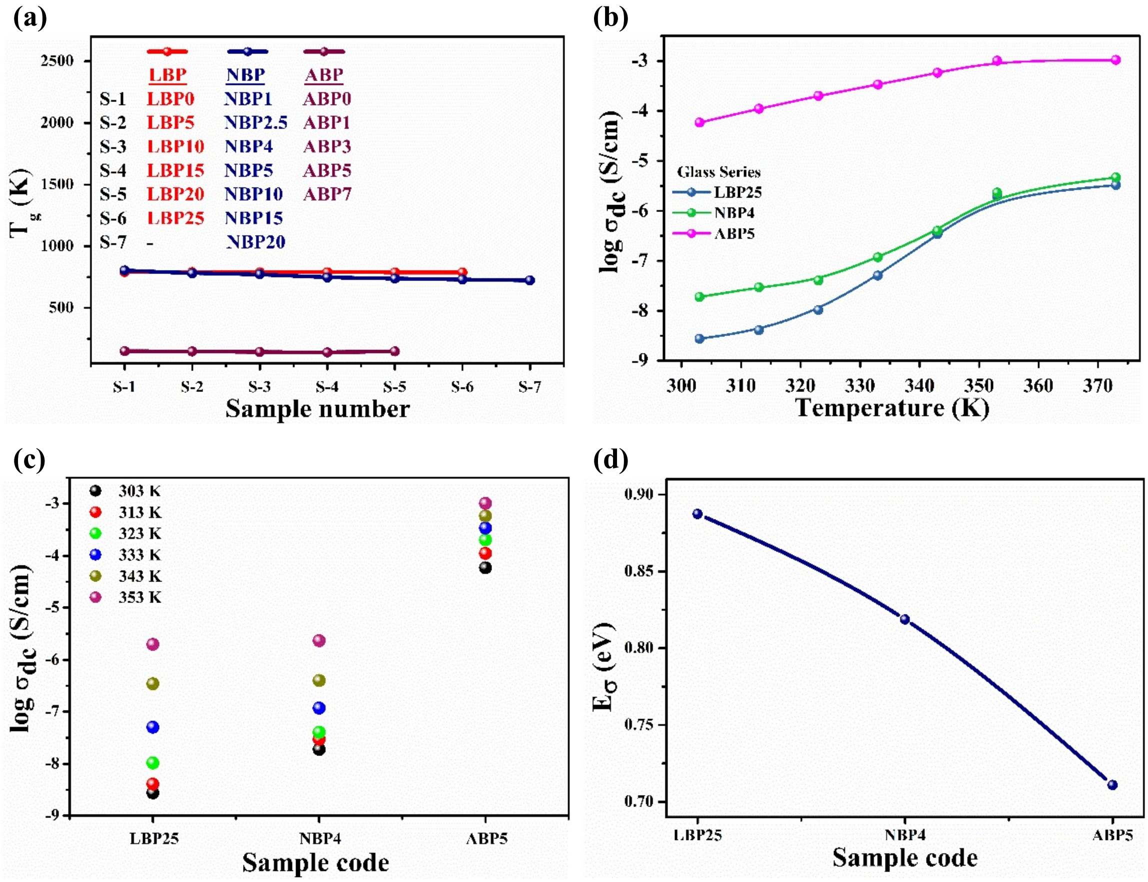

***Figure 7.1**: Qualitative comparison of (a) glass transition temperature, (b-c) dc conductivity as a function of temperature and the highest conductive samples at various temperature, respectively, (d) activation energy for ion diffusion.*

7.2.2 Ion transport study

(a) Conductivity study

Fig. 7.1(b-c) shows the non-zero limiting value of the dc conductivity (σ_{dc}) as a function of temperature and low frequency for borophosphate glasses with frequency-dependent conductivities. The dc conductivity of the investigated borophosphate glasses follows an Arrhenius law, where the conductivity exponentially increases with increasing temperature. Fig. 7.1(d) illustrates the activation energies for the dc conductivity of the most conductive sample from each of the three glass series. The activation energy represents the energy barrier that charge carriers must overcome to migrate within the glass structure. The dc conductivity in these borophosphate glasses is influenced by the presence of network-modifying cations that possess varying degrees of mobility and the ability to diffuse throughout the amorphous network. The different monovalent metal cations (Li^+, Na^+, and Ag^+) in the borophosphate glasses exhibit variations in charge transport, which can be attributed to the size of the metal ion and its Coulombic interactions with the glass network.

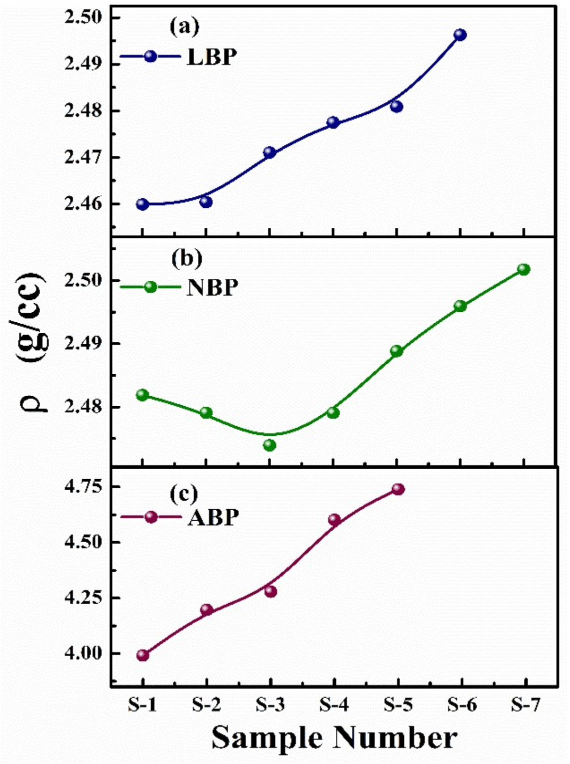

Figure 7.2: *Density (g/cc) of all glass series samples.*

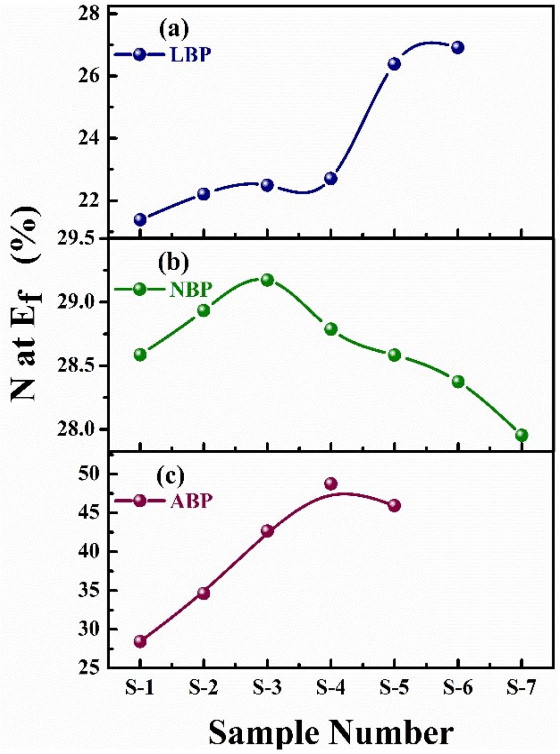

Figure 7.3: *N at E_f (%) of all glass series samples.*

Li^+ and Na^+cations, being smaller in size, are able to move within small structural traps in the glass framework. However, they experience strong Coulombic attraction from the terminal oxygen in the glass network, which binds them to their network sites.

On the other hand, Ag^+ cations have a larger effective radius and weaker bonding to the iodide molecule and the glass structure. This allows for greater mobility of Ag^+ within the glass network. As a result, the silver borophosphate glass series (ABP) exhibits the highest conductivity and the lowest activation energy among the investigated glass series.

The density of the ABP glass samples is comparatively higher than that of the NBP and LBP series samples, as depicted in Fig. 7.2(a-c). This difference in density also contributes to the variation in conductivity among the glass series. The observed phenomenon can be attributed to the correlation between the size and proximity of ions in the lattice and the amplitude of lattice vibration. Larger ions in closer proximity result in increased amplitude of lattice vibration, which enhances the probability of charge carrier migration. According to the data, Ag^+exhibits the greatest mobility, and the ABP5 sample of the ABP series displays the highest conductivity and the lowest activation energy, as shown in Fig. 7.1(d).

Furthermore, there is a favorable correlation between the increase in the count of liberated cations for conduction and the corresponding rise in conductivity. Fig. 7.3(a-c) illustrates that the ABP5 sample of the ABP series exhibits a significant increase in cations at the Fermi energy level compared to the other series samples. This increase suggests the presence of additional defect energy states and/or charge carriers, which contribute to the enhancement of ionic conductivity.

Overall, the enhancement of ionic conductivity in the borophosphate glasses is attributed to the influence of carrier concentration and the mobility of dissociated ions, which lead to increased mobility of charge carriers and lower activation energy for ion migration.

i. Ion transport model

The observed phenomenon in the studied glass systems suggests that when metal iodide salt is introduced, it induces a transformation of the glass into an ionic conductor.

- In the LBP series, the introduction of LiI leads to the dissociation of Li^+ ions, which then exhibit a hopping behavior as they conduct within the glass structure. This behavior is in line with the predictions of the Correlated Barrier Hopping (CBH) model.
- On the other hand, the NBP glass system characterizes the behavior of borophosphate glasses as electrolytes. Specifically, it focuses on understanding the conduction mechanism of Na^+ ions and their relaxation durations, which are explained by the Weak Electrolyte model established by Ravaine-Souquet.
- In the ABP glass system, the ion conduction mechanism is governed by the temperature-dependent Anderson-Stuart (A-S) model. According to this model, the mobility of Ag^+ ions exhibits a positive correlation with temperature. Additionally, the Non-Overlapping Small Polaron Tunneling Model (NSPT) suggests a strong interaction between the mobile ions and the ABP glass framework, which explains the significant modifications resulting from these interactions.

In all three borophosphate glass series, the conductivity follows the Jonscher's power law, which indicates that the conductivity varies with frequency.

ii. Decoupling Index (R_τ) and Mobile Carrier Concentration (K')

The current study utilized ac conductivity measurements and viscosity-derived mechanical relaxation times to investigate the relationship between R_τ (a measure of relaxation dynamics) and ion-pair content in glass compositions spanning a wide range. It has been systematically varied the salt concentration and observed corresponding variations in R_τ.

Fig. 7.4(a-b) illustrates the total count of cations that have become disengaged from the glass matrix across all the studied series. The trapping effect, where ions are immobilized within the glass structure, is more prominent in the LBP and NBP systems due to the relatively smaller size of the cations.

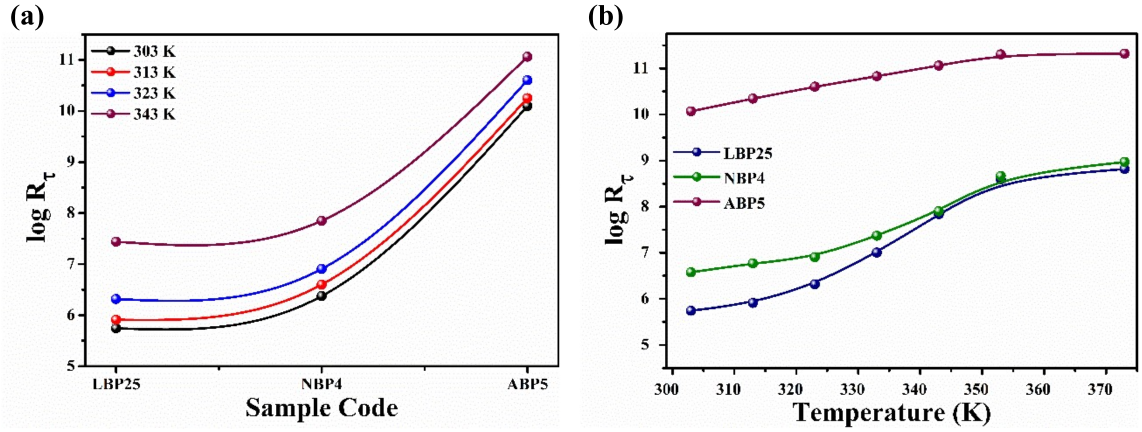

***Figure 7.4**: Decoupling index (R_τ), (a) as a function of highest conductive samples at various temperature, (b) as a function of temperature for highest conductive samples, of all three series.*

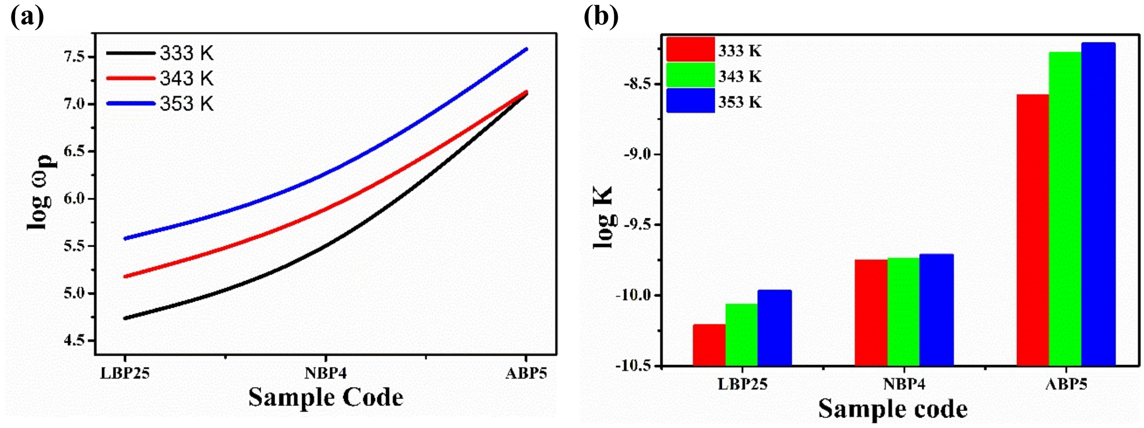

***Figure 7.5**: For the highest conductive samples from all three series and at various temperature points, the trend of (a) Hopping frequency ω_p,(b) total mobile ion concentration (K).*

Consequently, at a given temperature, these systems exhibit lower concentrations of decoupled Li^+ and Na^+ ions compared to the ABP glass system. Despite iodide ions being relatively immobile, their high polarizability and low charge create a relaxed environment that enhances the mobility of Ag^+ ions (mainly located in the iodide region). This results in conductivities ranging from 10^{-2} to 10^{-3} S/cm at room temperature [11].

The analysis of frequency-dependent conductivity provides insights into the hopping frequency (ω_p) shown in Fig. 7.5(a), which represents the onset of the relaxation phenomenon. It was observed that this frequency consistently shifts towards higher values as the temperature increases across all three glass series. The dc conductivity, temperature, and hopping frequency collectively determine the total mobile ion concentration (K) of a given sample, as depicted in Fig. 7.5(b).

(b) Dielectric Study

It is widely known that the electrical conductivity displayed by most inorganic glasses is electrolytic in nature and is primarily influenced by the concentration of alkali metal ions present within the glass. The high mobility of metal ions, particularly alkali ions, is also evidenced by significant dielectric losses observed in glasses incorporating these ions.

- In the studied LBP glass system, the dielectric relaxation strength shows a progressive increase with the addition of LiI and temperature, as observed in the frequency-dependent dielectric study. The incorporation of LiI into the glass matrix leads to a notable enhancement of dielectric permittivity and electrical conductivity parameters. This observation suggests that the inclusion of LiI improves the overall electrical characteristics of the glass. As the concentration of Li^+ ions in the glass matrix increases, there is a corresponding increase in dielectric loss. This phenomenon indicates that the inclusion of LiI promotes the mobility of charge carriers, resulting in increased dissipation of energy through the dielectric relaxation mechanism.
- In the NBP glass system doped with NaI, the polarization of the ionic medium at lower frequencies is primarily governed by the displacement of mobile ions in response to the applied electric field. This behavior is observed in the studied range of NBP glass samples. The reduction in the magnitude of polarization or dielectric relaxation strength ($\Delta\varepsilon$) of the medium is a consequence of this phenomenon. The dielectric relaxation strength exhibits dependence on both temperature and glass composition. The observed increase in dielectric relaxation strength ($\Delta\varepsilon$) is attributed to thermal effects and is found to be a gradual function of temperature. The observed polarization is a result of microscopic phenomena and is influenced by the concentration of mobile ions and the distance over which they hop.
- In the ABP glass series, the occurrence of the Non-Debye phenomenon suggests the presence of frequency-dependent space charge regions arising from ion diffusion and

the formation of a space charge region at the electrode-electrolyte interface. The conductivity of the ABP glass samples increases with temperature due to thermal stimulation. However, no significant loss peak is observed in any of the ABP glass samples across the analyzed frequency range. High dielectric loss is typically observed in electrolytes with high ionic conductivity. In this case, the high dielectric constant primarily stems from significant ionic conductivity, with electronic conductivity playing a minor role. The dissipation of energy, represented by migration losses, is mainly due to the dielectric loss, which is much higher than the energy storage capacity represented by the dielectric constant. As the temperature increases, the conduction loss also increases due to the corresponding increase in dc conductivity (σ_{dc}) and its shift towards lower frequencies at lower temperatures. By eliminating the dc contribution from the dielectric loss (ε''), the maximum of which shifts to higher frequencies as the temperature rises, the corrected value of ε'' indicates a reduction compared to the dielectric loss value, indicating the clear contribution of dipole relaxation.

(c) Modulus Study

In all three investigated glass series, the full width at half maximum (FWHM) of the modulus spectra shows significant variations with increasing dopant content within the studied frequency range.

- The findings from the LBP glass series indicate that the activation energy values for long-range ion migration (impedance) and short-range transport (modulus) are similar in magnitude. This suggests that the transportation of lithium ions in the system occurs through hopping mechanisms, regardless of whether the migration is long or short-range. According to this theory, ions undergo displacements by transitioning from one location to another within the glass matrix. The distribution of relaxation times and free energy barriers for ionic jumps are interconnected because the energy barriers affect the rates at which ions transition between different states or positions. Differences in energy barriers result in varying relaxation times for ions, leading to a broader distribution. The correlation between activation energy and the stretching parameter aligns with the coupling model proposed by Ngai.
- In the disordered structure of NBP glasses, the cooperative nature of the conduction process contributes to the distribution of relaxation times. A lower value of β in the glass composition indicates increased cooperation among the mobile ions. This means

that when one ion moves from one equilibrium position to another, it induces time-dependent movements of other charge carriers in its vicinity, resulting in further relaxation of the applied electric field.

- The distribution of relaxation times in the ABP glass series is associated with the distribution of free energy barriers for ionic jumps. This distribution increases due to either greater disorder in the system or the cooperative nature of the conduction process. The modulus component, which is temperature-dependent, accounts for the thermal activation of charge carriers. This leads to increased mobility and decreased relaxation time. The frequency exponent $n(T)$ in the studied silver iodide-doped glass series does not adhere to Ngai's relation. Additionally, it is important to note that the processes of dc conduction and conductivity relaxation are activated by different mechanisms due to differences in the activation energy for long-range and short-range migration.

(d) Time-Temperature Superposition Study

Table 7.2 provides the formulation of conductivity and modulus scaling parameters for the specific glass series, where the normalization curves converge to a single master curve. The models listed in the table demonstrate reasonable agreement with the corresponding experimental data.

Table 7.2: *List of suitable theoretical models for scaling aspects to understand relaxation mechanism in respective glass series under investigation.*

Glass series	**Formulation/ Theoretical model for relaxation mechanism**	
	Conductivity study	**Modulus study**
LBP	➢ Summerfield ➢ Roling	➢ Ghosh ➢ Roling ➢ Isard
NBP	➢ Summerfield ➢ Roling	➢ Ghosh ➢ Roling ➢ T-I-S
ABP	➢ Roling	➢ Summerfield ➢ Roling ➢ T-I-S

The interdependence between the conductivity and electric modulus relaxation processes is influenced by various factors, including the presence of mobile ions, glass composition, network modification, temperature, and the specific composition of the glass series.

These formulations or models describe the theoretical understanding of the relaxation mechanisms associated with conductivity and modulus in each respective glass series.

(e) Thermodynamic fragility ($F_{1/2}$)

The differences in the magnitudes of $F_{1/2}$ between the LBP and ABP glasses indicate that the structure of corresponding melts is indeed affected by the presence of cations such as $Li^+$and Ag^+ [12]. The objective of this study is to examine the relationship between the silver borophosphate glass (ABP), lithium borophosphate glass (LBP), and sodium borophosphate glass (NBP) in relation to the value of $F_{1/2}$. The thermodynamic fragility, $F_{1/2}$, was calculated using the formula

$$F_{1/2} = (0.151 - x)/(0.151 + x) \quad \ldots\ldots(7.1)$$

where x = $\Delta T_g/T_g$ and ΔT_g represents the range of glass transition temperature.

The results revealed that the value of $F_{1/2}$ was lowest for the ABP glass series, followed by the LBP glass series, and finally the NBP glass series. These findings suggest that the relationship between ABP, LBP, and NBP glasses may influence the value of $F_{1/2}$, with the ABP glass series exhibiting a higher degree of fragility compared to the other two glass series investigated. Furthermore, the study also indicates that the LBP glasses demonstrate a relatively higher degree of fragility compared to the NBP glasses (Fig. 7.6(a)). The presence of cations, namely Li^+, Na^+ and Ag^+, significantly influences the composition of the melts under investigation.

(f) Ionicity (ΔC_p)

In various crystallographic groupings, an increase in ionicity is observed as the bond character transforms from covalent to ionic. The investigated glass systems in this study exhibit different degrees of covalent bonding. Specifically, the LiI dopant forms a strong covalent bond, while NaI exhibits intermediate covalent bonding.

On the other hand, Table 7.1 shows that AgI predominantly displays ionic bonding. Previous studies by S. Kumar et al,; [12] have observed high magnitudes of ΔC_p, which indicate a strong ionic bond between the constituent atoms. Both sets of glasses, ABP and LBP, exhibit high values of ΔC_p, with ABP glasses showing a slightly higher elevation due to the additional degradation (B^{4-} to B^{2-}) resulting from Li_2O. This leads to an increase in the average ionic bonding in LBP glasses.

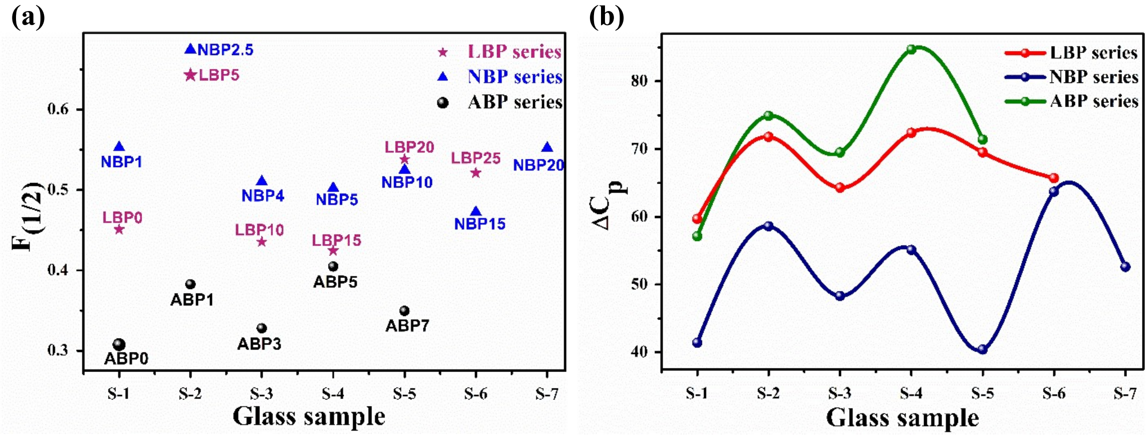

Figure 7.6: Comparison of (a) the thermodynamic fragility ($F_{1/2}$), (b) the ionicity (ΔC_p), for all the investigated glass series of borophosphate as host matrix.

The thermodynamic fragilities represented by $F_{1/2}$, show a characteristic range of 50% across all glass samples, indicating modified network glass systems.

These findings regarding ionicity in the present glass systems are consistent with previous investigations into their crystal structures [13]. They align with Zachariasen's postulates, which propose that the structure of glass is a random arrangement of units with the same short-range order as their corresponding crystals [14]. Therefore, a correlation can be drawn between the present system under investigation, as shown in Fig. 7.6(b), and the aforementioned findings.

Interestingly, despite the higher ΔC_pobserved in LiI-modified glasses, ABP glasses are found to be more fragile than NBP and LBP glasses. This deviation from the expected trend is unusual since higher ΔC_p in the case of the ABP glass system indicates a greater degree of ionicity, and such glasses are typically associated with higher $F_{1/2}$ values.

7.3 Conclusion:

In conclusion, the research work focuses on ion-conductive glasses and their advantages in electrochemical devices, such as high density, chemical resistance, thin film formation capability, and unique properties compared to crystalline ionic conductors. The study aims to gain a microscopic understanding of ion dynamics in glasses and utilizes conductivity measurements across a wide range of frequencies and temperatures to investigate the dynamics of Li^+, Na^+ and Ag^+ ions in borophosphate glasses.

The investigation reveals that the activation energy required for ion translation motion in these glasses is contingent upon the chemical properties of dopant molecules and the mass of the mobile charge carriers. The type of metal ion, Li^+, Na^+ or Ag^+, influences the structural, thermal, physical, and electrochemical properties of the borophosphate glasses. Smaller $Li^+$and Na^+ ions experience stronger Coulombic interactions, leading to lower conductivity due to restricted movement. In contrast, larger Ag^+ions experience weaker bonding and exhibit higher conductivity due to greater freedom of movement.

Correlations are observed in the ion dynamics across different glassy materials, stemming from structural disorder and interactions between mobile charge carriers and the network. Extensive efforts have been dedicated to enhancing the conductivity of ionically conducting glasses, and experiments with various mobile species have been conducted at different temperatures to improve their transport properties.

The research also investigates the relationship between metal cations (Li^+, Na^+, Ag^+) in metal halide dopants (LiI, NaI, AgI) and the network transformation facilitating ion transport in metal oxide-modified borophosphate glasses. The size and interaction of metal ions with the glass network play significant roles in determining the charge transport properties. The introduction of metal iodide dopants induces a transformation of the glass into an ionic conductor, affecting the structure and physical properties of the glass.

The study explores various properties of the metal iodide-doped borophosphate glasses, including glass transition temperature, density, activation energy for dc ionic conductivity, dielectric and conductivity isotherms, and their relation to frequency. It is found that the glass transition temperature decreases as the size of the metal ion in the metal iodide salt increases. The different glass series exhibit variations in conductivity, activation energy, and dielectric properties due to the presence of different metal cations and their interactions with the glass matrix.

The investigation also utilizes theoretical models to understand the relaxation mechanisms associated with conductivity and modulus in the different glass series. The findings highlight the influence of mobile ions, glass composition, temperature, and network modification on the interdependence of conductivity and modulus relaxation processes.

In conclusion, this research contributes to the understanding of how metal halides affect the properties and behavior of borophosphate glasses, particularly in terms of ion transport. The findings have implications for various applications, including solid-state electrolytes, optoelectronic devices, and sensors, where the properties of these glasses play a crucial role.

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