ABSTRACT

Solid State Ionics (SSI) is an interdisciplinary field of Solid State Physics that explores ionic solids with a wide range of ionic conductivity, from $10^{-13}\ S\ cm^{-1}$ to $10^{-1}\ S\ cm^{-1}$. The materials involved in SSI are known as Solid State Electrolytes (SSE) or Superionic Conductors (SC/SIC) and Fast Ionic Conductors (FIC) with ionic conductivities comparable to liquid electrolytes, making them suitable for electrochemical devices like batteries, fuel cells, and more.

To be a solid electrolyte (SE), a material should have an ion conductivity of about $10^{-3}\ S\ cm^{-1}$, higher than its electronic conductivity (about 0.01% of the ionic conductivity). The energy barrier for ion migration should be less than $1\ eV$, and the material should be physically and chemically compatible for electrochemical applications.

The backbone structure of SSI systems facilitates the transfer of ions over macroscopic distances. Solid electrolytes can be categorized based on their backbone structures: glass (amorphous) electrolytes, polymer (PE)/ gel polymer (GPE) electrolytes, composites, and NASICONs (crystalline/polycrystalline).

Glassy electrolytes, especially those containing oxides, have received significant attention due to their advantageous features, such as absence of grain boundaries, ease of shaping, and isotropic conduction. Various oxides and organic chemicals are used in glass production. The glasses have local, medium, and long-range structures but lack long-range order.

Solid-state ionic glasses are electrically insulating with conductivity around 10^{-12} S cm^{-1}, but this can be improved by altering the composition. Different glass-forming techniques like sol-gel, evaporation, and rapid quenching can be used. The crystallo-chemical postulates of Zachariasen and Goldschmidt's radius ratio requirement must be met to use oxides in ion-conducting glass formation.

The current research focuses on studying the ion transport mechanism in metal halide-doped borophosphate glass electrolytes for applications in electrochemical devices. The objectives include material preparation, structural and physical characterization, and investigation of electrical properties using techniques like Electrochemical Impedance Spectroscopy (EIS).

The thesis comprises seven chapters: Introduction & Literature Survey as **Chapter 1**, Model for Ion Transport in Glasses- **Chapter 2**, Material Preparation & Characterization Techniques as **Chapter 3**, Physical, Structural, Thermal, and Electrical Properties of Lithium Borophosphate Glass series as **Chapter 4**, Physical, Structural, Thermal, and Electrical Properties of Sodium Borophosphate Glass series- **Chapter 5**, Physical, Structural, Thermal, and Electrical Properties of Silver Borophosphate Glass series - **Chapter 6**, and Comparison of Glass Series and Conclusion as **Chapter 7** in the thesis.

The study focuses on examining the influence of various metal cation species (Li^+, Na^+, and Ag^+), their concentrations, and temperature variations on the properties and behavior of borophosphate glasses. The goal is to understand how these factors affect ion transport and conductivity in the materials, which can lead to the development of better ionically conducting glasses for different applications.

Ion-conductive glasses have significant advantages in electrochemical devices due to their high density, chemical resistance, ability to form thin films, and unique properties compared to crystalline ionic conductors. Understanding the ion dynamics in glasses is of great scientific and technological importance. Conductivity spectroscopy is commonly used to study the dynamic processes in glasses. The chapters in the thesis focused on three glass series doped with $LiI, NaI,$ and AgI, respectively.

The investigation aims to understand the correlation between metal cations (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 size and interaction of the metal ion with the glass network play significant roles in determining the charge transport properties of borophosphate glasses. Smaller Li^+ and Na^+ ions have stronger Coulombic interactions, resulting in lower conductivity, while the larger Ag^+ ion has weaker bonding and higher conductivity.

$Li^+$and Na^+ions, having smaller effective radii, are more restricted in their movement within the glass network due to strong Coulombic attraction from terminal oxygens, resulting in lower conductivity. In contrast, Ag^+ ions, with a larger effective radius and weaker bonding, have more freedom to move and exhibit higher conductivity.

The study also finds that the density of the glass samples affects their conductivity, with higher density leading to changes in ion packing and mobility within the glass structure.

The research aims to conduct a qualitative comparative analysis of the three glass series (LiI, NaI,and AgI dopants) regarding their structural, thermal, physical, and electro-chemical properties. By analyzing these properties, one can gain valuable insights into the behavior of borophosphate glasses with different metal cation dopants. The investigation further explores how the glass components, including the metal cation species, behave at varying temperatures to understand their contributions to the overall properties of the glass as temperature changes.

The electrochemical impedance spectra of the glass series are influenced by the type, nature, and relative population of the metal iodide (MI) molecules used as dopants, indicating that the choice and concentration of metal cation species significantly impact the electrical response of the material.

The study also examines other key properties of the MI-doped borophosphate glasses, such as glass transition temperature, density, activation energy for DC ionic conductivity, and dielectric and conductivity isotherms concerning frequency, to gain a comprehensive understanding of how the MI dopants affect the glass structure, dynamics, and electrical behavior. It is also a matter of investigation that how different metal cations (Li^+, Na^+, and Ag^+) influence the network structure and ion transport in borophosphate glasses. Comparison of various properties of $LiI, NaI,$ and AgI-doped glasses to identify correlations between the metal cation type and the glass network transformation. One significant finding is related to the glass-forming ability of NaI-doped glasses, which can be achieved by modifying the glass former to modifier ratio. The study focuses on qualitative analysis to understand the differences and similarities among the three glass series. The bonding characteristics of metal iodides (LiI, NaI, and AgI) influence the ion transport mechanisms in borophosphate glasses. Li^+ forms strong covalent bonds, Na^+ forms intermediate covalent bonds, and Ag^+ forms mainly ionic bonds.

The glass transition temperatures decrease with increasing metal ion size, resulting in a more flexible and less densely packed network. The ABP glass series (AgI-doped) exhibits the highest conductivity due to the greater mobility of Ag^+ ions.

The conductivities of the glasses follow an Arrhenius law, increasing exponentially with temperature. The dc conductivity is influenced by the presence of network-modifying cations and their mobility within the glass network. The ABP5 sample of the ABP series exhibits the highest conductivity and lowest activation energy. The conductivities are correlated with the increase in liberated cations, and there is a correlation between dc conductivity, hopping frequency, and total mobile ion concentration.

Dielectric studies show that LiI inclusion enhances dielectric permittivity and electrical conductivity parameters. NaI exhibits polarization at lower frequencies, with dielectric relaxation strength depending on temperature and composition. The ABP glass system shows frequency-dependent space charge regions and high dielectric losses due to high ionic conductivity.

Modulus studies reveal differences in activation energy for ion migration and short-range transport. The ABP and LBP glasses demonstrate higher fragility than the NBP glasses. The ionicity is higher in ABP and LBP glasses, and ABP glasses are more fragile despite higher ionicity.

The findings suggest that the size and interactions of metal ions significantly affect the charge transport properties of these glasses. The study provides valuable insights into the ion dynamics and conductivity in borophosphate glasses, with potential applications in solid-state electrolytes, optoelectronic devices, and sensors.

Overall, the investigation provides valuable insights into the relationship between metal cation dopants and network transformation mechanisms in borophosphate glasses, enhancing the understanding of ion transport and conductivity and potentially leading to improved ionically conducting glasses for various applications.

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