ABSTRACT

Keywords: *Solid Electrolyte, Ionic Conductivity, Glass, AgI, Differential Scanning Calorimetry, Ionic Transport Number, FTIR, Impedance Spectroscopy, Decoupling Index, Ion Relaxation, AC Conductivity, Dielectric Permittivity, Solid-State Battery.*

Solid electrolytes are a class of materials that conduct electricity by means of motion of ions like Ag^+, Na^+, Li^+, Cu^+, H^+, F^-, O^{-2} etc. in solid phase. The host materials include crystalline, polycrystalline, glasses, polymers and composites. Ion conducting glasses are one of the most sought after solid electrolytes that are useful in various electrochemical applications like solid state batteries, gas sensors, super-capacitors, electrochromic devices, to name a few.

Since the discovery of fast silver ion transport in silver oxyhalide glasses at the end of the 1960s, many glasses showing large ionic conductivity up to 10^{-4} ~10^{-2} S/cm at room temperature have been developed, chiefly silver and copper ion conductors. The silver ion conducting glasses owe their high ionic conductivity mainly to stabilized α-AgI. AgI, as we know, undergoes a structural phase transition from wurtzite (β phase) at room temperature to body centered cubic (α phase) structure at temperatures higher than 146˚C. The α-AgI possesses approximately six order of higher ionic conductivity than β-AgI. The high ionic conductivity of α-AgI is attributed to its molten sublattice type of structure, which facilitates easy Ag^+ ion migration, like a liquid. And hence, several attempts have been made to stabilize it at room temperature in crystalline as well as non-crystalline hosts like oxide and non-oxide glasses. Recently, in order to stabilize AgI in glasses, instead of directly doping it, indirect routes have also been explored. Where, a metal iodide salt alongwith silver oxide or silver phosphate is taken and an exchange reaction

permitted by Hard and Soft, Acid and Base (HSAB) principle occurs between the two and AgI and metal oxide form in the glass forming melt.

Keeping in view, the above facts, in the present work, transport properties of PbI_2 doped Ag_2O-V_2O_5-B_2O_3 glass systems has been investigated. For this purpose, three different glass series have been prepared and their physical and electrical properties have been investigated. For this purpose, three glass series having different stoichiometric ratios of PbI_2, Ag_2O, V_2O_5 and B_2O_3 were prepared using conventional melt quenching technique having following compositions.

Series (a): $x\ PbI_2 - (100-x)\ [Ag_2O - 2(0.7V_2O_5 - 0.3B_2O_3)]$

where, $5 \leq x \leq 25$ in steps of 5.

Series (b): $y\ (PbI_2{:}2Ag_2O) - (100-y)\ [0.7V_2O_5 - 0.3B_2O_3]$

where, $30 \leq y \leq 55$ in steps of 5.

Series (c): $z\ (PbI_2{:}Ag_2O) - (90-z)\ V_2O_5 - 10B_2O_3$

where, $30 \leq z \leq 50$ in steps of 5.

Work done in the present thesis has been organized in seven chapters as follows:

Chapter 1: A review and background information of different solid electrolyte materials and their development is presented. Along with that a detailed review on fast ion conducting glasses is included. At the end of the chapter, the aim of the present work has been given.

Chapter 2: A discussion about various theoretical models to explain fast ion conduction mechanism in superionic conductors in general and superionic conducting glasses in particular is given. In addition to that, impedance spectroscopy and its various formalisms are discussed.

Chapter 3: This chapter describes the method of preparation of the glass samples and various characterizations and techniques to study their various properties.

Chapter 4: Physical properties of the prepared glass samples are studied and discussed in this chapter. The glass samples are found to be fully amorphous as exhibited by x-ray diffraction studies. The density of the prepared samples is increasing consistently with increasing PbI_2 content in the glass. For glass series (a), the molar volume also increases with PbI_2 content. However, for glass series (b) and (c), molar volume is reducing with increasing PbI_2 content, showing that glass is getting compacted with increasing PbI_2 content.

Chapter 5: Transport properties of the prepared glass samples have been investigated using impedance spectroscopy and its various formalisms. The chapter discusses DC conductivity, AC conductivity, dielectric permittivity and modulus analysis of the obtained impedance spectra. The σ' spectra were scaled using Summerfield scaling law using $\sigma_{DC}T$ as the scaling factor for frequency axis and a well defined Time-Temperature Superposition (TTS) is observed as a function of temperature. The dielectric spectra show the presence of a dielectric relaxation in all glass samples. The dielectric permittivity, ε', spectra were scaled using the scaling law given by Sidebottom. The modulus spectra exhibit non-Debye relaxation of Ag^+ ions and could be explained using KWW (Kohlrausch-Williams-Watts) decay function. Scaling analysis of the modulus spectra as a function of temperature suggest of invariance of ion relaxation process with changing temperatures.

Chapter 6: Solid state battery studies: This chapter discusses about "solid state batteries" prepared by using the best conducting glass composition, from each glass Battery discharge characteristics, polarization measurements and other battery parameters like battery capacity, power density, energy, specific power etc. have been evaluated and summarized.

Chapter 7: A summary of the work done and future prospects are discussed.