

7.1 Summary of the results

- [1]. In the present study, transport properties of PbI_2 doped silver oxide containing vanado-borate glass systems have been investigated. The studies were undertaken with the aim of coming up with a suitable solid electrolyte system that can be used in a solid state battery. 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): $x \text{ PbI}_2 - (100-x) [\text{Ag}_2\text{O} - 2(0.7\text{V}_2\text{O}_5 - 0.3\text{B}_2\text{O}_3)]$

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

Series (b): $y (\text{PbI}_2:2\text{Ag}_2\text{O}) - (100-y) [0.7\text{V}_2\text{O}_5 - 0.3\text{B}_2\text{O}_3]$

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

Series (c): $z (\text{PbI}_2:\text{Ag}_2\text{O}) - (90-z) \text{V}_2\text{O}_5 - 10\text{B}_2\text{O}_3$

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

- [2]. The prepared glass samples are X-ray amorphous and show glass transition behavior, confirming their vitreous state. The glass transition temperature of all glass samples is below 100°C . And hence they may be utilized efficiently upto these temperatures only. The ionic transport number is almost unity and the prepared glass samples are principally ionic conductors.
- [3]. **Infrared** analysis reveals the presence strong and easily distinguishable absorption bands. In glass series (a), in which dopant salt concentration is varied against the glass matrix, a transition of VO_5 to VO_4 group is observed. In second glass series (b), vanishing of BO_4 stretching group after $y = 45\%$ is observed. In this glass series vibrational bands indicating presence of B-O-B bending and V-O-V symmetrical vibrations are present. In the glass series (c), in which V_2O_5 content is varied with respect to remaining glass matrix, BO_3 as well as BO_4

vibrational units are observed. The FTIR spectra clearly reveal the change of role of PbO from glass modifier to network former due to exchange coordination between PbI₂ and Ag₂O. Thus, presence of BO₃, BO₄ and B-O-B groups is there in all glass samples, which facilitate easy ion migration by providing NBOs in the glass network.

- [4]. **DC conductivity** of all glass samples is thermally activated and obeys Arrhenius law. For glass series (a), conductivity increases rapidly with increasing PbI₂ content. For glass series (b) and glass series (c), with changing compositions, conductivity initially decreases, attains a minimum at $M/F = 0.67$ ratio ($M = \text{PbI}_2 + \text{Ag}_2\text{O}$, $F = \text{V}_2\text{O}_5 + \text{B}_2\text{O}_3$, all in mole%) and then after it starts to increase. The reason for occurrence of such a minimum may be devoted to the change of role of PbO; it initially behaves as a glass former and higher values of M/F (>0.67), it gradually behaves as a modifier. The third glass series, $z(\text{PbI}_2:\text{Ag}_2\text{O}) - (90-z)\text{V}_2\text{O}_5 - 10\text{B}_2\text{O}_3$ possesses minimum conductivity. In this particular glass series, concentrations of Ag₂O and PbI₂ are same, and hence no Ag₂O is left in the end glass sample, at the end of the exchange reaction between the two. Lack of modifier Ag₂O leads to reduced concentration of NBOs. The compositional dependence of conductivity for all glass series is supported by **decoupling index**, R_τ . The glass compositions having higher decoupling index have higher ionic conductivity and vice-versa. Thus, compositional dependence conductivity is thus related to their 'looseness' of the glass structure, that is how easily it allows Ag⁺ ion migration in the glass matrix, and this is governed by decoupling indices of respective glass compositions. To understand the Ag⁺ ion conduction mechanism in these glass systems, the Anderson-Stuart formalism is most suitable.

- [5]. The **highest conducting composition** among all glass samples is $y = 55$ mole% in glass series (b); i.e.: $55(\text{PbI}_2:2\text{Ag}_2\text{O})-45[0.7\text{V}_2\text{O}_5-0.3\text{B}_2\text{O}_3]$, with $\sigma_{DC} = 1.94 \times 10^{-2}$ S/cm at room temperature. The transport number for this particular composition is also unity. Hence, this particular glass composition is the most justifiable contender as a solid electrolyte amongst all glass samples.
- [6]. The AC conductivity spectra obey the universal power law and exhibit a non-Debye type of relaxation behavior. The σ' spectra for all glass compositions follow Summerfield scaling law as a function of temperature and it a well defined time temperature superposition (TTS) exists in the studied temperature and frequency range. However no scaling as a function of composition for any of the glass series could be obtained; i.e. ion relaxation process varies from composition to composition.
- [7]. In **dielectric** analysis, the dielectric relaxation behavior is observed in all glass samples. The dielectric strength, $\Delta\epsilon$, is quite high for glass series (a) and (c), whereas for glass series (b) they are moderately high. The dielectric permittivity spectra obey Sidebottom scaling law (frequency axis is scaled by $\sigma_{DC} / \epsilon_o \Delta\epsilon$) as a function of temperature for all glass compositions. However, no scaling as a function of composition is observed. This can be attributed to that ion relaxation process is influenced by variations in ion hopping length as well as mobile ion concentration.
- [8]. In **modulus** analysis, non-Debye nature of ion relaxation process is observed. Moreover, the relaxation frequency is thermally activated. The relaxation time is Arrhenius in nature and its activation energy is very close to that of DC conductivity. Hence it is concluded that mobile Ag^+ ions may have to overcome similar energy barriers while conducting as well as while relaxing. Similar to AC

conductivity and dielectric permittivity, the modulus spectra also exhibit TTS behavior as a function of temperature, but not with composition. The stretched exponential constant, β , is independent of temperature as well as composition. However, β is found to be in the range of 0.3-0.7, which is usual for super ion conducting glasses.

Hence, the following inferences namely, (i) Arrhenius dependence of relaxation time with temperature and (ii) the comparable values of activation energy obtained from conductivity and modulus analysis suggest that the Ag^+ ion transport in the present glass systems follows hopping mechanism.

[9]. Battery application: The following optimum conducting compositions (OCC) from each glass series were chosen for solid battery application. They also possess unity transport number.

Series (a): $x = 25$ mole%: $25 \text{ PbI}_2 - 75 [\text{Ag}_2\text{O} - 2(0.7\text{V}_2\text{O}_5 - 0.3\text{B}_2\text{O}_3)]$

Series (b): $y = 55$ mole%: $55 (\text{PbI}_2:2\text{Ag}_2\text{O}) - 45[0.7\text{V}_2\text{O}_5 - 0.3\text{B}_2\text{O}_3]$

Series (c): $z = 50$ mole%: $50 (\text{PbI}_2:\text{Ag}_2\text{O}) - 40\text{V}_2\text{O}_5 - 10\text{B}_2\text{O}_3$

In addition to this, three different types of cathodes compositions are chosen and the polarization, and discharge studies of thus prepared cells has been carried out.

[10]. The Open circuit voltage of the prepared cells is very close to, 0.687 V, the standard value for Ag/I_2 type of cell reaction. The cells having $\text{C}+\text{I}_2+\text{SE}$ cathode show maximum stability against high discharge current, as well as they also show longest discharge times, whereas the cells having $\text{C}+\text{I}_2$ cathode $\text{C}+\text{I}_2+\text{TBAI}$ cathode show moderate and lowest responses respectively. The cell having $y = 55$ mole% glass composition as electrolyte with $\text{C}+\text{I}_2+\text{SE}$ cathode shows maximum stability amongst all investigated cells and in addition to that it

shows longest discharge time of more than 120 hr at a steady discharge current of 0.154 mA/cm^2 before reaching to 80% of OCV. And it has a discharge capacity of 0.819 mAh and its wattage is 0.559 mWh. One may conclude that this particular composition, i.e. the glass composition, **55(PbI₂:2Ag₂O)-45(0.7V₂O₅-0.3B₂O₃)** may be used as a suitable solid electrolyte for low and steady current requiring battery applications.

7.2 Future scope of the work

The future scope of the present work is given as follows.

- (a). In DC conductivity of glass series (b) and glass series (c), a minimum in conductivity isotherms is observed. As all prepared glass samples in these two glass series are principally ionic conductors in nature, ion-polaron interaction is not apparent here. Hence some more ion conducting systems with different metal halide salts and different glass formers in similar stoichiometric ratios may be prepared and investigated to see whether one ends up with similar results or not.
- (b). The glass composition **55(PbI₂:2Ag₂O)-45(0.7V₂O₅-0.3B₂O₃)** is having significant ionic conductivity and unity transport number. This particular glass composition may be optimized by replacing PbI₂ by some other metal halides, as lead is not an eco-friendly choice nowadays. Moreover this particular glass composition may be optimized using different glass formers instead of V₂O₅ and B₂O₃ to achieve still higher ionic conductivity.
- (c). Scaling of AC conductivity and dielectric spectra have been carried out using two separate approaches. And obtained results suggest of their equivalency. Hence, further theoretical insight is necessary to come up with a new scaling law that could accommodate both scaling laws in a single scaling law.

