Effect of Mixed Glass Former on Ionic Conductivity of Silver Boro Tungstate glass system \(x[0.75\text{AgI}:0.25\text{AgCl}]: (1-x)\) \([\text{Ag}_2\text{O-}\{\text{B}_2\text{O}_3:\text{WO}_3\}]\)

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Abstract. The idea to explore new ‘Superionic Electrolytes’, “Fast ionic conductors” is due to their tremendous potential applications in solid state electrochemical devices viz. solid state batteries , fuel cells, sensors, super capacitors. Superionic glasses have attracted great deal of attention due to their several advantageous over their crystalline counterparts such as high ionic conductivity, easy preparation, wide selection of compositions, isotropic properties and high stability etc [4-7]. Large numbers of silver ion based glasses have been reported in the literature for the glassy system of Agl-Ag2O: MxOy (MxOy = B2O3, SiO2, P2O5, GeO2, V2O5, As2O5, CrO3, SeO2, MoO3 & TeO3 etc) many of them shows high silver ion conductivity [8]. Ion transport behavior of Silver Boro Tungstate glass system \(x[0.75\text{AgI}:0.25\text{AgCl}]: (1-x)\) \([\text{Ag}_2\text{O-}\{\text{B}_2\text{O}_3:\text{WO}_3\}]\), where \(0 \leq x \leq 1\) in molar wt% prepared by melt quench technique were reported. The new host \([0.75\text{AgI}:0.25\text{AgCl}]\) was used as a better alternate in place of conventional host salt AgI. Conductivity measurement were carried out on this glass system as a function of frequency from 50 Hz to 5 MHz, over a temperature range of 27°C to 200°C, for different compositions by Impedance spectroscopy. The composition \(0.7[0.75\text{AgI}:0.25\text{AgCl}]: 0.3[\text{Ag}_2\text{O-}\{\text{B}_2\text{O}_3:\text{WO}_3\}]\) shows the highest conductivity of the order of \(\sigma_{rt} \approx 2.76 \times 10^{-2}\) S/cm, referred to as the Optimum Conducting Composition (OCC). The enhancement in the conductivity has been obtained by mixed former effect. XRD result shows that the system is completely amorphous. Temperature dependence of conductivity of all compositions were studied & reported. Activation energies (Ea) were also evaluated from the slope of \(\text{Log}(\sigma)\) vs \(1000/T\), Arrhenius plots.

1. Introduction
Ever since the discovery of MAg4I5 (M = Rb, K, NH4)[ 1-2] and fast ion conduction in Na-β alumina [3] a remarkable progress in the field of Solid State Ionics was made. This discovery had opened up the pathways to explore new superionic materials with different cations and anion conduction. Amongst these solids a great deal of effort has been made for the development of novel glassy electrolyte with innovative transport properties using various silver - oxy salts for their electrochemical device applications [4-7]. Since than a large number of Ag+ ion based oxide glasses with variety of glass former / glass modifier ratios with different doping salts were studied and reported [5,10-11]. In silver borate glasses, incorporation of Ag2O in B2O3 modifies the Boron-Oxygen network by converting some of the BO3 unit to BO4 units, which permits the dissolution of AgI salt in glass matrix providing Ag+ for the ion transport [9]. Conductivity of glasses can be enhanced by modification of the network by an alkali oxides or alkali sulphide by addition of dopant salt AgX (X=...
Cl, B, I) and by mixed glass former in the network. The enhancement in conductivity due to partial substitution of the network former by another, while network modifier is kept constant is called “mixed former effect” MFE[10].

In the present paper, we report here the effect of two glass formers [B2O3-WO3] on conductivity of new Silver Boro Tungstate system x[0.75AgI:0.25AgCl] : (1-x)[Ag2O;{B2O3-WO3}], where 0 ≤ x ≤ 1. An alternate dopant salt a quenched [0.75AgI]0.25AgCl mixed system solid solution has been used in place of conventional salt AgI [11]. Both the host exhibits identical transport properties, however new host salt yield better superionic glass/composite electrolytes as compared to those prepared with AgI [12]. Earlier attempts has been made to optimize the room temperature conductivity using single glass former such as B2O3[13], WO3[14], MoO3[15], CrO3[16] using a new host [0.75AgI:0.25AgCl] in place of conventional AgI salt. XRD of OCC of quenched system was performed to verify its amorphosity. Temperature dependence of conductivity of all compositions were studied and activation energy values (Ea) were evaluated from the slope of Log (σ) vs 1000/T Arrhenius plots.

2. Experimental
Solid electrolytes with the general composition x[0.75AgI:0.25AgCl]: (1-x) [Ag2O{B2O3:WO3}] for 0 ≤ x ≤ 1 have been prepared from analar grade chemicals (CDH) AgI, AgCl, Ag2O, H3BO3 and WO3. The appropriate amounts of the chemicals of the desired composition were weighed and grinded thoroughly by mortar and pestle. This powder was placed in a borosilica test tube and melted at 900°C in an electric muffle furnace. The melt was rapidly quenched by dropping the melt directly into liquid bath.

For ionic conductivity measurement the electrolytes were pulverized into fine powder and then pressed into pellets at a pressure of 2-3 ton/cm2 using perkin elmer hand press. The impedance studies in the present work were carried out using a HIOKI LCR HITESTER (3532-50) in the frequency range 50 Hz to 5MHz at different temperatures varying from 27°C to 200°C. Colloidal silver paint was painted on both sides of the electrolyte pellet as a reversible electrode and the true bulk resistance was calculated from the complex impedance plot.

3. Results and Discussion
Figure 1 shows the compositional dependence of ionic conductivity at room temperature for the system x[0.75AgI:0.25AgCl]: (1-x) [Ag2O{B2O3:WO3}] and x [AgI]: (1-x) [Ag2O{B2O3:WO3}] where 0 ≤ x ≤ 1. The ionic conductivity of all the compositions are ranging in order of 10-3 to 10-2 S/cm. We observe from figure that the conductivity increases as x increases, attains a peak value at x = 0.7, then decreases as x is increased further from 0.8 and 0.9. The system with composition 0.7[0.75AgI:0.25AgCl]: 0.3 [Ag2O{B2O3:WO3}] exhibited highest ionic conductivity of the order of σrt = 2.76 x 10-2 S/cm and referred to as “Optimum Conducting Composition” (OCC). Conductivity values were compared with glassy electrolytes prepared with AgI salts also for comparison which shows similar trends but have lower conductivity value. This increase in conductivity ‘σ’ has been attributed due to the mixed former effect. The reason for the decrease in conductivity for x = 0.8 & 0.9 may be due to blocked pathways for Ag+ ion migration created by interstitial borons. Boron may occupy interstitial positions of WO3 networks may cause hindrance to Ag+ ions which otherwise would have passed through those of WO3 interstitial windows. The ionic conductivities are relatively higher than those obtained for single former electrolyte [14]. This feature can be accounted for , on the basis of thermodynamic approach to the weak electrolyte theory [17] where GM/GFs ratios i.e. [Ag2O/B2O3-WO3] can be treated as ‘solvent’ and the Ag+ ion conduction occurs through a dissociation of the solute of the type AgI → Ag+ + I-.

The solvent of the amorphous solid electrolytes with an additional glass former can be characterized by a relatively high dielectric constant which increases the solubility and polarisability of the solute [0.75AgI:0.25AgCl], which thereby increases the silver ion conductivity over the ternary solid electrolytes with only single glass former.
Figure 1. Composition dependence of room temperature conductivity of Silver Boro Tungstate glass system \((\bullet\bullet\bullet)\) with \([0.75AgI:0.25AgCl]\) and \((-\bullet\bullet\bullet)\) with \([AgI]\).

Figure 2. XRD pattern of OCC 0.7\([0.75AgI:0.25AgCl]\): 0.3 \([Ag_2O\{B_2O_3:WO_3\}]\) quenched system.

Figure 2 shows the XRD results of OCC of quenched system. It is clearly observed from the diffractogram that the quenched composition \((x = 0.7)\) have diffused shallow peak which confirms the formation of completely glassy/amorphous phase of the system.

Figure 3 shows the temperatures dependence of conductivity for different compositions of \(x[0.75AgI:0.25AgCl]: (1-x) \ [Ag_2O\{B_2O_3:WO_3\}]\) where mol fraction \(x\) varies in range from 0 to 1. Conductivity plots for the host compound \([0.75AgI:0.25AgCl]\) is also drawn for comparison. One can

Figure 3. \(\log_{\sigma}\) vs \(1/T\) plots of Silver Boro Tungstate glass system \(x[0.75AgI:0.25AgCl]: (1-x) \ [Ag_2O\{B_2O_3:WO_3\}]\) for different compositions along with the host salt \([0.75AgI:0.25AgCl]\).

Figure 4. Composition dependence of activation energy of Silver Boro Tungstate glass system \(x[0.75AgI:0.25AgCl]: (1-x) \ [Ag_2O\{B_2O_3:WO_3\}]\).
note from the figure that although the high conducting α – phase of the host material appeared to be stabilized completely in the glass former/network modifier, however optimum conductivity enhancement from the host were achieved for the composition range x = 0.7 as observed from figure. This is in accordance with the behaviour generally observed in AgI- based glasses in which conductivity increases with AgI content.

Fig. 4 shows activation energy (Ea) verses compositional dependence of x. The activation energy (Ea) values were computed from the slope of Logσ vs 1/T Arrhenius plots. It is observed that the composition x = 0.7 have minimum activation energy Ea ~ 0.04 eV. The Arrhenius equation governing the variation of the quenched (OCC) 0.7[0.75AgI:0.25AgCl]- 0.3 [Ag2O{B2O3:WO3}] can be expressed as: \[ \sigma = \sigma_0 \exp(-E_a/kT) \], where Ea is the activation energy which is very small in comparison with that of host compound Ea ~ 0.234 eV. It can be noted that Ag⁺ ion transport in the glass system takes place with relative ease.

4. Conclusion
The effect of mixed glass formers on ionic conductivity of a new Ag⁺ ion conducting Silver Boro Tungstate glass system x[0.75AgI:0.25AgCl]: (1-x) [Ag2O{B2O3:WO3}] has been studied. An alternate host a quenched [0.75AgI:0.25AgCl] mixed system / solid solution has been used in place of conventional salt AgI. The ratio of two glass former B2O3 and WO3 was kept constant while salt concentration of Ag⁺ was varied. An enhancement of the order of ~10-2 S/cm was achieved at room temperature for composition 0.7[0.75AgI:0.25AgCl]: 0.3[Ag2O{B2O3:WO3}] which is referred as OCC. This has been attributed due to MFE. Glassy/amorphous phase of OCC was confirmed by XRD. Temperature dependence of conductivity shows that α - like phase of the host salt is completely stabilized in the glass matrix and mechanism of ion transport in OCC can be explained by weak electrolyte model suggested for glasses. Minimum activation energy value (Ea ~ 0.04eV) was obtained for OCC suggest the easy ion transport in the system.

5. Reference

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