# CHAPTER 6

# CONCLUSIONS

Super ion conductors in the solid state have attracted much attention both because of the technological needs of solid electrolytes of low ohmic resistance and because of the academic interest in understanding the conduction mechanism. AgI based super ionic conductors are extensively studied after the discovery of the high conducting phase of α-AgI. Recently, some studies have been reported which show high $Ag^+$ ion conducting silveroxysalt system which have a different dopant other than AgI. Hence, in order to know whether the silveroxysalt system such as $Ag_2O$-$V_2O_5$-$B_2O_3$ can serve as a host for the bivalent halide $CdI_2$, to have a cost effective system for electrochemical applications.

1. The samples of the system $CdI_2$-$Ag_2O$-$V_2O_5$-$B_2O_3$ were prepared by melt quenching technique. Three series were prepared out of this system.

   (1) $xCdI_2$-(100-x) [$2Ag_2O$-($0.7V_2O_5$-$0.3B_2O_3$)] where $5 \leq x \leq 30$ in steps of 5 keeping the modifier to former ratio 2:1.

   (2) $20CdI_2$-80[$xAg_2O$-y($0.7V_2O_5$-$0.3B_2O_3$)] where $1 \leq x/y \leq 3$ in step of 0.25.

   (3) $20CdI_2$-$53.4Ag_2O$-26.6[$xB_2O_3$-(1-x)$V_2O_5$] where x=0, 0.2, 0.4, 0.6, 0.8 and 1.

The prepared samples were subjected to characterization, ac conductivity and battery performance studies.

2. The X-ray diffraction studies of the first series show a peak free spectrum for 15-25 mole% of $CdI_2$ doped system. For 5 and 10 mole% of $CdI_2$ doped system, an amorphous background with a peak due to the agglomeration of $Ag_2O$ in the system is observed. The 30 mole% of $CdI_2$ doped system shows an amorphous background with peak due to β-AgI.

In the second series, the limit of glass formation has been set at $1.5 \leq x/y \leq 3$ among the samples prepared with different modifier to former ratio (x/y) from 1 to 3 in steps of 0.25. In the third series, all the samples show the peak due to agglomeration of $Ag_2O$, traces of AgI, metallic silver and some unidentified phases.

3. Differential Scanning Calorimetric studies show that the glass transition temperature, $T_g$ of the glasses decreases with increase of dopant concentration in the first series and in the second and third series $T_g$ is independent of modifier to former ratio (x/y) and $B_2O_3$ (x) content, means glass transition temperature mainly depends on the dopant concentration.

4. Infra red absorption spectra have been used to study the structure of the samples and its variation with the composition. The first series shows that the glass network is not affected by the addition of the dopant content. In the second series, the increasing addition of $Ag_2O$ to the system brings out the structural changes with composition and the transformation of $BO_3$ units to $BO_4$ and $VO_5$ to $VO_4$ units and observed the corresponding shift in the corresponding band towards the lower wave number. In the third series, where $V_2O_5$ is replaced by the $B_2O_3$ to the system, brings the changes due to the presence of constant amount of $Ag_2O$ Hence, it is modifier $Ag_2O$, not the dopant which is responsible for any structural changes brought in the glass system..

5. Thermo electric power studies show the thermo electric power (θ) value obtained is negative and arises due to the motion of $Ag^+$ ions in thermal gradient. The heat of transport obtained from the TEP plot is comparable to the activation energies obtained from the conductivity plot. The result obtained is in accordance with the theory of Rice and Roth, which states that in highly disordered materials heat of transport tends to be equal to the activation energy.

6. The ionic transport number found out from Wagner's polarization method and emf technique is almost unity. The high silver ionic transport number observed even if the silver vanadoborate system is doped with $CdI_2$ is due to the formation of AgI clusters in accordance with the theory of hard and soft acids and bases and $Ag^+$ ions from this AgI clusters results in high silver ion conductivity.

7. AC conductivity studies on the solid electrolyte system $CdI_2$ $Ag_2O$-$V_2O_5$-$B_2O_3$ have been studied over a range of frequency, temperature and composition. The dc conductivity of the bulk samples is found out from the resistance value obtained either from the low frequency intercepts of the impedance plots or from the frequency independent plateau region of the conductivity spectra.

8. The conduction mechanism in these systems has been explained by the diffusion path model. The conductivity is found to increase with the addition of $CdI_2$ to the silver oxysalt system for the first series and a maximum value is obtained for the 30 mole% $CdI_2$ doped system. In the second series, with the increase in the modifier to former (x/y) ratio the conductivity shows a non-linear behavior gives the idea that the glass modifier $Ag_2O$ content affects the ionic conductivity and a maximum of conductivity is obtained for the x/y ratio 1.75. In the third series, the substitution of $B_2O_3$ with $V_2O_5$ in the system, $CdI_2$-$Ag_2O$-$V_2O_5$, the conductivity shows a non-linear nature and a maximum value is obtained for 0.8% $B_2O_3$ doped system. There is no change in the order of magnitude of the conductivity and it has been explained that in these systems, the enhancement of conductivity mainly depends on the concentration of mobile ions, which is constant in the present series.

9. The frequency dependent conductivity of all the studied system shows a power law variation at high frequencies, a frequency independent plateau region (due to dc electrical conductivity) at low frequencies and a low frequency dispersion at lower frequency side (due to electrode polarization). The high frequency dispersion is found to shift to higher frequencies with increase in temperature and this dispersive nature is due to the many body effects commonly found in disordered materials. The hopping frequency, $\omega_p$ and mobile ion concentration has been evaluated and $\omega_p$ is found to be thermally activated in the same way as that of dc conductivity.

10. The Dielectric analysis on the system, $CdI_2$ $Ag_2O$-$V_2O_5$-$B_2O_3$ shows the dielectric permittivity which is found to decrease with the increase of frequency and saturate at higher frequencies and increases with temperature. Dielectric relaxation in these glasses has been explained by Stevels model. Dielectric loss, ε" is found to vary inversely with frequency due to the presence of dc conductivity. The frequency dispersion in tan δ manifests the persistence of $Ag^+$ mobility and dipolar relaxation losses are attributed for the dielectric loss. The activation energy obtained from the dielectric relaxation time is comparable with that of conductivity suggests the motions of the mobile charge carriers which are responsible for conductivity and relaxation effect.

11. The Modulus analysis of the present system, showing a broadened modulus spectrum, indicates the distribution of relaxation times in the conduction process. The relaxation frequency obtained from the modulus peak also thermally activated as that of dc conductivity suggests the transport of silver ions in the system and is probably due to hopping mechanism. The value of $M''_{max}$ remains almost constant with temperature but the frequency shifts to higher frequency side with temperature and composition. The

modulus spectra have been analyzed in terms of non-exponential decay function, giving a $\beta$ value ~0.6. The migration of mobile ions is responsible for the dispersion effects and relaxational spectra in these studied systems. The observed dispersion behavior and the relaxation phenomena in the presently investigated systems have been explained on the basis of the Diffusion Controlled Relaxation (DCR) model of Elliott. The obtained glass decoupling index increases with the increase in the dopant content and is in consistent with the conductivity with the increase in the dopant content. All these facts imply that the present system is also a practical solid electrolyte modeled by lumped RC circuits.

12. In order to see the applicability of this solid electrolyte to electrochemical applications, primary cells are fabricated using the electrolyte system $CdI_2$-$Ag_2O$-$V_2O_5$-$B_2O_3$ with varying cathode compositions and studied the polarization and discharge characteristics.

13. The battery performance is very sensitive to the composition of the cathode and the present study assists the choice of the best composition for the cathode constituents. The stability of these cells is improved appreciably by the addition of TAAI (tetra alkyl ammonium iodide, alkyl = ethyl or butyl) to the cathode. These results suggest that the cells fabricated with this present electrolyte material are suitable for low-power; ionic device applications that require long shelf life.