Chapter-VII

Conclusions and Summary

In this chapter, conclusions emerged out from the characterization results, ac and dc conductivity, dielectric and modulus studies and their dependence on the temperature and compositions are summarized.

Semiconducting transition metal oxide (TMO) glasses have been paid considerable attention because of their technical applications, namely optical and electrical memory switching, cathode materials and so on. It has been observed that the electrical conduction in the transition metal oxide glasses occurs by the hopping of small polarons between two different valence states of the TM ions such as V^{+4} and V^{+5} in vanadate glasses. When an alkali oxide is added in transition metal oxide glasses during glass preparation, one may also expect mobile alkali ions to contribute to the charge transport and mixed conductivity to be observed. Purely ionic conducting glasses can be used as solid electrolytes and those exhibiting mixed conduction can be employed as cathode materials in novel advanced electrochemical cells. In the present work a systematic study on silver based barium vanado-tellurite glasses is performed using x-ray diffraction, differential scanning calorimetry, fourier transform infra-red spectroscopy, transport number measurement, dc and ac conductivity in order to understand the effect of modifier on conduction and relaxation mechanism.

1. The samples of the system $BaO-Ag_2O-V_2O_5-TeO_2$ were prepared by splat quenching technique. Three series were prepared out of this system.
   (i) $x\,(BaO{:}1.5\,Ag_2O) - (95-x)V_2O_5 - 5TeO_2$
   where x = 25, 30, 35, 40, 45 mol %.
   (ii) $10\,BaO - y\,Ag_2O - (85-y)\,V_2O_5 - 5\,TeO_2$
   where y = 20, 25, 30, 35, 40, 45, 50, 55 mol %.
   (iii) $5\,BaO - z\,Ag_2O - 35\,V_2O_5 - (60-z)\,TeO_2$
   where z = 25, 30, 35, 40, 45, 50, 55, 60 mol %.

2. The x-ray diffraction study on the above mentioned three different series based on silver, barium, vanadium and tellurium have been performed. The diffraction spectra of all series show peak free pattern i.e., no phase of crystallinity is observed. Thus, the XRD curves confirm the amorphous nature of the glass samples studied.
3. Differential scanning calorimetry studies of the prepared glass samples provide the valuable information about the glass transition temperature (T_g) and the crystallization temperature (T_c). In the first series, glass transition temperature (T_g) is found to be independent of increasing both modifiers i.e., with the variation of BaO and Ag_2O , but in the second and third series where BaO is kept constant at 10 and 5 mol % respectively, T_g decreases with increasing modifier i.e., Ag_2O. The decrease of glass transition temperature with increasing modifier i.e., Ag_2O, suggests that a larger number of bonds are broken within the glassy network because the Ag^+ ions goes to interstitial sites which opens up the structure to form a more open type thermodynamically stable and amorphous phase. Presence of double and triple crystalline peaks in second and third series may be due to different crystalline phases appearing during heating up.
4. Infra red absorption spectra have been used to study the structure of the samples and its variation with the composition. An IR spectrum of first series shows the broadening of the absorption spectra due to the increase of BaO and Ag_2O both in this series. The transition from VO_5 to VO_4 group is observed by the corresponding shift in the bands towards the lower wave number. In the second series, as Ag_2O increases, transition from TeO_4 to TeO_3 occurs. It is also observed that the VO_5 groups are present in addition with VO_4 groups.

Some new bands, due to the increase of Ag_2O content are also visible in this series which are not observed in first series. In the IR spectrum of third series, transition from TeO_4 to TeO_3 occurs with increasing modifier. In this series also VO_5 groups are present along with VO_4 group. Since BaO is constant in this series, it confirms that new sharp peaks are due to the addition of Ag_2O that are assigned to vanadium groups. Thus, FTIR results confirm that the structure of the silver based barium vanado-tellurite glass matrix is formed of tellurite and vanadate oxides.

5. Silver ion transport number (t_{Ag}) of all the samples of three different series was measured by EMF method which shows the mixed conducting nature of the samples. The dominance of electronic transport number (t_e) over ionic transport number (t_{Ag}) in first series is observed whereas ionic transport number dominance is observed in the glasses of the second and third series except for y=20-30 mol% of second series, which shows dominancy of electronic component (t_e).
6. DC Conductivity studies on the system $BaO\text{-}Ag_2O\text{-}V_2O_5\text{-}TeO_2$ have been performed over a range of composition and temperature. The dc conductivity of the bulk samples is found out from the resistance value obtained from the low frequency intercepts of the impedance plots. Temperature dependence of dc conductivity obeys the Arrhenius behavior in all series. The variation of conductivity with the increase in modifier is clearly observable. The dc conductivity is electronic in nature in the samples of first series where BaO along with Ag_2O is increased whereas the dc ionic conductivity is found in the glasses of second and third series except for y=20-30 mol% of second series where glass samples show electronic nature. The results of these series thus

confirm that the present glasses of BaO-Ag_2O-V_2O_5-TeO_2 system are of mixed conducting nature.

7. The analysis of dc conductivity for the glasses of first series is adequately explained by Mott's small polaron theory. The average distance R_V between V-V ion increases with increasing modifier, since dc conductivity is due to electron hopping from V^{+4} to V^{+5}, then with increasing R, it is reasonable to expect a decrease in dc conductivity. The small value of polaron radius (r_p) suggests that the polarons are highly localized. The calculated values of density of states confirm for the localized states. In the second series conductivity decreases initially upto 30 mol % of Ag_2O then on further increasing Ag_2O, conductivity increases. Thus, the conductivity isotherm can be seen as intersect of two curves corresponding to electronic and ionic conductivity and the curve exhibit a sharp minima. For the samples y= 20, 25 and 30 mol % of Ag_2O, polaronic conductivity parameters are calculated which confirms the applicability of Mott's model of small polaron hopping. In the third series, conductivity of the samples increases while the activation energy decreases with modifier increase. This is because of the fact that as the modifier increases larger number of oxygen bridges are broken and the breaking of the bond, facilitates ion migration. The increasing number of non-bridging oxygen with increasing alkali or silver oxide content is also clearly visible from the decrease in the T_g with increasing Ag_2O content in second and third series.
8. The nature of hopping mechanism has also been ascertained for electronically conducting glass samples. Non-adiabatic nature of hopping is observed in all samples of the first series and for y= 20, 25 and 30 mol % samples of second series which show polaronic conductivity. Hence, non adiabatic nature of

hopping is confirmed only for these samples. Rest of the glass samples exhibit the dominance of ionic conductivity.

9. The frequency dependent conductivity shows a power law variation at high frequencies and a frequency independent plateau region at low frequencies which corresponds to dc conductivity. The ac conductivity behavior with frequency has been fitted to Almond West type of expression using a single exponent *n*. The variation of power law exponent *n* for first and third series is increasing with temperature while in second series it is independent of temperature. The hopping frequency is found to be thermally activated and Arrhenius in nature. The activation energy values calculated from hopping frequency are close to the values calculated from the dc conductivity. This indicates that the ions in these glasses also have to overcome the same barrier while conducting by hopping as well as relaxing. The calculated values of mobile ion concentration factor for all samples in different series using the values of σ_{dc} and ω_h are found to be temperature and compositional independent.
10. Scaling of the conductivity have been performed using σ_{dc} as the scaling parameter for the conductivity axis and ω_h is used as the scaling parameter for the frequency axis according to Ghosh's scaling model. It is concluded from scaling that the conductivity spectra are independent of temperature and composition. This implies that the relaxation mechanism is independent of temperature and composition under the conductivity formalism.
11. The dielectric response of the glasses was examined using impedance data. The logarithm of real part of dielectric constant (ε') is found to decrease with

the increase of frequency and saturates at higher frequencies whereas the dielectric loss varies inversely with frequency due to the presence of dc conductivity. The frequency and temperature dependent dielectric studies show the ion migration and polarization as per Stevel's model. The dielectric loss angle i.e., tan δ increases with the increase of temperature at low frequencies, in the mid frequency region it shows a peak while in the high frequency region it is constant with increase in temperature. The dispersion in tan δ with frequency is found to shift towards high frequency with increase in temperature. The dielectric relaxation time (τ) follows the Arrhenius behavior and the activation energies calculated from the dielectric relaxation time matches with that of conductivity plots attributing that mobile charge carriers are responsible for conductivity and relaxation effect in the present glass systems.

12. The conductivity relaxation of the mobile ion was examined using electrical modulus formalism. The modulus plot shows the non-Debye behavior and is asymmetric with respect to the peak maximum, which confirms the distribution of relaxation time in the conduction process. The relaxation frequency obtained from the modulus peak (f_{max}) is thermally activated. The normalized plot of modulus spectra confirms the temperature and composition independent relaxation mechanism. Non exponential decay function from modulus spectra provides β values close to 0.6-0.7 and is found to be independent of temperature and composition. The correlation between n and β namely $n=1-\beta$ proposed by Ngai, does not satisfy in our case. The calculated values of glass decoupling index R_τ for the first series suggests that the motion

of Ag^+ ions are coupled more and more with the viscous motion of the glass network as the amount of BaO is high in this series. For the second series R_τ values suggests that the decoupling of silver ions decreases upto 30 mol % of Ag_2O afterwards decoupling of Ag^+ ions increases with the viscous motion of glass network, facilitating the increase in conductivity. In the third series also, the motion of Ag^+ ions are decoupled more and more as Ag_2O increases because R_τ increases with increasing Ag_2O suggesting an increase in conductivity with the increase in modifier Ag_2O in the glass system which perfectly agrees with the results obtained from the conductivity and emf measurements.