A NEW FAST AG$^+$ ION CONDUCTING COMPOSITE ELECTROLYTE SYSTEM: DIELECTRIC INVESTIGATIONS

R. K. NAGARCH

Department of Physics, SVN University, Sagar, (M.P.), India

ABSTRACT

A fast Ag$^+$ ion conducting composite electrolyte system: $0.9[0.75AgI:0.25AgCl]: 0.1TiO_2$ has been prepared by quenching route of material preparation. At this particular composition the system exhibits better ionic conductivity and can be used in solid state battery fabrication as an electrolyte. Some basic dielectric parameters such as: dielectric constant (ε'), dielectric loss (ε") and tangent loss (tanδ) were studied as a function of temperature and frequency. Frequency dependence of dielectric constant (ε') and dielectric loss (ε") exhibit frequency dispersion, which is due to polarization effect and contribution of charge accumulation at the electrode-electrolyte interface. The observed behavior of ε' & ε" in the present study may be associated with space charge effect arising from the electrode. The variation of ε" and tanδ with temperature indicated that present system shows space charge polarization and dipole relaxation character of system.

KEYWORDS: Composite Electrolyte, Dielectric Constant, Dielectric Loss, Dispersion

INTRODUCTION

The dielectric relaxation as well as conductivity relaxation can be explained and understood easily through ionic conduction studies in solids. At sufficiently higher temperature all materials are liable to show increasing movements of ions, either intrinsic to their lattice as in the cases of ionic solids, or extrinsic due to impurity in purely covalent lattice including many polymers. This is normally expected to lead to dc conduction, although in many cases there is evidence of low frequency dispersion in data which on superficial analysis may be considered to represent dc conduction [1-3].

Generally materials exhibits fast ion conduction at ambient temperature known as fast ion conductors or superionic solids. Silver ion conducting superionic solids are well known due to their high ionic conductivity at ambient temperature [4]. Majority of these Ag$^+$ ion conducting superionic solids a large number of systems have been developed and reported in glassy/amorphous and composite phase [5-8]. In these systems AgI was used as a host salt material. After the investigation of a superionic solid solution: [0.75AgI:0.25AgCl] [9-10] a number of glassy/amorphous and composite electrolyte systems have been reported in the past, in which this solid solution was used as a host salt in place of traditional host matrix AgI [11-13]. The Ag$^+$ ion conducting superionic systems in composite phase, have attracted wide spread attention in recent year due to their possible technological application in solid state batteries, fuel cell, sensor etc. [4]. The new alternative host salt [0.75AgI:0.25AgCl] mixed system/solid solution which not only exhibited transport characteristics similar to AgI but has several transport parameters superior to those of convential host salt AgI. The β → α - like phase transition takes place at a subsequently reduced temperature at ~135ºC [9-10]. It has been reported that this new solid solution: [0.75AgI:0.25AgCl] yield better composite electrolyte as well glassy/ amorphous electrolyte systems [11-13].

In the present paper, we report here the dielectric relaxation studies of a new quenched composite electrolyte system: 0.9[0.75AgI:0.25AgCl]: 0.1TiO$_2$. The present system was prepared by melt quenching route of preparation (quenched in liquid nitrogen). At this particular composition the present system shows better ionic conductivity as well as other transport parameters. Several transport parameters such as: conductivity (σ) ionic mobility (μ), mobile ion concentration (n), ionic drift velocity (v$_d$) and transference number (t$_{ion}$) etc. as well as structural characterization i.e. XRD and DSC have already been reported on this system [14-15]. In the present paper, some basic dielectric parameters such as: dielectric constant (ε'), dielectric loss (ε") and tangent loss (tanδ) etc were studied as a function of frequency and temperature.

EXPERIMENTAL DETAILS

Sample Preparation

Commercially available reagent grade chemical compounds; AgI and AgCl (purity >98%) [Supplied by Reidel Pvt. Ltd. India] and TiO$_2$ (purity >99%) [Loba Pvt. Ltd. India] were used, as supplied. The AgI & AgCl were mixed homogeneously to form the new host salt [0.75AgI:0. 25AgCl] and heated at ~ 700^{0}C in electric furnace. The heated precursor melt was cooled rapidly (i.e. quenched in liquid nitrogen). Finally the finished product was thoroughly ground and then pure TiO$_2$ was mixed in the form of 0.9[0.75AgI:0.25AgCl]: 0.1TiO$_2$ superionic system. This mixture was heated at ~ 700^{0}C in electric furnace and then cooled rapidly i.e. quenched in liquid nitrogen. The details of material preparation have already been reported [14-15]. The finished product was thoroughly ground then pressed at 2-3 ton/cm^2 to form pellets of dimension of area 1.3 cm^2 and thickness 0.1 to 0.25cm. The surfaces of pallets were coated with silver paint for dielectric measurements.

Dielectric Studies

The frequency and temperature dependence dielectric measurements in terms of Z, θ, D and C$_s$ have been made on the present composite electrolyte system: 0.9[0.75AgI:0.25AgCl]: 0.1TiO$_2$ in the frequency range of 42Hz to 5MHz and temperature range of 30-200ºC. these data have been used calculate other parameters such as: Z', Z", ε', ε" and tanδ using standard relations and experimental constants [16]. A HIOKI LCR bridge (model 3532-50 Japan) was used for these measurements.

RESULTS AND DISCUSSIONS

The basic dielectric parameters have been measured using Z, θ, D and C$_s$ data in the frequency range of 42Hz to 5MHz and temperature range of 30-200ºC for the present system. The dielectric parameters have been evaluated using standard relations and constants which are discussed below in brief.

The complex permittivity is given by

$$\varepsilon^* = \varepsilon' - j \, \varepsilon'' = \varepsilon' - j(\sigma/\omega\varepsilon_0) \tag{1}$$

here ε' & ε" are real and imaginary parts of dielectric permittivity and σ is conductivity, the real and imaginary parts of complex permittivity can be measured using impedance data by the following equation:

$$\varepsilon^* = 1/(j\omega CZ^*) \tag{2}$$

Where Z* is complex impedance, C = (ε_0 A)/l, here 'l' is thickness of the sample and A is cross section area of the

sample. In the present investigation dielectric constant or real part of dielectric constant has been evaluated using relation:

$$\varepsilon' = C_s \, l / \varepsilon_0 A \tag{3}$$

Where 'C_s' is capacitance of the sample and ε_0 is dielectric permittivity for free space. The tangent loss is expressed as:

$$\tan\delta = \varepsilon'' / \varepsilon' = -Z'/Z'' \tag{4}$$

where Z' (= Z cos θ) and Z" (= Z sin θ) are real and imaginary impedance of the sample.

Frequency Dependence Dielectric Studies

The real component of the dielectric constant (ε') was studied as a function of frequency in the temperature range of 30–200°C for quenched composite electrolyte system: $0.9[0.75AgI:0.25AgCl]: 0.1TiO_2$. The variation of dielectric constant (ε') with temperature is shown in Figure 1 for the system. All these plots depict dispersion at higher frequency and decrease in dielectric constant with increasing frequencies. It is observed that both the dielectric constant and its dispersion are higher at higher temperature. It can also be seen from these plots that dielectric constant is almost independent with frequency in lower frequency region for all temperatures. Variation of (ε') with frequency could be attributed to the formation of space charge region at the electrode and electrolyte interface [16], which is familiarly known as $\omega^{(n-1)}$ variation or non Debye type of behavior. The space charge region with respect to the frequency is explained in the form of ion diffusion [16].
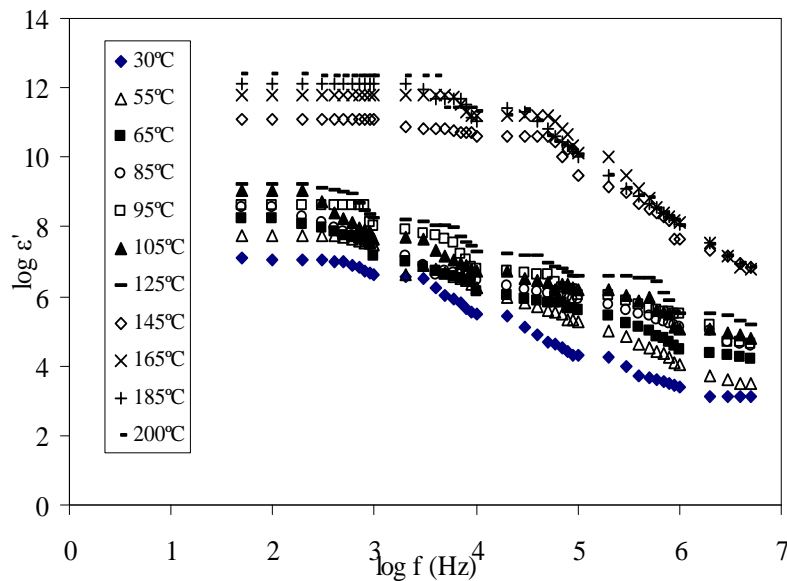

**Figure 1: Log F vs. Log E' Plots Composite Electrolyte System: 0.9
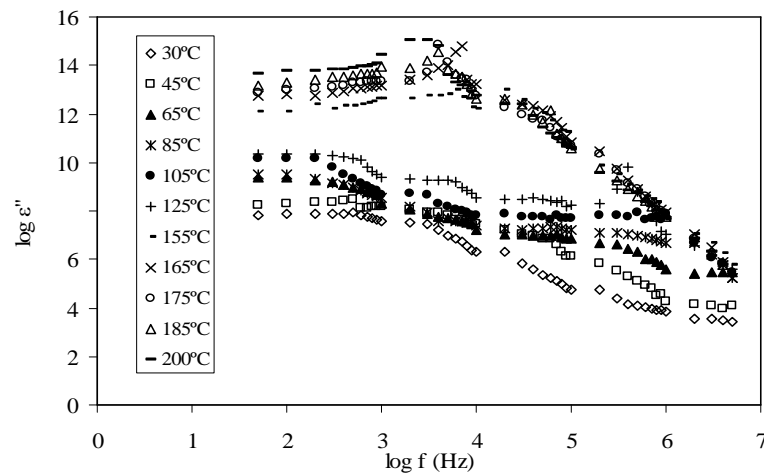[0.75agi:0.25agcl]: 0.1tio₂ at Different Fixed Temperatures**

Figure 2: Log F vs. Log E" Plots for Plots Composite Electrolyte System: 0.9 [0.75agi:0.25agcl]: 0.1tio$_2$ at Different Fixed Temperatures

In the low frequency region variation of dielectric constant is almost independent, which is due to the contribution of accumulation of charge at the interface and probably due to an interfacial ionic polarization caused by the localized Ag$^+$ ion motion in its potential well. At high frequency, this observed variation is attributed to high periodic reversal of the field charge carrier so the dielectric constant decreases with increasing frequency. The log ε" vs. log f behavior for new alternative host salt at various fixed temperatures in the range of (30-200°C) is shown in Figure 2. It is observed from Figure 2 that dielectric loss ε" decrease slightly with increasing frequency in lower frequency region and ε" decreases sharply with increasing frequency in higher frequency region. This type of behavior of ε" can also be associated with space charge effect arising from the electrode [16-18]. The frequency dispersion is attributed to the polarization effect and contribution of charge accumulation at the electrode electrolyte interface [19-20]. It is also observed from Figure that the dielectric loss ε" increases with increasing temperature, which is attributed to both the conduction and dipole relaxation loss [21]. The dispersion of dielectric loss ε" at higher frequency may also be due to the high periodic reversal of the field at the electrode-electrolyte interface. It is also clearly seen from this Figure 2 that dielectric loss ε" becomes high at lower frequency due to free charge motion within the materials [22]. These high values do not corresponds to the bulk dielectric process but are due to free charge build up at the interface between the electrolytes and electrodes. In lower frequency region there is particularly time for charges to build up at the interface before the field changes the direction and this contributes to very large apparent value of dielectric loss. This phenomenon leads to the so called conductivity relaxation [23].

Temperature Dependence Dielectric Studies

Dielectric constant ε' has been studied as a function of temperature at various fixed frequency (i.e. 1MHz, 100 KHz, 10 KHz, 1 KHz and 100 Hz). The log ε' vs. temperature plots for new host salt: [0.75AgI:0.25AgCl], at various fixed frequencies is shown in Figure 3. It is observed in all plots that dielectric constant ε' increases slowly up to approximately 125°C, beyond this temperature quick change occurs in ε', then dielectric constant again increases faintly with temperature. It is has been reported earlier that the present system exhibits β→ α -like phase transition at about 135°C.
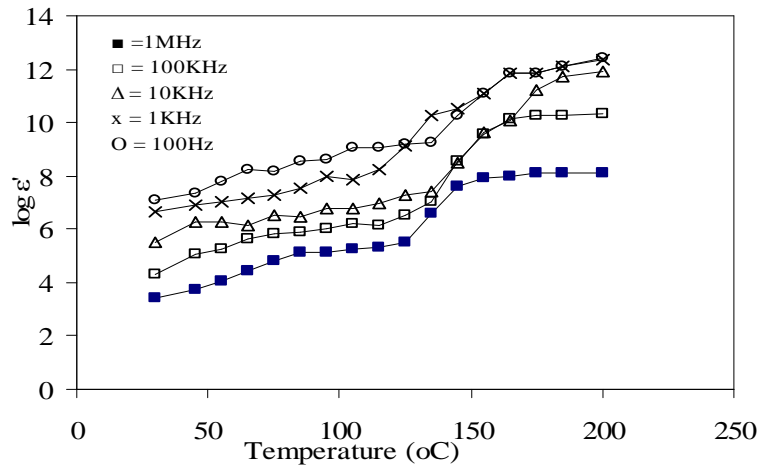
Figure 3: Variation of Dielectric Constant with Temperature at Different Fixed Frequencies for Composite Electrolyte System: 0.9[0.75agi:0.25agcl]: 0.1tio₂
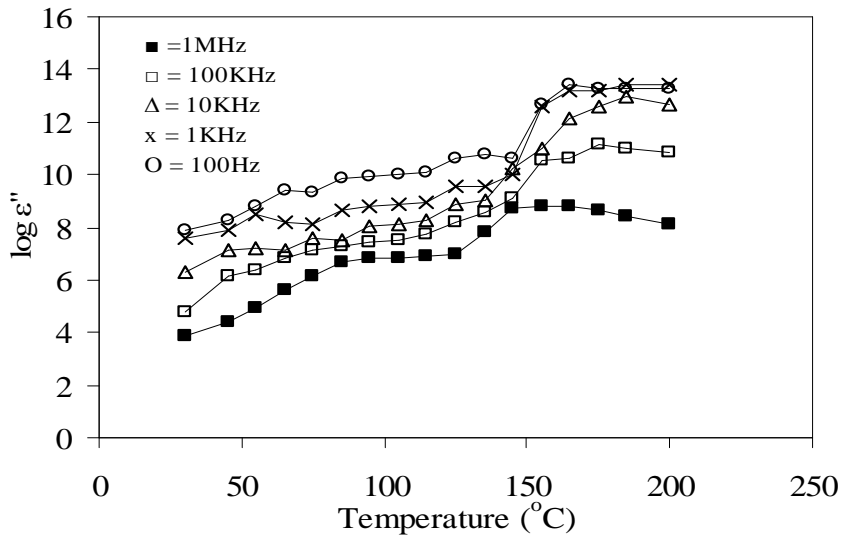

Figure 4: Variation of Dielectric Loss with Temperature at Different Fixed Frequencies for Composite Electrolyte System: 0.9[0.75agi:0.25agcl]: 0.1tio₂
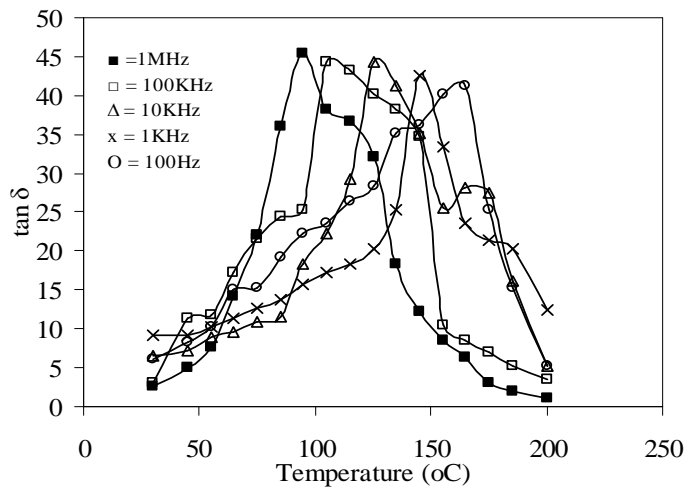

Figure 5: Variation of Tangent Loss (Tanδ) with Temperature at Different Fixed Frequencies for Composite Electrolyte System: 0.9[0.75agi:0.25agcl]: 0.1tio₂

Hence in the present investigation the dielectric constant exhibits abrupt change with temperature at this temperature. It is clear from this study that the dielectric constant strongly depend on frequency, also it is obvious from these plots that ε' is high at lower frequency and dielectric constant decreases with increasing frequency. It is well known that electronic, ionic, dipolar; ion jump or orientation and space charge polarizations contribute the dielectric constant. Among these all type of polarizations orientation and space charge polarizations depend on the purity & perfection of the ionic conduction in superionic solids. The present investigation shows slight increase in the dielectric constant ε' with temperature, which seems to be due to combined effect of ion jump polarization and space charge polarization [16]. At higher temperature there is an increasing hopping role contributing to the ion jump polarization and hence it enhances the dielectric constant with increasing temperature. It is also inferred that the electronic and ionic polarization are not affected significantly by temperature in the temperature range of the present study. Figure 4 depicts the temperature dependence of dielectric loss (ε") plots for host salt at various fixed frequencies. It is clearly seen from Figure 4 that dielectric loss increases with increasing temperature and attains a peak value than decrease slightly with temperature. It is also obvious from these all plots that the value of dielectric loss increase with decreasing fixed frequency. Hence in present investigation the highest value of ε" was obtained at 100Hz for the system. It is also indicates that the variation of dielectric loss for all plots with temperature has exhibited broad distinct maxima; with increasing frequency, the temperature maxima shift slightly towards higher temperatures and with increasing temperatures. The maxima shift towards higher frequencies indicating dipolar relaxation character of dielectric loss in the system. The temperature has an influence on dielectric loss, in the present investigations. The present system shows dipole relaxation which is attributed to the space charge polarization and may be due to the bonding effect in the system. Relaxation phenomenon is associated with the frequency dependence of orientational polarization and hence with polar dielectric substance. In static or slowly varying frequency the permanent dipoles align themselves along the applied field direction, upon them and thus contribute fully to the total polarization of the dielectric [24-25].

The variation of tangent loss (tanδ) with temperature at different fixed frequencies is shown in Figure 5 for the system. It is obvious from this Figure that in all these curves tangent loss (tanδ) has a relaxation peaks as maximum temperature (t_{max}) which depend on the frequency. It is clearly seen from Figure 5 that as the frequency increase the peak of the relaxation of tangent loss shift towards higher temperature region. Hence all these systems exhibits relaxation behavior and also the present system shows higher value of $tan\delta_{max}$ at higher frequency and temperature. From the temperature dependence of tangent loss studies it is obvious that present system shows the dipole relaxation which is mainly due to the space charge polarization [26-27].

CONCLUSIONS

A fast silver ion conducting composite electrolyte system: $0.9[0.75AgI:0.25AgCl]: 0.1TiO_2$ has been synthesized by quenching route of material preparation. The frequency dependence of dielectric parameters (ε' & ε") exhibited frequency dispersion behavior, which indicated that present system shows space charge effect arising from the electrode-electrolyte interface. It is also observed that present system exhibited higher values of ε' & ε" at lower frequency. It can be observed from temperature dependence of dielectric constant (ε') study, that ε' increase with increasing temperature, which is due to combined effect of ion jump polarization and space charge polarizations. The variation of dielectric loss and tangent loss with temperature indicated that present system shows maxima at particular temperature at fixed frequency which shows space charge polarization and dipole relaxation character of system.

ACKNOWLEDGEMENTS

REFERENCES

1. L.L. Hench and J.K. West, *"Principles of Electronic Ceramics"* John Wiley & Sons New York 1990.

2. V. Raghvan, *"Material Science and Engineering"- A first course,* Prentice –Hall (New Delhi) 1998.

3. S. R. Elliott, *Phys. of Amorphous Materials* Langmann (New York) 1990.

4. S. Chandra, *"Superionic Solids – Principles and Application"* (North Holland, Amsterdam) 1981.

5. M.C.R. Shastry and K.J. Rao *Solid State ionics*, **51** 331 1992.

6. Shahi K. and J.B Wagner. Jr. *Solid State Chem.* **42** 107 1982.

7. A. Chiodelli and A. Magistris *Solid State Ionics*, **18-19** 356 1986.

8. R.C. Agrawal and R.K. Gupta, *J. of Mater Sci.* **34** 1131 1999.

9. R. C. Agrawal, R. K. Gupta, R. Kumar and A. Kumar, *J. Mater Sci.* **29** 3673 1994.

10. R.C Agrawal., R. Kumar R.K. Gupta, M. Saleem, J. *Non-Crystalline Solids,* **181** 110 1995.

11. R.C Agrawal. And R. K. Gupta *J. Mater. Sci.,* **32** 3327 1997.

12. R.C. Agrawal, R. K. Gupta, C.K. Sinha, Kumar and G. P. Pandey, *Ionics* **10** 113 2004.

13. R. C. Agrawal, Mohan L. Verma, R. K. Gupta and S. Thaker, *Solid State Ionics* **473** 136 2000.

14. R. K Nagarch, R. Kumar and R. C. Agrawal, *J. Non – Cryst. Solids* **352** 450 2006.

15. R. K Nagarch and R. Kumar, *"Solid State Ionics-Materials and Applications" (eds.)* B.V.R. Chowdari, et al (World Scientific, Singapore) 2006.

16. J.R. Macdonald, (eds.), *Impedance Spectroscopy*, Wiley New York, 1987.

17. S. Selvasekarapanian and M. Vijay Kumar, *Materials Chemistry and Physics* **80** 29 2003.

18. R. Suresh and K. Hariharan, Materials *Chemistry and Physics* **60** 28 1990.

19. R. Mishra and K.J. Rao, *Solid State Ionics***106** 113 1998.

20. F.S. Howell R.A. Bose P.B. Macedo and Moyrihan C.J., *J. Phys. Chem.* 1974 **78** 639

21. S. Kumar K. Hariharan, *Mater. Chem. & Phys* **60** 28 1998.

22. A. Kyristis P. Pissis J. Grammatakakis, *J. of Polym. Csi. Part B: Polym. Ohys* 1995.**33** 1737

23. J.C. Dyre, *J. of Non Cryst. Solid* **135** 219 1991.

24. S. R. Elliott *"Phys. of Amorphous Materials"* Langmann New York 1990.

25. M.M. EI-Desoky K. Tahoon M. Y. Hassan *Mater. Chem. & Phys*. **89** 180 2001.

26. N. E. Hill W.E., VAghan A. H. Price, M. Devices *Dielectric properties and Molucular Behavior*. Van Nostrand Reinbuld Landon 1969.

27. Ravi Kumar V. and N Veeraiah., *J. of Phys. Chem. Solids* **1** 911998.