New Journal of Glass and Ceramics, 2011, 1, 125-129
doi:10.4236/njgc.2011.13018 Published Online October 2011 (http://www.SciRP.org/journal/njgc)

The Effect of Mixed Iodide Salts on the Conductivity Behavior in Ag_2O-V_2O_5-B_2O_3 Superionic Glass System

Poonam Sharma[1], D. K. Kanchan[1]*, Nirali Gondaliya[1,2], Meenakshi Pant[1], Manish S. Jayswal[1]

[1]Solid State Ionics & Glass Laboratory, Department of Physics, Faculty of Science, The M. S. University of Baroda, Vadodara (Gujarat) India; [2]Department of Engg Physics, SVMIT, Bharuch, Gujarat, India.
Email: *d_k_kanchan@yahoo.com

Received June 14th, 2011; revised July 19th, 2011; accepted August 23th, 2011.

ABSTRACT

A superionic mixed metal iodide glass system [(PbI_2 –CuI) - Ag_2O- V_2O_5- B_2O_3] *has been prepared by splat quenching technique. The prepared glass samples are characterized by X-ray diffraction* (*XRD*) *and differential scanning calorimetry* (*DSC*)*. The effect of mixed metal iodide salts concentration on electrical properties has been investigated by the complex impedance spectroscopy* (*CIS*)*. AC conductivity analysis is carried out in the frequency range of* 2*MHz*-1*Hz at different temperatures and an enhancement in the conductivity with iodide salts is the main feature of the observed results with an anomaly at* 20 *mole % of* PbI_2 –*CuI.*

Keywords**:** *Iodide Salts, Ag-Ion Conductors, XRD, Impedance*

1. Introduction

Super-ionic solids are known as potential candidates for application to electrochemical devices and solid state batteries. Electrical properties of silver oxy-salt based solid super ionic electrolytes with different glass modifyers and formers have been widely reported in the past [1-3]. Some reports on the replacement of Ag^+ ion with other feasible cation like CdI_2, PbI_2, CuI in the glass electrolytes are also available in literature [3-5]. Many interesting results have been obtained regarding the nature of electrical conductivity of these glasses. Instead of directly doping pure AgI in a host glass, some different routes by doping with a suitable MI_n type salt in an Ag_2O containing glass and thereby forming AgI as a result of exchange reaction between the two, based on Lewis HSAB (Hard and Soft Acids and Bases) principle [6], where a hard acid ion prefers to co-ordinate to a hard base ion and vice-versa are reported to have a favorable effect by increasing the electrical conductivity. According to the HSAB theory, Pb^{+2} ion is a borderline acid and I^- is a soft base while Ag^+ is a soft acid and O^{-2} is a borderline base, hence an exchange reaction between PbI_2 and Ag_2O takes place as per the following equation

$$Pb^{+2}\,[\mathrm{I}] + 2\,Ag^{+}\,[\mathrm{o}] \ldots\ldots 2\,Ag^{+}\,[\mathrm{I}] + Pb^{+2}\,[\mathrm{o}] \qquad (1)$$

From the above reaction we see that for one molecule of PbI_2 and one molecule of Ag_2O, as a result of the exchange reaction, two AgI and one PbO molecules are formed in the glass network. Damravi *et. al*. reported the more open volume are created by PbI_2 based glass system than by AgI [7]. However, many reports are available on PbI_2 and CuI based glasses, but up to author's knowledge no report is available on mixed iodide salts in literature. In the presently investigated system, an attempt is made to observe the effect of varying mixed metal iodide salts concentration on electrical properties in a silver-vanado-borate glass system.

2. Experimental

Sample preparation:

PbI_2 and CuI doped Silver-Vanado-Borate glasses in the composition of

$$x\,[(PbI_2 - CuI) - (100\text{-}x)\,\{2Ag_2O{:}3\,(0.7V_2O_5 - 0.3B_2O_3\}]$$

where $10 \le x \le 30$, in steps of 5, were prepared by the melt-quenching process. Required quantities of materials were weighed according to their molecular weight percentage and mixed thoroughly by wet grinding method. The mixer is then taken in an alumina crucible in a controlled electrical furnace and then the furnace temperature was raised gradually up to 873 K and kept for 2 hours to melt the mixture. Then the obtained homogeneous melt was quenched by pouring in between two Copper block plates to form the glass at room temperature. The obtained solid material was used for conductivity and other studies.

Characterization:

The as quenched glass samples were ground into fine powder and were characterized by X-ray diffraction (XRD) and differential scanning calorimetric (DSC) techniques. X-ray diffraction patterns of the powdered samples were recorded by X-ray diffractometer (Schimadzu) using Cu-K_α radiation for 2θ values between 10 and 80 degree at 2 deg/min scan rate. Differential scanning calorimetry is considered as a sensitive recorder to examine the thermal stability of the prepared samples. DSC analysis was performed in the temperature range 323 K - 673 K using differential scanning calorimeter (SII EXSTAR-6000) with a heating rate of 10K per min.

The electrical conductivity measurements of the glasses were carried out at various temperatures by complex impedance method. For this, the glass samples of about 1 mm thickness were used and the measurements were made by the two-probe method. The sample inside the sample holder is kept in contact with two polished, cleaned and spring-loaded copper electrodes. The complex impedance measurements were carried out using Solartron 1260 Impedance analyzer interfaced with computer in the frequency range of 1 Hz to 2MHz at various temperatures.

3. Results and Discussion

All the samples were examined by X-ray diffraction (XRD) technique to confirm their glassy nature. **Figure 1** shows X-ray diffraction pattern for x = 15 mol% and 20mol% glass samples. These patterns show a broad halo at $2\theta \sim 30^0$, beyond that no further oscillations are observed. The peak free pattern reveals the glass/amorphous nature of the samples. **Figure 2** represents the DSC thermogram of x = 10 mol% and 15 mol% glass sample which shows an endothermic peak of glass transition temperature (T_g) followed by two exothermic peaks corresponding to multiple crystallization. Presence of glass transition temperature is a signature of glassy nature of the prepared samples. N.H. Ray reported that the glass transition temperature depends on the density of covalent cross-linking, the number and strength of the cross links between oxygen and the cation and the oxygen density of the network [8]. In presently investigated system, T_g values are observed to increase with mixed iodide salt concentration which may be linked to lowering of the energy barrier for migration of the mobile Ag^+ ions.

Complex Impedance measurements were carried out to determine the electrical conductivity and the ac behavior of glasses over a range of temperature and frequencies.

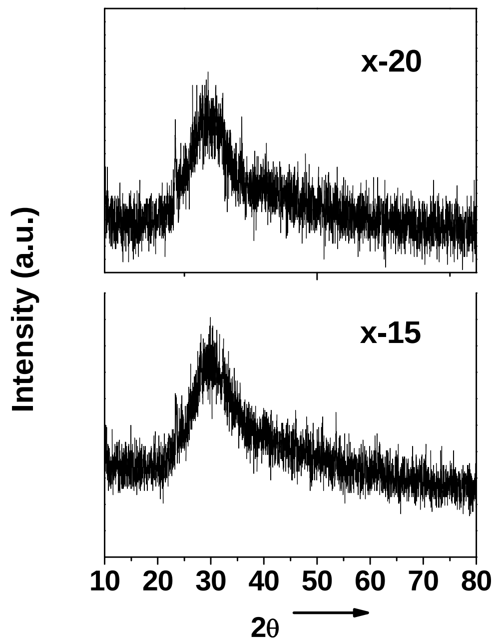

Figure 1. XRD patterns, for x = 15 and 20 mol%.

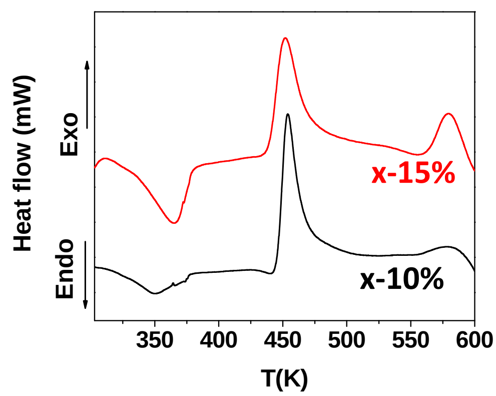

Figure 2. DSC thermogram for x = 10 mol% and 15 mol%.

Figure 3 shows the impedance plot (z′(ω) vs. z″(ω)) for all the prepared glass samples which consists of one arc and a spur at low frequencies. The observed spur at low frequencies shows the appearance of ionic conductivity in presently investigated system. The value of the bulk resistance of the sample was estimated from the low frequency intercept of the complex impedance plot using this resistance value, the dc conductivity is estimated [9]. **Figure 4** and **5** represents the temperature dependence and compositional variation of dc conductivity, respectively. Log σ vs. inverse of temperature plot shows a straight line indicating a thermally activated Arrhenius behavior. Similar behavior with different values is observed for other compositions too. More than one order enhancement in conductivity is observed by increasing the concentration of iodide salts. The increase in conductivity values is in consistent with reports based on iodide

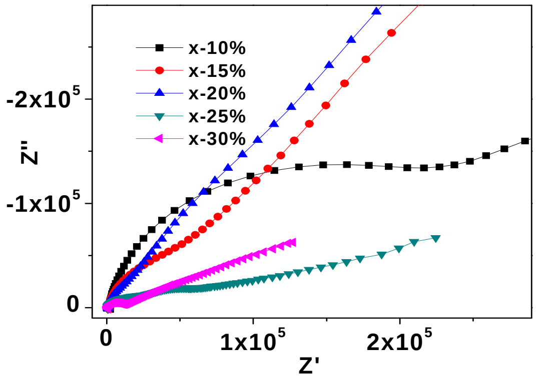

Figure 3. Complex impedance plots of (PbI_2–CuI-Ag_2O -V_2O_5-B_2O_3) glass series at 303K.

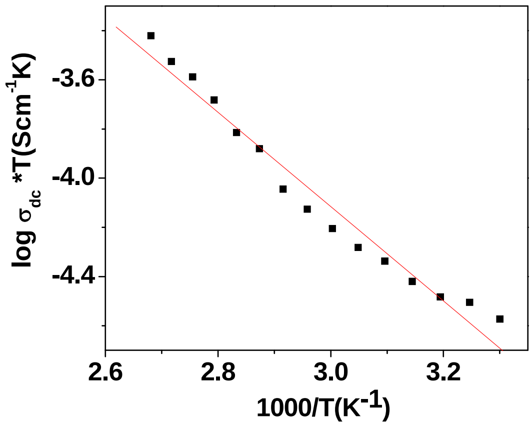

Figure 4. log σ vs. inverse temperature plot for x-10 mol%.

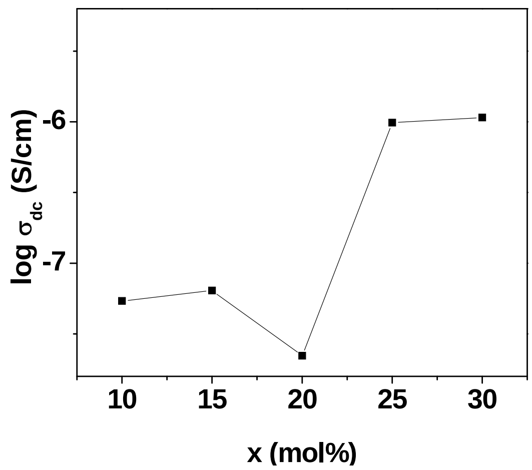

Figure 5. Composition-wise variation of dc conductivity at ambient temperature.

salts [3-6]. In the presently investigated system, the Ag^+ ions bonded to the non-bridging oxygen have less freedom to move and are expected to be less mobile compared to the Ag^+ ions in an iodine environment. The diffusion path model [10] requires that the different anion potentials are formed by the interaction of a mobile cation, Ag^+, with anions I^- and O^-. The potentials made with I^- ions by Ag^+ are smaller than those made with O^- ions. The Ag^+ ions in the shallow iodide potential are more mobile than Ag^+ ions in deep oxide potentials. The increase in AgI content increases the number of Ag + ions in the shallow iodide potential and simultaneously decreases the number of Ag^+ ions in the Oxy-Anion potentials. When these potentials are connected for a long period, they form a favorable path for ion transport known as diffusion path. Thus, the increase in (PbI_2 –CuI) concentration creates more and more diffusion paths increaseing the conductivity. In the present case, Cu^+, a transition metal cation is expected to be a soft acid, does not undergo exchange reaction under HSAB whereas, AgI, which is formed by the ion exchange reaction between PbI_2 and Ag_2O by the Hard and Soft Acids and Bases (HSAB) principle, participates in the conduction process. Since, PbI_2 is a heavy metal salt which is reported to behave as modifier as well as former, the increase in concentration may produce structural alteration and formation of inhomogeneous ionic clusters [3,4,11]. It is also known that borate glass is assumed to consist of a random three-dimensional network of nearly flat BO_3 triangles with a comparatively high fraction of six member boroxol rings [12]. In the borate glass systems, addition of glass modifier oxide changes the coordination numbers of boron polyhedral *i.e.*, the boron polyhedral changes from BO_3 to BO_4 [12] and borate functional groups are reported to exist in bridging and non-bridging oxygen configurations [13,14]. This change in boron structure might be reduceing the pathways for the migration of mobile cationic species and reduces the conductivity at 20 mol%. Beyond 20 mol% of iodide salt, the local environment of the Ag^+ ions changes to induce an enhancement in the conductivity. More thoroughly research in this direction is under progress. Same type of conductivity behavior in AgI-based glass system is reported in literature [15,16].

AC conductivity plots were analyzed and fitted according to Jonscher's universal power [17] law $\sigma(\omega) = \sigma_0 + A\omega^n$, where $\sigma(\omega)$ is frequency dependent conductivity, σ_0 is dc conductivity, A is a constant and ω is the angular frequency and n is the frequency exponent (usually $0 < n < 1$). **Figure 6** shows the frequency dependent conductivity plot at different temperatures for a sample x = 10 mol%. The plots exhibit double relaxations which merge into single one as can be observed from the high temperature.

The conductivity exhibits a typical frequency independent plateau at lower frequencies and a crossover or a dispersive region at higher frequencies. Similar behavior is observed for other compositions also. The frequency response of conductivity in glasses may be entirely due

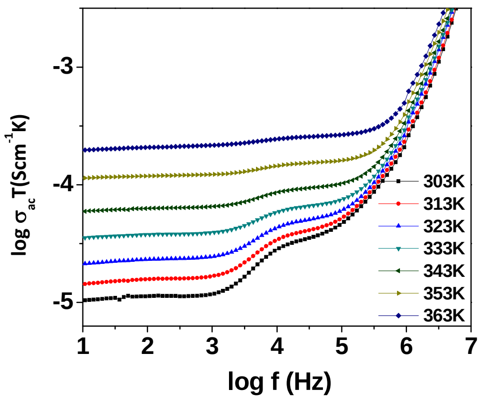

Figure 6. Frequency dependence of ac conductivity for x = 10 mol% sample.

to the translational and localized hopping of ions [18,19]. The translational hopping gives rise to long range electrical transport at very low frequencies, while the high frequency dispersion may be correlated to the forward–backward hopping of the ions at high frequencies which requires only a fraction of energy that is involved in the Long-Range diffusion of ions. The frequency independent plateau at low frequency region arises due to contribution of DC conductivity and the switch over of the frequency independent region to frequency dependent region at higher frequencies implies the onset of conductivity relaxation [20]. The onset frequency of conductivity relaxation shifts towards higher values with increasing temperature, as shown in **Figure 5**.

4. Conclusions

The enhancement in conductivity with mixed metal iodide salts PbI_2 and CuI content is observed with an anomaly at x = 20 mol%. PbI_2 is responsible for enhancement of conductivity due to the formation of AgI by exchange reaction between Ag_2O and PbI_2. In copper iodide salt, Cu^+, a transition metal cation, is expected to be a soft acid, does not undergo exchange reaction under HSAB. The increase in conductivity is due to Ag^+ ions in the shallow iodide potential which create more and more diffusion path ways for mobile cations. A sudden decrease in conductivity at 20 mol % of iodide salts is attributed to change in structure due to boron anomaly which is not favorable for migration of mobile cationic species.

REFERENCES

[1] D. Dutta and A. Ghosh, "Ionic Relaxation in AgI-Ag_2O-TeO_2 Glasses," *Journal of Physics: Condensed Matter*, Vol. 16, No. 15, 2004, pp. 2617-2624. doi:10.1088/0953-8984/16/15/013

[2] M. Pant, D. K. Kanchan, P. Sharma and M. Jayswal, "Mixed Conductivity Studies in Silver Based Barium Vanado-Tellurite Glasses," *Material Science and Engineering B*, Vol. 149, No. 1, 2008, pp. 18-25. doi:10.1016/j.mseb.2007.11.037

[3] K. Padmasree and D. K. Kanchan, "Conductivity and Dielectric Studies on 20CdI_2-80[xAg_2O-y(0.7V_2O_5-0.3B_2O_3)] Super Ion Conducting System Where 1 ≤ x/y ≤ 3," *Journal of Non-Crystalline Solids*, Vol. 352, No. 36-37, 2006, pp. 3841-3848. doi:10.1016/j.jnoncrysol.2006.06.012

[4] S. A. Suthanthiraraj and V. Methew, "AC Conductivity, XRD and Transport Properties of Melt Quenched PbI_2-Ag_2O-Cr_2O_3 System," *Ionics*, Vol. 14, No. 1, 2008, pp. 79-83. doi:10.1007/s11581-007-0151-6

[5] M. S. Jayswal, D. K. Kanchan, P. Sharma, M. Pant, "The Effect of PbI_2 on Electrical Conduction in Ag_2O-V_2O_5-B_2O_3 Superionic Glass System," *Solid State Ionics*, Vol. 186, No. 1, 2011, pp. 7-13. doi:10.1016/j.ssi.2011.01.016

[6] R. S. Kumar and K. Hariharan, "Ion Transport Studies in PbI_2-Ag_2O-V_2O_5 Glassy System," *Solid State Ionics*, Vol. 104, No. 3-4, 1997, pp. 227-237. doi:10.1016/S0167-2738(97)00419-0

[7] G. El-Damrawi, A. K. Hassan and H. Doweidar, "Silver Ionic Conductivity of Mixed Cationic Glasses," *Physica B*, Vol. 291, No. 1-2, 2000, pp. 34-40. doi:10.1016/S0921-4526(99)01875-X

[8] N. H. Ray, "Composition—Property Relationships in Inorganic Oxide Glasses," *Journal of Non-Crystalline Solids*, Vol. 15, No. 3, 1974, pp. 423-434. doi:10.1016/0022-3093(74)90148-3

[9] M. Pant, D. K. Kanchan, N. Gondaliya, "Transport Properties and Relaxation Studies in BaO Substituted Ag_2O-V_2O_5-TeO_2 Glass System," *Materials Chemistry and Physics*, Vol. 115, No. 1, 2009, pp. 98-104. doi:10.1016/j.matchemphys.2008.11.047

[10] T. Minami, "Fast Ion Conducting Glasses," *Journal of Non-Crystalline Solids*, Vol. 73, No. 1-3, 1985, pp. 273-284. doi:10.1016/0022-3093(85)90353-9

[11] P. S. S. Prasad and S. Radhakrishna, "Transport and Dielectric Studies on Silver Based Molybdo-Tungstate Quaternary Superionic Conducting Glasses," *Solid State Ionics*, Vol. 28-30, No. 1, 1988, pp. 814-820. doi:10.1016/S0167-2738(88)80153-X

[12] H. Doweidar, "Consideration of the Boron Oxide Anomaly," *Journal of Material Science* Vol. 25, No. 1, 1990, pp. 253-258. doi:10.1007/BF00544216

[13] E. I. Kamitsos and G. D. Chryssikos, "Borate Glass Structure by Raman and Infrared Spectroscopies," *Journal of Molecular Structure,* Vol. 247, 1991, pp. 1-16. doi:10.1016/0022-2860(91)87058-P

[14] P. J. Bray, S. A. Feller, G. E. Jellison Jr. and Y. H. Yun, "B^{10} NMR Studies of the Structure of Borate Glasses," *Journal of Non-Crystalline Solids*, Vol. 38-39, No. 1, 1980, pp. 93-98. doi:10.1016/0022-3093(80)90400-7

[15] N. Satyanarayana, R. Patcheammalle, P. Murlidharan, M. Venkateswarlu and B. Rambabu, "Preparation, Characterization and Characterization Studies of the Superionic Conducting AgI-Ag_2O-CrO_3-V_2O_5 Glassy System," *Solid*

State Ionics, Vol. 136-137, 2000, pp. 1097-1100. doi:10.1016/S0167-2738(00)00545-2

[16] R. V .G. K. Sarma and S. Radhakrishna, "Glass Formation and Conductivity Studies in Silver Boromolybdate Systems," *Material Science and Engineering B*, Vol. 7, No. 4, 1991, pp. 267-273. doi:10.1016/0921-5107(91)90003-E

[17] A. K. Jonscher, "The 'Universal' Dielectric Response," *Nature*, Vol. 267, 1977, pp. 673-679.

[18] N. Baskaran, G. Govindaraj and A. Narayanasamya, "A.c. Conductivity and Relaxation Processes in Silver Selenochromate Glass," *Solid State Ionics*, Vol. 98, No. 3-4, 1997, pp. 217-227. doi:10.1016/S0167-2738(97)00110-0

[19] S. H. Chung, K. R. Jeffrey, J. R. Stevens and L. Borjesson, "Dynamics of Silver Ions in $(AgI)_x$-$(Ag_2O$-$nB_2O_3)_{1-x}$ Glasses: A 109Ag Nuclear Magnetic Resonance Study," *Physical Review B*, Vol. 41, No. 10, 1990, pp. 6154-6164. doi:10.1103/PhysRevB.41.6154

[20] B. Deb and A. Ghosh, "Dielectric and Conductivity Relaxation in AgI Doped Silver Selenite Superionic Glasses," *Journal of Applied Physics*, Vol. 108, No. 7, 2010, Article ID: 074104.

