

Microstructure Dependence of Electrical Properties in AgI- and Ag₂S-Doped Glass Nanocomposites

Bijan Deb

Department of Physics, Ramkrishna Mahavidyalaya (Tripura University), Kailashahar, Tripura, India

Abstract

In this paper, we report the study of microstructure dependence of ion conduction for several AgI- and Ag₂S-doped glasses and glass nanocomposites systems. The structure and electrical properties of these samples have been studied and the effects of formation of nanocrystalline phases on the electrical properties of these glasses are presented. The microstructure of these glasses was studied employing transmission electron microscope (TEM). The temperature dependence of dc conductivity shows an Arrhenius nature with an activated type behavior for both the AgI- and Ag₂S-containing glasses. The comparative study revealed that the formation of nanocrystallites considerably influences the electrical conductivity of these glasses, the degree of influence being dependent on the glass composition and nature of dopant.

Keywords: conductivity, glass, microstructure, nanocomposites

***Corresponding Author**

E-mail: debbijan@gmail.com

INTRODUCTION

Glasses, nanocomposites and ceramics materials are significant from technological as well as scientific point of view.^[1-4] Silver ion conducting glasses are studied extensively for their high electrical conductivity, making them potentially suitable for various applications in sensors and electrochemical devices.^[2,5] The freezing of superionic α -AgI phase within glassy matrix at ambient temperature have shown to cause an enhancement in the ionic conductivity by many orders of magnitude^[6] making them suitable for various applications.

Several theoretical and experimental studies have been devoted to understand the structural features in these materials and to correlate the macroscopic properties to microscopic parameters.^[3,4] The ion transport behavior is observed to be influenced in few cases by the mobility of

the cations whereas in some other cases by the change in the concentration of mobile ions. Few study based on extended X-ray absorption fine structure (EXAFS)^[7] and Monte Carlo and molecular dynamics simulations reveal that the expansion of the glassy network caused by an addition of dopant salts increases the volume of the conduction pathways which effects the conductivity. The formation and growth of nanocrystallites within the glassy matrix can considerably influence the ion transport behavior. In a few silver ion conducting glass nanocomposites, an increase of the conductivity has been observed which is related to distribution of nanocrystallites embedded within the glass matrix.^[8] In few cases for lithium ion conducting glass ceramics, an increase of the conductivity with the increase of particle size and crystallinity has been observed.^[9] Thus, the microstructure of the glass nanocomposites plays a crucial role

in determining the variation of the conductivity and relaxation dynamics. In this work, we focus our attention to study the microstructure and the electrical properties in several AgI- and Ag₂S-doped glass systems with an attempt to correlate the ion transport to the microscopic modification of the glass structure.

EXPERIMENTAL TECHNIQUES

All the glass samples were synthesized by conventional melt quenching technique.^[10,11] We have prepared two glass systems namely AgI-doped glasses of composition $x\text{AgI}-(1-x)(0.60\text{Ag}_2\text{O}-0.40\text{SeO}_2)$ where $x = 0.15, 0.20, 0.25$, and 0.30 and Ag₂S-doped glass systems of composition $y\text{Ag}_2\text{S}-(1-y)(0.30\text{Ag}_2\text{O}-0.70\text{MoO}_3)$ where $y = 0.05, 0.10, 0.15$, and 0.20 mol fraction. The formation of glasses and glass nanocomposites were confirmed from the X-ray diffraction patterns recorded in X-ray diffractometer (Bruker, model D8 Advanced AXS) using CuK α radiation (wavelength = 1.54 Å). The microstructures of the samples were studied employing transmission electron microscope (TEM) (JEOL, model-JEM 2010). The conductivity measurements were accomplished using an LCR meter

(QuadTech, Model 7600) in the frequency range of 10 Hz to 2 MHz and in a wide temperature range.

RESULTS AND DISCUSSION

AgI–Ag₂O–SeO₂ Glass Systems

The dc conductivity of the glasses was obtained from complex impedance plots. The dc conductivity for all the compositions is plotted as a function of reciprocal temperature in Figure 1(a). It is clearly observed that the conductivity shows a linear dependence on reciprocal temperature following the Arrhenius relation given by

$$\sigma_{dc}T = \sigma_0 \exp(-E_\sigma/k_B T) \quad \text{Eq. (1)}$$

where σ_0 is the pre-exponential factor, T the absolute temperature, E_σ the activation energy, and k_B is the Boltzmann constant. The values of activation energy E_σ have been calculated from the least-squares straight line fits to the data. The variation of σ_{dc} with AgI content (x mol fraction) at a fixed temperature is shown in Figure 1(b). It is noted that the conductivity increases with the increase of AgI content. The activation energy shows opposite trend to that of dc conductivity.

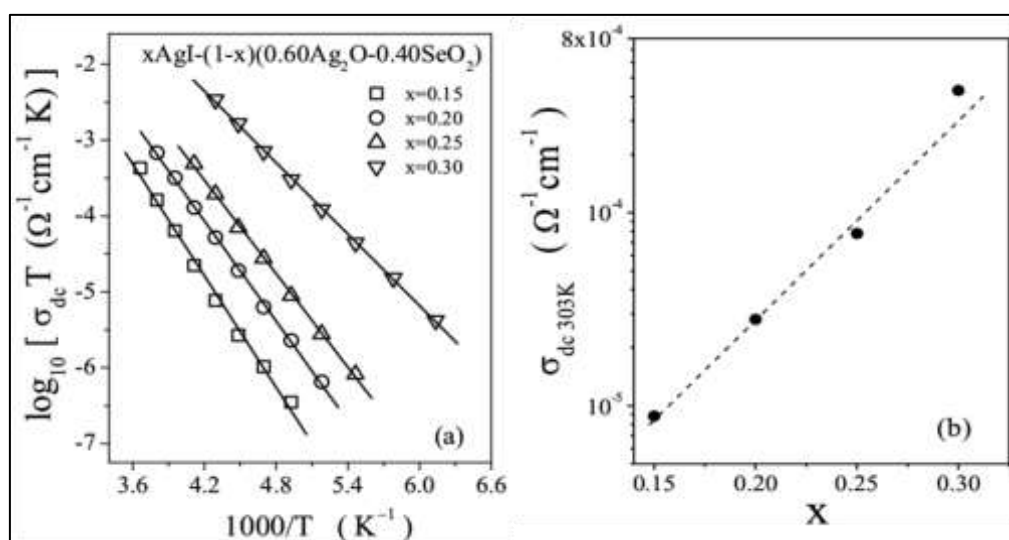


Fig. 1. (a) Reciprocal Temperature Dependence of dc Conductivity (σ_{dc}) for All the Glasses of Composition $x\text{AgI}-(1-x)(0.60\text{Ag}_2\text{O}-0.40\text{SeO}_2)$ Shown. Solid Lines Are Linear Fit to the

Data. (b) Variation of σ_{dc} With AgI mol Fraction (x) At a Fixed Temperature 303 K. Dotted Line Is a Guide to the eye.

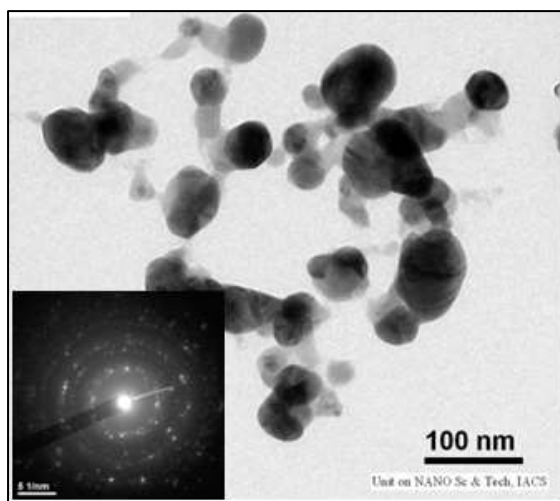


Fig. 2. TEM Images for $x = 0.15$ of Where x = AgI Mole Fraction. The Inset Is the Corresponding SAED Pattern.

The increase of dc conductivity can be understood qualitatively from the Anderson–Stuart model.^[12] According to this model the total activation energy consists of two terms namely the electrostatic binding energy and the strain energy. The decrease of binding and strain energy is related to modification of the network structure of the glasses on AgI doping. The addition of halide salt modifies the glass network and leads to the lowering of strain energy needed for migration between barriers and the binding energy of the mobile cations thus creating favorable pathways for ion conduction which leads to the enhancement of conductivity.

To quantify the microstructure dependence of ionic conductivity depending on composition the transmission electron micrograph of the samples were analyzed. Figure 2 shows the TEM images for selected compositions. The presence of crystallites particles of nanometer dimensions are also clearly observed for all the samples. The inset of Figure 2 is the selected area electron diffraction (SAED) pattern which shows different sharp spots. From the SAED pattern the crystalline

phases present was determined by comparing with standard ICDD datasheet which confirms the presence β -AgI and Ag₂SeO₃ phase in all the AgI containing samples. The average sizes of the nanocrystallites were determined for all the compositions and it is observed that the average size decreases with increase of AgI content. The decrease of particle size with the increase of AgI content might be due to the decrease of strain between the crystallite particles and the glassy matrix. This result thus leads to the fact that a part of AgI content causes expansion of the glassy network and so the growth of the size of the nanocrystallites within the glassy matrix is hindered with the increase of AgI content. Thus, the increase of conductivity is correlated to the decrease of nanocrystallite size with the increase of AgI content, favoring more open network and thus faster ionic conduction.

Ag₂S–Ag₂O–MoO₃ Glass Systems

The temperature dependence of dc conductivity for all the Ag₂S-doped samples is plotted in Figure 3(a). It is noted that the dc conductivity follows the Arrhenius relation given by Eq. (1). The variation of σ_{dc} with Ag₂S content (y) at a fixed temperature is shown in Figure 3(b). It is observed that σ_{dc} increases with increase of Ag₂S content up to $y = 0.15$ and then decreases for $y = 0.20$. The dc conductivity of these Ag₂S glass systems behavior is different from that of AgI glass systems signifying that the conductivity variation depends on the composition.

The compositional variation of the dc conductivity can be explained on the basis of structural details of the glass nanocomposites. The volume expansion^[13] of the samples was determined from glass compositions. It is obtained that the volume expansion increases with increase of y up to 0.15 and then decreases for

$y = 0.20$. The increase of the volume expansion creates more open network structure for ion migration so that the mobility of ions increases. Similarly, the decrease of the volume expansion decreases the pathway volume for ion migration. Thus, an initial increase of the conductivity for $y \leq 0.15$ is attributed to

the increase in the volume expansion of the glass matrix, whereas for Ag_2S content $y = 0.20$ the decrease of volume expansion decreases the conductivity. The Ag_2S addition thus modifies the glassy network depending on compositions and consequently effecting the conduction.

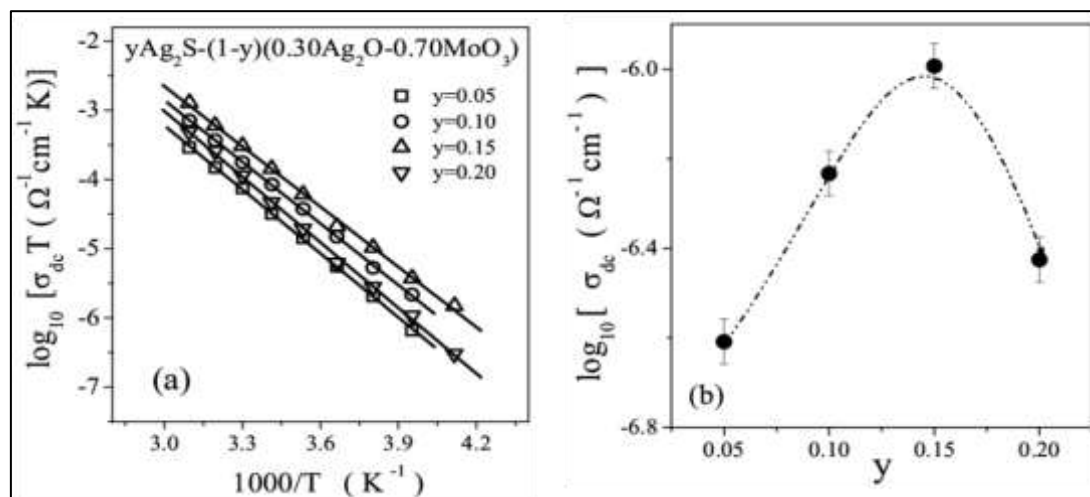


Fig. 3. (a) Reciprocal Temperature Dependence of dc Conductivity (σ_{dc}) for All the Glasses of Composition $y\text{Ag}_2\text{S}-(1-y)(0.30\text{Ag}_2\text{O}-0.70\text{MoO}_3)$ Shown. Solid Lines Are Linear Fit to the Data. (b) Variation of σ_{dc} With Ag_2S Mol Fraction (y) at a Fixed Temperature 303 K. Dash Line Is a Guide to the Eye.

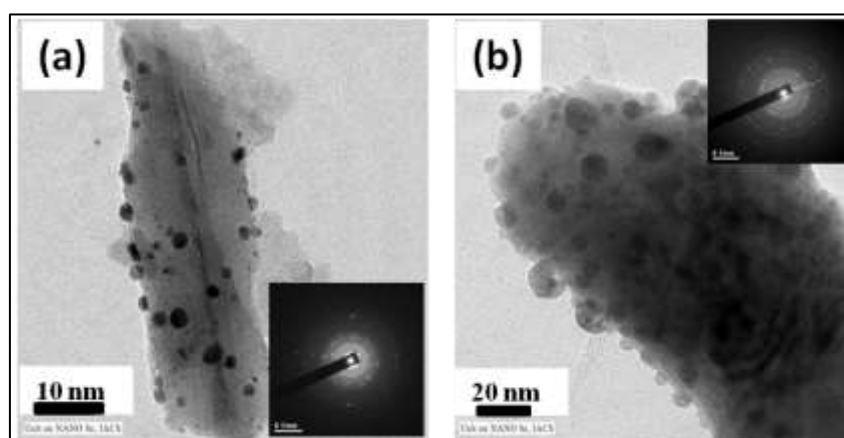


Fig. 4. TEM Images for Samples with Ag_2S Mol Fraction of (a) $y = 0.05$ and (b) $y = 0.20$. The Inset Shows the Corresponding SAED Pattern.

Figure 4 shows TEM images for selected samples of Ag_2S glass systems. The insets in Figure 4(a) and (b) show the corresponding SAED patterns. The formation of nanoparticles is clearly observed in the images for all the samples.

The SAED patterns show sharp bright spots along with characteristic amorphous rings for the as-prepared samples. From the diffraction spot in the SAED patterns, the interplaner distances (d values) have been calculated and the different

crystalline phases have been obtained by comparing them with those given in ICDD datasheet. The presence of Ag₂Mo₂O₇ crystallites has been identified in the compositions with $y = 0.05$ and 0.10 . The presence of crystalline phases of α -Ag₂MoO₄, Ag₂Mo₂O₇, and γ -Ag₂S crystallites has been observed in samples with $y = 0.15$ and 0.20 .^[11] We have determined the average crystallites size from TEM, and it is observed that there is a slight increasing tendency of the average particle size with increasing Ag₂S content. The crystalline fraction (ratio of crystalline area to total area) is lower for $y \leq 0.15$ whereas the crystalline volume fraction is significantly high for $y = 0.20$ sample, so that the ion dynamics is affected by the nanocrystallites formation within the glass matrix for higher Ag₂S content which lowers the conductivity.^[14]

CONCLUSIONS

Electrical properties for several AgI- and Ag₂S-based glasses and glass nanocomposites and its dependence on microstructure were presented. For the AgI-doped glass systems the average nanocrystallites size decreases with increase of AgI content and causes an enhancement of conductivity with increase of AgI content. In Ag₂S-doped systems addition of Ag₂S also causes the conductivity to increase, however, at highest Ag₂S content the formation of larger nanocrystallites and high crystalline fraction causes the conductivity to decrease. The modification in the microstructure thus depends on composition and considerably influences the electrical conductivity.

ACKNOWLEDGEMENTS

The author thanks UGC, NERO for financial support for the work via MRP grant file No. F.5-387/2014-15(MRP/NERO)/3610.

REFERENCES

1. (a) Suthanthiraraj S.A., Sarumathi R. *Appl Nanosci.* 2013; 3: 501p; *J Maier Nat Mater.* 2005; 4: 805p.
2. (b) Mandanici A., et Al. *J Noncrystal Solids.* 2014; 401: 254p; (b) Boolchand P., Bresser W.J. *Nature.* 2001; 410: 1070p.
3. Dyre J.C., Maass P., Roling B., et al. *Rep Prog Phys.* 2009; 72: 046501p.
4. Sidebottom D.L. *Rev Mod Phys.* 2009; 81: 999p.
5. Knauth P. *J Electroceram.* 2000; 5: 111p.
6. Tatsumisago M., Shinkuma Y., Minami T. *Nature.* 1991; 354: 217p.
7. Sanson A., Rocca F., Armellini C., et al. *Phys Rev Lett.* 2008; 101: 155901p.
8. Bhattacharya S., Ghosh A. *J Phys Chem C.* 2010; 114: 5745p.
9. Narvaez-Semanate J.L., Rodrigues A.C.M. *Solid State Ionics* 2010; 181: 1197p.
10. Deb B., Bhattacharya S., Ghosh A. *Euro Phys Lett.* 2011; 96: 37005p.
11. Deb B., Ghosh A. *J Alloys Compd.* 2011; 509: 2256p.
12. Deb B., Ghosh A. *J Appl Phys.* 2012; 112: 094110p.
13. Kabi S., Ghosh A. *J Phys Chem C.* 2011; 115: 9760p.
14. Deb B., Ghosh A. *J Phys Chem C.* 2011; 115: 14141p.