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Superlinear frequency dependence of AC conductivity and its scaling behavior in xAgI-$(1-x)$ $AgPO_3$ glass superionic conductors

D.P. Singh [a,*], K. Shahi [b], Kamal K. Kar [c]

[a] Materials Science Programme, Indian Institute of Technology Kanpur, India
[b] Department of Physics and Materials Science Programme, Indian Institute of Technology Kanpur, India
[c] Department of Mechanical Engineering and Materials Science Programme, Indian Institute of Technology Kanpur, India

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ABSTRACT

Low temperature AC conductivity studies on melt quenched xAgI-$(1-x)$ $AgPO_3$ glass electrolytes are presented. It is observed that doped glasses show Jonscher power law behavior at all temperatures, however, undoped $AgPO_3$ glass also shows superlinear frequency-dependent conductivity at very low temperatures apart from the usual Jonscher power law behavior. This behavior in undoped $AgPO_3$ glass is not yet reported in literature. The Summerfield scaling law is used to demonstrate that Jonscher power law behavior and superlinear power law behavior have different physical origins as scaling law is not followed in the superlinear regime. Moreover, scaling behavior of AC conductivity also indicates that conduction mechanisms are slightly different in doped and undoped glasses. However, scaling behavior provides only qualitative information about the conduction mechanisms. The conductivity spectra of doped and undoped glasses can be merged into a super-master conductivity curve except in the transition zone (where AC conductivity starts dominating over DC conductivity) where the conductivity master plots of doped and undoped glasses do not merge.

1. Introduction

A great deal of work on the electrical properties of xAgI-$(1-x)$ $AgPO_3$ and $x$$Ag_2S$-$(1-x)$ $AgPO_3$ glass electrolytes has published in the past [1–23]. In these glasses, a silver ion conductivity of ~10^{-2} S/cm has been achieved by doping silver iodide (AgI) in high concentrations. Such high ionic conductivity here is achieved by adding the silver iodide in the glass matrix $AgPO_3$ during preparation [4,6,24,25]. These glasses possess an ion transport number ~0.99 [25]. In many of the above reports the conductivity spectra of the doped and undoped $AgPO_3$ glass electrolytes have been studied and it is found that they obey the Jonscher power law (JPL) behavior at ambient conditions. There are not many reports available on the low temperature electrical properties of these glasses. In particular, the reports about the presence/absence of nearly constant loss (NCL) and/or superlinear power law (SPL) behaviors in these glass systems are contradictory. The details about JPL, NCL, and SPL behaviors can be found in above mentioned references including our previous work [26]. Few researchers [8,19] have observed SPL behavior while others [18] have observed NCL behavior in xAgI-$(1-x)$ $AgPO_3$ glasses. Some [12] have neither observed NCL nor SPL behavior. Others either have not studied or have not mentioned anything about the observation of NCL/SPL behavior. In this work, low temperature AC conductivity properties of xAgI-$(1-x)$ $AgPO_3$ ($x = 0$–0.5) glasses are studied in the frequency range of 20 Hz–2 MHz. We suspect that this inconsistency in NCL/SPL observation in the published literature in this system has something to do with preparation conditions like humidity, melting temperature quenching rate, etc., because laboratory ambience may differ in different places and generally researchers do not control the quenching rate accurately while preparing the glass. Here we report an SPL behavior in undoped glass that has not been reported earlier in undoped $AgPO_3$. Moreover, we have applied Summerfield scaling to show that SPL behavior has different origin than JPL behavior.

2. Experimental

The doped and undoped $AgPO_3$ glasses were prepared by melt quenching method using a brass twin roller operated at 2000 rpm. The chemicals used were $NH_4H_2PO_4$, $AgNO_3$, and AgI, all from Sigma Aldrich, USA. The melting of chemicals in appropriate stoichiometric amounts was done in two steps. Initially, the mixture was heated in quartz crucible at 300 °C for 2 h to remove the evolving gases and finally it was heated at 700 °C for 6 h before being quenched to room temperature using twin roller. The typical heating rate of the furnace was kept at 100 °C/h, and the room temperature and humidity were around 25 °C and 30%, respectively. The melting and quenching were done in open air atmosphere. The sub-millimeter thick flakes obtained after quenching were crushed by a mortar pestle and a fine powder was made. This powder was used for x-ray diffraction to confirm the amorphous

* Corresponding author at: Department of Physics, Banasthali University, India.
E-mail address: dpphysics@gmail.com (D.P. Singh).

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phase. For electrical measurements, pellets of 10 mm diameter and 1 mm thick were made from the glass powder by applying a pressure of ~1 GPa. The pellets were annealed for several hours at temperature ~80 °C to remove the internal stresses. After coating with silver paint, these pellets were used for electrical measurements using Agilent precision LCR meter in the frequency range 20 Hz–2 MHz and temperature range 120–360 K. A liquid nitrogen-based cryogenic system was used to reduce the temperature of the samples during measurements.

3. Results and discussion

(i) DC conductivity

The DC conductivity was calculated using Nyquist plots. A Nyquist plot is a graph between real part of impedance (Z') and imaginary of impedance (Z''), which for dielectric and conductive samples comes out to be a semicircle or a depressed semicircle with centre being below the real axis. The intercepts of the Nyquist plot semicircles with the x axis (i.e., axis corresponding to Z'), R_{dc}s gave DC conductivity according to relation $\sigma_{dc} = \frac{l}{A}\left(\frac{1}{R_{dc}}\right)$ where l and A are the sample thickness and electrode surface area of the sample pellets, respectively. The Nyquist plots for one sample are shown in Fig. 1 as representative, at few selected temperatures. Similar plots were obtained in other samples. The plots of temperature dependence of DC conductivity (obtained by above method) of all glass compositions are shown in Fig. 2. The DC conductivity follows the typical Arrhenius temperature dependence for all glass compositions. The activation energy for DC conduction is also shown in the plot for different glass compositions, which is calculated using Aarhenius temperature dependence (detailed calculations not shown). It is clear from Fig. 2 that with the addition of AgI to the glass matrix, activation energy first decreases rapidly, and then saturates around 0.26 eV for $x = 0.5$ sample. It is because, in silver iodide rich glasses, micro-domains of amorphous silver iodide are formed and the silver iodide ions surrounded by only iodide ions are more mobile than those surrounded by glass network [27]. Moreover, Silver iodide expands the glass network which facilitates high ionic conductivity [12]. The DC conductivity varies nearly exponentially with the mole fraction of silver iodide (x) in the whole composition range studied, which can be described as

$$\sigma_{dc} = \sigma_{x0} e^{mx} \quad (1)$$

where σ_{x0} and m are constants. Fig. 3 shows the dependence of DC conductivity of xAgI-$(1-x)$ $AgPO_3$ glass electrolytes on the mole fraction of silver iodide. Constant σ_{x0} simply represents the DC conductivity for $x = 0$ composition, i.e., for undoped $AgPO_3$ glass. The constant m could be determined from the slope of the line $\ln\sigma_{dc}$ vs x. The activation energies and DC conductivities from literature are compared with the present work in Table 1. The values of activation energies agree well with each other, within experimental limits and they all saturate in

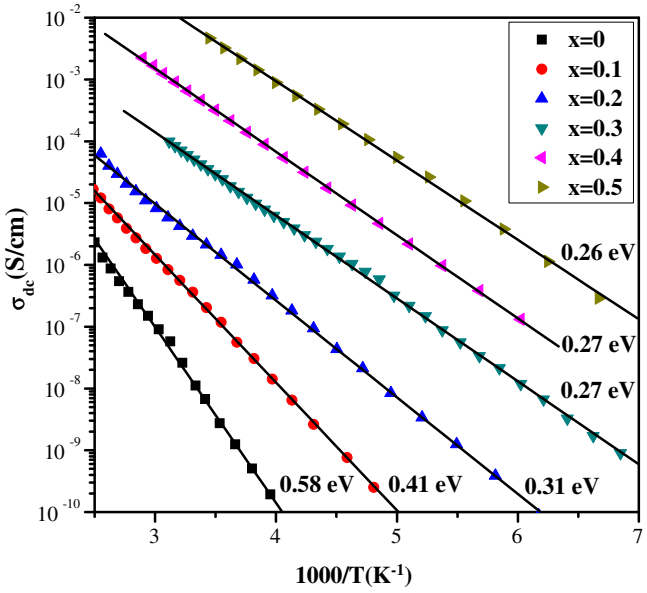

Fig. 2. Arrhenius plots of DC conductivity for xAgI-$(1-x)$ $AgPO_3$ glass electrolytes. Different symbols indicate different compositions. The obtained activation energies are also mentioned for different compositions.

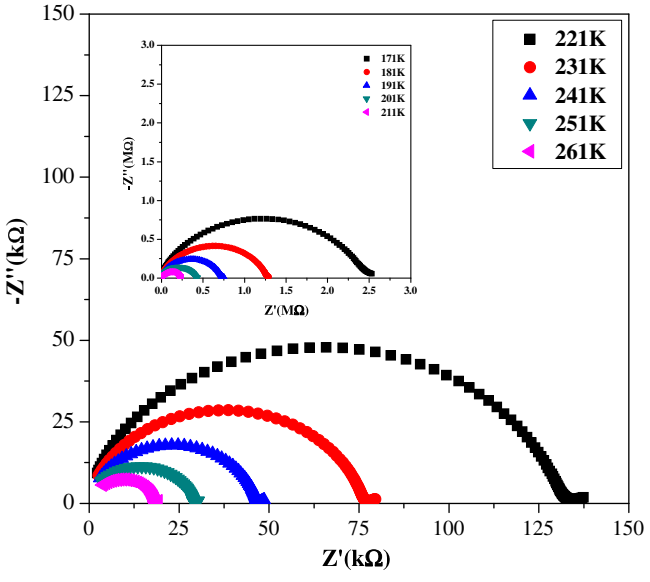

Fig. 1. Nyquist plot between real (Z') and imaginary (Z'') parts of complex impedance for xAgI-$(1-x)$ $AgPO_3$ glass electrolytes for $x = 0.3$ at few selected temperatures. The intercepts of these plots were used for the evaluation of DC conductivity.

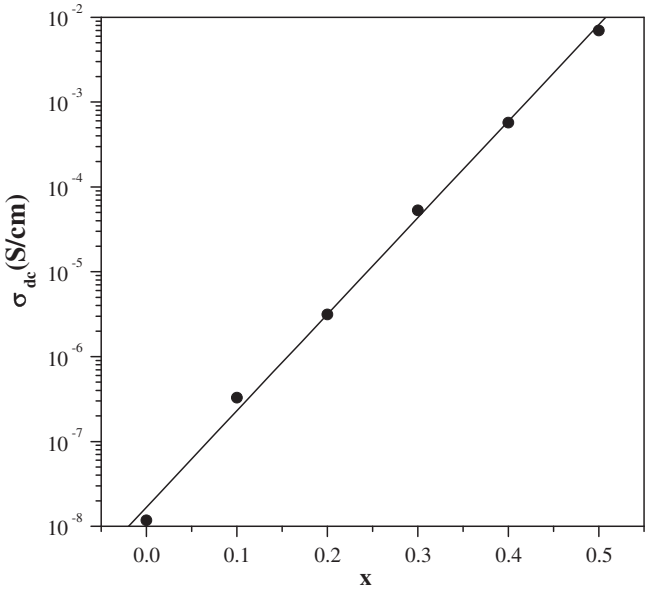

Fig. 3. Composition dependence of DC conductivity for xAgI-$(1-x)$ $AgPO_3$ glass electrolytes.