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Conductivity percolation transition of $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses

A. Piarristeguy [*], J.M. Conde Garrido, M.A. Ureña, M. Fontana, B. Arcondo

Laboratorio de Sólidos Amorfos, Departamento de Física, Facultad de Ingeniería, Universidad de Buenos Aires,
Paseo Colón 850, Buenos Aires 1063, Argentina

Abstract

The ionic conductivity of several chalcogenide glasses increases abruptly with mobile ion addition from values typical of insulating materials (10^{-16}–$10^{-14}\ \Omega^{-1}\ cm^{-1}$) to values of fast ionic conductors (10^{-7}–$10^{-1}\ \Omega^{-1}\ cm^{-1}$). This change is produced in a limited concentration range pointing to a percolation process. In a previous work [M. Kawasaki, J. Kawamura, Y. Nakamura, M. Aniya, Solid State Ionics 123 (1999) 259] the transition from semiconductor to fast ionic conductor of $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses was detected at $x^* \cong 10$ at.% in the form of a steep change in the conductivity. $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses with $x \leqslant 25$ at.%, prepared by a melt quenching method, are investigated by impedance spectroscopy in the frequency range 5 Hz–2 MHz at different temperatures, T, from room temperature to 363 K and by DC measurements at room temperature. The conductivity of the glasses, σ, was obtained as a function of silver concentration and temperature. For $x \geqslant 10$ at.% our results are in agreement with those reported by Kawasaki et al. [M. Kawasaki, J. Kawamura, Y. Nakamura, M. Aniya, Solid State Ionics 123 (1999) 259]. The percolation transition was observed in the range $7 \leqslant x \leqslant 8$. The temperature dependence of the ionic conductivity follows an Arrhenius type equation $\sigma = (\sigma_o/T) \cdot \exp(-E_\sigma/kT)$. The activation energy of the ionic conductivity, E_σ, and the pre-exponential term, σ_o, are calculated. The results are discussed in connection with other chalcogenide and chalcohalide systems and linked with the glass structures.

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Keywords: Fast ion conduction; Chalcogenides

1. Introduction

In general, the ionic conductivity of the chalcogenide glasses increases significantly with the increase in the metal content from very low conductivity to values larger than $10^{-7}\ S\ cm^{-1}$, behaving as fast ionic conducting materials. In some cases, this colossal change in the conductivity occurs in a limited concentration range indicating a percolation transition [1–5]. As it was reported by [1], the $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses behave as ionic conductors ($x \leqslant 25$) showing a very sudden increase of the conductivity from $10^{-13}\ S\ cm^{-1}$ to $10^{-5}\ S\ cm^{-1}$ at $x^* \approx 10$. For the AgGeS and AgGeSeSb systems, the conductivity transition was observed at a very low value of the metal content (Ag concentration $\ll$1 at.%) [2–5]. These authors also proposed a percolation transition.

These sulphide and selenide glasses have several common structural characteristics: (a) the network-structural units of the chalcogenide glasses are $GeCh_4$ (Ch = Se, S) tetrahedra linked by edge- and corner-sharing, (b) the first diffraction peak (FSDP), which seems to be related to the intermediate range (IRO), is about $q \approx 1$ Å, and (c) the silver content increment decreases the IRO by a fragmentation of the tetrahedra chains [1–6].

The main aim of our work is to study the ionic conduction in the AgGeSe system in order to find common tendencies in sulphide and selenide glasses doped with silver and to analyze the percolation transition.

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[*] Corresponding author.
E-mail addresses: apiarri@fi.uba.ar (A. Piarristeguy), murena@fi.uba.ar (M.A. Ureña).

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2. Experimental

$Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ samples with $x = 0$, 0.5, 1, 3, 5, 7, 8, 9, 9.3, 9.6, 9.9, 10, 15, 20 and 25 at.%, were prepared with high-purity (4N) elements. In all cases, batches weighting 5 g were placed in quartz ampoules (10 mm inner diameter). The ampoules were evacuated to a pressure of $\approx 10^{-8}$ bars and sealed. After synthesis and homogenization (7 h at $T \approx 1200$ K) the ampoules were quenched in an ice-water bath.

The electric measurements were made on bulk samples conformed in rectangular geometry with platinum electrodes by a sputtering technique. The temperature was determined using a calibrated thermo-resistance of Pt ($\Delta T < 1$ K). Glasses have been studied by impedance spectroscopy in the frequency range 5 Hz–2 MHz at different temperatures, from room temperature to 363 K. Also, DC measurements at room temperature were carried out applying a voltage $V = 1.9$ V.

3. Results and discussion

The complex impedance spectra from samples in the composition range $8 \leqslant x \leqslant 25$ at.% show: (a) for higher frequencies an arc linked with the electrolyte and (b) for lower frequencies the beginning of a second arc linked with electrolyte–electrode interfaces [7]. However, due to the high impedance values of samples with $x < 8$ at.%, the complex impedance measurements could not be carried out. Fig. 1 depicts the impedance imaginary component vs. its real component as a function of frequency for the sample with $x = 9.3$ at.% at $T = 298$ K.

For samples with $x \geqslant 8$ the resistive impedance of the bulk electrolyte, R_∞, was determined from the cross point of the arc, fitted according to the cell equivalent circuit, with the horizontal line [8]. The conductivity values at different temperatures are calculated following $\sigma = d/R_\infty A$, where d is the thickness of the sample and A its area.

DC measurements were performed on samples with Ag concentration $x \leqslant 9.9$ at.%. For $8 \leqslant x \leqslant 9.9$ at.%, the time dependence of the electric current, $i(t)$, corresponds to fast ionic conductor behavior. Due to Ag^+ accumulation on the lower potential electrode (polarization), $i(t)$ decreases as the measurement is performed. Fig. 1 shows the DC values of $i(t)$ measured at room temperature, $T = 298$ K, on the sample with $x = 9.3$. Conductivity values (obtained at $t = 0$), $\sigma_{DC} = \frac{d \cdot i(t=0)}{A \cdot V}$, agree with those determined by means of the impedance spectroscopy method. Measurements of DC conductivity performed on samples with $x < 8$ give results below 10^{-13} S cm^{-1}.

Table 1 reports the conductivity values, σ_{298}, at room temperature. The conductivity values obtained for samples with $x \geqslant 8$ ($\sim 10^{-5}$ S cm^{-1}) are characteristic of fast ion-conducting glasses.

The Ag content dependence of conductivity in $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ glasses (this work and Ref. [1]) is shown in Fig. 2. The values of conductivity are in

Table 1
Composition dependence of the ionic conductivity at room temperature σ_{298}, the activation energy E_σ, and the pre-exponential factor σ_o

x	σ_{298} (S cm^{-1}) ± 5%	E_σ (eV) ± 1.5%	σ_o (S cm^{-1} K) ± 15%
$x \leqslant 7$	$<10^{-13}$	–	–
8	1.1×10^{-5}	0.361	4284
9	1.1×10^{-5}	0.370	5993
9.3	1.2×10^{-5}	0.375	7867
9.6	1.1×10^{-5}	0.382	9406
9.9	1.6×10^{-5}	0.375	10527
10	1.3×10^{-5}	0.367	6350
15	4.8×10^{-5}	0.352	12969
20	6.6×10^{-5}	0.347	14493
25	1.1×10^{-4}	0.339	17511

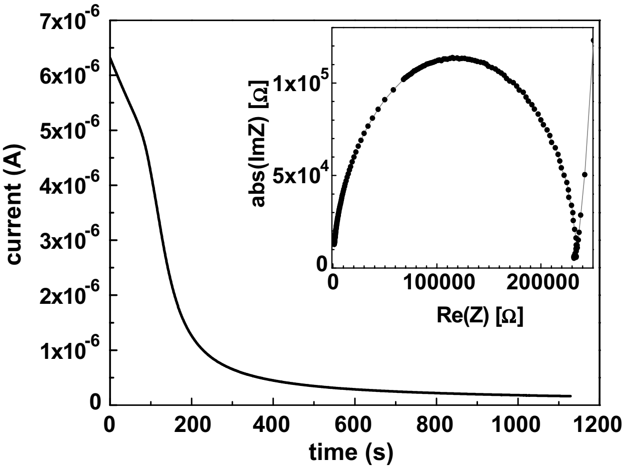

Fig. 1. DC current vs. time (t) for the sample with $x = 9.3$ at.% at $T = 293$ K. In the inset, complex impendance spectrum for the same sample at the same temperature.

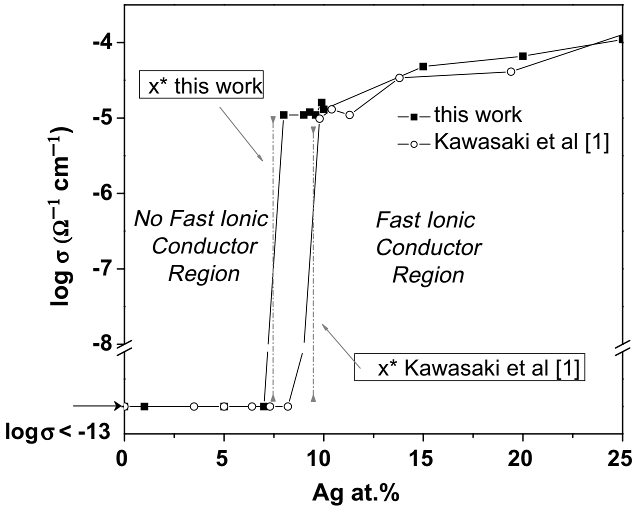

Fig. 2. Conductivity of $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ ($0 \leqslant x$ (at.%) $\leqslant 25$) glasses vs. Ag content. The error bars are smaller than the symbol size ($\Delta[\log\sigma] \sim 0.02$). The lines are to guide the eye (this work and Ref. [1]).