Study of temperature and pressure dependences of electric properties of amorphous Ag-Ge-As-S chalcogenides containing carbon nanotubes

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K V Kurochka, N V Melnikova, V E Zaikova and Ya Yu Volkova

Ural Federal University, 19 Mira str., Ekaterinburg, 620002, Russia

e-mail: kirill.k.v@yandex.ru

Abstract. Frequency and temperature dependences of impedance of $AgGe_{1+x}As_{1-x}(S+CNT)_3$, $x = 0.4$; 0.5; 0.6 were measured. There are maxima on frequency dependences of tangent of loss, which can be connected with relaxation processes inside the sample (the maximum at high frequencies) and the second maximum can be connected with processes occurring on the sample-electrode border. Activation energy of all synthesized materials was estimated to be near 0.5 eV. The relaxation of electric resistance at fixed pressures within the pressure range of 30 to 50 GPa was observed. It is established that the resistance decreases exponentially with time within this range of pressures.

1. Introduction

Multicomponent silver chalcogenides with a silver ion conductivity have been known as promising materials for scientific and applied purposes. They can be applied in a wide range of devices such as memory cells [1], solid state batteries, different kind of sensors etc. Materials of the Ag-Ge-As-S system have a significant share of ionic component in conductivity [2, 3]. In order to obtain materials with a higher ionic conductivity component, glassy silver chalcogenides $AgGe_{1+x}As_{1-x}(S+CNT)_3$ with the addition of carbon nanotubes (CNT) were synthesized. The obtained materials have the ionic conductivity share not less than 99 percent [4].

This paper is devoted to the study of temperature dependences of electric properties at ambient pressure and resistance relaxation at fixed pressure in the pressure range of 30 to 50 GPa in glassy $AgGe_{1+x}As_{1-x}(S+CNT)_3$ ($x = 0.4$; 0.5; 0.6).

2. Materials and methods of study

The synthesis of $AgGe_{1+x}As_{1-x}(S+CNT)_3$ ($x = 0.4$; 0.5; 0.6) with about 7 additional atomic percent of CNT was carried out by means of alloying initial components in the quartz containers evacuated to residual pressure of 10^{-4} Pa, filled with a superpure argon to $0.5 \cdot 10^5$ Pa. The initial components were the chemical reagents of high purity and nanotubes added to the blend as a composite with dehydrated sulfur.

The materials were investigated by an X-ray diffractometer Shimadzu XRD 7000 (monochromatic radiation CuKα). An Auriga CrossBeam Zeiss scanning electron microscope providing the X-ray microanalysis (EDS) was used to confirm the homogeneity of glasses as well as to estimate the atomic percent ratio of elements. The synthesis and properties of materials at room temperature are described in detail in [4, 5].

Electrical properties in the temperature range of 300 to 383 K were investigated by impedance spectroscopy in the frequency range of 1 Hz to 32 MHz in the cells with graphite electrodes. Measurement and analysis of impedance was performed by a universal frequency response analyzer Solartron 1260A.

Experiments under high pressure (within the range of 15 to 50 GPa) were performed using powder samples in rounded cone – plane type high pressure cell (HPC). Conductive synthetic carbonado diamonds were used as a material for anvils. These diamonds are good conductors, which allow measuring the electrical properties of materials placed in the pressure cell [6]. The measurements of the electrical resistance of materials in HPC were performed using an Agilent 34970A.

3. Results and Discussion

Since the materials under study have the ion component of conductivity of about 99 percent, applying an external electric field results in observing the polarization phenomena near electrodes. In case of alternating current these phenomena appear much weaker than at direct current and depend on the frequency of alternating current and the electrodes' material.

Thus, the studies of temperature dependences of impedance in the frequency range of 1 Hz to 32 MHz (figure 1) in the cells with the electrodes blocking the ion component of conductivity (graphite) were performed. As it can be seen in figure 1, these materials are characterized by two well separated areas on the frequency dependence (in the whole temperature range from 300 to 383 K): the high-frequency one characterizing properties of the sample, and the low-frequency one characterizing the influence of the electrode impedance.
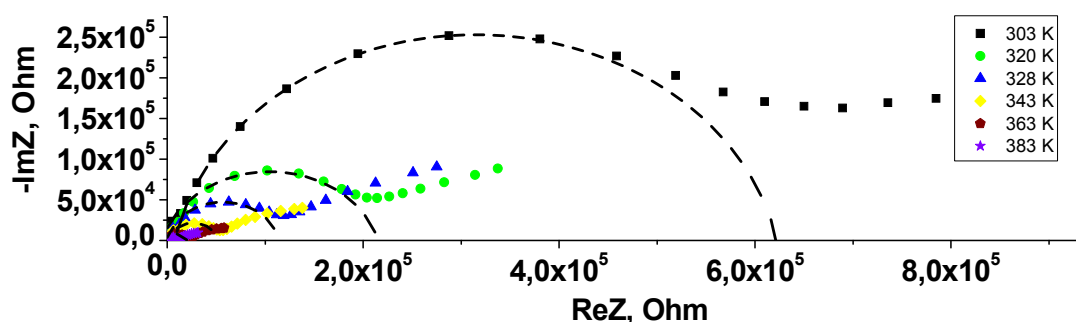

Figure 1. Hodographs of impedance of $AgGe_{1.4}As_{0.6}(S+CNT)_3$ in the cell with graphite electrodes in the temperature range of 300 to 383 K. Dash lines indicate the circle approximation of high frequency parts of hodographs which characterize properties of the sample.

There are relaxation maxima on the frequency dependences of tangent of dielectric loss for the sinthesized materials (figure 2 (b)). The maximum at high frequencies is associated with the relaxation processes in the sample, and the estimated relaxation time is typical for the ion-relaxation polarization. The appearance of the maximum at low frequencies can be connected with the processes occurring on the sample-electrode border [7]. It is also confirmed by the dramatic increase of permittivity determined by the double dielectric layer capacitance at low frequencies (figure 3). The maxima shift towards higher frequencies with increasing temperature as it is shown in figure 2 (a) for $AgGe_{1.5}As_{0.5}(S + CNT)_3$. The same dependence of dielectric loss tangent was also observed in the materials without CNT. The high frequency peak in the frequency dependence of tangent of dielectric loss shifts toward higher frequencies with increasing temperature because the time required for the completion of this relaxation process decreases with increasing temperature that results from weakening of bonds between ions, increasing number of mobile ions and easier electron transport. The frequency at which polarization occurs on the electrodes because of accumulation of space charge on

the sample-electrode border also becomes higher with increasing temperature. Adding nanotubes also leads to the fact that the silver ions can move inside CNTs [8] that increases their mobility resulting in the decrease of the relaxation time.
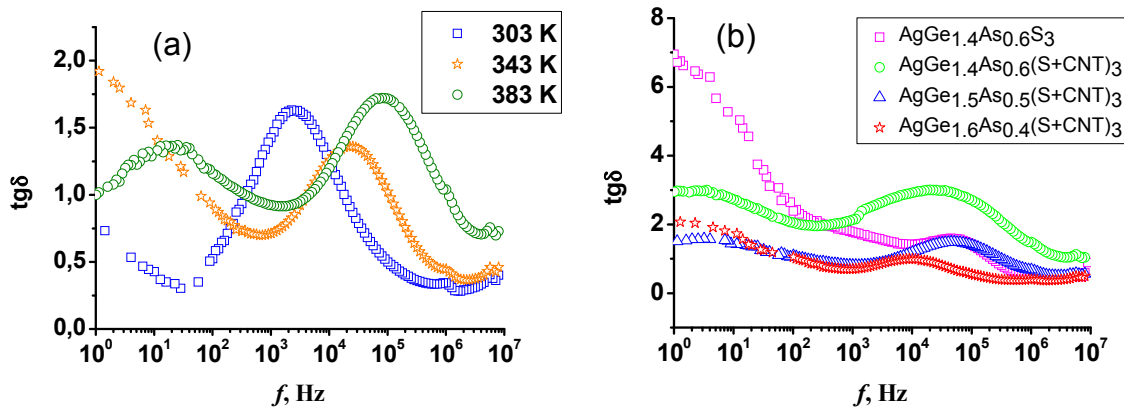

Figure 2. Frequency dependences of tangent of dielectric loss (tgδ): (a) for AgGe$_{1.5}$As$_{0.5}$(S+CNT)$_3$ ($x = 0.5$) at different temperatures; (b) – for AgGe$_{1.4}$As$_{0.6}$S$_3$ and AgGe$_{1+x}$As$_{1-x}$(S+CNT)$_3$ ($x = 0.4$; 0.5; 0.6) at 363 K.
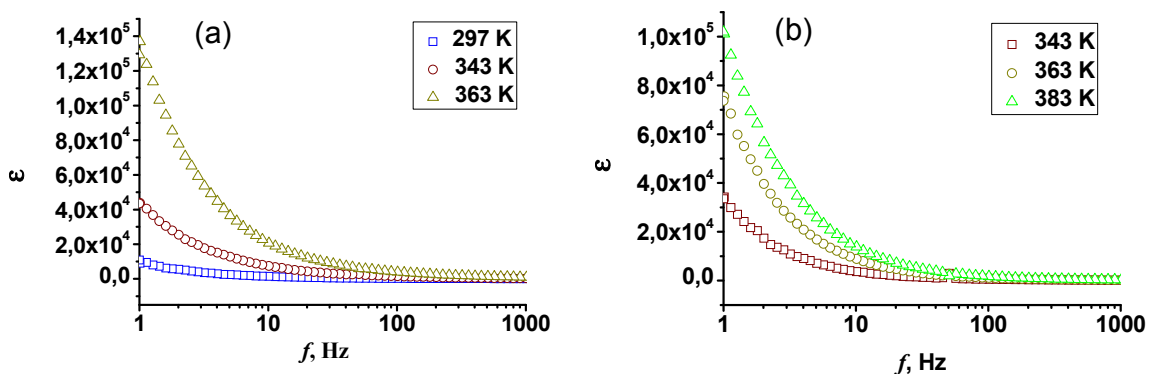

Figure 3. Frequency dependences of permittivity at different temperatures: (a) for AgGe$_{1.4}$As$_{0.6}$(S+CNT)$_3$ ($x = 0.4$); (b) for AgGe$_{1.4}$As$_{0.6}$S$_3$.

The activation energy of all studied materials was estimated based on the temperature dependences of resistivity. In the temperature range of 300 to 383 K it is equal to 0.51 eV for the compounds containing CNT with $x = 0.4$; 0.5 and to 0.54 eV for $x = 0.6$ (table 1).

The values of activation energy we obtained are in a good agreement with the values obtained in [2] for AgGe$_{1+x}$As$_{1-x}$S$_3$ ($x = 0.4$; 0.6) compounds.

In the AgGe$_{1+x}$As$_{1-x}$S$_3$ and AgGe$_{1+x}$As$_{1-x}$(S+CNT)$_3$ compounds the increase of resistivity and decrease of conductivity with time at ambient pressure were observed in other works [2, 4] that is typical for the materials with an ionic conductivity component. However, it can be assumed that with increasing pressure ion transport practically disappears at some pressure, and only electrons are the charge carriers. In fact, the investigation of resistivity relaxation at fixed pressures above 30 GPa confirms that the processes occurring in AgGe$_{1.4}$As$_{0.6}$S$_3$ and AgGe$_{1.4}$As$_{0.6}$(S + CNT)$_3$ are typical for the

materials with only electron transport. The study of the electrical relaxation at fixed pressure in the range of 30 to 50 GPa showed that the resistance decreases exponentially with time for both materials (figure 4).

Table 1. The activation energy of compounds with/without CNT (including the data from [2])

Compound	Activation energy	Temperature range
$AgGe_{1.4}As_{0.6}(S+CNT)_3$	0.51	300 – 383 K
$AgGe_{1.5}As_{0.5}(S+CNT)_3$	0.51	300 – 383 K
$AgGe_{1.6}As_{0.4}(S+CNT)_3$	0.54	300 – 383 K
$AgGe_{1.4}As_{0.6}S_3$	0.40	300 – 383 K
$AgGe_{1.6}As_{0.4}S_3$	0.47 [2]	240 – 300 K
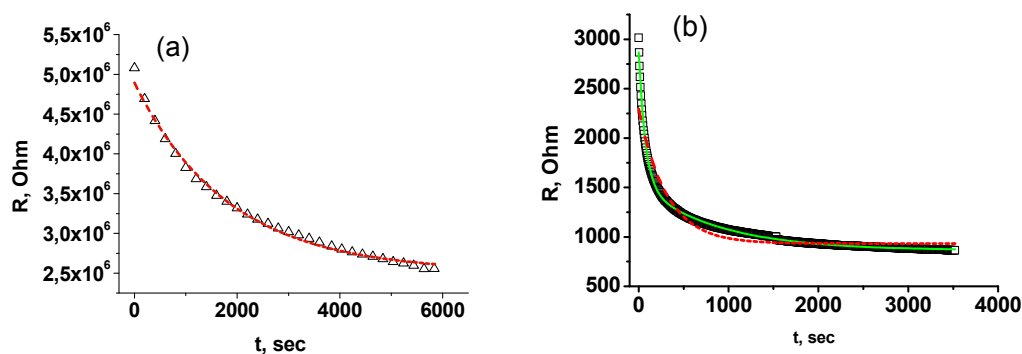
Figure 4. Time dependence of resistance at 46 GPa: (a) for $AgGe_{1.4}As_{0.6}S_3$ (b) for $AgGe_{1.4}As_{0.6}(S+CNT)_3$. The dash and solid lines show the exponential and two exponential approximations of experimental data respectively.

Exponential time dependence of the resistance can be approximated by the expression [9]:

$$R(t) = (R_0 - R_\infty)\exp(-\frac{t}{\tau}) + R_\infty, \tag{1}$$

where τ is the relaxation time, R_0 and R_∞ - the resistance at $t = 0$ and in the saturated state respectively.

However, the approximation of experimental data by (1) can be not satisfactory enough for the materials containing CNT. In this case, the approximation by an exponential function of the form:

$$R(t) = (R_0 - R_\infty)\exp(-\frac{t}{\tau_1}) + R_{int}\exp(-\frac{t}{\tau_2}) + R_\infty, \tag{2}$$

can be more exact (figure 4 (b)).

Then the total relaxation process is characterized by two different relaxation times, one of them (τ_1) describes the relaxation processes occurring at deformation of CNTs and resulting in increasing

electron conductivity, while the second one (τ_2) may be connected with the increase in electrical conductivity during deformation and compaction of glass network with increasing static pressure. In this case the time τ, determined by the expression (1) is an average relaxation time.

The relaxation times for different values of fixed pressure can be estimated using the exponential approximation (1). The pressure dependences of the relaxation times for $AgGe_{1.4}As_{0.6}S_3$ and $AgGe_{1.4}As_{0.6}(S + CNT)_3$ compounds are shown in figure 5.

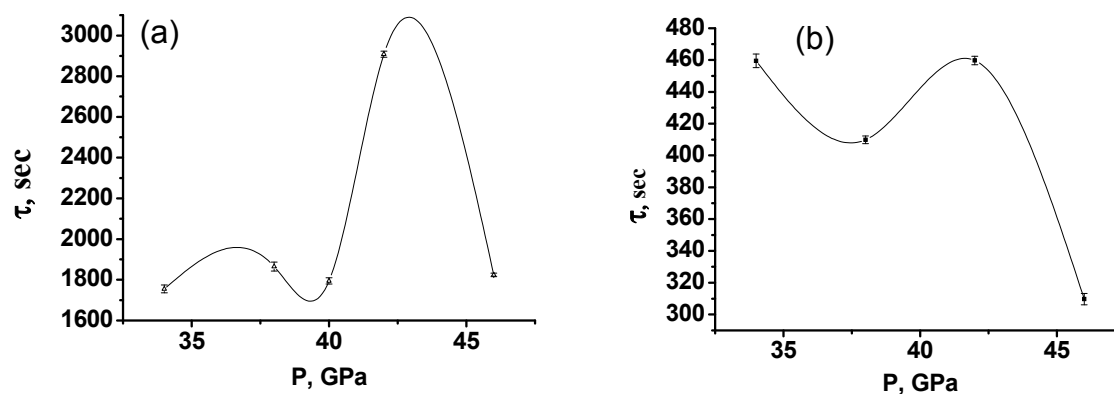**Figure 5.** Variation of the average relaxation time defined by (1) with pressure: (a) for $AgGe_{1.4}As_{0.6}S_3$; (b) for $AgGe_{1.4}As_{0.6}(S+CNT)_3$.

As it can be seen in figure 5, introduction of CNTs into the glass network leads to increasing of electronic conductivity of glass [8], which results in a decrease of resistance and relaxation time under high pressure. Moreover, there are the specific features in the distribution of relaxation times near the pressure value of 42 GPa for both materials.

4. Conclusion

The temperature dependences of the electrical properties of $AgGe_{1+x}As_{1-x}(S+CNT)_3$ with $x = 0.4$; 0.5; 0.6 at alternating electric field within the frequency range of 1 Hz to 32 MHz and in the temperature range of 300 - 383 K have been studied. There are two peaks in frequency dependences of tangent of loss for all the materials. The first maximum observed at high frequencies is associated with the relaxation phenomena occurring in the sample. The second maximum observed at low frequencies may be associated with the phenomena at the sample-electrode border. Maxima shift towards higher frequencies with increasing temperature. The activation energy for all the materials studied was estimated based on the temperature dependences of resistivity. In the temperature range of 300 to 383 K it is equal to 0.51 eV for the compounds containing CNT with $x = 0.4$; 0.5 and to 0.54 eV for $x = 0.6$.

The relaxation of the resistivity for $AgGe_{1.4}As_{0.6}(S+CNT)_3$ and $AgGe_{1.4}As_{0.6}S_3$ at fixed pressures in the range of 30 to 50 GPa has also been investigated. The resistance decreases exponentially with time for both materials. Analysis of pressure dependences showed that specific features in the distribution of relaxation times near the pressure value of 42 GPa are observed for both materials that can be associated with structural changes in glasses and the features of electron transport process.

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