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Electrical conductivity and impedance response of arsenic-sulphide glasses doped with Pb

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Abstract
Bulk samples of $Pb_x(As_2S_3)_{100-x}$ chalcogenide glassy system obtained by melt quenching method were subjected to the measurement of their electric and dielectric properties over the temperature and frequency ranges (323-423 K) and (0.1 Hz-100 kHz) respectively. The introduction of lead into the system significantly increases DC and AC conductivity. Hoping between the localized states was identifed as a dominant conductivity mechanism in DC regime. The results of ac conductivity measurements are explained based on the correlated barrier hopping CBH model. The AC impedance analysis by means of an equivalent circuit model was used to found correlation between the distinct microstructures and electrical properties of these compounds. The high insulating nature of investigated samples in the whole frequency range was established. The frequency dependence of dielectric losses at different temperatures was also analyzed.

Keywords—chalcogenide glasses, conductivity, impedance analysis

I. INTRODUCTION

In the modern era of technology, semiconducting chalcogenide glasses became materials of a significant scientific interest due to their specific physical characteristics which provide them a wide application in fabrication of solid-state devices [1]. These semiconductors explore high transmittance in IR region, high non-linear refractive index, low phonon energy, mouldability, etc, that are advantageous to optical and opto-mechanical designers [2]. Therefore, they have been considered as materials applicable for mid-infrared (IR) optics, used as amplifiers, thermal imaging and chemical sensors [3, 4]. Also, doping of host material with impurity atoms or modification in the technological procedure of chalcogenide glasses preparation causes variation in their physical properties, which allowed the possibility of using such materials for various commercial applications [5].

Metal chalcogenide semiconductors of the group V–VI found extensive applications in solid state optical and electrical devices, and novel memory devices [6]. Particularly, they are being considered as core material for transmitting optical fibers, having an advantage when short length and flexibility are required [7]. Impurity effects in chalcogenide glasses may have importance in the production of these materials, especially in the sense of modification of their transport properties. [8]. The working principle of phase-change devices (PCM) is based on rapid reversible phase transformations between amorphous and crystalline state, which are accompanied by abrupt changes in optical and electrical properties of the materials [9]. A special interest for those applications is connected with doping of the glasses by active impurities which alter the optical and electrical properties of the host material. Therefore, it is necessary to find alloying elements which have a positive influence on the properties of amorphous and crystalline phases, as well as on the parameters and performance of PCM devices in general. Bi and Pb are the only known dopants that cause carrier-type reversal in chalcogenide glasses by melt doping. Investigation of AC conductivity and dielectric measurements in order to understand the mechanisms of conduction processes in these materials and the types of their polarization have been reported for a wide variety of amorphous chalcogenide semiconductors [10].

Our previous studies have shown that increasing the lead content in arsenic-sulphide matrix significantly modifies the network structure [11,12]. Therefore, a better understanding of the correlation between the structural modification of glass network and electrical properties as a function of composition is required. A common approach to characterize transport properties of multicomponent chalcogenides is based on application of AC impedance spectroscopy (IS) [13]. IS is widely used technique employed to study electrical responses of different electrical active regions in a material. The IS analysis

consists in choosing the equivalent electric circuit, whose elements will consistently represent the electrical properties of the material in the view of physicochemical characteristics of its structure.

II. Experimental

Chalcogenide glasses of the system $Pb_x(As_2S_3)_{100-x}$ (x=1, 2, 3 at.%) were synthesized from high purity elementary components (99.999 %) by the melt quenching method in a cascade regime of heating as described in previous investigations [11]. For the needs of performing the measurements of electrical and dielectric properties selected samples (x=1 and 3 at.%) were prepared in a form of plane–parallel plates and coated with a conductive graphite layer on contact surfaces. For determination of the DC conductivity, electric current was measured at a constant voltage of 1 V using Novocontrol Concept 90 (Frankfurt, Germany) [14], in the temperature range from 323 K up to 423 K. The upper limit of temperature interval was specified considering glass transition temperature of investigated compounds [11]. The current was determined by picoammeter Keithley 6517B (London, UK) ([15]. The temperature was measured using a Pt/PtRh thermocouple, with an accuracy of ±1 °C. Temperature dependences of the DC conductivity were measured at increasing temperature, with a heating rate 5 °C/min. For AC measurements (from 293 up to 423 K), LCR Hi-tester Hioki 3522-50 (Shangai, China) [16] in frequency range 0.1 Hz-100 kHz was used. Measurements were done in steps of 10 °C, after 20 min's tempering at chosen temperatures. From the experimentally determined values of R_p and C_p connected in parallel, the complex impedance Z^* was calculated according to following relation:

$$Z^* = Z_{real} - jZ_{imag} = \left(\frac{1}{R_p} + j\omega C_p\right)^{-1} \quad (1)$$

where ω is angular frequency of the field.
The obtained impedance spectra were analyzed and simulated using EIS Spectrum Analyzer sofware [17].

III. Results and Discussion

The results of DC conductivity measurements of investigated chalcogenides are shown in Fig. 1. DC conductivity increases exponentially with increasing temperature which indicates the presence of a thermally activated conduction mechanism and semiconducting character of studied materials. In general, the observed increase in the conductivity with Pb content could be caused by increase in the density of localized state in the mobility gap [18] or due to the shift of Fermi level [19]. Namely, the introduction of dopant atoms can influence the charge carrier concentration and produce creation of new states which in return may alter the position of Fermi level. Our previous research indicated modifying influence of dopant on the network structure for x= 3 at.% of Pb [11]. Also, nano-scale phase separation was found to be more pronounced in glasses with higher amount of Pb. Therefore, higher conductivity of the sample with higher Pb content can be attributed to the new structural units As-S and PbS whose existence was confirmed by X-ray analysis of annealed samples [11].

The activation energy of conduction for each sample was determined from the slope of the linear plots using the well-known Arrhenius equation [20]. The calculated values of activation energy and pre-exponential factor σ_0 are given in Table 1.

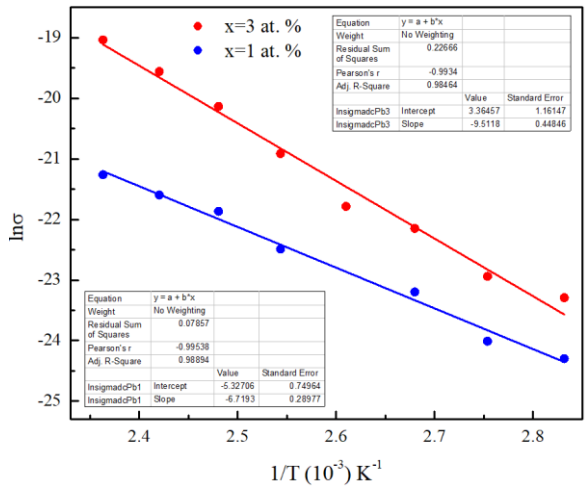

Fig. 1: Dependence of $\ln\sigma_{dc}$ on 1/T for the glassy system $Pb_x(As_2S_3)_{100-x}$

According to the criteria of Daviss and Mott [21], the value of factor σ_0 should be in the range between 10 000 and 50 000 $\Omega^{-1}m^{-1}$ for hopping between the delocalized states beeing a dominant transport mechanism. If conduction mainly occurs between the localized states, parameter σ_0 takes much lower values (by 2-3 orders of magnitude) due to lower density of states. Considering data listed in Table 1 it can be concluded that charge carrier transport in given temperature interval of both samples is determined with hoping between the localized

Table 1: DC conductivity data for the glassy system $Pb_x(As_2S_3)_{100-x}$

x (at. %)	DC Conductivity data	
	σ_0 ($\Omega^{-1}m^{-1}$)	E_a (eV)
1	205.83	0.579 (25)
3	28.92	0.819 (39)

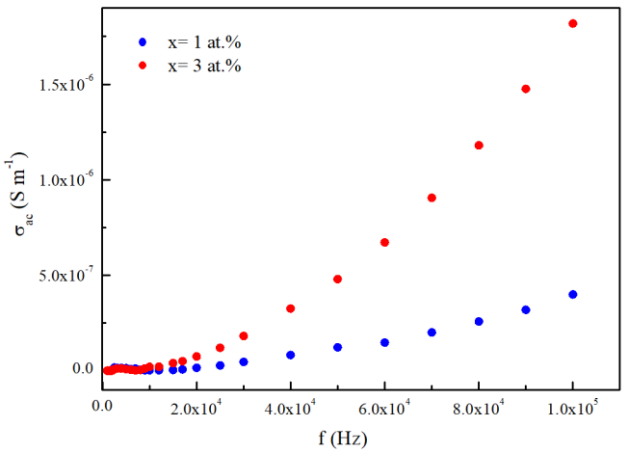

Fig. 2: Dependence of σ_{ac} on frequency for the glassy system $Pb_x(As_2S_3)_{100-x}$ at T= 323 K

states. In that case, the value of parameter E_a designates the sum of the energy distances between the localized states and the Fermi level, i.e. the activation energy of hopping between these states. Its higher value for the compound with x=3 at.% of Pb can be explained with occurrence of new structural units in the amorphous network.

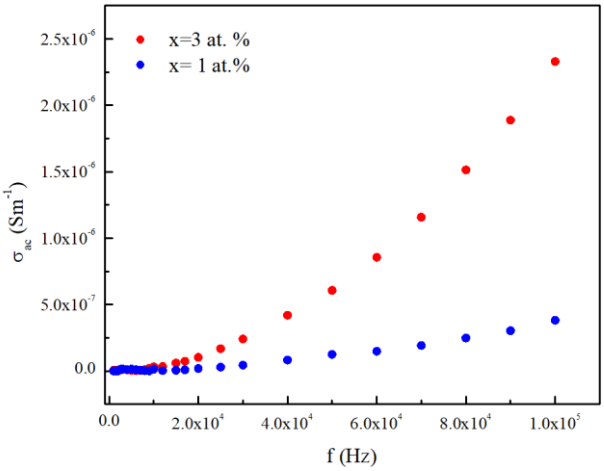

Fig. 3: Dependence of σ_{ac} on frequency for the glassy system $Pb_x(As_2S_3)_{100-x}$ at T= 423 K

The frequency dependence of the AC electrical conductivity for $Pb_1(As_{40}S_{60})_{99}$ and $Pb_3(As_{40}S_{60})_{97}$ glasses at selected temperatures (T= 323 K and T= 423 K) is shown in Fig. 2 and 3 respectively. The recorded plots explore the typical behavior found for amorphous semiconductors [22]. In low frequency range the conductivity is almost independent of the frequency and can be ascribed to DC conductivity, whereas AC conductivity exhibits dispersion in power law fashion at higher frequencies.

The correlated barrier hopping (CBH) model proposed by Elliott [23] has been extensively applied to the chalcogenide glassy semiconductors for explaining AC conduction mechanism. According to this model, the conduction in AC regime can be interpreted in terms of pair approximation via bipolaron hopping procces. Bipolarons occurs when two electrons simultaneously hop over a potential barrier between D^+ and D^- states. The barrier height is correlated with the inter-site separation via a Coulombic interaction [24]. Since the concentration of these diamagnetic defects states is very large in low and intermediate temperature ranges, bipolaron hopping is the dominant conduction mechanism in this domain [25].

Table 2: IS data for the glassy system $Pb_x(As_2S_3)_{100-x}$

Temperature (K)	x=1 at. %		x=3 at. %	
	C_1 (pF)	C_2 (pF)	C_1 (pF)	C_2 (pF)
293	3.06	3.64	3.08	2.1
313	3.06	2.68	3.08	1.4
333	3.06	2.95	3.08	1.6
353	3.07	2.61	3.08	1.4
373	3.07	6.19	3.09	3.1
393	3.08	132.5	3.09	66.5
423	3.08	266	3.09	132.5

To provide more details about the conduction mechanism in studied samples and potentially highlight the role of Pb doping, experimental data are presented in the form of Nyquist plots. They are analyzed in terms of equivalent circuits made of components describing the contribution of different electrical active regions in a material. It was found that impedance spectra of both samples at all temperatures can be described with two capacitors connected in parallel. As a representative example, Fig. 4 presents the Nyquist plots obtained at temperature of 423 K. The curves tend to be linearly lined up towards the Z_{imag} in the whole frequency range which refers to high insulating nature of both compounds. It is important to highlight a strong agreement between the experimental data points and the fitted spectrum for both samples (errors below 10 %). Fitting with the model above using the Powel algorithm and amplitude function yielded the values of parameters as presented in Table 2.

The loss tangent graphs of investigated materials at selected temperatures (T= 323 K and T= 423 K) given in Figs. 5 and 6 show the variation of the loss tangent against the frequency. The

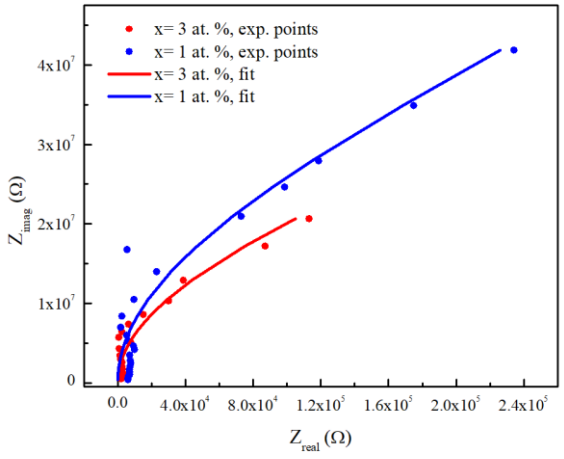

Fig. 4: Nyquist plots for the glassy system $Pb_x(As_2S_3)_{100-x}$ at T= 423 K

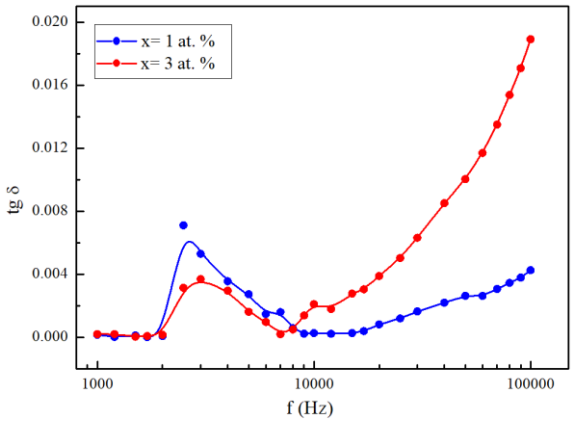

Fig. 5: Frequency dependence of tgδ for the glassy system $Pb_x(As_2S_3)_{100-x}$ at T= 323 K

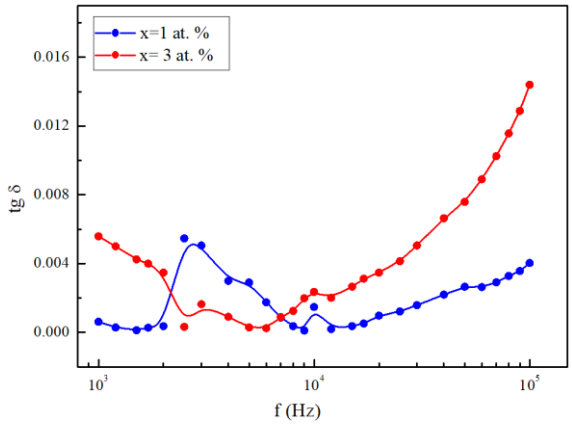

Fig. 6: Frequency dependence of tgδ for the glassy system $Pb_x(As_2S_3)_{100-x}$ at T= 423 K

low-temperature plots indicate an increase in the loss with frequency, followed by a maximum at particular frequency (Figure 5). The low-frequency region (left side of the peak) is associated with the dominated Ohmic component and maxima at a particular frequency (relaxation frequency) is observed where the frequency of applied electric field matches with the frequency of molecule rotation. At this frequency, maximum power transfer occurs. This is the high-frequency region which is associated with the dominated capacitive behavior [26-28], as already established on the basis of impedance spectra analysis. This behavior is especially pronounced in $Pb_1(As_{40}S_{60})_{99}$ sample. On the other hand, significant increase of tgδ of the sample with higher Pb content at high frequencies accompanied with peak shift to a lower frequencies at high-temperatures (see Fig. 6) can be attributed to an increase in conductivity, confirming the previous results.

IV. CONCLUSION

The measurements of the DC conductivity of the glasses from the system $Pb_x(As_2S_3)_{100-x}$ (x=1 and 3 at.%) showed that the increase in this parameter as a function of the dopant content can be explained as a consequence of network modification, due to formation of new structural units AsS and PbS, as established in previous research. Also, analysis of the temperature dependent DC conductivity revealed that dominant mechanism of transport of charge carriers in the investigated temperature interval for both samples is hoping between the localized states. The nature of variation of AC conductivity spectra is found to obey Jonscher's universal power law and suggest that correlated barrier hopping model (CBH) is the most suitable model to characterize the electrical conduction mechanism of prepared chalcogenides. Further, analysis of impedance spectra by means of an equivalent circuit model revealed the presence of a single temperature dependent relaxation and high insulating nature of investigated compounds. The frequency dependence of dielectric losses at different temperatures confirmed these conclusions.

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