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dc electrical properties of some metal–chalcogenide glassy alloys of the Cu–As–Se system

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Abstract

The dc electrical conductivity of metal–chalcogenide glassy alloys $Cu_xAs_{50-x}Se_{50}$, with $x=5$, 10 and 20 at%, derived from their linear current–voltage characteristics, and its variation with temperature, have been studied. The electrical conductivity, plotted versus inverse temperature, obeys an Arrhenius-type dependence, and the calculated preexponential factors seem to indicate that the electrical conduction mechanism is the so-called hopping between localized states, both in the band tails and near the Fermi level. Nevertheless, the electrical conductivity–temperature characteristics show a slight curvature, that could be explained by the influence of the variable range hopping conduction mechanism on the main conduction mechanism, or by the consideration of the small polaron model as the only electrical conduction mechanism.

1. Introduction

The electrical properties of Se-based glasses are very interesting, since these materials exhibit effects such as optical memory and photodarkening [1,2], for which the study of their electrical behaviour could shed some light. Generally, the undoped chalcogenide glasses show low values of the electrical conductivity, which means a serious limit to their technological applications and to the electrical measurements. The addition of transition metals into these amorphous materials, even at very low concentrations, leads to a significant increase in their electrical conductivities [3]. Several authors have reported on the marked influence of copper on arsenic selenides [4]. This study is aimed at determining the influence of copper content on the electrical conductivity and its dependence on temperature. It is focused on three samples of composition $Cu_xAs_{50-x}Se_{50}$, with $x=5$, 10 and 20 at% (in the following, M1, M2 and M3, respectively), i.e. from the binary alloy $As_{50}Se_{50}$, part of the As-content has been substituted by Cu, fixing the content of the chalcogen.

2. Experimental details

The bulk glasses were prepared according to the conventional melt–quench method. The elements were heated to 950°C approximately, and kept at that temperature for 15 h. Meanwhile, the ampoules that contained them were rotated so as to ensure a good mixture. Then, the ampoule was quenched in air. The non-crystallinity of the samples was checked by X-ray diffraction analysis [5] and by differential scanning calorimetry (DSC) [6]. Also, the composition of the ingot thus obtained, was determined by atomic absorption analysis, attaining good agreement with the proposed chemical composition. Some results obtained from these preliminary characterization

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techniques are shown in Table 1. One can notice that, as copper content is increased, the average coordination number of the amorphous material also increases. This fact has been explained in detail through the hypothesis of tetracoordinated copper atoms, in such a way that the structural configuration which most agrees with the experimental X-ray diffraction data, in all cases, consists of a network of tetrahedral units centered on Cu atoms and on As atoms, joined together through Se atoms, as a consequence of their high tendency to form chains [5]. Similar results have also been reported for other Cu–As–Se glassy alloys [7,8].

The samples were prepared by cutting the ingot, obtained after the quenching process, and by embedding these cylinders (approximately 7 mm high) in an epoxy-type resin. To ensure the electrical contacts with the electrode system, the parallel sides of the samples were carefully polished with alumina powder, of different grain sizes, until they showed mirror-like surfaces. The electrodes were made of graphite paint, deposited over these surfaces, and they were subjected to a curing process, where the device was heated to a temperature of 80°C for several hours, until the electrical resistance of the sample was stable.

The samples were put inside a cylindrical furnace, controlling its temperature by means of a PID-type temperature controller of ±0.3°C accuracy (Omron E5AX). The temperature range under study was between 30 and 100°C, considering that this latter value is sufficiently lower than the glass transition temperature and so, no structural changes should occur during the electrical stimulation. All the measurements were made in darkness.

Generally, when a constant voltage pulse is applied to a bulk chalcogenide glassy semiconductor, the Joule self-heating makes the sample temperature rise, therefore the electrical resistance of the sample decreases and, consequently, the current also increases during the pulse width. So, it is very important to accurately determine the current *at the beginning* of the pulse (i.e. I at $t=0$). To obtain the $I(t=0)-V$ characteristics of the samples, a memory oscilloscope (Trio, model MS-1650B) was used to record the voltage drop on a fixed resistor in series with the glassy sample. From this voltage drop, the current can be continuously calculated during the application of the pulse (the pulses were 60 s wide). Furthermore, it is worth mentioning that a double recording system was used, since we recorded simultaneously the first second of the pulse (by means of the aforementioned memory oscilloscope) and its full width (using a chart recorder).

Table 1
Average coordination number, n_{avg}, glass transition temperature, T_g, and actual composition for the three glassy alloys under study

Glassy alloy	n_{avg} [a]	T_g (K) [b]	Actual composition [c]
M1	2.66	449	$Cu_{4.9}As_{45.7}Se_{49.4}$
M2	2.93	453	$Cu_{9.7}As_{40.4}Se_{49.9}$
M3	3.23	446	$Cu_{20.2}As_{30.5}Se_{49.3}$

[a] X-ray diffraction. [b] DSC ($\beta=4$ K min^{-1}).
[c] Atomic absorption.

3. Results and discussion

The $I(t=0)-V$ characteristics of the bulk glassy samples, shown in Figs. 1a–1c, exhibit a clear ohmic behaviour, in the range of voltage and current provided by the voltage source used in the present work (up to 1000 V and up to 20 mA). So, the experimental values are well fitted to a straight line, whose slope is, obviously, the inverse of the electrical resistance. Other bulk chalcogenide glassy samples have shown $I(t=0)-V$ characteristics, exhibiting a non-ohmic behaviour, using a different measurement technique [9,10]. Such a method implies the fitting of the experimental $I(t)$ values to a phenomenological time dependence which agrees with the thermal balance equation for this process [10,11]. The current increase for an applied voltage V at an instant t, $\Delta I_{JH}(V, t)$, is given by

$$\Delta I_{JH}(V,t)=\Delta I_{JH}(V,\infty)\ [1-\exp(-t/\tau_{th})]\ , \qquad (1)$$

where τ_{th} is a time constant for the thermal process produced by Joule self-heating, and $\Delta I_{JH}(V,\infty)$ is the current increase at the steady state, i.e. the state at which the heat generated by the Joule effect and the heat removed from the sample to the surrounding ambient are balanced.

With our experimental results, the $I(t=0)$ values calculated with this technique, were always higher than those shown by the memory oscilloscope. As the difference increases when the pulse voltage increases,

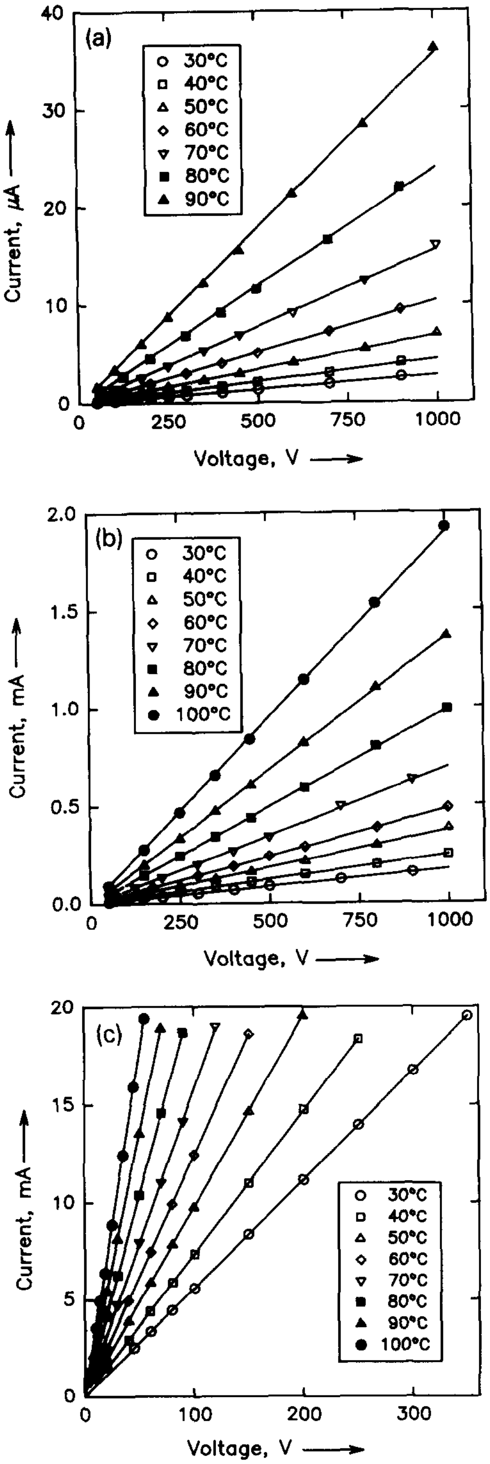

Fig. 1. The current–voltage characteristics for the glassy alloys under study: (a) M1, (b) M2 and (c) M3.

this method could mislead one to consider a non-ohmic behaviour for the present bulk samples. It should be noted that Eq. (1) was theoretically explained by considering several approximations (such as the homogeneous heating of the sample during the electrical stimulation), and this fact could be the reason for the departure of the experimental results from those predicted by the above-mentioned time dependence, specially at the beginning of the pulse.

From the electrical resistance values, obtained at different ambient temperatures, and considering the geometrical parameters of each sample, the electrical conductivity was calculated. These results are shown in Fig. 2, in a semilogarithmic plot, versus the inverse of the temperature.

On the other hand, according to the Mott–Davis model for the electrical conduction in chalcogenide glassy solids [12], not only the energy bands show limited tails (this is the reason why it is better to consider the *mobility gap* instead of the energy gap for these amorphous materials), but also some energy states exist near the center of the gap, originated from lattice defects, such as valence alternation pairs, dangling bonds, etc., which can be subdivided into donor and acceptor states. These states have the effect of pinning the Fermi level at the center of the mobility gap. In this case, the electrical conduction takes place

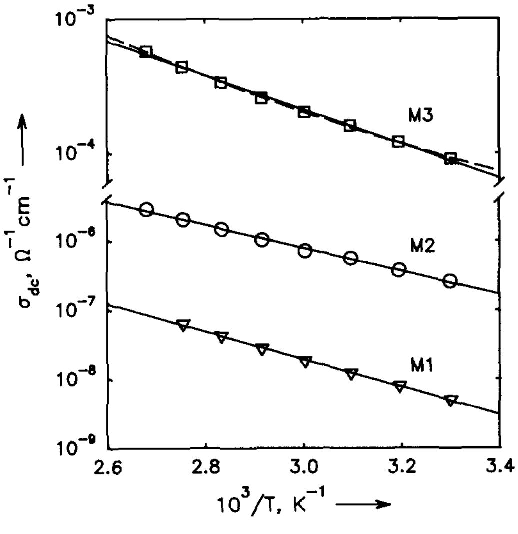

Fig. 2. Semilogarithmic plot of the electrical conductivity versus inverse temperature for the glassy alloys under study. The dashed line that connects the points of the sample M3 is a guide for the eyes.

both in the band tails and in the states near the Fermi level, by means of a phonon-assisted tunnelling hopping [12]. The dependence of the electrical conductivity on temperature is then given by a typical Arrhenius-type relationship

$$\sigma=\sigma_0 \exp(-\Delta E/k_B T) , \qquad (2)$$

where k_B is the Boltzmann constant, ΔE is the activation energy, and σ_0 is the pre-exponential factor, that, in this case, is lower than the *minimum metallic conductivity*, i.e. the corresponding pre-exponential factor for the extended states' conduction mechanism, theoretically estimated by Mott as approximately $2\times10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ [13]. The activation energy will be the sum of several contributions: the energy difference between the Fermi level and the edge of the valence band tail and both hopping energies required for phonon-assisted tunnelling in the band tails and near the Fermi level.

According to Eq. (2), the plots of σ versus inverse temperature, shown in Fig. 2 are well fitted to a straight line, from which the pre-exponential factor and the activation energy can be calculated. Table 2 shows these values for the three glassy alloys under study.

Regarding the composition dependence of the dc electrical properties, as the copper content is increased (and so, the arsenium content is decreased), the electrical conductivity also increases (the same for the pre-exponential factor). In turn, the activation energy decreases with increasing copper content. This fact is not due to the narrowing of the band gap, but to the shift of the valence band towards the Fermi level [14,15], caused by the occurrence of defects generated by the presence of copper atoms and the partially ionic nature of Cu–Se chemical bonds, which can produce a higher number of defects [16]. Amorphous semiconductors from the Cu–As–Se system seem to be similar to the amorphous Si:H, because the tetrahedrical bonds predominate and most of the defects must have positive correlation energies, but there is a significant difference between these two doping mechanisms: the ionicity of the Cu–Se bonds instead of the covalent character of the Si–H bonds. The ionicity of the Cu–Se bond has been calculated, being similar to that of most II–VI semiconductors [16]. As in these materials, the ionicity results in the formation of cationic and anionic vacancies. For several reasons (as the atomic size, for example), a type of vacancy is generally preferred from a thermodynamic point of view. Alloys in the Cu–As–Se system are p-type materials [15], this fact being a logical consequence of the copper and selenium electronegativity and the ionic radius values.

Table 2
Parameters deduced from the fitting of the electrical conductivity to the Arrhenius-type dependence of eq. (2).

Parameter	Glassy alloy		
	M1	M2	M3
$\sigma_0\ (\Omega^{-1}\ \mathrm{cm}^{-1})$	4.81×10^{-2}	1.71×10^{-1}	2.71
ΔE (eV)	0.42	0.36	0.27
r	0.9994	0.998	0.998

In the electrical conductivity versus inverse temperature plot, a slight curvature can be noticed (to show this behaviour clearer, the conductivity axis in Fig. 2 was expanded, in the region where the conductivity values for the M3 alloy appear). This electrical behaviour is mentioned in the literature for lower ranges of temperature [17], and it is considered as an indication of the influence of another conduction mechanism in this kind of glassy materials. Two physical models are plausible for explaining this small curvature: the variable range hopping [18] and the mechanism of conduction by small polarons [19].

When the temperature decreases, the number and energy of phonons available for absorption also decrease, and so, tunnelling is restricted to those centers that, although they are not the nearest neighbours, they are energetically closer, being inside the range $k_B T$. This is the so-called variable range hopping mechanism [18], for which the following dependence of the electrical conductivity on ambient temperature can be obtained

$$\sigma=\sigma' \exp(-B/T^{1/4}) , \qquad (3)$$

where σ' is the pre-exponential factor for variable range hopping and B is a parameter which depends on the density of states at the Fermi level, $N(E_F)$, through the expression

$$B=16\alpha^3/k_B N(E_F) , \qquad (4)$$

α being the exponential decay coefficient for the localized wavefunction, estimated by Fritszche [20] as 0.125 Å^{-1}.

Although $T^{-1/4}$ behaviour usually appears at lower temperature than the range studied here, several authors have found that the maximum temperature at which the variable range hopping mechanism dominates can range up to room temperature for glasses in the Cu–As–Se system [21]. Nevertheless, with our experimental results, the calculated values of $N(E_F)$ are higher than those predicted by the model (greater than 10^{24} cm^{-3} eV^{-1}, for the three glassy alloys under study). Therefore, it would be necessary to study this kind of electrical behaviour at lower temperatures in order to obtain a more accurate value of $N(E_F)$, as the temperature range analysed is, perhaps, too close to the abovementioned maximum temperature found for these particular amorphous materials.

The second possible explanation for the observed curvature is the occurrence of the electrical conduction mechanism corresponding to the small polaron model, proposed by Emin et al. [19]. They suggested that the motion of the charge carrier is slowed down by the disorder, leading to the localisation of the carrier and the polarisation of the neighbouring lattice. The result is a potential well that traps the carrier, creating an unit formed by the lattice deformation and the carrier, i.e. a polaron. The polaron has a lower energy than the free electron, but a larger effective mass, since any movement also involves its induced deformation. Also, we can pointed out that as the holes interact less strongly than the electrons, their mobility will be higher and they will dominate the electrical conduction. At low temperatures, the electrical conduction takes place by band conduction. At higher temperatures, the polaron can hop from one position to an equivalent one, providing the phonons have the necessary energy for the lattice deformation, i.e. it is also a phonon-assisted tunnelling. Although the small polaron theory was developed for crystalline materials, the disorder is assumed to have no influence on the polarons, due to their local nature. Furthermore, it should be stressed that the probability for the small polaron formation is increased when the material is disordered.

The expression for the electrical conductivity for this conduction mechanism is similar to Eq. (2), but with a different physical significance for the activation energy parameter. In this particular case, this parameter is the sum of the energy required to generate the carriers and an activation energy associated with the hopping of small polarons. Then, the activation energy will depend on the temperature through the following relationship [21]

$$\Delta E = W_h \cosh^{-2}(\Theta_D/4T) + W_d/2 , \quad (5)$$

where W_h is the hopping energy of the small polarons, Θ_D is the Debye temperature of the solid and W_d is the disorder energy. According to Emin et al., the continuous curvature of the log σ versus inverse temperature characteristics is due to the fact that the mobility of the small polarons is thermally activated for temperatures higher than one third of the Debye temperature, which in this kind of materials ranges from 500 to 700 K [21]. The application of the small polarons model to our experimental data gave values for the Debye temperature excessively high, since the temperature range under study was limited.

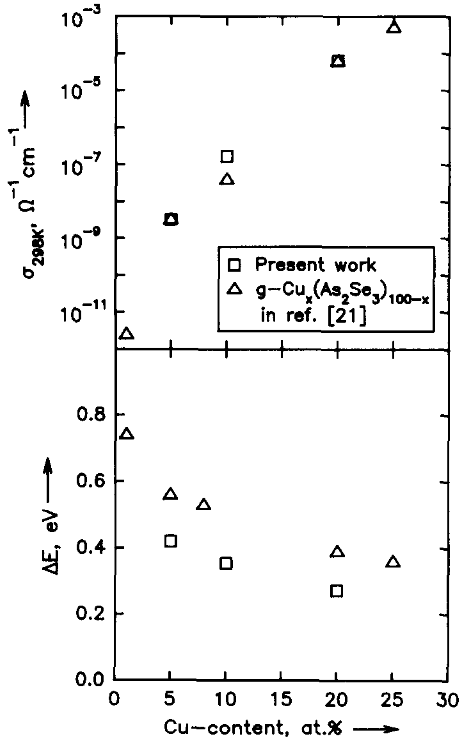

Fig. 3. Electrical conductivity (at 298 K) and hopping energy versus copper content for the three glassy alloys. Values for other alloys of near chemical composition, found in the literature, are also shown.

Finally, Fig. 3 shows the values of the electrical conductivity (at 298 K) and the activation energy for the three glassy samples, plotted versus copper content. Some values found in the literature, are also shown, being in excellent agreement with those obtained in the present work (considering the different As–Se content ratio between both sets of glassy alloys).

4. Acknowledgement

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