

# DC conductivity in GeSb<sub>2</sub>Te<sub>4</sub> and (GeSb<sub>2</sub>Te<sub>4</sub>)<sub>90</sub>(SnSe<sub>2</sub>)<sub>10</sub> phase change materials

M. POPESCU<sup>a\*</sup>, M. KUBLIHA, J. KALUŽNÝ, A. VELEA<sup>a</sup>, A. LÖRINCZI<sup>a</sup>

<sup>a</sup>National Institute R&D of Materials Physics, Atomistilor str. 105 bis, 077125-Bucharest – Măgurele, P.O.Box MG. 7, Romania

Institute of Materials, Faculty of Materials Science and Technology of the Slovak University of Technology, Böttova 9, 91724 Trnava, Slovakia

The dc electrical conductivity of the bulk amorphous GeSb<sub>2</sub>Te<sub>4</sub> material has been investigated. Pure and samples doped by 10 at. % SnSe<sub>2</sub> have been measured. The conductivity in the samples has been compared with that of SnSe<sub>2</sub> bulk sample. The activation energy of the doped sample is 0.165 eV. During heating the conductivity of doped material increases, reaches a maximum and then decreases. The comparison with the pure SnSe<sub>2</sub> samples allows to explain this behavior by the release above 148 °C of a small amount of selenium not bonded in the network.

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The chalcogenides in the non-crystalline state are flexible electronic materials that are now largely used in optoelectronic devices, in switches, CD recording devices and are proposed for smart memories [1-11]. Many papers have been published recently on switching mechanism in chalcogenides and phase change materials properties, as well as modeling [12-15]. The Ge-Sb-Te materials have been recently proposed as phase change materials for random access memories [16-25]. The memory effect is based on the rapid phase change produced under the action of electrical current pulses. Two conduction states are typical for such materials: the high conductivity state, which corresponds to the crystalline state, and the low conductivity state which is proper to the amorphous state of the investigated material.

We have prepared two phase change materials: the first composition is GeSb<sub>2</sub>Te<sub>4</sub> labelled L1, while the second one is (GeSb<sub>2</sub>Te<sub>4</sub>)<sub>90</sub>(SnSe<sub>2</sub>)<sub>10</sub> which has been labelled L2.

Pure elements (p.a. purity) have been introduced in a quartz ampoule in a proportion that corresponds to the stoichiometry of the ternary compound, adding appropriate amount of SnSe<sub>2</sub> in the case of the second, doped, composition. The ampoules were evacuated to 10<sup>-3</sup> Torr, sealed and heated in a tubular furnace at around 1050 °C (a temperature above the melting point of germanium) for 24 h. The ampoules were periodically shaken during heating and thereafter quenched in air. Sn and Se were introduced in the doped composition as SnSe<sub>2</sub> compound previously prepared by synthesis from elements. Cylindrical ingots were obtained.

The SnSe<sub>2</sub> ingots were prepared by mixing Sn and Se elements (5n purity) in quartz ampoule and then heating up to the melting point of SnSe<sub>2</sub> (657 deg. C) [26]. Periodic shaking and rocking of the ampoule was made in order to get a homogeneous composition. Finally the

ampoule was cooled down to 0 °C in a mixture of ice and water. An ingot of 19 mm in diameter and length of ~ 60 mm was obtained. Disc-shaped samples have been cut from the ingot.

The X-ray diffraction data show that both L1 and L2 samples are vitreous. The sample SnSe<sub>2</sub> is a mixture of polycrystalline and amorphous phase. The main crystalline phase is hexagonal SnSe<sub>2</sub>. A minor cubic SnSe<sub>2</sub> phase has also been found.

The direct current (dc) electrical conductivity measurements were carried out with conducting electrodes based on copper. The temperature dependence of the dc-conductivity ( $\sigma_{dc}(T)$ ) has been measured at a heating rate of 5 °C/min, using a Keithley 2000 digital multimeter in four-wire resistance setup, to compensate resistance of connected wires.

Temperature was measured by means of an S(Pt-PtRh) type thermocouple and a Greisinger GMH 3210 thermometer [27]. The measured data were monitored in steps of 1 °C.

The charge carriers move under the applied electric field but the free movement is impeded by the scattering on the lattice vibrations. As a consequence an Arrhenius law is obtained:

$$\sigma_{dc} = \sigma_0 e^{-(E_a/kT)} \quad (1)$$

where  $\sigma_0$  is a pre-exponential factor,  $E_a$  is the activation energy,  $k$  is Boltzmann's constant and  $T$  is temperature.

The results of the measurements are given in Fig. 1, where the conductivity  $\sigma_{dc}$  (in logarithmic scale) is plotted versus 1000/T.

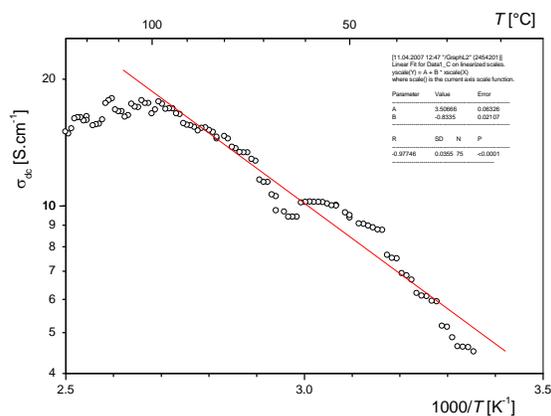


Fig. 1. The dc electrical conductivity of the bulk phase change material based on Ge, Sb and Te with SnSe<sub>2</sub> addition.

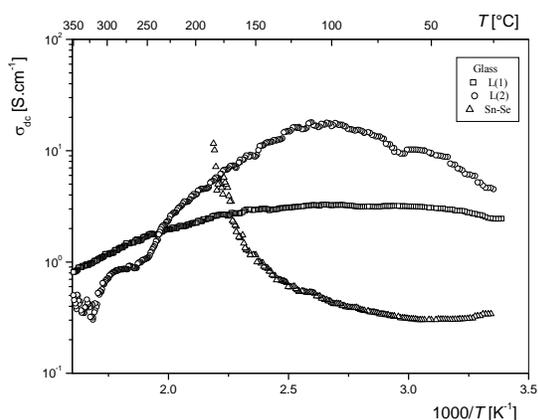


Fig. 2. The dc conductivity curves for the Ge-Sb-Te phase change material pure and doped, and for the pure dopant of SnSe<sub>2</sub>.

Fig. 2 shows the conductivity curves of the Ge-Sb-Te phase-change material compared to the material doped by SnSe<sub>2</sub> and with pure SnSe<sub>2</sub> sample. The figure evidences the effect of SnSe<sub>2</sub> on the Ge-Sb-Te major compound. The dc electrical conductivity of the doped material (L2) reaches a maximum at ~ 148 °C, after which it decreases. The conduction mechanism seems to change at that temperature from one characterized by hopping (semiconductor-like) to a metallic one.

In the case of the amorphous sample L1, the conductivity is practically constant (around 3 S.cm<sup>-1</sup>) up to ~140 °C. Then, a slight decrease occurs.

The conductivity of the SnSe<sub>2</sub> sample increases steeply up to around 184 °C. This special behavior is probably due to the release of a small amount of selenium which significantly influences the conductivity, due to its metallic character.

Taking into account the behavior of SnSe<sub>2</sub>, the conductivity curve of the L2 (doped) sample seems to be explained by the role played by the doping fraction: SnSe<sub>2</sub>. In the doped sample the selenium regulates the conductivity due to its valence properties. For significant

amount of SnSe<sub>2</sub> the semiconducting properties are evidenced.

The activation energy of the material is E<sub>a</sub> = 0.165 eV. At a certain temperature some selenium is released (at the temperature point corresponding to the steep increase of the conductivity of SnSe<sub>2</sub>). Thus the conduction character of the sample is changed drastically and the conductivity decreases.

It is possible to conclude that the conductivity in phase change memory material GeSb<sub>2</sub>Te<sub>7</sub> could be controlled by small amount of SnSe<sub>2</sub> introduced into the composition. This effect could be of interest for the control of the energy dissipation during the action of the electrical pulses responsible for the change of the conductivity state during switching.

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\*Corresponding author: mpopescu@infim.ro