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Semiconducting Ge-Se-Sb-Ag chalcogenides as prospective materials for thermoelectric applications

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A B S T R A C T

Chalcogenide as thermoelectric materials have shown a large power factor to yield a high figure of merit. In this work we report the study of *Ag* doped $Ge_{20}Se_{60}Sb_{20-x}Ag_x$(0 ≤ x ≤ 20 at%) chalcogenide materials in thin film form for the thermoelectric behaviour in the temperature range 300–450 K. Thin films have been prepared from the bulk samples by thermal evaporation. Electrical characterization analysis has also been reported. The dc conductivity increases while the activation energy decreases with the increase in *Ag* concentration. The type of the conductivity has been found to be *p*-type throughout the entire investigative temperature range where the sign of the thermoelectric power is positive. The concentration of the free carriers has been determined from dc conductivity and thermoelectric power measurements. The activation energy obtained from the thermoelectric power decreases while the power factor, which is one of the important thermoelectric parameters, increases with increasing silver content.

1. Introduction

The growing energy challenge around the globe can be countered to some extent with the development of new thermoelectric devices which converts waste heat into electric power without emitting greenhouse gases. The development of new and efficient thermoelectric devices requires new thermoelectric materials. Thermoelectric materials utilize the temperature difference for the conversion into electricity by tapping the flow of electron from a hotter part to a colder part. An effective thermoelectric material has to take care of good electric conduction otherwise shortly the temperature throughout the material will become equal. The ability of Peltier elements to heat and cool with great accuracy, have established their usefulness in various sectors like optical, automobile, electronics *etc*. Seebeck based products are instead immature. Bringing again into activity and prominence in exploring new thermoelectric materials for high thermoelectric conversion efficiency, we have chosen chalcogenide materials ($Ge_{20}Se_{60}Sb_{20-x}Ag_x$(0 ≤ x ≤ 20 at%)) to understand their thermoelectric behaviour particularly based on Seeback effect.

Chalcogenide materials have great potential due to their wide applications in electronic, optoelectronic and thermoelectric devices [1,2]. Thermoelectric materials are receiving increasing attention because of their prospective applications in solid state cooling and power generation [3,4]. The thermoelectric power measurements are expected to provide some information about the electrical transport mechanism for amorphous semiconductors. The dc conductivity and thermoelectric power measurements of amorphous semiconductors gives the mobility activation energy as the difference in the activation energy of thermal conductivity (ΔE) and the activation energy of thermoelectric power (ΔE_s) [5]. The dc conductivity and thermoelectric power measurements of a series of materials with systematic compositional change should be examined to figure out the conduction mechanisms of amorphous semiconductors.

Synthesis and compositional dependence of the optical and other physical properties (density, molar volume, compactness, mean coordination number, cohesive energy and the overall mean bond energy) for various related materials have been reported [6–9].

The present work reports the investigation of $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ (0 ≤ x ≤ 20 at%) chalcogenide thin films for their thermoelectric behaviour particularly Seeback effect. Along with thermoelectric behaviour the activation energy, the relaxation time and the free carriers concentration have also been determined.

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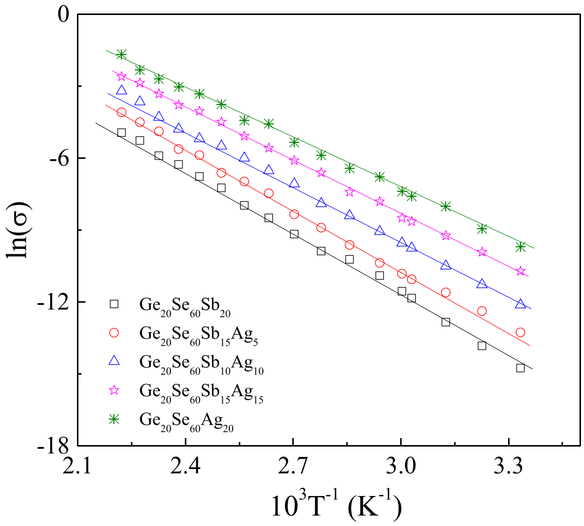

Fig. 1. ln (σ) vs. 1000/T for $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ (where *x = 0, 5, 10, 15 and 20 at%*) thin films.

2. Experimental details

Different compositions of bulk $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ (0 ≤ x ≤ 20 at%) chalcogenide glasses were prepared from 5 N pure constituent elements by the melt-quenching technique. Further details for preparation conditions can be found in a previous work [9]. Thin films of $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ have been prepared by the thermal evaporation of the bulk samples. For the thermoelectric power and conductivity measurements two gold electrodes with a spacing of 0.015 m and length of 0.014 m were deposited. For making the contacts silver paste is used. An ohmic character was obtained for the electrode contacts as confirmed by current–voltage measurements. The temperature difference between the ends of the sample has been kept 15 °C throughout the measurements of the thermoelectric power and the mean value of the temperatures at the ends has been taken as the specimen temperature. Two calibrated copper constantan thermocouples have been used to measure the temperatures near the two electrodes. To measure the thermo electromotive force a Keithley electrometer (model 6517A) was used. A voltage of 1.5 V (from a dry cell) has been applied across the planar films for the dark conductivity measurements, and the resulting current has been measured with the electrometer. The measurements of the dark conductivity and the thermoelectric power have been obtained in a vacuum ≈10^{-1} Pa. The error in the experimental measurements has been approximately ± 2%.

3. Results and discussion

The experimental dc conductivity data for amorphous $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ (0 ≤ x ≤ 20 at%) thin films are plotted in Fig. 1. A linear nature of the plots (ln(σ) versus 1/T) clearly indicates that the conduction is through an activated process having single activation energy in the investigative temperature range (300–450 K) for $Ge_{20}Se_{60}Sb_{20-x}Ag_x$(0 ≤ x ≤ 20 at%) thin films. The dc conductivity, σ, obeys the Arrhenius law

$$\sigma = \sigma_o exp\left(\frac{-\Delta E}{k_B T}\right) \tag{1}$$

where σ_o is the conductivity pre-exponential factor, ΔE is the activation energy for dc conduction and k_B is the Boltzmann constant.σ_o and ΔE were obtained by a least square fit to experimental data. The conductivity results are listed in Table 1 including ΔE, σ_o and room temperature dc conductivity σ^*. It is observed that, σ^* increases while ΔE decreases with an increase of Ag content for the $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ (0 ≤ x ≤ 20 at%) thin films. The activation energy is equal to 0.749 eV for $Ge_{20}Se_{60}Sb_{20}$ and decreases to 0.605 eV for the $Ge_{20}Se_{60}Ag_{20}$ sample. The activation energy for $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ films is for the electronic conduction. By known the conductivity pre-exponential factor (σ_o), the free carrier relaxation time (τ) can be calculated from the relation [10]

$$\sigma_o = \frac{2e^2\tau}{m^*}\left(\frac{2\pi m^* k_B T}{h^2}\right)^{3/2} \tag{2}$$

where the effective mass, m^*,equals 0.11 m_e [11] and h is Planck's constant. The temperature dependence of free carrier relaxation time for $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ (0 ≤ x ≤ 20 at%) thin films is shown in Fig. 2. From this figure we can notice that τ decreases on increasing both of the Ag content and the temperature. The estimated values of the free carrier relaxation time at room temperature (τ*) for $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ (0 ≤ x ≤ 20 at%) thin films are presented in Table 1. The free carriers concentration (n_σ) for $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ (0 ≤ x ≤ 20 at%) thin films has been calculated from the values of the activation energy, ΔE, in the equation [11]

$$n_\sigma = 2M^{3/2} exp\left(\frac{-\Delta E}{k_B T}\right) \tag{3}$$

where $M = 2\pi m k_B T/h^2$, m is the mass of the charge carrier. The estimated values of the free carriers concentration at room temperature (n_σ^*) are presented in Table 1. The concentration of the free carriers as a function of temperature for $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ (0 ≤ x ≤ 20 at%) thin films is represented in Fig. 3. It is evident from Fig. 3 and Table 1 that the free carrier's concentration increases with both of the temperature and the Ag content.

The mobility (μ) of free charge carriers in $Ge_{20}Se_{60}Sb_{20-x}Ag_x$ (0 ≤ x ≤ 20 at%) thin films at different temperatures has been calculated by using the concentration of the free carriers in connection with the conductivity measurements according to the relation [12]; $\mu = e\tau/m^*$. The estimated values of the mobility at room temperature (μ^*) are given in Table 1. The temperature dependence of the mobility for $Ge_{20}Se_{60}Sb_{20-x}Ag_x$(0 ≤ x ≤ 20 at%) thin films is displayed in Fig. 4. Fig. 4 shows that the mobility decreases with an increase in both of the temperature and the *Ag* content. Substituting the values of μ and ΔE

Table 1
Values of the conductivities σ and σ0, thermoelectric power S, the activation energies ΔEand ΔE_s, δ and free carrier concentrations n_σ and n_s.

Composition	σ^a (10^5 Ω m)$^{-1}$	σ_0 10^6 (Ω m)$^{-1}$	S^b μV K^{-1}	ΔE eV	ΔE_s	δ	n_σ 10^{14} m^{-3}	$n_s^b 10^{14}$	μ^a (10^{-5}) $m^2 V^{-1} s^{-1}$	E_f meV	τ^a 10^{-12} s
$Ge_{20}Se_{60}Sb_{20}$	0.044	1.616	2108	0.749	0.703	0.046	0.068	0.0849	0.4022	1.413	2.29
$Ge_{20}Se_{60}Sb_{15}Ag_5$	0.155	1.419	1997	0.713	0.665	0.047	0.274	0.3396	0.3533	3.56	2.012
$Ge_{20}Se_{60}Sb_{10}Ag_{10}$	0.550	1.15	1886	0.678	0.628	0.050	1.190	1.085	0.2863	7.723	1.63
$Ge_{20}Se_{60}Sb_5Ag_{15}$	2.122	1.072	1766	0.638	0.586	0.052	4.97	4.569	0.2669	20.14	1.52
$Ge_{20}Se_{60}Ag_{20}$	6.470	0.9139	1652	0.605	0.550	0.055	17.78	19.26	0.2275	52.54	1.295

δ = ΔE-ΔE_s.
[a] at 300 K.
[b] at 333 K.