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ELECTRICAL CONDUCTIVITY AND THERMOELECTRIC POWER OF a-$Se_{80-x}Ga_{20}Te_x$ ($x = 0, 5, 10, 15$ AND 20) THIN FILMS

ZISHAN H. KHAN[a], M. ZULFEQUAR[b], M. ILYAS[b] AND M. HUSAIN[b]

[a]Department of Applied Sciences & Humanities,Faculty of Engineering & Technology
Jamia Millia Islamia, New Delhi-110025, India
[b]Department of Physics, Jamia Millia Islamia, New Delhi-110025 India

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The dc conductivity and thermoelectric power of a-$Se_{80-x}Ga_{20}Te_x$ ($x = 0, 5, 10, 15$ and 20) thin films were reported in the present work. The free charge carrier concentration was calculated with the help of dc conductivity and thermoelectric power measurements. The calculated values of free charge carrier concentration were used to evaluate the free charge carrier mobility from which grain boundary potential was evaluated. The results are interpreted in terms of small polaron hopping, the structure of Se-Te and the grain boundary potential barrier.

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1. Introduction

The present paper gives information about the transport mechanism of a-$Se_{80-x}Ga_{20}Te_x$ system, since these materials have applications in various solid state devices. In recent years, the optical memory effects in amorphous semiconducting films have been investigated and utilized for various applications. These have distinct advantages, viz., large packing density, mass replication, fast data rate, high signal-to-noise ratio and high immunity to defects [1–5]. Among amorphous semiconductors, glassy chalcogenides (Se, Te, S) are more important because they have great varieties of band gaps and are transparent in IR region [6]. Recently, various workers [7–10] have reported the use of these materials for reversible optical recording by amorphous to crystalline phase change.

In amorphous semiconductors, charge transport occurs through participation of both electrons and holes. The mechanism of transport involves the hopping of both free carriers and polarons and the conduction of electrons and holes in the extended states [11–14]. One of the important and apparently anomalous situations in carrier transport among amorphous semiconducting chalcogenides is the so-called "*n–p* anomaly" in which the Hall and Seebeck coefficients indicate opposite signs for the predominant carriers [13–18]. However, this anomaly has apparently been resolved [13–18] and the sign of the charge carrier is indicated by thermoelectric power (S) measurements. It is also known that the temperature variation of the mobility gap is best determined in amorphous semiconductors by a study of S. Measurements of S also give a fair indication of the existence of polaron hopping and in conjunction with conductivity data such measurements can be used to determine the hopping barrier for polarons.

The paper reports dc conductivity and thermoelectric power (TEP) of a-$Se_{80-x}Ga_{20}Te_x$ as a function of temperature. Se has been selected because of its wide commercial applications. Its device applications like rectifiers, photocells, xerography, switching, and memory etc. made it attractive. However, pure selenium has short lifetime and low sensitivity. Se-Te alloys are useful due to their greater hardness, higher photosensitivity, higher crystallization temperature and smaller aging effects compared to the pure amorphous selenium. It has also pointed out that Se-Te alloys have extra advantages over amorphous selenium as far as their use in xerography is concerned [19–21]. We have chosen gallium as an additive material because it appears to be quick hardener when added to pure selenium. It is also a typical metal having low melting point (286°C) and a very high boiling point (2403°C). Recently, gallium was used in doping semiconductors and producing solid state devices. Moreover, gallium readily alloys with most metals and has been used as a component of low-melting alloys. The addition of third element (Te) expands glass forming area and also creates compositional and configurational disorder in the system. The lattice perfection and the energy band gap of the material play a major role in the preparation of the device for a particular wavelength, which can be modified by the addition of dopants [22]. Several workers [23–31] have conducted electrical, structural, and optical studies of a-Se-Ga and other amorphous alloys.

2. Experimental

Glassy alloys of a-$Se_{80-x}Ga_{20}Te_x$ were prepared by melt-quenching technique. The elementary constituents (purity 99.999%) of specific glass compounds were mixed together and sealed in evacuated fused quartz ampoules, and they were heated to 600–800°C for 16–18 h at a rate of 3–4°C·min^{-1}, quenched in ice water, and finally annealed just below each glass transition temperature for 20 h. The glassy alloys were characterized by X-ray diffraction. X-ray diffraction patterns showed the absence of sharp Bragg reflections. Vacuum evaporation technique was used to prepare the thin films of these glassy alloys keeping the substrates at room temperature and at a base pressure of $\approx 10^{-5}$ Torr. Predeposited thick indium electrodes on well degassed glass substrate were used for electrical contact.

The measurements were made in a vacuum $\approx 10^{-3}$ Torr. Planar geometry of the thin films (thickness $\approx$ 5000 Å, electrode gap 1.5 cm) was used for thermoelectric power and conductivity measurements. Temperature difference ($\approx$ 15°C) was maintained at the ends of the amorphous films during thermoelectric power measurements. Temperature was measured by two calibrated copper–constantan thermocouples mounted near two electrodes. Thermo emf. was measured by a nanovoltmeter (Keithley model 181). For the electrical conductivity measurements, a voltage of 1.5 V (from a dry cell) was applied across the planar films and the resulting current was measured by a Keithley electrometer (model 617). The measurements were made in a vacuum of $\approx 10^{-3}$ Torr by mounting the films in a specially designed sample holder. The experimental error during the measurements was $\pm 3\%$ approximately.

3. Results

The temperature dependence of dc conductivity for thin films of a-$Se_{80-x}Ga_{20}Te_x$ is shown in Fig. 1. It is clear from the figure that, in all the samples, the plots of $\ln \sigma_{dc}$ vs. $1000/T$ are straight lines, indicating the conduction in these glasses through an activated process having single activation energy in temperature region (287–318 K). The dc conductivity (σ_{dc}) can, therefore, be expressed by the usual relation

$$\sigma_{dc} = \sigma_0 \exp(-\Delta E_\sigma / k_B T), \tag{1}$$

where k_B is the Boltzmann constant and σ_0 is the pre-exponential factor. The values of ΔE_σ have been calculated using the slopes of Fig. 1. The calculated values of ΔE_σ are given in Table. Figure 2a shows that ΔE_σ decreases with the increase in concentration in $Se_{80-x}Ga_{20}Te_x$.

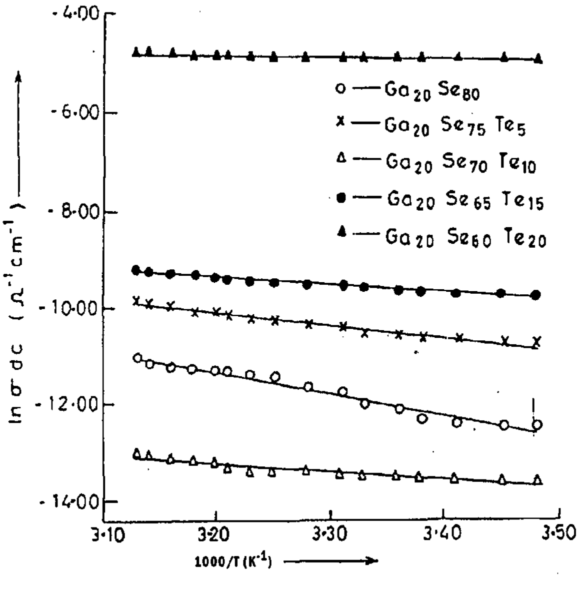

Fig. 1. Variation of dc conductivity vs. $1000/T$ for a-$Se_{80-x}Ga_{20}Te_x$.

TABLE

Electrical parameters of a-$\mathrm{Se}_{80-x}\mathrm{Ga}_{20}\mathrm{Te}_x$ ($x = 0, 5, 10, 15,$ and 20). n_s is the free charge carrier concentration calculated from thermoelectric measurements. n_σ is the free charge carrier concentration calculated from dc conductivity measurements.

x	σ_{dc} ($\Omega^{-1}\cdot\mathrm{cm}^{-1}$) at T = RT	ΔE_σ (eV)	S (μV/K) at 333 K	ΔE_s (eV)	$\Delta E_\sigma - \Delta E_s$ (eV)	n_s (1/cm^3)	n_σ (1/cm^3)	μ (cm$^2\cdot$V$^{-1}\cdot$s^{-1})	ΔE_μ (eV)
0	8.21×10^{-6}	0.31	721.24	0.21	0.10	2.04×10^{22}	1.96×10^{20}	2.35×10^{-7}	0.09
5	4.59×10^{-5}	0.22	320.21	0.14	0.08	2.13×10^{24}	6.75×10^{21}	4.25×10^{-8}	0.08
10	1.71×10^{-6}	0.15	251.90	0.09	0.06	4.71×10^{24}	9.36×10^{22}	1.14×10^{-10}	0.05
15	7.19×10^{-5}	0.07	122.52	0.04	0.03	2.11×10^{25}	1.89×10^{24}	2.38×10^{-10}	0.03
20	8.06×10^{-3}	0.04	98.82	0.02	0.02	2.78×10^{25}	5.38×10^{24}	8.64×10^{-9}	0.02

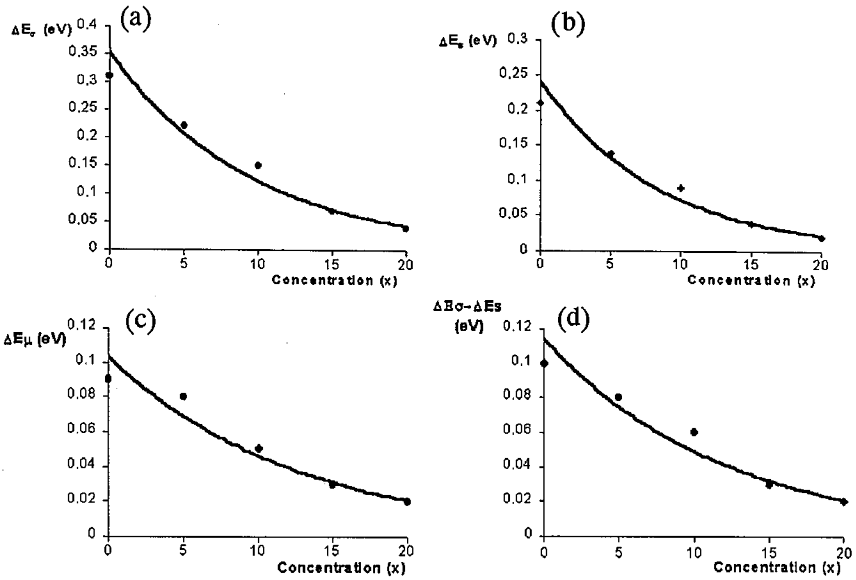

Fig. 2. Variations of (a) ΔE_σ, (b) ΔE_s, (c) ΔE_μ, and (d) $\Delta E_\sigma - \Delta E_s$ with concentration (x) for a-$\mathrm{Se}_{80-x}\mathrm{Ga}_{20}\mathrm{Te}_x$.

The general expression for S in the case of amorphous semiconductors has been extensively discussed in the literature [32, 33]. In the case where carriers are excited to appropriate extended states beyond the mobility edges, or where charge carriers form small polarons and are transported by hopping near the band edges, the expressions for S are formally identical. S is given by [33]

$$S = (k/e)[(\Delta E_s/k_\mathrm{B}T) + A], \tag{2}$$

$$\Delta E_s = (E_\mathrm{F} - E_\mathrm{V}) \quad \text{or} \quad (E_\mathrm{C} - E_\mathrm{F}), \tag{3}$$

where A is small constant between 1 to 4 [11, 12] and represents the thermal energy transported by carriers. Its magnitude is, therefore, dependent on the nature of scattering processes. As already mentioned, ΔE_s may be in general lower than ΔE_σ and this difference is considered as equal to the mobility activation energy [32] or to the polaron hopping barrier if the conduction is by small polaron [34]. Figure 3 gives the temperature dependence of thermoelectric power (S) for the thin films of a-$\mathrm{Se}_{80-x}\mathrm{Ga}_{20}\mathrm{Te}_x$. It is seen from Fig. 3 that the S vs. $1000/T$ curves are straight lines with a positive slope indicating that S decreases linearly with temperature. The activation energy (ΔE_s) has been calculated by using the slopes of Fig. 3. Figure 2b shows that ΔE_s decreases with the increase in tellurium (Te) concentration in a-$\mathrm{Se}_{80-x}\mathrm{Ga}_{20}\mathrm{Te}_x$. Figure 2d shows that the difference $\Delta E_\sigma - \Delta E_s$ also decreases with the increase in Te concentration in a-$\mathrm{Se}_{80-x}\mathrm{Ga}_{20}\mathrm{Te}_x$.

From the thermoelectric measurements, the free charge carrier concentration was calculated using the equation [35]

$$n_s = 2M^{3/2}\exp(2k_\mathrm{B} - S)/k_\mathrm{B}, \tag{4}$$

where $M = 2\pi m k_\mathrm{B}T/h^2$, k_B is the Boltzmann constant (taken in eV/K) and

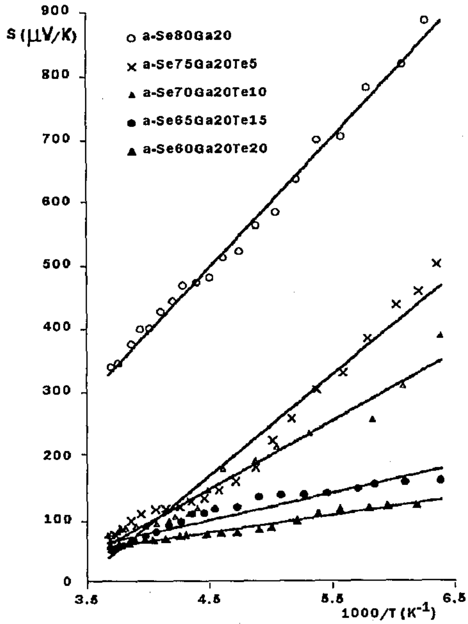

Fig. 3. Variation of thermoelectric power vs. $1000/T$ for a-$\mathrm{Se}_{80-x}\mathrm{Ga}_{20}\mathrm{Te}_x$.

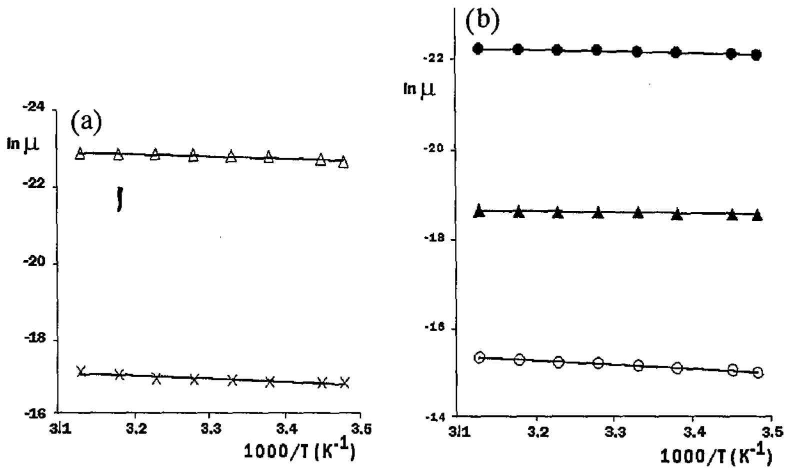

Fig. 4. Variation of mobility (μ) vs. $1000/T$ for a-$\mathrm{Se}_{80-x}\mathrm{Ga}_{20}\mathrm{Te}_x$: (a) $x = 5$ (crosses) and 10 (open triangles), (b) $x = 0$ (open circles), 15 (dark circles), 20 (dark triangles).

S is the thermoelectric power (taken in μV/K). It is evident from Table that the free charge carrier concentration increases on increasing Te concentration in a-$\mathrm{Se}_{80-x}\mathrm{Ga}_{20}\mathrm{Te}_x$ system.

Knowing the values of thermal activation energy (ΔE_σ), the free charge carrier concentration for different samples can be calculated using the equation

$$n_\sigma = 2M^{3/2}\exp(-\Delta E_\sigma/k_{\rm B}T), \tag{5}$$

where $M = 2\pi m k_{\rm B}T/h^2$, m is mass of charge carrier. The calculated values of free charge carrier are given in Table. It is evident from Table that the free charge carrier concentration increases with the increase in Te concentration. As observed, the free charge carrier concentration calculated from the conductivity measurements is lower than that calculated from thermoelectric power.

The grain boundary potential barrier model as proposed by Petriz [36] is based upon the consideration that the grain boundaries have an inherent space charge region due to the interface. The exponential temperature dependence of the mobility can be represented by the following relation:

$$\mu = \mu_0 \exp(-\Delta E_\mu/k_{\rm B}T), \tag{6}$$

where μ_0 is the grain boundary limited mobility. The value of ΔE_μ (mobility activation energy) can be estimated from the plots of $\ln\mu$ vs. $1000/T$ (Fig. 2c).

To calculate μ at different temperatures some authors [37, 38] made use of the free charge carrier concentration calculated from the Hall coefficient measurements in connection with the conductivity measurements at the same temperature. Because of very low conductivity in the present samples, it was not possible to measure the Hall coefficient either at room temperature or any other elevated temperature. Therefore, this problem was treated in another way. The free charge carrier concentration obtained from thermoelectric power measurements given in Table in connection with the conductivity measurements were used to calculate μ at any given temperature

$$\mu = \sigma/ne. \tag{7}$$

For each set of samples, the mobility activation energy has been calculated using $\ln\mu$ vs. $1000/T$ plots (Fig. 4). The calculated values of mobility activation energies are given in Table and the variation of mobility activation energy (ΔE_μ) with concentration (x) is shown in Fig. 2c for a-$\mathrm{Se}_{80-x}\mathrm{Ga}_{20}\mathrm{Te}_x$. It can be seen from the figure that ΔE_μ decreases on increasing Te concentration.

4. Discussion

The temperature dependence of thermoelectric power (S) measures the energy difference between the Fermi level and the energy where charge transport occurs. In simple one-band model with the Fermi energy pinned near the middle of the band gap, S is thermally activated with the activation energy of carrier density activation energy. The difference between ΔE_σ and ΔE_s can be attributed to the mobility activation energy. Table shows that $\Delta E_\sigma - \Delta E_s$ decreases with the increase in Te concentration in a-$\mathrm{Se}_{80-x}\mathrm{Ga}_{20}\mathrm{Te}_x$, which indicates that the band tailing increases as Te concentration increases in this system. In addition to transport of holes among the extended states, small polarons near the band edges may also contribute to conductivity. These small polarons are usually associated with the structure of Se [39]. Scottmiller et al. [40] have studied the effect of addition of various elements (S, Te, Bi, As, In, Ge etc.) on the structure of glassy Se by infrared and Raman spectroscopy. According to them, in glassy Se about 40% of the atoms have the ring structure and 60% of the atoms are bonded as polymeric chains. In case of a-Se-Te, tellurium glass contains short chains, while Se glass contains a mixture of long chains and rings. As the Te concentration increases, the number of Se rings decreases and the number of long Se-Te polymeric chains and Se-Te mixed ring increases [41] resulting the decrease in $\Delta E_\sigma - \Delta E_s$. In such a situation, neighbouring site polaron hopping would be involved in carrier transport and this is possible if Se-Te bonds are available in the structural contiguity throughout the samples of a-$Se_{80-x}Ga_{20}Te_x$.

The difference between the conductivity and TEP activation energies may also be attributed to a "grain boundary" limited mobility. Since the films are deposited from the vapour, the growth process involves the nucleation and growth of amorphous domains. As these domains grow together, an interface region exists between domains. Donovan and Heinemann [42] (evaporated a-Ge) and Hauser and Staudinger [43] did transmission electron microscopy on rf sputtered films of a-Ge up to 600 Å thick. Both teams of investigators report the existence of voids of approximately 10 Å diameter. If thus void-network continued to exist in the 5000 Å thick films, it could serve as "domain boundary" network that impedes the carrier mobility; $\Delta E_\sigma - \Delta E_s$ could then be attributed to the activation energy necessary for the carrier to be transported across the voids. For crystalline material in which grain boundaries cause the mobility to be thermally activated, mobility activation energies as great as 0.2 and 0.3 eV have been measured [44]. Although the postulated void-network provides a possible description of the electronic behaviour of a-Ge, it is not possible to verify its effect on the electronic properties experimentally. It is not possible to do transmission electron microscopy on films of the thickness required to do TEP measurements.

The difference $\Delta E_\sigma - \Delta E_s$ may be interpreted in terms of mobility activation energy. It can be seen from Table that the $\Delta E_\sigma - \Delta E_s$ is approximately equal to the mobility activation energy. Therefore, one can suggest that this difference may be due to the potential barriers at grain boundaries. Hence the potential barrier at grain boundaries play a distinguishable role in the samples.

5. Conclusion

From the above results and discussion, one can conclude that the thermal activation energy ΔE_σ and activation energy ΔE_s calculated using thermoelectric power measurements decreases with the increase in Te concentration. The free charge carrier concentration calculated from conductivity measurements is lower than that calculated from thermoelectric power measurements. The difference $\Delta E_\sigma - \Delta E_s$ decreases with the increase in Te concentration in a-$Se_{80-x}Ga_{20}Te_x$ resulting in decrease in band tailing. The difference $\Delta E_\sigma - \Delta E_s$ may be most likely due to small polaron hopping.

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