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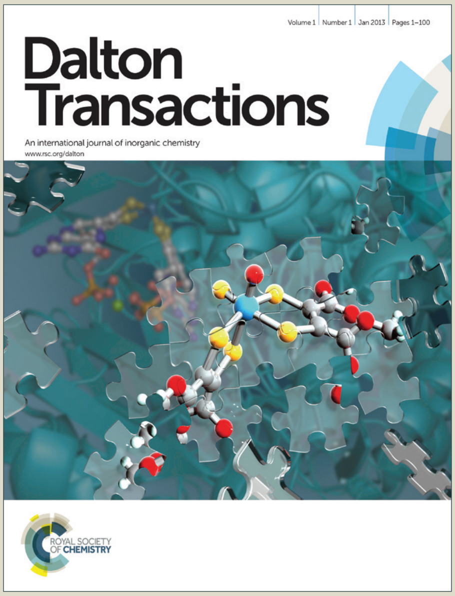

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ARTICLE

Semiconducting quaternary chalcogenide glasses as new potential thermoelectric materials: an As-Ge-Se-Sb case

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The performance of thermoelectric materials may be improved via complex structures, impurities, disorder etc. Chalcogenide glasses possess such properties. In the present paper, we report the electrical and thermoelectric properties of $As_{14}Ge_{14}Se_{72-x}Sb_x$ (where x = 3, 6, 9, 12, 15 at.%) chalcogenide glasses in the temperature range of 300 K to 450 K. The electrical conductivity has been observed to increase from $1.46\times10^{-9}\Omega^{-1}cm^{-1}$ to $1.80\times10^{-6}\Omega^{-1}cm^{-1}$ for x = 3at.% to x = 15at.%. The addition of Sb increase the Seebeck coefficient to large value 1124 μVK^{-1} for x = 15at.% at 333K. As a result of increased electrical conductivity and Seebeck coefficient for enhanced values of Sb, power factor (a measure of the performance of the thermoelectric energy converters) has been observed to increase strongly. Results indicate that the investigated chalcogenide glassy compositions may be potential candidates for incurring high action thermoelectric materials.

Introduction

To cope with the rising demand of energy in various sectors, a socio-political unrest in the recent years has been dramatically intensified. Similarly, there are lots of worries over environmental issues with the burning of fossil fuels [1]. Thermoelectricity is the one mode to meet the demands of our energy requirements. Thermoelectricity has to be valued as a fascinating mean of low-cost conversion of waste heat to useful electrical energy with a small environmental impact. Now to tap the waste heat we require thermoelectric materials which have ability to convert thermal energy into electrical energy (Seebeck effect) and, reversibly, electrical energy into thermal energy (Peltier effect). These materials provide an important solution to energy problems through the conversion of thermal energy into electrical energy. The thermoelectric devices has proved to be highly attractive and reliable (NASA Voyager space-crafts have used *SiGe*-based thermoelectric generators working smoothly for more than 30 years) [2].

Unused waste heat generated from home heating, automotive exhaust, and various industrial appliances could be converted to electricity by using thermoelectrics. Since thermoelectric generators are solid-state devices with motionless parts and being silent, reliable and scalable, makes them suitable for miniature and distributed power generation. The thermoelectric properties of solids vary dramatically from one material to other both in magnitude and temperature dependence. This is brought on by variation in sample sizes for single crystals or grain sizes for polycrystalline samples, lattice defects or imperfections, dislocations, anharmonicity of the lattice forces, carrier concentrations, interactions between the carriers and the lattice waves, interactions between magnetic ions and the lattice waves, *etc.*[3].

The thermoelectric analysis of amorphous semiconductors has been anticipated to provide some information about the electrical transport mechanism. Measurements of dc conductivity and thermoelectric power gives the mobility activation energy, which can be calculated from the difference between activation energy of thermal conductivity (ΔE_σ) and the activation energy of thermoelectric power (ΔE_s) for amorphous semiconductors [4]. Among amorphous semiconductors, chalcogenides have attracted much attention due to versatility in their synthesis and thermal, optical and electrical properties. So the thin films of chalcogenide have a wide range of applications in *viz.* advanced energy conversion and storage (ECS), thermoelectrics, electronic and optoelectronic devices *etc.*[5-7].

Chalcogenides are known to form various series of good thermoelectric materials *e.g.* Bi_2Se_3, Bi_2Te_3 and $Bi_2Te_{2.7}Se_{0.3}$, $PbTe$, $AgSbSe_xTe_{2-x}$, $TeAgGeSb$ and $AgPb_mSbTe_{2+m}$ materials [8-10] Among various chalcogenide glassy systems, *As–Se–Ge* is an important system due to the fact that *Ge*, *As* and *Se* are the elements of same period in groups IV to VI and brings about the covalent character of the interaction between their atoms resulting a broad glass formation region among all investigated three component chalcogenide systems [11-13]. The optical and thermal parameters of amorphous semiconductors have been extensively studied on *As–Se–Ge* system [14-17]. Since the properties of chalcogenide glasses changes significantly

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with the variation in their compositions [13-18]. So a good glass forming system (*As-Se-Ge*) has been chosen and is alloyed with antimony (Sb). *As-Ge-Se-Sb* system has shown high glass transition temperature and high crystallization temperature in comparison to other chalcogenide glasses [15,19,20]. So *As-Ge-Se-Sb* system provides a high working range ~436 K to 506K [15].The dc conductivity and thermoelectric power measurements with systematic compositional change should be investigated to understand the conduction mechanisms in these amorphous semiconductors.

In the present paper we report a systematic investigation of *As-Ge-Se-Sb* thin films (where *Se* is replaced with *Sb* for various compositions), for electrical conductivity and thermoelectric power. Also the activation energy, the free carrier relaxation time and the free carrier concentration have been investigated for the studied films from the measured values of the electrical conductivity and the thermoelectric power. A correlation has been drawn between the composition and thermoelectric parameters.

Experimental details

Bulk compositions of $As_{14}Ge_{14}Se_{72-x}Sb_x$ (where x = 3, 6, 9, 12, 15 at.%) chalcogenide glasses have been synthesized using melt-quench technique from the high purity (99.999%) constituent elements. Melt quenching substantially enhances the glassy domain due to the faster quenching rate. Glasses with wide varietyof compositions, up to ten kinds of elements at several ratios are possible. Moreover, melt quenching technique does not require stoichiometry. Further details for preparation conditions and the nature of the samples can be found in previous works [13-15]. Thin films of $As_{14}Ge_{14}Se_{72-x}Sb_x$ samples have been deposited on glass substrates by the thermal evaporation at a pressure of approximately 10^{-4} Pa. Film thickness was controlled in the range 200 nm – 220 nm using a quartz crystal (Edward FTM5) thickness monitor. For the thermoelectric power and conductivity measurements, two gold electrodes were deposited with an electrode gap of 0.015 m and electrode length of 0.014 m. For making the contacts silver paste has been used. An ohmic character has been obtained for the electrode contacts as confirmed by current–voltage measurements. The temperature difference between the ends of the sample has been about 15°C during the measurements of the thermoelectric power and the mean value of the temperatures at the ends was 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) has been used. A voltage of 1.5 V has been applied across the planar thin films for the dark conductivity measurements, and the resulting current was measured with the electrometer. The measurements of the dark conductivity and the thermoelectric power have been made for 300 K to 450 K in a vacuum $\approx 10^{-1}$Pa. The error of the experimental measurements has been approximately ± 2%.

Results and discussion

Figure 1 shows the dependence of dc conductivity (σ) on temperature for the thin films under investigation. The dc conductivity can be expressed by the conductivity relation

$$\sigma = \sigma_o e^{-\Delta E / k_B T} \qquad (1)$$

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 the plotted experimental data. It is clear from the Figure1 that for all the thin film samples, the plots of ln(σ) vs. *1000/T* are straight lines for the studied temperature range 300 K to 450 K. This indicates that in the investigated samples conduction occurs via an activated process having single activation energy in different temperature regions. Various parameters *i.e.* ΔE, σ_o and room temperature dc conductivity σ^*calculated from the Figure 1 are listed in table 1. It has been observed that σ^* increases whereas ΔE decreases with an increase of *Sb* content for the $As_{14}Ge_{14}Se_{72-x}Sb_x$ (where x = 3, 6, 9, 12, 15 at.%) thin films. The activation energy decrease from 0.765 *eV* for x = 3 to 0.628 *eV* for x = 15at.% of *Sb* content.

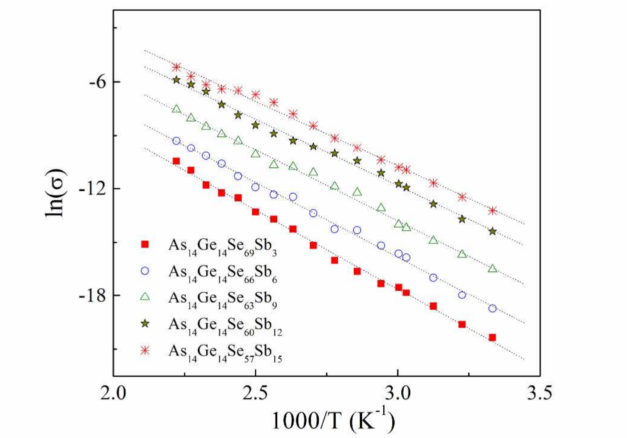

Figure 1 Electrical conductivity (σ) as a function of temperature for $As_{14}Ge_{14}Se_{72-x}Sb_x$ (where x = 3, 6, 9, 12 and 15 at. %) thin films.

With increase in Sb at.%, Sb-Se bonds (bond energy = 43.96 kcal/mol) supplant the Se-Se bonds (bond energy = 44 kcal/mol) which caused the reduction in band energy of the system and hence, in turn gradually decreases the activation energy [12].The decrease in activation energy with increasing Sb at.% has been supported by the similar results obtained for optical band gap [14]. Further, it has been well-established that glasses having Se form a polymeric network and the formation of homopolar bonds quenched qualitatively [18]. Now when *Se* is cross-linked with *Ge*, *As* and *Sb*, the probability of heteropolar bonds increase which may lead to the formation of high bond energy *As-Se*, *Ge-Se* in comparison to low energy homopolar Se-Se bonds [13]. But still the average bond energy of the system goes on decreasing with the addition of *Sb* content due to increased *Sb-Se* low energy bonds as reported earlier [13] and hence the energy barrier height decreases which successfully explains our results reported in table 1.

Table 1 Some electrical parameters as a function of *Sb* content for the $As_{14}Ge_{14}Se_{72-x}Sb_x$ (where *x* = 3, 6, 9, 12 and 15 at. %) thin films (* at 300 K and ** at 333 K).

x	σ* ×10^{-9} $(\Omega\ cm)^{-1}$	σ_0 ×10^{3} $(\Omega\ cm)^{-1}$	S** μVK^{-1}	ΔE eV	ΔE_s eV	δ eV	n_σ* ×10^{15} cm^{-3}	n_s** ×10^{18} cm^{-3}	μ* ×10^{-6} $cm^2 V^{-1} s^{-1}$	E_f meV	τ* ×10^{-15} s
3	1.46	7.76	855.2	0.765	0.620	0.145	4.31	4.867	1.677	9.75	1.049
6	7.31	10.16	955.3	0.721	0.602	0.119	23.51	4.123	2.196	8.73	1.374
9	68.50	22.59	999.2	0.685	0.571	0.114	93.32	3.854	4.883	8.34	3.055
12	566.20	42.00	1055.0	0.647	0.563	0.084	410.70	3.554	9.079	7.91	5.680
15	1801.00	66.78	1124.0	0.628	0.547	0.081	835.60	3.229	14.43	7.42	9.030

The free carrier relaxation time (τ) can be calculated by using the pre-exponential conductivity factor (σ_o), from the relation [21]; $\sigma_o = (2e^2\tau/m^*)(2\pi m^* k_B T/h^2)^{3/2}$, where $m^*$is the effective mass and is equals $0.11m_e$ and *h* is Planck's constant. Figure 2 shows the temperature dependence free carrier relaxation time. It can be clearly seen that the relaxation time increases with increase in *Sb* content for a particular temperature whereas with increase in temperature it decreases. The estimated values of the free carrier relaxation time at room temperature (τ^*) for the studied thin films are listed in Table 1.

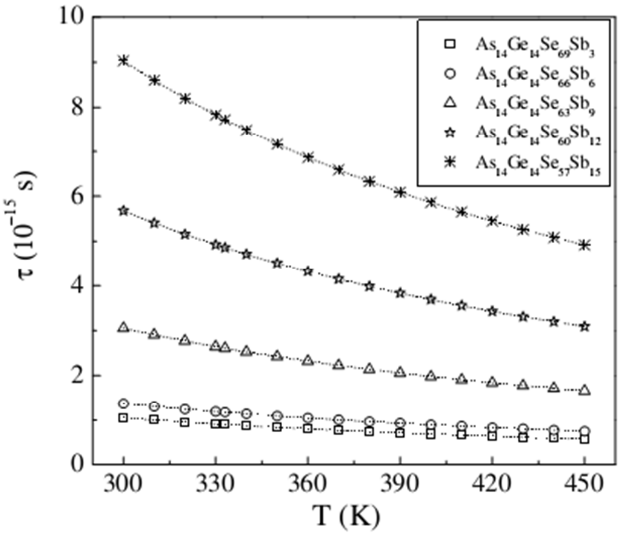

Figure 2 Free carrier relaxation time (τ) as a function of temperature for $As_{14}Ge_{14}Se_{72-x}Sb_x$ (where *x* = 3, 6, 9, 12 and 15 at. %) thin films.

The free carrier concentration (n_σ) for $As_{14}Ge_{14}Se_{72-x}Sb_x$(where *x* = 3, 6, 9, 12, 15 at.%) thin films can be computed from the values of the activation energy (*ΔE*), by using the equation [22], $n_\sigma = 2(2\pi m k_B T/h^2)^{3/2} e^{-\Delta E/k_B T}$, where *m* is the mass of the charge carriers. The computed values of the free carrier at room temperature (n_σ^*) have been listed in Table 1. Figure 3 shows the concentration of the free charge carriers as a function of temperature and it has been observed that with *Sb* content as well as with temperature it increases. With the increase in temperature electrons in the valence band acquire enough energy to surpass the band gap and go to the conduction band, becoming free to conduct and the empty states (holes) left behind in the valence band are also free to move and hence leading to an increase in charge carrier concentration with increase in temperature [23].

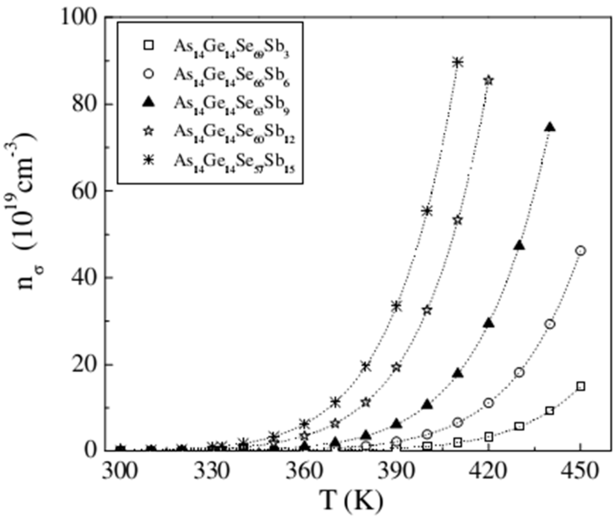

Figure 3 Free carrier concentration (n_σ) obtained from electrical conductivity as a function of temperature (T) for $As_{14}Ge_{14}Se_{72-x}Sb_x$ (where *x* = 3, 6, 9, 12 and 15 at. %) thin films.

The mobility (*μ*) of charge carriers at different temperatures in $As_{14}Ge_{14}Se_{72-x}Sb_x$ (where *x* = 3, 6, 9, 12, 15 at.%) thin films can be calculated by using the concentration of the free charge carrier in relation to the conductivity measurements according to the expression [24]: $\mu = \sigma/ne$. The values of mobility of free carriers at room temperature are listed in Table 1. It has been observed that mobility increases with the increase of *Sb* content. Since mobility is proportional with conductivity so the trend can be correlated with the same.

The Seebeck coefficient also called thermoelectric power (*S*), has more information than just measuring the induced voltage as a result of temperature difference. The parameter *S* is a highly useful quantity for distinguishing semiconductor materials and from its sign the dominant type of charge carrier can directly be figured out. Its magnitude is determined by the density of states, the energy dependence of the carrier relaxation time and the Fermi level. The temperature dependence of thermo-electric power measures the energy difference between the Fermi level and the energy where charge transport occurs. In a simple one-band model with the Fermi energy trapped near the center of the energy gap, *S* is thermally activated with the activation energy of the carrier density. A detailed discussion on the thermoelectric power can be seen at [4,25].

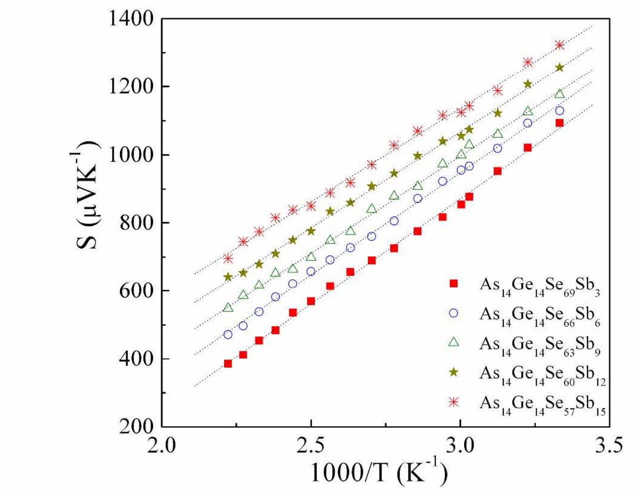

Figure 4 Variation of thermoelectric power or Seebeck coefficient (S) with temperature for $As_{14}Ge_{14}Se_{72-x}Sb_x$ (where x = 3, 6, 9, 12 and 15 at. %) thin films.

For amorphous semiconductors, where carriers are excited to states beyond the mobility edges, the thermoelectric power can be calculated using the relation [25],

$$S = \frac{k_B}{e}\left[\frac{\Delta E_s}{k_B T} + A\right] \qquad (2)$$

and $\Delta E_s = (E_F - E_V)$ or $(E_C - E_F)$,
where A is a constant representing the thermal energy carried by the carriers and its value lies between 1 and 4[4]. E_F, E_V and E_C are energies corresponding to Fermi level, valence band and conduction band respectively. The magnitude of A depends on the nature of the scattering processes. The difference $\delta = \Delta E - \Delta E_S$ (where $\Delta E_S < \Delta E$) may be equals to mobility activation energy [4] or equals the polaron-hopping barrier if the conduction is by small polarons [26]. These small polarons are usually associated with the structure of *Se* [27]. Figure 4 shows the variation of thermoelectric power as a function of temperature of temperature and it has been observed that with increasing temperature thermoelectric power decreases whereas with increasing *Sb* content it increases corresponding same temperature. The variation thermoelectric power as a function of temperature is linear with a positive slope indicating that the majority of the charge carriers are holes and thereby the samples under investigation are *p*-type. Moreover, the variation of S measures the energy difference between the Fermi level and transport level. From Figure 4, it is clear that thermoelectric power is thermally activated, *i.e.* the conduction is via an activated process having single activation energy. This behavior is as mentioned in the simple one-band model where the Fermi energy trapped near the center of the energy gap. Now from the slope of the plots in Figure 4, we can calculate the activation energy (ΔE_S) and hence the parameter δ. The calculated values of thermoelectric power at 333 K, ΔE_S and δ have been listed in Table 1. A decrease of δ (= $\Delta E - \Delta E_S$) with an increase of the Sb content may also be attributed to a grain boundary limited mobility. Since the films have been deposited *via* thermal evaporation process, the growth process may involve the nucleation and growth of amorphous domains. These domains grow together by forming an interface region between them. This may lead to a decrease in the mobility gap with the increase of *Sb* content. These results are in good agreement with the earlier reported band gap calculated both theoretically and optically [13,14].

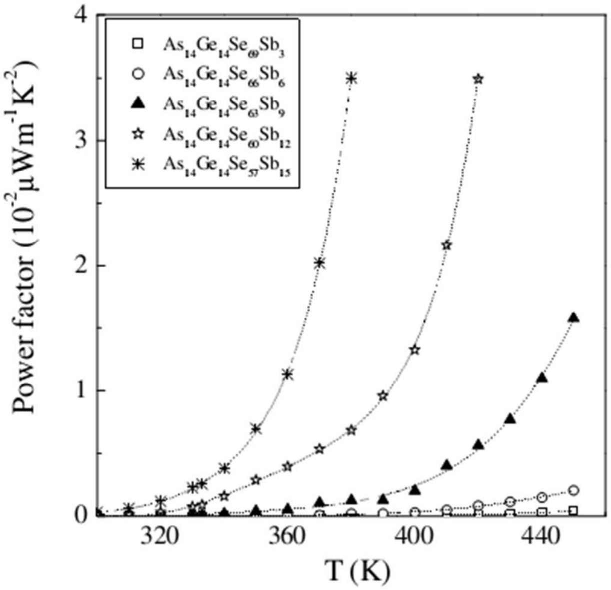

Figure 5 Power factor (P) for $As_{14}Ge_{14}Se_{72-x}Sb_x$ (where x = 3, 6, 9, 12 and 15 at. %) thin films as a function of temperature.

Also, it is well familiar concept that the Seebeck coefficient (S) gives a larger value for materials having only one type of carrier concentration (electrons or holes) contribute to thermal conduction. On the other hand, the Seebeck coefficient decreases if conduction is dominated by a high concentration of mixed carriers. In present case we have observed that Seebeck coefficient increases with increase in *Sb* content.

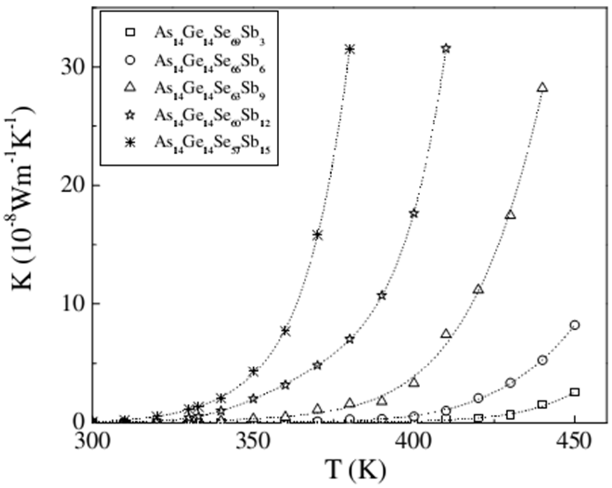

Figure 6 Thermal conductivity (K) as a function of temperature for $As_{14}Ge_{14}Se_{72-x}Sb_x$ (where x = 3, 6, 9, 12 and 15 at. %) thin films.

The concentration of free charge carriers (n_s) has also been determined by using the thermoelectric power, in the equation [28];

$$n_s = \frac{\pi}{3}\left(\frac{8\pi^2 k_B^2 m^* T}{3Seh^2}\right)^{3/2} \quad (3)$$

where m^* is the effective mass of free charge carriers. The values of n_s calculated at 333 K are listed in Table 1. This is observed that with the increase in Sb content the concentration of free charge carriers decreases. It has been observed that the free charge carrier concentration determined from the conductivity data is less than that calculated from the thermoelectric power data. Using the concentration of free charge carriers (n_s) determined from thermoelectric power, we have calculated Fermi energy (E_F) for $As_{14}Ge_{14}Se_{72\text{-}x}Sb_x$ (where x = 3, 6, 9, 12, 15 at.%) samples from the relation [29]; $E_F = \{h^2(3\pi^2 n_s)^{2/3}\}/2m$, where h is the Planck's constant and m is the mass of the charge carrier. The values of E_F are listed in Table 1 and found to decrease from 9.75 *meV* to 7.42 *meV* with increase in *Sb* content from 3 at.% to 15 at.%. This decrease can be simply correlated with the decrease in concentration of free charge carriers (n_s).

The thermoelectric efficiency of a device is mainly controlled by dimensionless figure of merit (*ZT*), which is given by [24,25], $ZT = PT/K$, where P is the power factor, T is absolute temperature, K is thermal conductivity and only depends on the material. *ZT* can be maximized by maximizing the power factor and/or minimizing the thermal conductivity. Thus, the performance of the thermoelectric energy converters may be determined from their power factor (P), calculated using the relation [30,31]; $P = S^2\sigma$. The variation of power factor has been illustrated in Figure 5 as a function of temperature. It has been observed that P increases strongly with an increase in temperature. This increase in P can be correlated with the increasing concentration of the charge carriers. Moreover, P increases with the increase of Sb content.

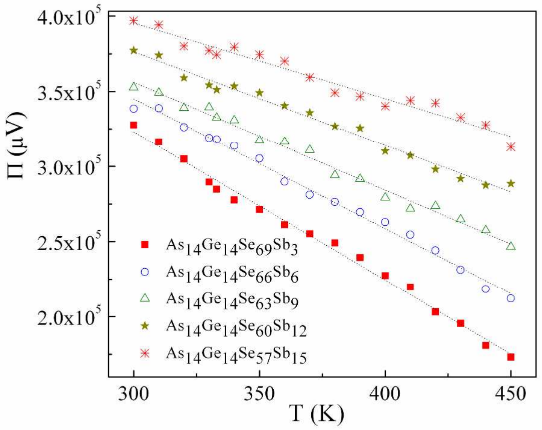

Figure 7 Variation of Peltier coefficient (Π) with temperature for $As_{14}Ge_{14}Se_{72\text{-}x}Sb_x$ (where x = 3, 6, 9, 12 and 15 at. %) thin films.

Thermal conductivity (K) can be considered as a sum of two different contributions [2], *i.e.* $K = K_L + K_E$, where K_L and K_E are phonon and electronic contributions respectively. The electrical conductivity and thermal conductivity are interrelated *via* the Wiedemann–Franz law, $K_E = L\sigma T$, where L is Lorentz factor $\left(L = (\pi^2/3)(k_B/e)^2\right)$. Assuming only the electronic contribution to thermal conductivity, the temperature dependent variation of K as a function of T has been plotted in Figure 6. It has been observed that the values of K increase with temperature strongly for high Sb content because the investigated compounds are semiconductors. The values of K also enhance due to the higher mobility of the charge carriers. These effects are an outcome of the increased excitations of the charge carriers from valence band to conduction band states with an increase in temperature [32]. Finally, from our results of Seebeck coefficient and thermal conductivity, which are based on the electronic contribution, one can easily observe that samples under investigation are very good thermoelectric materials and could be used as potential candidates for thermoelectric applications.

Using thermoelectric power (S) and the temperature at the junction (T_1), Peltier coefficient or coefficient of performance (Π) can be evaluated; $\Pi = ST_1$. So the values of Π depend on the nature of contacting materials and the contact temperature. Figure 7 shows the variation of Peltier coefficient with temperature. It has been observed that the coefficient of performance decreases linearly with temperature.

Conclusions

Thin films of the $As_{14}Ge_{14}Se_{72\text{-}x}Sb_x$ (where x = 3, 6, 9, 12, 15 at.%) chalcogenide glasses have been investigated for electrical and thermoelectric properties. Electrical conductivity has been observed to increase by three orders for x = 3 at.% to x = 15at.% of *Sb* content. The free charge carrier concentration calculated both from electrical and thermoelectric measurements have also been found to increase with *Sb* content. The thermoelectric power has been observed to increases with Sb content from 855.2μVK^{-1} for x = 3 at.% to 1124μVK^{-1} for x = 15at.% at 333K. The power factor has also been observed to increase sharply with enhanced value of *Sb*content. The obtained results suggest that the investigated chalcogenide may appear as potential candidate for obtaining high performance thermoelectric materials.

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