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# TRANSPORT PROPERTIES OF THE QUATERNARY SYSTEMS OF Bi-Sb-Te-Se

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Transport properties namely electrical conductivity σ, Hall effect ($R_H$) and thermoelectric powers (S) have been measured for thin films of the quaternary $BiSbTe_2Se$, $BiSbTe_{1.5}Se_{1.5}$, $BiSbTeSe_2$ and the ternary system $BiSbTe_3$ as function of temperature in the range 300-500K. S and $R_H$ measurements indicate p-type conduction except for that $BiSbTe_{1.5}Se_{1.5}$ show n-type conduction. The results were analyzed in order to establish the conduction mechanism in these compounds. The aim of the present study is to characterize transport properties of the thin film and to detect the possibility of using these materials in thermoelectric devices.

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*Keywords*: Bi-Sb-Se-Te, Transport propert6ies ; Thin films

## 1. Introduction

A large number of studies have been reported on the $(Bi, Sb)_2$, $(Te, Se)_3$ based thermoelectric materials as devices, because of their excellent performance in thermoelectric refrigeration and power generation at room temperature [1-2]. Single crystal grown by travelling heater method with higher thermoelectric efficiency could be achieved in the case of bismuth telluride and antimony telluride [3- 5].

Antimony telluride [6], Bismuth telluride [7,8] as well as mixed crystals of intermediate compounds $Sb_{2-x}Bi_xTe_3$ [9] mixed crystals rank among the narrow gap semiconductors and also, are among the best p-type materials available for thermoelectric devices at room temperature. Also, there were many reports on electrical and thermoelectrical of intermetallic compounds Bi-Te-Sb, Bi-Te-Se ternary alloys systems. However, systemic studies on Bi-Sb-Te-Se are no well performed [10]. Moreover, no previous works have been reported up to our knowledge on thin films of the quaternary system Bi-Sb-Te-Se.

## 2. Experimental

Spec pure of the constituent materials were used for the preparation of the bulk material by direct fusion in sealed, evacuated silica tubes. Thin films were prepared by thermal vacuum evaporation of the bulk compounds.

Using the four probe method, the electrical conductivity $\sigma_{d.c}$ the thermoelectric power S and the Hall effect $R_H$ measured simultaneously on the same samples over the temperature range between 300 and 500 K.

All measurements were made on well annealed films at about 470 K for two hours in vacuum ($10^{-3}$ Torr) to eliminate most of the irreproducible behavior. All measurements were performed on films with thickness greater than 1000 Å (~ 1200- 2000 Å) where thickness had a negligible effect on the transport properties.

## 3. Results and discussion

### 3.1 Electrical conductivity

The temperature dependence of the electrical conductivity of $BiSbTe_x Se_{3-x}$ (x =1, 1.5, 2, and 3) in the temperature range from 300 to 500 K under vacuum is shown in Fig. (1). The general features of these curves for all compositions are that:

-The conductivity of all samples increase as the temperature increase showing normal semiconducting behavior of these alloys, exponential increase of the conductivity with temperature.

-At any certain temperature the conductivity decreases as the tellurium content decrease, except that $BiSbTe_{1.5}Se_{1.5}$ which show the lowest conductivity. The conductivity increases exponentially over the entire temperature range. The plots of Ln σ against 1000/T are straights lines indicating that the conduction in these samples is through thermally activated process which agree well with the results of other workers [11, 12].

-The conductivity for each composition indicates two straight lines with different slopes the first line is in the temperature range 300- 360 K, while the other line is in the temperature range 390- 500 K. The activation energy has been calculated using the slope of the curve and found to be in the temperature range 300- 360 K are 61.2, 35.3, 48.6 and 33.9 meV for x = 3, 2, 1.5, 1 respectively.

-Also, the activation energy in the temperature range 390- 500K were calculated and found to be half the optical energy gap indicating that the conduction mechanism in $BiSbTe_xSe_{3-x}$ at temperature greater than 390K is intrinsic where as extrinsic conduction dominates in the temperature range 300- 360K.

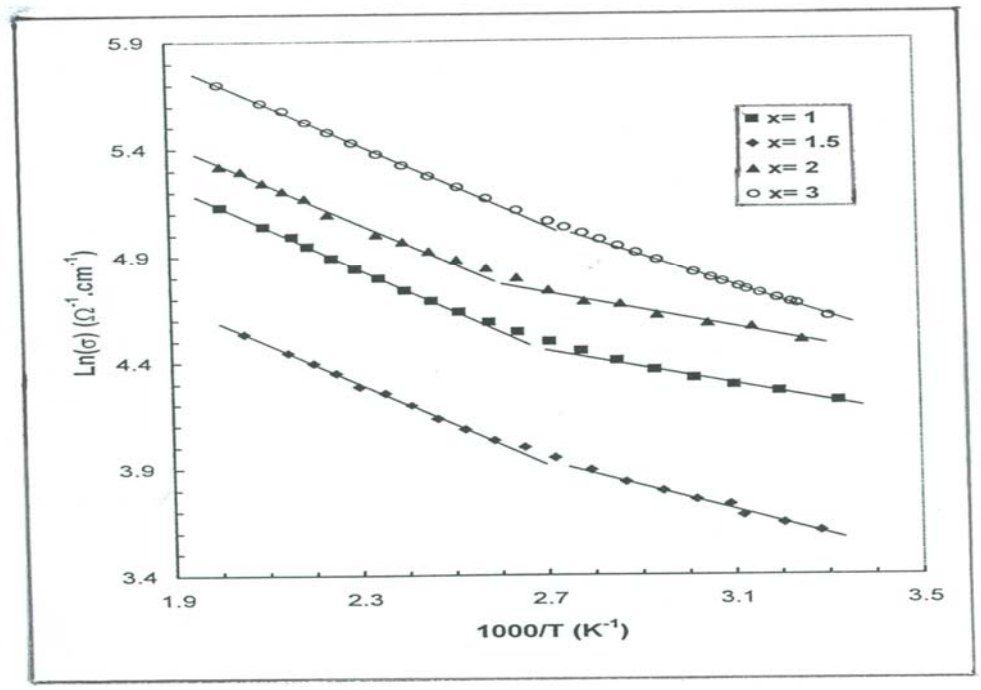


*Fig.(1) Lnσ Vs 1000 / T for the different compositions $BiSbTe_xSe_{3-x}$.*

The calculated electrical energy gap together with the optical energy gap is given in Table (1) for comparison [13]. However, these results agree well with our Hall effect measurements as will be shown in the following.

*Table 1: The dependence of the optical band gaps of $BiSbTe_xSe_{3-x}$ films on composition, x, value.*

| Mole fraction x | Observed Optical Transitions | |
|---|---|---|
| | $Eg_1$ (meV) | $Eg_2$ (meV) |
| 1 | 169.9 | 192.5 |
| 1.5 | 165.2 | 200.4 |
| 2 | 163.7 | 217.0 |
| 3 | 167.7 | 194.1 |

### 3.2 Hall effect

The Hall effect had been investigated for the different compounds $BiSbTe_xSe_{3-x}$ (x = 1, 1.5, 2 and 3) in the range of temperature from 300 to 480K. The value of $R_H$ is positive indicating p-type conduction for composition $BiSbTe_3$, $BiSbTe_2Se$ and $BiSbTeSe_2$ while the value of $R_H$ is negative indicating n- type conduction for composition $BiSbTe_{1.5}Se_{1.5.}$ This may due to the resulting deviation from stoichiometry. Since it is known that for Bi or Sb chalcogenides, the resulting deviation from stoichiometry are expressed of native defects, which are electrically active. Thus the material rich in Bi or Sb is of P- type and that rich in Te or Se is of n- type [3].

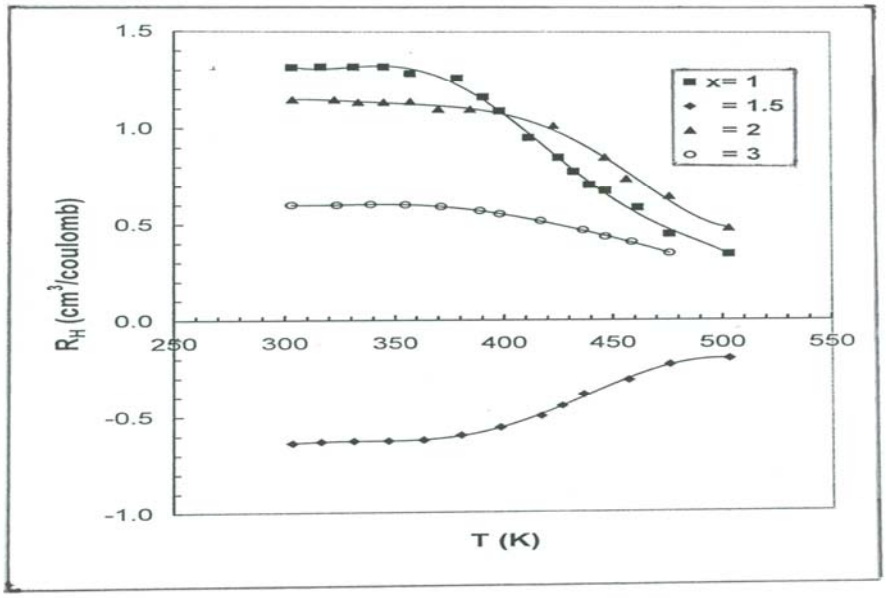


*Fig.(2) $R_H$ Vs temperature for the different compositions $BiSbTe_xSe_{3-x}$.*

The variation of the Hall coefficient $R_H$ with temperature is shown in Fig. (2). It is seen that the Hall coefficient is fairly constant in the vicinity of room temperature (300- 360K) indicating that the extrinsic material is in the saturation range where no further ionization takes place and this in this temperature range, the material could be considered as partially degenerate. The carrier concentration has been calculated from the familiar relation, $R_H = (3\pi / 8) (1 / ne)$, where n and e are the electron concentration and electronic charge respectively and was found to of the order $10^{19}$ $cm^{-3}$ (as well be shown later) at the saturation temperature region. From this concentration the degeneracy temperature has been estimated using the relation [14].

$$T_{deg} = (3/\pi) \frac{h^2}{8km} n^{2/3} \quad (1)$$

Where k is the Boltzman's constant, m is the free electron mass and h is planks constant, from this we get a degeneracy temperature of 330 K.

As the temperature is increased beyond the saturation region, a very steep fall in the Hall coefficient is observed, with a tendency to change its sign at higher temperatures. This obviously is due to the film becoming intrinsic in nature. This type of behavior has been reported in bismuth telluride in bulk form [15-17] as well as in thin films [5]. These results are in fair agreement with the electrical conductivity data.

### 3.3 Thermoelectric Power

Fig. (3) Shows the temperature dependence of the thermoelectric power S for the different compositions $BiSbTe_xSe_{3-x}$ (x =1, 1.5, 2 and 3) in the temperature range 300- 500 K, it is worthy to note that:

- The thermoelectric power for compositions $BiSbTe_3$, $BiSbTe_2Se$, $BiSbTeSe_2$ had a positive sign over the whole investigated temperature range indicate p-type conduction, while the thermoelectric power for $BiSbTe_{15}Se_{1.5}$ had a negative sign indicating n-type conduction, which is in agreement with the Hall effect measurements.

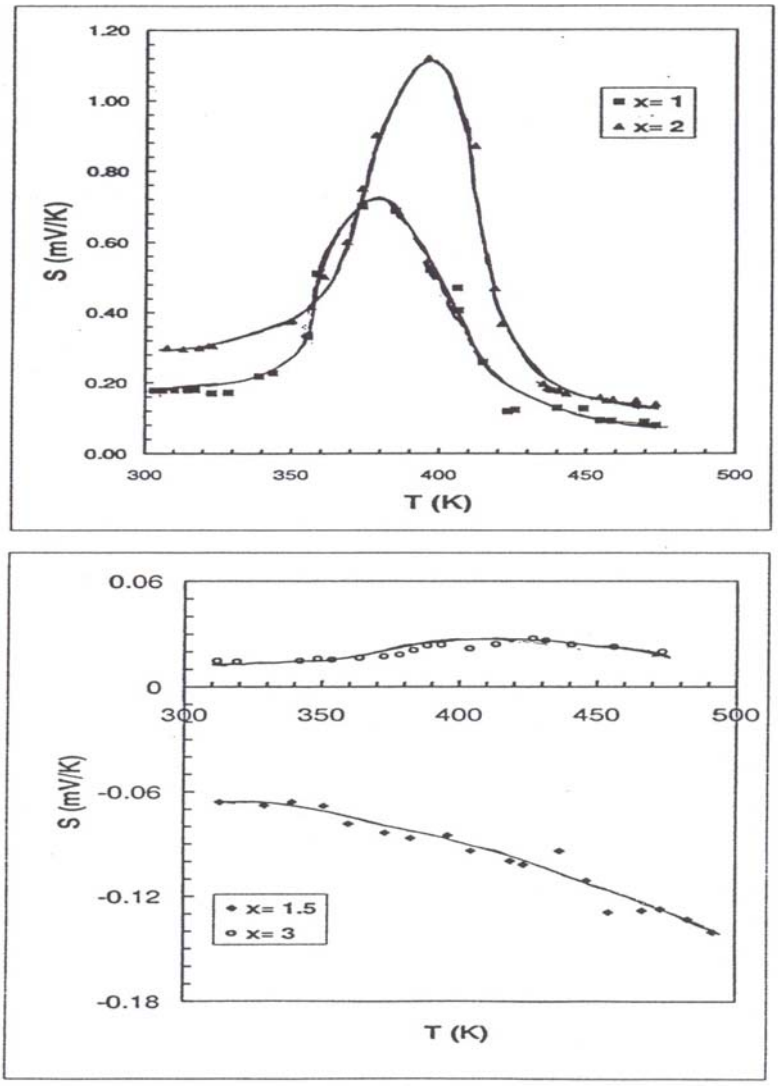


*Fig. (3) Variation in the thermoelectric power S with Temperature for the different compositions $BiSbTe_xSe_{3-x}$.*

It is seen that the thermoelectric power for $BiSbTe_2Se$ and $BiSbTeSe_2$ p-type conduction compositions, increase with increasing the temperature up to (~ 360- 370K) i.e. in extrinsic range, due to the degenerate nature of the materials and attains a maximum value of 1.15 and 0.78 respectively. Thus it is found to decrease with increasing temperature, in the intrinsic range which may be due to the generation of electrons from the valence band to the conduction band.

- For both $BiSbTe_2Se$ and $BiSbTeSe_2$, the room temperature thermoelectric power is high being ~ 0.3 and 0.2 mV respectively and increase with temperature to reach ~ 1mV, while the room temperature thermoelectric power of both $BiSbTe_3$ & $BiSbTe_{15}Se_{1.5}$, are quite small being 0.03 & -0.06 respectively and not vary much with temperature.

### 3.4 Hall mobility

The temperature dependence of the mobility will be discussed to determine the dominant scattering in the different composition $BiSbTe_xSe_{3-x}$.

From electrical conductivity ($\sigma$) and Hall coefficient ($R_H$), the temperature dependence of the Hall mobility ($\mu_H$), could be determined using the relation:

$$\mu_H = R_H \sigma \tag{2}$$

Also, Hall mobility can be described as a function of temperature as:

$$\mu_H = \mu_0 \, T^a \quad \text{or} \quad \text{Log } \mu_H = \text{Log } \mu_0 + a \, T \tag{3}$$

Where (a) value depends on the scattering mechanism. A log –log plot of $\mu_H$ versus T is represented in Fig. (4) to deduce the power variation law of mobility ($\mu \alpha T^a$). These curves show that:

- The room temperature Hall mobility of these compositions have the highest value (97 $cm^2$ / volt sec) for $BiSbTe_2Se$, and lowest value (23 $cm^2$ / volt sec) for $BiSbTe_{1.5}Se_{1.5}$, while the Hall mobility 89 and 66 ($cm^2$ / volt sec) for $BiSbTeSe_2$ and $BiSbTe_3$ respectively.

- The Hall mobility for the different compositions $BiSbTe_xSe_{3-x}$, first increase linearly in accordance to the relation $\mu \alpha T^a$ in the temperature interval of 300- 370K. The calculated values of "a" in this temperature range are 1.232, 1.394, 1.311 and 1.64 for x = 1, 1.5, 2 and 3 respectively. These values are very close to 3/2 i.e. $\mu \alpha T^{3/2}$ indicating that the mobility is in this temperature range is mainly limited by ionized impurity scattering.

-For temperatures higher than 370K (370 < T < 500 K) the Hall mobility for different compositions decrease linearly in accordance to the relation $\mu \alpha T^{-a}$. The calculated values of "a" in this temperature range are a = 2.194, 2.11, 2.107 and 2.108 for x = 1, 1.5, 2 and 3 respectively. Acoustic phonon scattering leads to a $T^{-3/2}$ variation law for mobility, and this deviation from this law indicates that additional scattering mechanism should be taken into account.

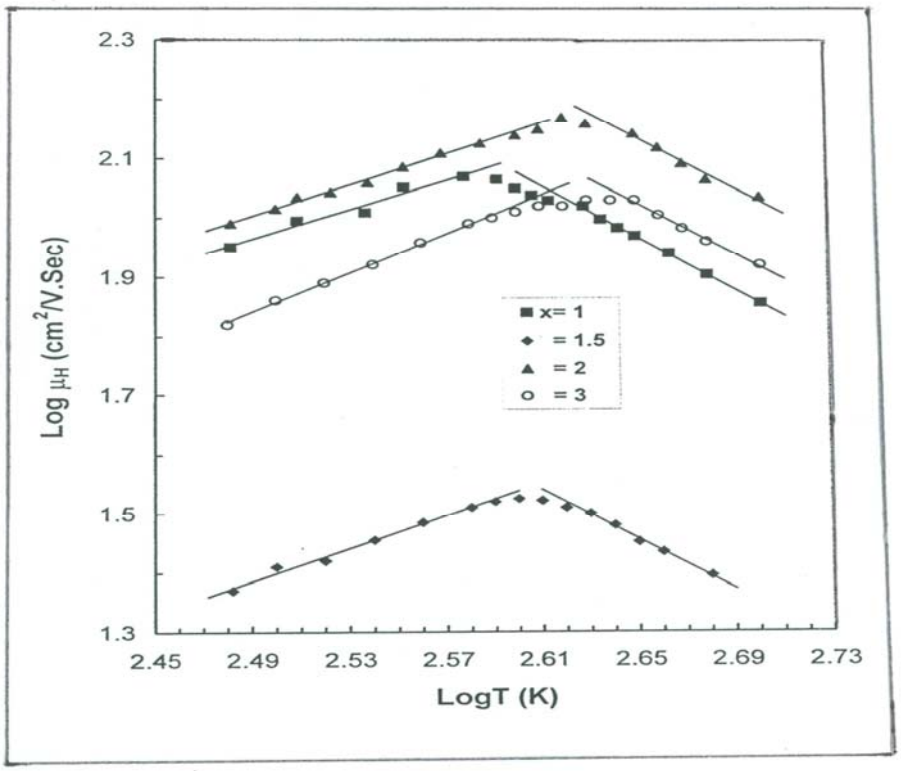


*Fig. (4) Log $\mu_H$ Vs Log T for the different compositions $BiSbTe_xSe_{3-x}$.*

In addition to the classical acoustic phonon, ionized impurity scattering mechanism could occur. The high carrier concentration obtained demonstrated that the number of ionized defects is not negligible in our samples.

### 3.5 Number of free carriers

The number of free carriers was calculated from $R_H$ data using the relation:

$$N = (3\pi / 8)\,(1/ R_H\, e) \qquad (4)$$

Obviously the temperature dependence of N for the different compositions $BiSbTe_xSe_{3-x}$ is the inverse image of $R_H$, namely that the number of free carriers in the interval from 300- 360K is constant indicating full ionization of the impurity centers, while for temperatures greater than 370K, the number of free carriers increase markedly as the temperature increases indicating the intrinsic conduction.

It is well known that the number of free carriers (electrons or holes) in the range where the impurity does not play any role in the conduction mechanism i.e. in the intrinsic range is given by the relation [18].

$$N = N_{eff}\,(e^{-EA / 2KT}) \qquad (5)$$

Fig. (5) Shows the relation between Ln N and the reciprocal of the absolute temperature. These curves show that for temperature greater than 370K, the number of free carriers varies exponentially with temperature, i.e. linear relation, indicating the validity of the above relation.

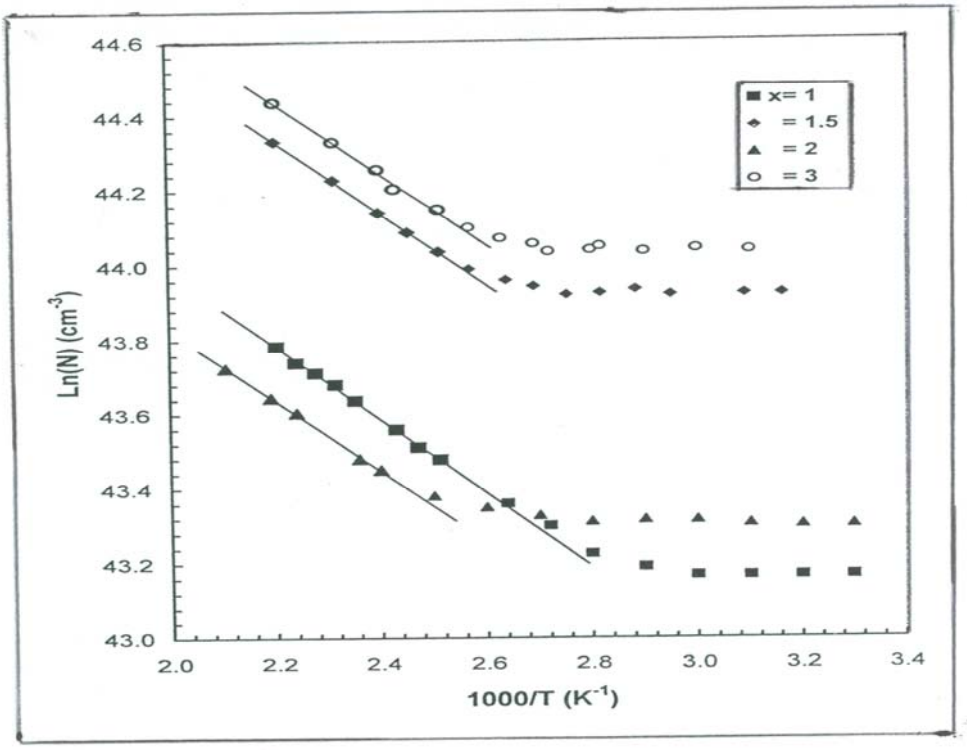


*Fig. (5) Ln N Vs 1000 / T for the different compositions $BiSbTexSe_{3-x}$.*

From the slopes of these curves, the energy gaps for different compositions were calculated. The calculated energy gaps were found to be in good agreement with these obtained from either the optical absorption or the electrical conductivity as shown in Table (2).

*Table (2) the calculated values of the energy gap are shown below:*

| Composition X | $E_g$ Opt. | $E_g$ Elec. | $E_g$ N | (ΔE) elec. Activation energy |
|---|---|---|---|---|
| 3 | 0.1677 | 0.165 | 0.164 | 61.2 |
| 2 | 0.1639 | 0.161 | 0.163 | 35.3 |
| 1.5 | 0.1653 | 0.165 | 0.166 | 48.6 |
| 1 | 0.1706 | 0.171 | 0.1708 | 33.9 |

### 3.6 Effective mass

The effective mass ($m^*/ m_0$) is one of the most important physical parameters as the other physical parameters strongly depends on the value of m*, e.g. mobility, thermal conductivity and others. In the following we will determine the effective mass and its temperature dependence.

It is known that the thermoelectric power S is related to the effective mass by the relation:

$$S = \pm \frac{k}{e} \left[ C + \mathrm{Ln} \frac{2 ( 2\pi m^* kT)^{3/2}}{h^3 n} \right] \quad (6)$$

Where k is Boltzmann′s constant, e is the electron charge, h is Plank′s constant, n is the number of free carriers as deduced from Hall effect measurements, T is the absolute temperature and C is a constant determined from the scattering mechanism, (C is equal to 2 in atomic lattices). This relation is valid for non- degenerate semiconductors, also for a large group of semiconductors have high electrical conductivity (this last condition is in agreement with our results).

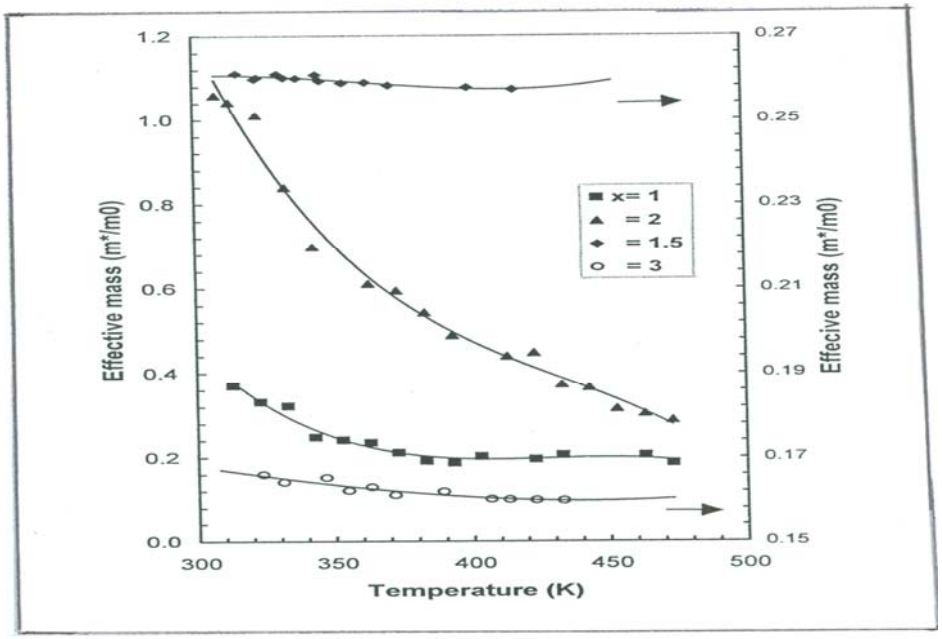


*Fig. (6) Temperature dependence of ($m^*/ m_o$) the $BiSbTe_xSe_{3-x}$ compounds.*

Fig. (6) shows the temperature dependence of the calculated values of $m^*/ m_0$ for the different compositions $BiSbTe_xSe_{3-x}$ (x = 1, 1.5, 2 and 3) in the temperature interval from 300 to ~ 500 K. These curves show two distinct features:

1- For $BiSbTe_2Se$ and $BiSbTeSe_2$ the effective mass ($m^*/m_0$) decrease with increasing temperature.

2- The room temperature effective masses ($m^*/m_0$) for two compositions $BiSbTeSe_2$ and $BiSbTe_2Se$ are quite high being 0.4 and 1.1 respectively, while for the other two compositions, $BiSbTe_{15}Se_{1.5}$ and $BiSbTe_3$ the effective masses are relatively small being 0.26 and 0.16 respectively.

## 4. Conclusions

Measurements of the Hall effect and thermoelectric power indicate that the films of the compositions $BiSbTeSe_2$, $BiSbTe_2Se$ and $BiSbTe_3$ were p-type conduction while they show n-type conduction for $BiSbTe_{1.5}Se_{1.5}$ only.

The electrical conductivity variation with temperature shows good semiconducting behavior and Lin σ versus 1/ T shows a linear fit with different slopes indicating extrinsic conduction in the temperature range 300- 360 K with activation energies of 33.9 to 61.2 meV and intrinsic for temperature greater than 380 K ranging between 0.161 and 0.171 eV depending on composition.

From the temperature dependence of the mobility, it was found that the mobility was

affected by both impurity scattering in the temperature range 300- 360 K, while for higher temperature T > 370 K the mobility was controlled by acoustic phonon scattering and ionized impurity scattering.

## References


[1] A.F. Semizorev. Inorganic Materials **316**, 675 (1995).
[2] W.M Yim, and F.D Rosi, Solid state electronics **15**, 1121-1140. (1972)
[3] J.P. Fleurial, L.Gailliard, R.Triboulet, H. Scherrer and S. Scherrer, J. Phys. Chem. Solids **49**(10), 1237 (1988).
[4] L.Gailliard, L. Caillat, H.Scherrer, and S. Scherrer, in the Eighth International Conference on Thermoelectricity Nancy [ Edited by H.Scherrer and S.Scherrer (1989)].
[5] J. George, and B. Pradeep, solid state communications, **56**(1), 117 (1985).
[6] J. George, and M.K. Radhskrishnan, Solid State Commun.33, (1980) .
[7] Y.H.Shing, Y. Chang, A.Mirshafii, L.Hayashi, S.S.Roberts, J.Y. Josefwicz, N. Tran, J.Vac.Sci. Technol. A.**1**, 503 (1983).
[8] J. R. Drabble, R.D. Grove, and R. Wolfe, proc. phys. soci. London, 71, 430 (1958).
[9] T.Caillat, M.Carle, P.Pierrat, H.Scherrer, and S.Scherrer, J.Phys.Chem. Solids, **53**(8), 1121 (1992).
[10] K. Masui, Y. Kanamitu, S. Hotta, K. Nakayoshi, (Dep. electrical and computer Eng. Nagoya. Inst. Tech.; Nagoya, Japan 466) proc. Int. conf.Thermoelectric1993. (pub.1994).12$^{TH}$, 155–160 (Eng.Proc.Int.conf. Thermo.) (1989).
[11] S. Espevick, Wu. Chen-ho, R.H.Bube, Journal of applied physics, **42**, 3513 (1971).
[12] F. Briones, D. Galmoga, and C.Dritz, Thin solid films, **76**, 385 (1981).
[13] W.Shockly, Electron and Holes in Semiconductors, p.242, Affiliated East-West press., India (1968).
[14] S. Shigetomi and S. Mori, J.Phys.Soci. Japan **11**, 915, (1956).
[15] C.B. Sattertwaite, and R.W. Ure, Phys.Rev. **108**, 1164 (1957).
[16] J. Black, E.M. Conwell, L. Seigle, and C.W. Spencer, J.Phys.Chem. Solids, **2**, 240 (1957).
[17] A. M. ABOU EL SOUD, B. S. FARAG, I. S. AHMED FARAG, S. A. GAD and H. A. ZAYED, FIZIKA A (Zagreb) 17 (2008) 1, 15–28.
[17] A.F. Ioffe, Physics of semiconductors, (London, Infosearch 1960).