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*Research Article*

# Electrical and Thermoelectric properties of $Bi_2(Te_{1-x}Se_x)_3$ thin films

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## *Abstract*

*The alloys of $Bi_2[Te_{1-x}\ Se_x]_3$ (were prepared by melting technique with different values of the Se percentage (x=0,0.1,0.3,0.5,0.7,0.9 and 1)..Thin films of these alloys were prepared using thermal evaporation technique under vacuum of $10^{-5}$ Torr on glass substrates, at room temperature with deposition rate (12nm/min) with constant thickness (450±30 nm).The D.C conductivity measurements showed two stages of activation energy and hence two transport mechanisms for $Bi_2[Te_{1-x}\ Se_x]_3$ thin films, throughout the heating temperature range (323-433)K. The results of Hall Effect measurement show that all thin films have p-type conductivity. The carrier concentrations of charge carriers $n_H$ decrease with increasing of Se percentage, from $2.32*10^{19}cm^{-3}$ at x=0 to $9.40*10^{17}cm^{-3}$ at x=1, while the Hall mobility $\mu_H$ showed opposite manner which increases with increasing of Se percentage from $3.51*10^{-1}$ $cm^2/V.s$ when x=0 to $7.54cm^2/V.s$ at x=1. The carrier mobility increases with increasing of Se percentage. Thermoelectric properties of $Bi_2[Te_{1-x}\ Se_x]_3$films were measured from (323 to 433) K. The values of Seebeck coefficient, the power factor and thermal conductivity $K_{el}$ were decreased with increasing of Se percentage in all samples of $Bi_2(Te_{1-x}Se_x)_3$ thin films. The figure of Merit (ZT) decreases by increasing (Se) percentage for all investigated $Bi_2(Te_{1-x}Se_x)_3$ thin films, from 0.7048 at x= 0 to 0.1298 at x=1.*

**Keywords:** *Electric and thermoelectric properties, $Bi_2(Te_{1-x}Se_x)_3$ thin films , thermal evaporation technique*

## Introduction

Compounds of $Bi_2[Te_{1-x}\ Se_x]_3$ have the scientific and practical important as it is considered as a very good thermoelectric material which they are having the possibility of the direct converting heat to electricity or vice versa, so they are used for manufacturing many eco-friendly devices so it regarded as one of important green technologies . $Bi_2Te_3$ compound and its alloys intervention in the industry of a very important thermoelectric devices especially refrigeration and power generation also used as sensors and solar cell [D. M. Rowe, (1995)].

Bismuth telluride and its alloys has been widely studied as a thermoelectric material, especially in the temperature range about 300 K. It has a rombohedral structure with space group $R^3m$, and the lattice is stacked in a repeated sequence of five atom layers: $Te^1$-Bi-$Te^2$ -Bi-$Te^1$along the c-axis. Te and Bi layers are held together by strong ionic-covalent bonds ($Te^1$ -Bi and Bi_$Te^2$). The $Te^1$ bonds between cells are of the Van der Walls type and are extremely weak [T.M.Tritt. , 2002]. Bismuth telluride compounds can be doped as either n- or p-type material by creating either a tellurium-rich composition or a bismuth-rich composition respectively; therefore they are very sensitive to Te and Se percentage [Nolas, *et al*, 2001].

## Experimental Procedure

Alloys of $Bi_2[Te_{1-x}\ Se_x]_3$ were fabricated by using exact amount of (Redal De Hien Germany Assay of high purity 99.99%) powders of source materials (Bi, Te and Se elements ), accordance with their atomic percentages of Se (x=0,0.1,0.3,0.5,0.7,0.9 and 1), then put each alloy in an evacuated quartz ampoule to vacuum ~$10^{-4}$ Torr , then put them in thermal oven to temperature of 650 °C for 6 hours until ensuring homogeneous components and fused with each other, then leave them cooled gradually until they reached room temperature. The alloys were grinded well until they became powder to be manufacture a $Bi_2[Te_{1-x}\ Se_x]_3$ thin films with thicknesses (450±30 nm) and deposition rate (12 nm\min), which were deposited at room temperature on corning 7059 microscopic glass substrate by thermal evaporation method under suitable vacuum ($10^{-5}$ Torr). Then we calculated the electrical measurements which included D.C. conductivity, Hall effect, seebeck coefficient, thermal conductivity and figure of merit.

## Results and Discussion

For getting the information about the nature of the conduction mechanism in the $Bi_2(Te_{1-x}Se_x)_3$ thin films, we were studying the temperature dependence of

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electrical conductivity by calculating the relation between the nature logarithm of the conductivity (ln σ) as a function of 1000/T in the range of a temperature (323 K -433K) by using sensitive digital electrometer type keithley (616) and electrical oven and that's very useful to determine the extrinsic range of the activation energies from the slope of (-ΔE/K) by using the relation(1) [A. Beiser, 1980].

$$\sigma = \sigma_\circ \exp(-\Delta E/K_B T) \qquad (1)$$

σ: the electrical conductivity

$\sigma_\circ$: the minimum electrical conductivity at( 0)K,

$E_a$: is the activation energy which corresponds to ($E_g/2$) for intrinsic

T: is the temperature and $k_B$ is the Boltzmann's constant.

From the above relation between the temperature and electrical conductivity of $Bi_2(Te_{1-x}Se_x)_3$ thin films for deferent values of Se percentage (x) ,where x=(0,0.1,0.3,0.5,0.7,0.9 and 1), we can investigate the behavior of these thin films, as the behavior of semiconductor materials. From the figure (1),

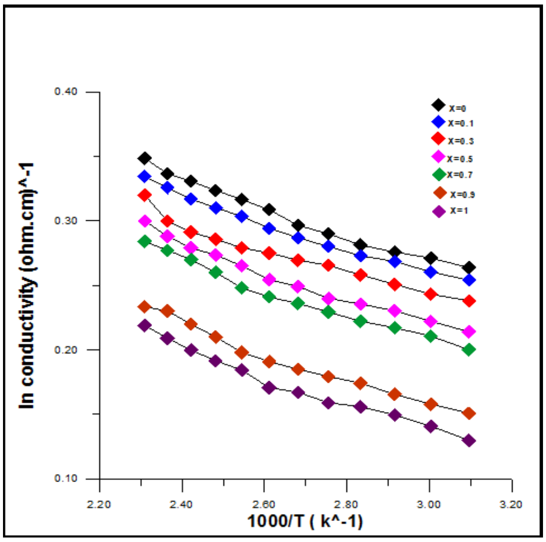

**Figure 1:** the electrical conductivity for deferent Se percentage

We see two stages of conductivity throughout the heating temperature range. In this case the first activation energy ($Ea_1$) occurs at low temperature within range (323-383) K and the conduction mechanism of this stage is due to carriers transport to localized states near the valence and conduction bands, while the second activation energy ($Ea_2$) occurs at higher temperature within range (383-433) K, and this activation energy is due to conduction of the carrier excited into the extended states beyond the mobility edge , for all samples of $Bi_2(Te_{1-x}Se_x)_3$ thin films as shown in figure (2). These two conduction mechanism means that the d.c. conductivity is nonlinear with temperature.

From table (1) we noticed that the values of activation energies increasing with the increasing of the percentage of (x). The values of activation energy $E_{a1}$ increase from (0.00666-0.00733) eV when x increase from (0 to 1). The values of $E_{a2}$ increase from (0.0108-0.01321) eV when x increase from (0 to 1). We conclude that the increasing in the percentage of (Se) leads to increase in the activation energies which leads to saturate the dangling bonds, i.e. there is rise in the density of state which occurs at Fermi level which caused to the transfer from conductivity near Fermi level to the thermal activation conductivity at band gap, these results indicate that the crystalline of the compounds changed with changing of the (Se) percentage for the $Bi_2(Te_{1-x}Se_x)_3$ thin films.

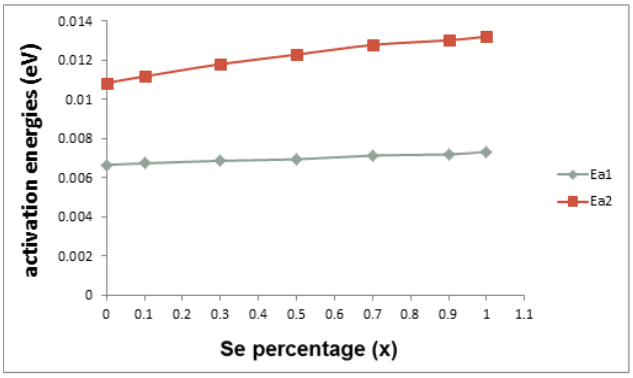

**Figure 2:** The variation of activation energies [$E_{a1}$and $E_{a2}$] of $Bi_2 (Te_{1-x} Se_x)_3$ thin films

**Table 1:** The activation energies of $Bi_2 (Te_{1-x} Se_x)_3$ thin films

| X | σ(Ω.cm)^-1 | $E_{a1}$(eV)Range (323-383)K | $E_{a2}$ (eV) Range (383-433)K |
|---|---|---|---|
| **0** | 1.305 | 0.0066 | 0.0108 |
| **0.1** | 1.289 | 0.0067 | 0.0111 |
| **0.3** | 1.268 | 0.0068 | 0.0118 |
| **0.5** | 1.232 | 0.0069 | 0.0123 |
| **0.7** | 1.197 | 0.0071 | 0.0128 |
| **0.9** | 1.144 | 0.0072 | 0.0130 |
| **1** | 1.134 | 0.0073 | 0.0132 |

From fig.(3) we noticed that ln σ decreased with increasing x , this is due to the relation between the electrical conductivity and the carrier concentrations, which is greatly affected by the structure and crystal defects, also we notice that, the carrier concentrations and carrier mobility changeable with variation of (x) and that agree with many researcher [Carle M. 1995 ; L.I. Soliman, *et al* 2010] This behavior can be explained as due to change in the localized states, structure, and composition of films as well as to the re-arrangement of atoms which yields more defects.

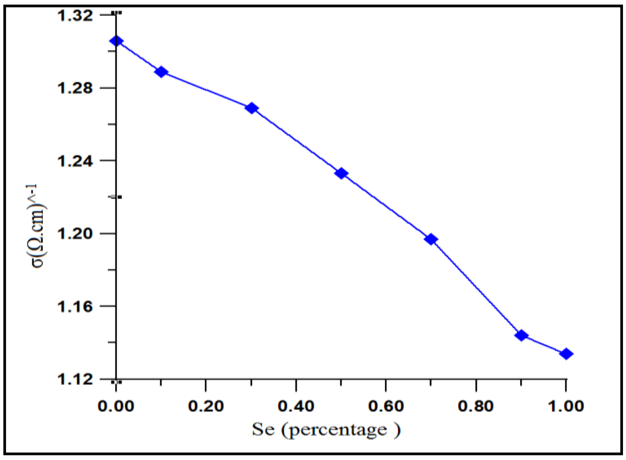

**Figure 3:** The electrical conductivity as function of Se percentage

The Hall measurements which includes carrier concentration, Hall coefficient, Hall mobility, electrical conductivity and type of conductivity for as deposited $Bi_2(Te_{1-x}Se_x)_3$ thin films at different values of Se percentage (x=0, 0.1,0.3,0.5,0.7,0.9,and 1). The results show that all thin films have p- type conductivity and that coincide with the original compounds $Bi_2Te_3$ and $Bi_2Se_3$, that indicates there is no deviation in the percentage of Se and/or Te in our fabricated alloys, then this will be changing the type of conductivity. Figure (4) shows that the hall coefficient of $Bi_2(Te_{1-x}Se_x)_3$ thin films as a function of Se percentage, which indicates that increasing of hall coefficient with increasing of Se percentage[ M. Neuberger, 1966].

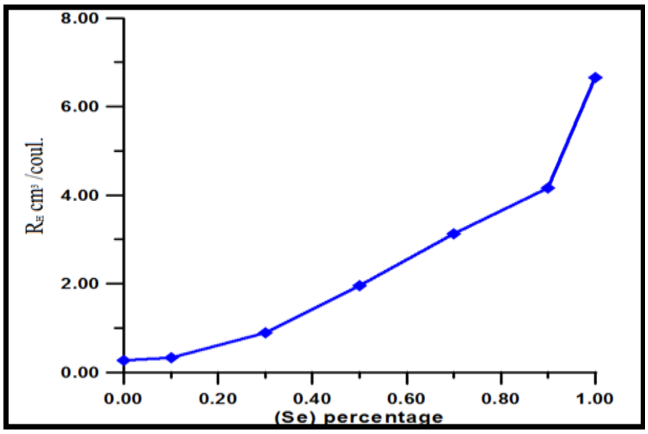

**Figure 4:** Hall coefficient for all samples as a function of Se percentage

The variation of carrier concentrations as function of (Se) percentage for $Bi_2(Te_{1-x}Se_x)_3$ thin films deposited at R.T have been shown in Figure(5), we notice that the carrier concentrations decrease with increasing of Se percentage, from $2.32*10^{19}cm^{-3}$ at x=0 to $9.40*10^{17}cm^{-3}$ at x=1 , this behavior is due to the structure defects . The hole concentrations generally are created by the structure defects which generated by the occupation of Te and Se sites with Bi atoms and that agree with [Nolas, *et al*, 2001].

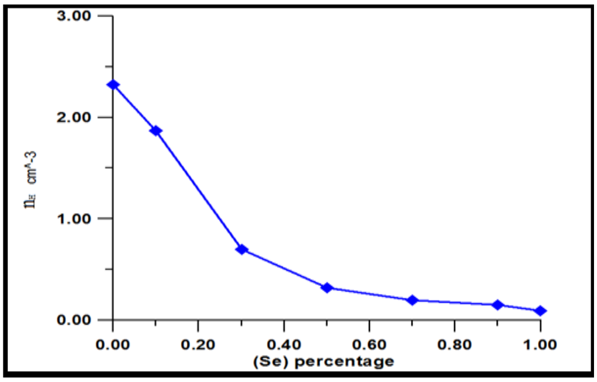

**Figure 5**: Carrier concentration for all samples as a function of Se percentage

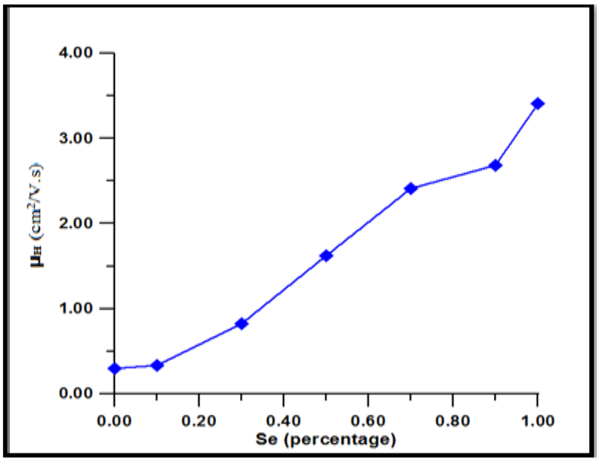

**Figure 6:** Hall mobility for all samples as a function of Se percentage

**Table 2:** Carrier concentration ($n_H$) ,Hall coefficient ($R_H$),Hall mobility( $\mu_H$)
Electrical deposited at RT of $Bi_2(Te_{1-x}Se_x)_3$, where(x=0, 0.1 , 0.3,0.5,0.7, 0.9 and 1)

| X Percentage of Se | Electrical conductivity (σ)at R.T. $(\Omega.cm)^{-1}$ | Carrier concentration $n_H$ $(cm^{-3})$ | Hall coefficient $R_H$ $(cm^3/coul.)$ | Hall mobility $\mu_H$ $(cm^3/v.s)$ |
|---|---|---|---|---|
| 0 | 1.106 | $2.32*10^{19}$ | 0.269 | 0.298 |
| 0.1 | 1.009 | $1.87*10^{19}$ | 0.334 | 0.337 |
| 0.3 | 0.926 | $7.00*10^{18}$ | 0.893 | 0.828 |
| 0.5 | 0.832 | $3.20*10^{18}$ | 1.95 | 1.63 |
| 0.7 | 0.772 | $2.00*10^{18}$ | 3.13 | 2.41 |
| 0.9 | 0.644 | $1.50*10^{18}$ | 4.17 | 2.69 |
| 1 | 0.513 | $9.40*10^{17}$ | 6.65 | 3.41 |

The formation of structure defects in $Bi_2(Te_{1-x}Se_x)_3$ thin films crystals was considered to be caused by the low polarity of Bi–Te bonds, which decreased the carrier concentration with increasing of Se percentage . Also this behavior may be attributed to the difference of the electro-negativity and the atomic radii of both Se and Te atoms. The carrier mobility increases with increasing of Se percentage as shown in figure(6),$\mu_H$ equal to 3.51*$10^{-1}$ $cm^2/V.s$ when x=0 increasing to 7.54$cm^2/V.s$ at x=1 and this results agree with [Junqiang Song, *et al*, 2013.]. All the obvious results are listed in table (2).

To investigate the thermoelectric properties for as deposited $Bi_2(Te_{1-x}Se_x)_3$ thin films with deferent values of Se percentage (x=0.0.1 ,0.3 ,0.5 ,0.7,0.9,1) ,we measured the variation of the gradient of voltage as a function of temperature in the range of (323 to 433) K as shown in figure (7) . We calculate Seebeck coefficient for each sample of $Bi_2(Te_{1-x}Se_x)_3$ thin films. From the relation(2)[ D. M. Rowe, 1995;T.M.Tritt. 2002; Nolas, *et al*, 2001].

$$S = -\frac{dV}{dT} \tag{2}$$

The value of Seebeck coefficient, decreases as increasing of Se percentage in all samples of $Bi_2(Te_{1-x}Se_x)_3$ thin films , as shown in Figure(8)[M.Takashiri *et al*, 2008], we notice a linear behavior which indicates that there is increasing in voltage with increasing of temperature . The sign of Seebeck coefficient indicates that the conductivity of $Bi_2(Te_{1-x}Se_x)_3$ thin films is p-type, which agree with our results of Hall effect , and this behavior was due to the small excess of Bi and there are no excess of Te and Se which responsible for transfer their type of conductivity from p- to n- type.

We calculated the power factor of as deposited $Bi_2(Te_{1-x}Se_x)_3$ thin films ,and we noticed that, when we increase the (Se) percentage in $Bi_2(Te_{1-x}Se_x)_3$ thin films there is a decrease in power factor, as shown in figure (9),this behavior is due to decrease in carrier concentration. The results of power factor are tabulated in the Table (3) agree with [Nolas, *et al*, 2001 and L.I. Soliman, *et al* ,2010].

***Thermal conductivity*** can be measured for as deposited thin films of $Bi_2(Te_{1-x}Se_x)_3$ with different (Se) percentage (x=0,0.1,0.3,0.5,0.7,0.9and 1), with taking into account that the thermal lattice has negligible because it has a small value for the material under study [Vasilevskiy D, *et al*, 2002].From figure (10) we notice that the compositional dependence of electronic thermal conductivity $K_{el}$ for the as deposited thin films . It appears that, $K_{el}$ decreases sharply by increasing Se percentage, these results are in good agreement with the electrical conductivity data as discussed before. That results were observed is agree with other workers [Carle M(1995) and Saji A, *et al.* 2003] .for composition $Bi_2(Te_{1-x}Se_x)_3$ single crystal with x =0, x = 1, and x< 0.15, with polycrystalline $Bi_2(Te_{1-x}Se_x)_3$ thin films with ( x= 0,0.2,0.4,0.6,0.8 and 1)and with reports study x=0.3 and x=0.1 a comparison for x = 0.1, 0.3, 0.5, 0.7,0.9 could not be made since there is no report on thermal conductivity K for these compositions.

To calculate the ***figure of merit*** for thin films of $Bi_2(Te_{1-x}Se_x)_3$ deposited at RT with different (Se) percentage (x=0,0.1,0.3,0.5,0.7,0.9and 1), we calculated thermoelectric figure of merit ZT at 323 k, and we found that ZT decreases by increasing (Se) percentage for all investigated samples agree with [Soliman *et al.* 2010], from 0.7048 at x= 0 to 0.1298 at x=1 ,as shown in figure (11), this happen because increasing in power factor, agree with [Gross, A.J., 2010], the values of Figure of merit and other thermoelectric parameter are mentioned in the Table (3).

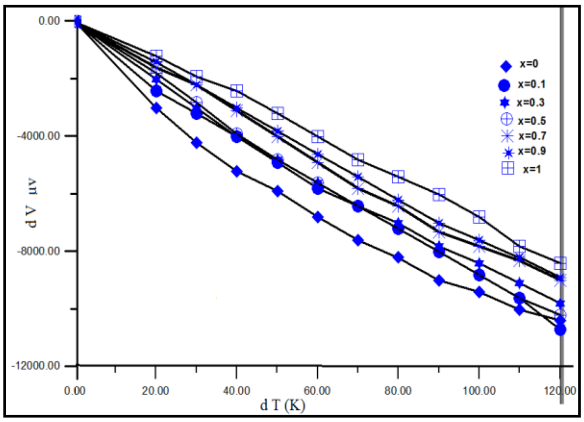

**Figure 7:** The relation between voltage gradient with the temperature

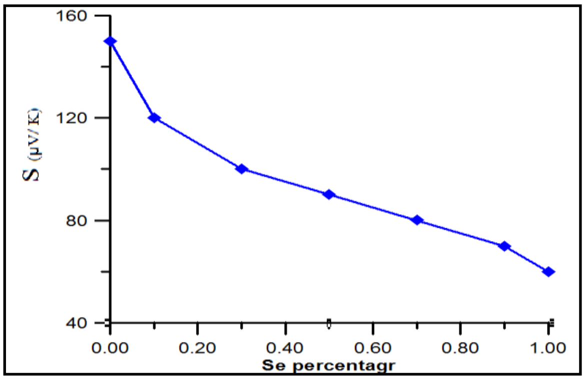

**Figure 8:** Seebeck coefficient with Se percentage

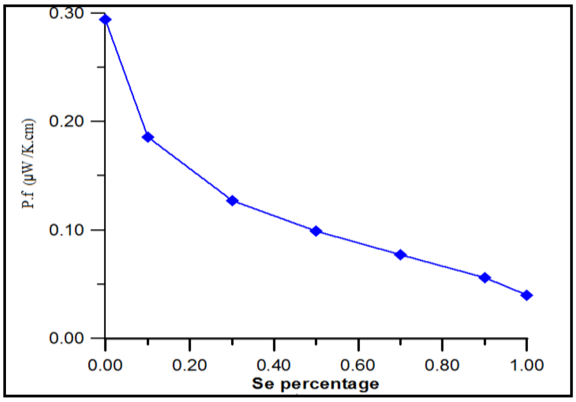

**Figure 9:** The power factor with Se percentage

**Table 3:** The parameters of thermoelectric properties Seebeck coefficient, electrical conductivity, thermal conductivity , power factor and figure of merit

| X | s(μv/k) | $\sigma(\Omega.cm)$^$^{-1}$ | k( w/cm.K) | p.f(μw/k.cm) | ZT |
|---|---|---|---|---|---|
| **0** | 150 | 1.306 | $1.035*10^{-5}$ | 0.294 | 0.705 |
| **0.1** | 120 | 1.289 | $1.0184*10^{-5}$ | 0.186 | 0.457 |
| **0.3** | 100 | 1.269 | $1.002 *10^{-5}$ | 0.127 | 0.322 |
| **0.5** | 90 | 1.233 | $9.738*10^{-6}$ | 0.099 | 0.269 |
| **0.7** | 80 | 1.197 | $9.455*10^{-6}$ | 0.077 | 0.219 |
| **0.9** | 70 | 1.144 | $9.038*10^{-6}$ | 0.056 | 0.175 |
| **1** | 60 | 1.134 | $8.957*10^{-6}$ | 0.040 | 0.129 |

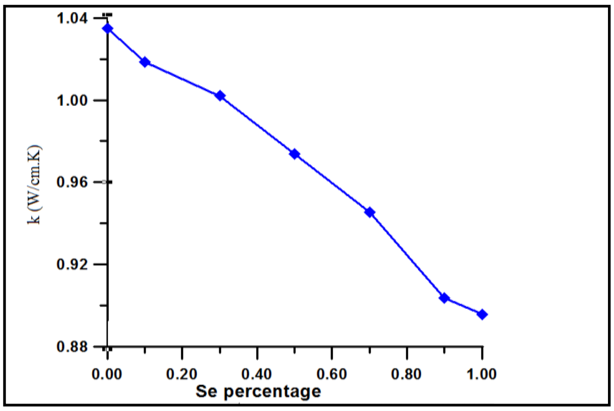

**Figure 10:** Thermal conductivity with Se percentage

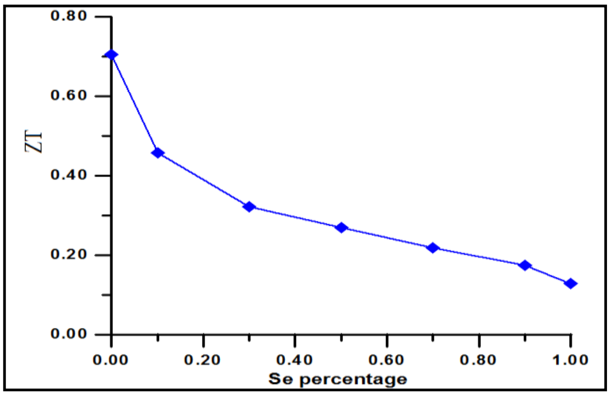

**Figure 11:** The figure of merit (ZT) with Se percentage

## Conclusion

From the study of electrical and thermoelectric properties for $Bi_2(Te_{1-x}\ Se_x)_3$ thin films with different Se percentage (0 ,0.1 ,0.3 , 0.5 ,0.7, 0.9 and 1) , which deposited by thermal evaporation technique at R.T .we notice the following results:

The electrical conductivity of $Bi_2(Te_{1-x}\ Se_x)_3$ thin films decreasing with increasing the Se percentage, also we found there are two activation energies $E_{a1}$ and $E_{a2}$ , which they are increasing with increasing of the Se percentage .

$Bi_2(Te_{1-x}\ Se_x)_3$ films have p- type conductivity, the carrier concentration decreasing with increasing the Se percentage , but the Hall coefficient and Hall mobility increasing with increasing the Se percentage.

The thermoelectric properties were determined by Seebeck coefficient, power factor , thermal conductivity and figure of merit which represented as the most important parameter to have the knowing about the efficiency of thermoelectric materials. Seebeck coefficient, power factor, thermal conductivity and figure of merit decreasing with increasing of the Se percentage.

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