JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 2, February 2009, p. 180 - 185

Semiconductor parameters of Bi_2Te_3 single crystals

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Single crystals of Bi_2Te_3 were grown in our laboratory by a special modified Bridgman technique method and were characterized by measurements of electrical conductivity and Hall effect in two crystallographic directions (parallel and perpendicular to the *c*-axis). From these measurements the investigated sample was found to be p-type conductivity. The carrier concentration was evaluated as 2.64×10^{17} cm^3. Also, the present investigation involves the thermoelectric power measurements of Bi_2Te_3 samples in the wide range 176-550 K in the two crystallographic directions. The combination of the electrical and thermal measurements in the present investigation makes it possible find various physical parameters such as diffusion coefficients, diffusion lengths, the mean free time between collision and effective masses of carriers were evaluated. The variation of the Hall mobility with temperature was studied and hence the scattering mechanism was discussed.

(Received January 7, 2009; accepted February 23, 2009)

Keywords: Bi_2Te_3, Hall and Seebeck coefficients, Electrical conductivity

1. Introduction

Bismuth telluride Bi_2Te_3 is one of the widely investigated substances. Thus several earlier authors [1-10] studied this compound. Anisotropy of the transport properties of single-crystal Bi_2Te_3 disordered by electron bombardment was studied by A. E. Kar'kin et al [5]. M. Situmorang and H. J. Goldsmid [1] have been studied anisotropy of the Seebeck coefficient in Bi_2Te_3 where they were used the theoretical predictions and compared with experimental data. J. Nagao et al [7] have been prepared Bi_2Te_3 crystals, they employed the Bridgman technique for growing the crystals and also they studied anisotropic factor of electrical conductivity in p-Bi_2Te_3 crystals. The anisotropic factor, $\sigma_{//}/\sigma_{\perp}$, shows an exponential form involving an activation energy. V. A. Kul'bachinskii et al [8] have been prepared the Bi_2Te_3 crystals by using Bridgman method and found that X-ray lattice parameters of these crystals, a = 0.43821 nm and c = 3.0481 nm and determined of the dielectric constant of Bi_2Te_3 was very large ($\varepsilon_{\infty} \approx 80$) and also found that the magnetic susceptibility χ of the Bi_2Te_3 single crystals.

The present work is study of some physical properties of Bi_2Te_3 single crystal over a wide temperature range extending to 163-550 K in an attempt to obtain as much as possible information about the semiconducting properties of these compounds. The properties investigated were the electrical conductivity σ, Hall coefficient R_H and Seebeck coefficient α and the dependence of these properties on temperature where this is important for investigation of transport phenomena in these materials. The work conducted is intended to supply for obtain of information about electrical conduction, forbidden gap width and mobility of current carriers and obtain to the semiconductor parameters of this compound.

2. Experimental Arrangement

Bi_2Te_3 single crystals, in the present investigation, were grown from melt by the modified Bridgman-Stockbarager technique, which constructed locally in our laboratory. This modification aimed to get suitable rate of the motion in order to obtain slow cooling rate of crystal growth. The charged ampoule is allowed to lowered inside the furnace at very constant rate (40 mm/day or 1.66 mm/h). More details about the design, modification, the pulling system and the three-zone tube furnace were described by [11]. For Bi_2Te_3 crystals the ampoule charged with the required amount of material 4.917 g of pure Bismuth (99.999 %) representing 52.19 % and 4.503 g of pure Tellurium (99.999 %) representing 47.81 % of the compound. The chemicals were introduced into a silica tube, which was then evacuated to 10^{-6} Torr and sealed under this vacuum. At the beginning of the growth run, the ampoule was held in the hot zone of the furnace about 24 hours for complete melt of the composition. Then, the ampoule was shaken during heating several times to accelerate the diffusion of the constituents through each other in order to perform homogenization. The charged ampoule moves from zone to another with the required rate 1.66 mm/h. The temperature of the middle zone 859 K corresponding to the crystallization temperature of Bi_2Te_3 according to the phase diagram [12]. The duration time for producing Bi_2Te_3, as a silvery dark metallic crystal is about eleven days. The produced ingot of Bi_2Te_3 compound was identified by means of X-ray diffraction technique. The results indicated that the ingot was good crystalline material with the required phase without any secondary phases. X-ray diffraction of the Bi_2Te_3 powder was compared with ASTM cards that indicated rhombohedral structure with lattice parameters in agreement with the parameters reported by V. A. Kul'bachinskii et al [8].

For studying the electrical conductivity and Hall effect, the used sample was cut with care from regions of

the ingots in which the layers of the crystal lattice were nearly parallel to another. The sample was prepared in a rectangular shape with dimension 8.3× 2.6×0.5 mm^3. Silver paste contact was used as ohmic contact. Recording the current-voltage characteristics checked the ohmic nature of the contacts. The electrical conductivity and the Hall coefficient were measured by a compensation method in a special cryostat [13] with a conventional D.C. type measured by using (UJ 33E Mark) potentiometer in a magnetic field of 5000 G which supplied from an Oxford N177 electromagnet. The temperature range of investigation was between 163 K and 528 K. We used liquid nitrogen for low temperature and electric heater for high temperature above room temperature. According to the anisotropy of Bi_2Te_3, the electrical conductivity was measured in two directions parallel and perpendicular to cleavage plane. All measurements were carried out under vacuum condition of about 10^{-3}Torr. This vacuum was necessary for the following reasons, firstly to avoid contamination of vapor in the low temperature range of measurements. Secondly to avoid oxidation of the sample in the high temperature range of measurements.

For studying thermoelectric power (TEP) measurements, an evacuated calorimeter (10^{-3} Torr) was used to protect the sample from oxidation and water vapor condensation at high and low temperatures respectively. The calorimeter has two heaters. The outer heater (the external source) discharges its heat slowly to the specimen environment. The inner heater (connected to the lower end of the crystal) was made purposely to control the temperature and its gradient along the specimen. The TEP is calculated at different temperatures by dividing the magnitude of the thermovoltage difference across the crystal by the temperature difference between the hot and cold ends. The thermoelectric power were measured throughout the temperature range extended from 176 K up to 550 K. According to the anisotropy of Bi_2Te_3, the thermoelectric power measurements carried out in two directions for the heat flow parallel and perpendicular to cleavage plane.

3. Results and discussion

3.1 Temperature dependence of electrical conductivity and Hall effect for Bi_2Te_3

For investigation the anisotropic phenomena in the layered Bi_2Te_3 crystal, the influence of temperature on the electrical conductivity was examined in two crystallographic directions (i.e $\sigma_{//}$ and $\sigma_{\perp}$). The measurements were carried out in temperature range 163-528 K. Figure1 shows the temperature dependence of the electrical conductivity σ along and across to the layers in Bi_2Te_3 single crystals. Both curves a typical semiconductor behavior. In Fig. 1 the electrical conductivities $\sigma_{//}$ and $\sigma_{\perp}$ increases slowly at low temperature corresponding to the extrinsic region. This is due to liberation of the ionized acceptors and their transition from the impurity level. From these regions the ionization energies were calculated as 0.036 eV and 0.0196 eV for $\sigma_{//}$ and $\sigma_{\perp}$, respectively. The second part of these curves lies between 328-398 K for $\sigma_{\perp}$ and 293-388 K for $\sigma_{//}$, which represents the transition region were the behavior of $\sigma_{//}$ and $\sigma_{\perp}$ is governed by the behavior of both the charge carrier concentration and their mobility. Above 398 K and 388 K intrinsic conduction region begins for $\sigma_{\perp}$ and $\sigma_{//}$, respectively where $\sigma_{\perp}$ and $\sigma_{//}$ increases sharply with increasing temperature. This predicts that both electron and holes contribute in the conduction at this high temperature range. The dependence in this temperature range follows the relation,

$$\sigma = \sigma_o \exp\left(-\Delta E_g / 2KT\right) \tag{1}$$

from the above formula we can deduce from these curves the energy gap width $\Delta E_{g\perp}$ and $\Delta E_{g//}$. It was found to be $\Delta E_{g\perp}$ = 0.151 eV agreement with [14] and $\Delta E_{g//}$ = 0.152 eV which equal to that in perpendicular direction. It's evident from Figure1 that the values of $\sigma_{//}$ are always much higher than those of $\sigma_{\perp}$. For instance at room temperature $\sigma_{//}$ equals $7.69\,\Omega^{-1}\,cm^{-1}$, while $\sigma_{\perp}$ equals $1.89\,\Omega^{-1}\,cm^{-1}$. This reveals the anisotropic nature of the physical quantity σ in the Bi_2Te_3 semiconductor compound. Values of $\Delta E_{g\perp}$ and $\Delta E_{g//}$ are the same as estimated from the two curves of $\sigma_{\perp}$ and $\sigma_{//}$, respectively. This means that ΔE_g is independent of direction. For gaining much understanding about the anisotropy of σ values, Figure 2 is depicted. This figure shows that the ratio of the electrical conductivities, $\sigma_{\perp}/\sigma_{//}$, as a function of reciprocal temperature in the same investigated temperature range (i.e 163-528 K). The anisotropy ratio, as evident from the curve, has a general mode of variation similar to the variation of the electrical conductivity (Fig. 1). The origin of the anisotropy, $\sigma_{\perp}/\sigma_{//}$, (which equal to 0.247 at room temperature) has been attributed to the one-dimensional disorder due to stacking faults or inclusions which can easily appear between layers due to weak interlayer bonding [7,15].

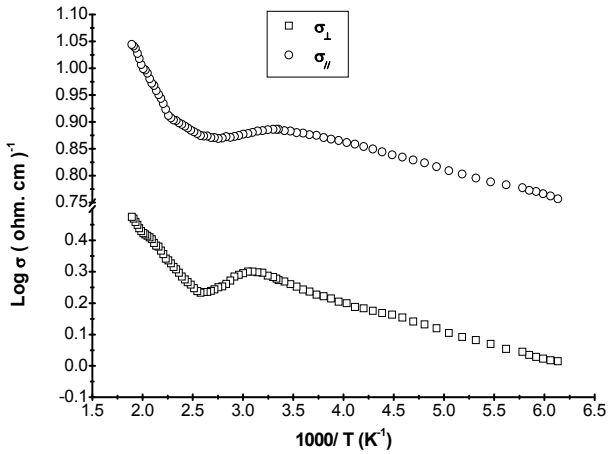

Fig. 1. Temperature dependence of the electrical conductivity for Bi_2Te_3 (Perpendicular and Parallel to the cleavage plane).

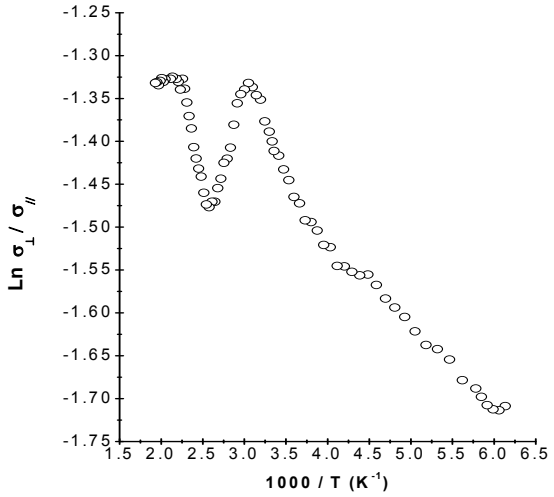

Fig. 2. Anisotropic factor vs temperature for Bi_2Te_3.

As for the importance of the Hall effect measurement, the present investigation is extended to cover this unique phenomenon. In the same limited temperature range (163-528 K). From measurements of Hall coefficient, it obvious that the sign of the Hall coefficient is positive in the entire temperature range of investigation. This indicates that the compound Bi_2Te_3 is a brilliant p-type semiconductor and inducting that the holes are a major contribution to the conductivity. It must be mentioned that the values of R_H were found to be the same in both the two crystallographic directions indicating that R_H is isotropic in these materials. The isotropy of the Hall coefficient suggests that the top of the valence band be at the center of the Brillouin zone. Fig. 3 depicts the relation between $R_H T^{3/2}$ and 10^3/ T. From the above relation we computed the value ΔE_g in the intrinsic region (388-528 K). It is 0.152 eV. In the extrinsic range (163-293 K), the value ΔE_a is estimated to be 0.0198 eV. These data are approximately in a good accordance with those obtained from the electrical conductivity $\sigma_{//}$ work (see Fig. 1). Simultaneous measurements of the electrical conductivity and Hall effect permit us to investigate the influence of temperature on the Hall mobility. Thus the Hall mobility was examined in two crystallographic directions. This influence of temperature on $\mu_\perp$ and $\mu_{//}$ is typically presented in Figure 4. Both $\mu_\perp$ and $\mu_{//}$ have the same behavior where in the low temperature part, which represents the extrinsic region, Both $\mu_\perp$ and $\mu_{//}$ decrease with increasing temperature obeying the law $\mu_\perp \alpha T^{-1.01}$ and $\mu_{//} \alpha T^{-1.59}$. Such behavior is characteristic of a scattering mechanism of the charge carriers with ionized impurities. In the high temperature range, corresponding to the intrinsic region, $\mu_\perp$ and $\mu_{//}$ decrease sharply according to the law $\mu_\perp \alpha T^{-1.55}$ and $\mu_{//} \alpha T^{-1.84}$, indicates that stoichiometric vacancies and certain of defects are responsible for scattering processes. This usually occurs in defect-semiconductor at high temperatures. In the intermediate part, which represents the transition region, $\mu_\perp$ and $\mu_{//}$ decrease slowly with increasing temperature.

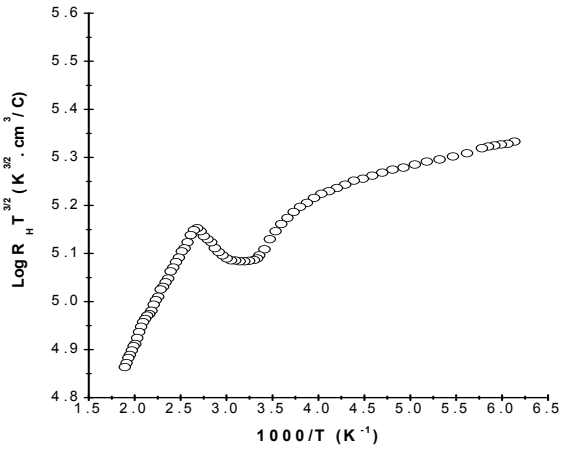

Fig. 3. Temperature dependence of the Hall effect for Bi_2Te_3.

From Fig. 4 we can conclude the following: -

* The Hall mobility parallel to cleavage plane ($\mu_{//}$) is much higher than the Hall mobility perpendicular to cleavage plane ($\mu_\perp$). For instance, at room temperature $\mu_{//}$ = 182.03 cm^2/Vs, while $\mu_\perp$ = 44.89 cm^2/Vs.

* Very strong anisotropy in the Hall mobility parallel and perpendicular to the cleavage plane is clearly observed throughout the temperature range of experiment. For the Bi_2Te_3 crystals, the anisotropic of the Hall mobility at room temperature can deduce as $\mu_{\perp} / \mu_{//} = 0.247$.

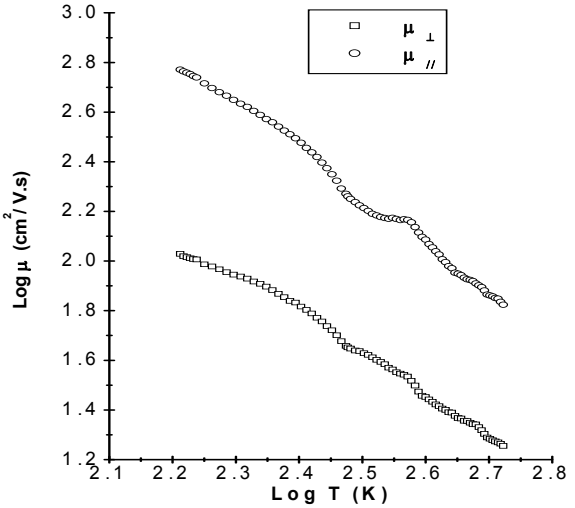

Fig. 4. Behaviour of Hall mobility as a function of temperature for Bi_2Te_3 (Perpendicular and Parallel to the cleavage plane).

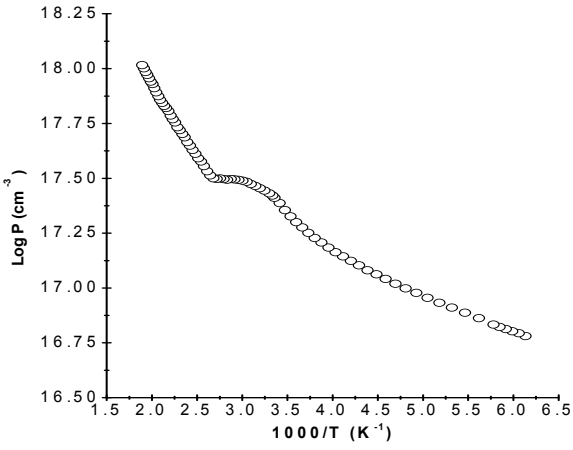

Fig. 5. Variation of carrier concentration with temperature for Bi_2Te_3.

From Hall coefficient data the charge carriers concentration was calculated by using the relation ($P = 1/R_H\, e$) where, (P) is the hole concentration and (e) is the electron charge. The variation of number majority carriers against reciprocal temperature is depicted in Fig. 5. The value of the hole concentration at room temperature is $2.64 \times 10^{17}\, cm^{-3}$.

3.2 Temperature Dependence of Thermoelectric Power of Bi_2Te_3

The thermoelectric power (Seebeck coefficient α) was measured as function of environmental temperature, T. Measurements were carried out with the two directions of the temperature gradient perpendicular and parallel to cleavage plane [16]. The temperature dependence of (Seebeck coefficient α) perpendicular $\alpha_{\perp}$ and parallel $\alpha_{//}$ to cleavage plane in the temperature range extended from 176 K up to 550 K, as function of reciprocal of absolute temperature, is given in Figure 6. In this figure, $\alpha_{\perp}$ and $\alpha_{//}$ decrease sharply as the temperature rises till reaching the temperature equals to 215 K for $\alpha_{\perp}$ and 218 K for $\alpha_{//}$ this may be due to the presence of some crystal defects or trapping centers in the direction of the carrier flow. Above these points, $\alpha_{\perp}$ and $\alpha_{//}$ increase monotonically with temperature increase up to its maximum value 156.5 μ V/K at a temperature equals to 363 K for $\alpha_{\perp}$ and 897.64 μ V/K at a temperature equals to 328 K for $\alpha_{//}$, where the increment of α is interpreted as a result of the thermal generation of the charge carriers with increasing the temperature. After that the values of $\alpha_{\perp}$ and $\alpha_{//}$ decrease with increasing the temperature as a result of the compensation process which takes place in this temperature. Then $\alpha_{\perp}$ increases slightly with increasing ambient temperature, while $\alpha_{//}$ is approximately temperature independent.

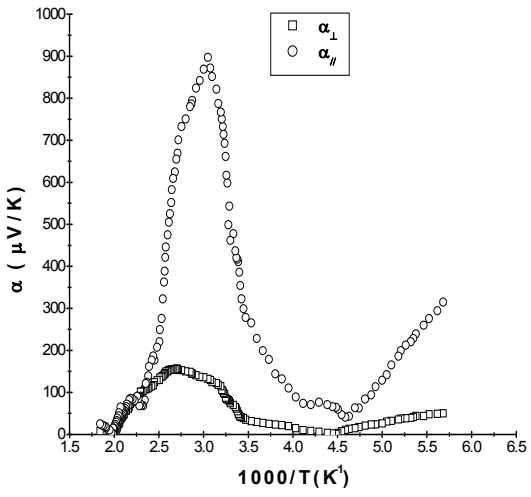

Fig. 6. Temperature dependence of the thermoelectric power for Bi_2Te_3 (Perpendicular and Parallel to the cleavage plane).

From Fig. 6 we note that

* Values of $\alpha_{//}$ is always higher than that of $\alpha_{\perp}$. This reveals the anisotropic nature of the Seebeck coefficient α in the Bi_2Te_3 semiconductor compound [1].

* Values of $\alpha_{//}$ exceed the values of $\alpha_{\perp}$ by several orders of magnitude. For example, $\alpha_{//}$ = 477.69 μ V/K while $\alpha_{\perp}$ = 103.41 μ V/K at room temperature.

The discussion of the results should be, then, separated into two parts: the intrinsic and the extrinsic region. This enables us to estimate many physical parameters. In intrinsic region we can apply the following formula [17] :-

$$\alpha = \frac{K}{e}\left[\frac{b-1}{b+1}\left(\frac{\Delta E_g}{2KT}+2\right)+\frac{1}{2}Ln\left(\frac{m_n^*}{m_p^*}\right)^{3/2}\right] \quad (2)$$

Where, K is Boltzmann's constant, b is the ratio of the electron to hole mobilities, ΔE_g is the energy gap width, m_n^* ,m_p^* are the effective mass of both electron and holes respectively. In accordance with this equation a plot of $\alpha_{\perp}$ and $\alpha_{//}$ as function of reciprocal of absolute temperature is a straight line as shown in Figure 6. The measured thermoelectric power in conjunction with the previously Hall data is used to calculate the required physical parameters. The slope of the linear part of the dependence in the intrinsic region were used to estimate, the ratio of the electron and hole mobilities, and was found to be $\mu_{n\perp}/\mu_{p\perp}$ = 3.22 and $\mu_{n//}/\mu_{p//}$ = 3.84. Since, $\mu_{p\perp}$ = 44.89 cm^2/V.s and $\mu_{p//}$ = 182.03 cm^2/V.s. The electron mobility can be deduced and its value amounted to be $\mu_{n\perp}$ = 144.47 cm^2/V.s, $\mu_{n//}$ = 699.01 cm^2/V.s using ($\Delta E_{g\perp} = \Delta E_{g//}$ = 0.15 eV). The knowledge of the mobilities of the majority and minority carriers enables us to compute the diffusion coefficients. They were evaluated and were found to be $D_{p\perp}$ = 1.16 $cm^2\ s^{-1}$, $D_{p//}$ = 4.71 $cm^2\ s^{-1}$ and $D_{n\perp}$ = 3.74 $cm^2\ s^{-1}$, $D_{n//}$ = 18.10 $cm^2\ s^{-1}$. Also, the ratio between the effective masses of both electrons and holes can be evaluated from the intersection of the curve with $\alpha_{\perp}$, $\alpha_{//}$ -axis. We evaluated this ratio as $m_{n\perp}^*/m_{p\perp}^*$ = 0.181, $m_{n//}^*/m_{p//}^*$ = 0.142, and assume that these ratios does not vary with temperature. In the extrinsic part we can apply the following formula (Wilson 1953) [18] :

$$\alpha = \frac{K}{e}\left[2 - Ln\frac{ph^3}{2(2\pi\, m_p^* KT)^{3/2}}\right] \quad (3)$$

The plot of $\alpha_{\perp}$ and $\alpha_{//}$ versus LnT yields a straight line (in the impurity region). Calculation of the effective mass of holes from the intersection of the two curves, the values of $m_{p\perp}^*$ = 5.85×10^{-34} kg and $m_{p//}^*$ = 7.63×10^{-33} kg. Combining these values with the above-mentioned results for the ratio m_n^*/m_p^*, for two directions, we obtain the effective mass of electrons $m_{n\perp}^*$ = 1.06×10^{-34} kg, $m_{n//}^*$ = 1.08×10^{-33} kg. The calculated values of the effective masses for both minority and majority carriers can be used for the determination of the relaxation time for both current carriers. These values for holes comes to be $\tau_{p\perp}$ = 1.64×10^{-20} s, $\tau_{p//}$ = 8.68×10^{-19} s, whereas for electrons equals to $\tau_{n\perp}$ = 9.57x10^{-21} s, $\tau_{n//}$ = 4.72×10^{-19} s. The diffusion length, as another important physical parameter, can deduce by using the formula ($L = \sqrt{D\,\tau}$). The diffusion length for holes, $L_{p\perp}$ =1.38×10^{-10} cm, $L_{p//}$ = 2.02×10^{-9} cm, while for electrons, $L_{n\perp}$ = 1.89×10^{-10} cm, $L_{n//}$ = 2.92×10^{-9} cm.

4. Conclusions

The results of the characterization of Bi_2Te_3 crystals lead to the following conclusions :-

1- The temperature dependence of the electrical conductivity (in two crystallographic directions, i.e $\sigma_{//}$ and $\sigma_{\perp}$) and Hall effect were investigated in temperature range from 163 to 528 K for Bi_2Te_3 single crystal.

2- The conductivity type throughout the entire temperature range was found to be p-type for our Bi_2Te_3 single crystal as concluded from the positive sign of both the Hall coefficient and thermoelectric power. Combination of the electrical conductivity and Hall effect measurement enables us to study the influence of temperature on the Hall mobility and to discuss the scattering mechanism of the charge carriers.

3- The crystal has an energy gap of 0.151eV, which was the same in two crystallographic directions and ionization energy of 0.036 eV and 0.0196 eV for parallel and perpendicular to the cleavage plane.

4- The present investigation involves the thermoelectric properties of Bi_2Te_3 single crystal. These

were carried out with the two directions of the temperature gradient perpendicular and parallel to the cleavage plane in the temperature range from 176 to 550 K. For the purpose of measurement, we designed the calorimeter from brass material. It was suitable, easy to control the temperature and to achieve the measurement under vacuum condition.

Acknowledgments

The authors would like to acknowledge Professor Dr. S. A. Hussein., Prof. of Solid State Physics, Physics Department, Faculty of Sciences, South Valley University, Qena, Egypt, for valuable discussion and encouragement during this work.

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