Growth and thermal transport properties of some ternary Thallium Dichalcogenide semiconductor compounds

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Abstract: In the present study high quality of TlBiTe2 crystals were prepared by modified Bridgman technique. The thermal transport properties were investigated. The thermoelectric power measurements were carried out in the temperature range (220K-480K). From these measurements the conductivity of the crystals was found to be p-type. The mobility of charge carriers, holes and electrons was found to be 2257.53cm^2/V.sec and 5024.226cm^2/V.sec respectively. The effective masses of the majority and minority carriers were deduced to be 6.0933x10^{-27}kg and 1.821x10^{-29}kg respectively. The diffusion coefficient, relaxation time and diffusion length for holes was calculated to be 58.4701cm^2/sec, 8.54 x 10^{-10}sec and 2.234x10^{-4}cm respectively. Also D_n, τ_n and L_n for electrons were found to be 130.127cm^2/sec, 5.68x10^{-14} sec and 2.7187x10^{-6} cm respectively. In addition to these pronounced parameters, the efficiency of the thermoelectric element (figure of merit) was evaluated which leads to better applications in many fields especially in the field of energy conversion.
[S. R. Alharbi, A. T. Nagat, E. M. Saed, M. H. Al-Hussiny and S. A. Hussein. **Growth and thermal transport properties of some ternary Thallium Dichalcogenide semiconductor compounds.** *Life Sci J* 2013;10(2):1233-1237] (ISSN:1097-8135). http://www.lifesciencesite.com. 170

Keywords: $TlBiTe_2$, thermoelectric power, effective mass, diffusion coefficient, relaxation time.

1. Introduction

In the past three decades, significant increase in chalcogenide semiconductor has been shown by various worker, because of their interesting physical properties as well as their wide technological application[(1)]. Thallium compounds have recently attracted interest as promising thermoelectric[(2)] materials. Over the last four decades, narrow band-gap semiconductors have played a dominant role in providing efficient materials for thermoelectric power application[(3)]. Among these are Tl-based ternary chalcogenides, $TlBiTe_2$ has been suggested as a candidate materials since 1970, but its use has been limited due to the fact that Tl and its compound have to be carefully handled[(4)]. $TlBiTe_2$ is a narrow gap semiconductor, which belongs to the family of pseudo IV-VI semiconductors[(5)]. Most of the developments in the field of materials for thermoelectric applications have been rather empirical, that is various materials were tested for the properties of interest in this application, and the best available material was then chosen and adjusted for best results**.** As the field progresses, it becomes increasingly evident that new materials will have to be found to realize fully the possibilities of thermoelectric power production. In a previous paper[(6)], we reported the electrical conductivity and Hall effect. This paper reports on a preliminary attempt at a prior design of materials for thermoelectric power production. As far as we know there are no good experimental results in the literature[(7)] about thermoelectric power of $TlBiTe_2$. In the present work, our aim is to investigate the thermoelectric power (TEP) in the temperature range 220-480K. Since the published literature does not provide a adequate information for the TEP of $TlBiTe_2$, this gives us the opportunity to report this work.

2. Experimental Arrangement

2.1 preparation of $TlBiTe_2$.

The $TlBiTe_2$ single crystal ingots have been grown by the modified Bridgman. The present samples were obtained by fusing the proper components taken in their stoichiometric proportions. Thallium of 99.9999% purity (Aldrich mark), Bismuth and Tellurium of the same purity and mark were used as starting material in the growth experiments. The components of the required composition 15.2853g of Tl representing 30.5706%, 15.6291g of Bi representing 31.2581% and 19.0857g of Te representing 38.1714% were placed in a silica ampoule, coated internally with a thin layer of carbon to prevent contamination of the charge and evacuated down to 10^{-6} Torr. The silica tube has a constricted sharp end at the bottom to facilitate seeding in the growth process. The quartz ampoule is washed with pure alcohol and hot distilled water. The ampoule with its charge had been introduced in a tray placed inside a

programmable muffle furnace controlled within ±1°C. The furnace temperature was regulated to reach 700K rapidly, then increased in steps of 20°C/h up to 840K, at which it was kept steady for five continuous hours. After this period, the temperature was allowed to decrease gradually with the same rate, until the sample reached its crystallization temperature (812K) as it was deduced from the reported phase diagram[8]. At this stage the furnace temperature was kept constant for forty hours, after it was commenced to decrease gradually till 700K in steps of 10°C/h, and finally in steps of 100°C to reach the room temperature. The time required for this process is about two weeks. A visual examination of the $TlBiTe_2$ ingot showed clearly gray opaque color which is in good agreement with the reporting data[9]. The single crystallinity of the product was verified by means of x-ray diffraction technique. The prepared material showed that it is strongly crystalline as identified with diffraction chart, and the diffraction data did not show the presence of any other phases.

2.2 Measuring technique.

The thermoelectric power (TEP) of bulk specimen at different temperature was measured. The used sample holder was of pressure contact type. A vacuum working chamber was locally constructed for the present work and was designed[10,11] in a way, that it allows measurements at a wide range of temperature. In this work, a compensation method is used for measuring voltages without drawing an appreciable current using a Tensily potentiometer type (U33E). The potentiometer is used for measuring the thermo-e.m.f, while T_1 and T_2 are measured using digital multimeter model HC-5010. In the TEP measurements, an evacuated calorimeter (10^{-3} Torr) was used to protect the sample from oxidation and water vapour condensation at high and low temperature 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 properly control the temperature and its gradient along the specimen. The direction of the temperature gradient was perpendicular to the natural cleavage planes. More details about the apparatus and technique of measuring have been published[12]. The thermoelectric power of the investigated $TlBiTe_2$ is measured throughout a temperature range 220-480K.

3. Results and Discussion

The results of the temperature dependence of thermoelectric power (TEP) of $TlBiTe_2$ single crystals are given in figure 1. The results and the figure indicate the following points : (1) Our sample shows p-type conductivity within the temperature range of investigation, which is agreement with our previous data[6] of the Hall coefficient. (2) The room temperature TEP value for $TlBiTe_2$ is mounted to 383.33μV/deg. (3) At the beginning of the curve TEP increases with temperature, reaching a maximum value at α equal to $500\mu VK^{-1}$ at 320K, such behaviour led to the assumption that, more holes are generated and contribute to the increment of α values as the temperature rise due to thermal generation of free charge carriers. (4) With further rise of temperature a sharp drop of TEP is observed after 320K until it reaches a minimum value of α equal to $30\mu VK^{-1}$ at 345K. This decrease in α reveals that the compensation process takes place in this range of temperature and the presence of some crystal defects and trapping centers in the direction of the carrier flow. (5) A third region in the same figure is observed where α increases with further rise of the temperature. Such behaviour is expected in this intrinsic range where generation of both carriers (electrons and holes) contribute to the increment of α value. The discussion of the results could be divided into two regions. The intrinsic and extrinsic region. This enable us to estimate many physical parameters: As follows from the expression of TEP of a semiconductor in the intrinsic region is given by[13]

$$\alpha = -\frac{k}{e}\left[\frac{\mu_n - \mu_p}{\mu_n + \mu_p}\left(\frac{\Delta E_g}{2kT} + 2\right) + \frac{3}{4}\ln\frac{m_n^*}{m_p^*}\right]$$

Where μ_n and μ_p are the electron and hole mobilities, k is Boltzman constant, m_n^* and m_p^* are the effective masses of electrons and holes respectively, and ΔE_g is the width of the forbidden band, this formula predicts that a plot of α as a function of the reciprocal of temperature, in the intrinsic range, should be a straight line.

Figure 2 shows the relation between α and $10^3/T$. It is clear from the graph that the general mode of α variation against T, decrease linearly and rapidly with temperature. The ratio of the electron and hole mobilities was found to be b= 2.226. On considering the value of μ_p=2257.53$cm^2V^{-1}s^{-1}$ which was obtained from the Hall measurements data, the value of electron mobility estimates and found to be μ_n =5024.23 $cm^2V^{-1}s^{-1}$. Also the ratio between the effective masses of both electrons and holes can be evaluated as m_n^* / m_p^*=2.989×10^{-3}, means that the effective mass of hole is greater than that of electron.

Another formula has been suggested by Wilson[14] to be employed in the extrinsic region was used

$$\alpha = \frac{k}{e}\left[2 - \ln\frac{ph^2}{2\left(2\pi m_p^* kT\right)^{3/2}}\right]$$

Plotting the above relation between α and lnT we obtain figure 3. This figure shows that α increases linearly with temperature increase in the temperature range corresponding to the impurity region. From the intercept of the line with the α-axis we got m_p^*=6.0933x10^{-27}kg. Combining this value with the above maintained results for the ratio m_n^* / m_p^* allows us to determine the effective mass of electrons. This value equal to m_n^* =1.821x10^{-29}kg. The calculated value of the effective masses of both minority and majority carriers can be used to determine the relaxation time for both current carriers. Its value for electrons comes to τ_n=5.68x10^{-14}s and for holes equal to τ_p= 8.54x10^{-10}s. Another important parameter can be deduced with the aid of the obtained values of μ_p and μ_n using the Einstein relation(D=kTμ/e), from which the diffusion coefficient for both carrier (electrons and holes) can be evaluated to be D_n=130.127cm^2/s and D_p=58.47cm^2/s. The diffusion coefficient as noticed is inversely proportional to the effective mass of holes and electrons. The electron mobility as calculated is much higher than the hole mobility, this result is acceptable, since the hole effective mass is greater than that of the electron. Combining the values of diffusion and relaxation time, one can obtain the diffusion length of free carriers L_p=2.2345x10^{-4}cm and L_n=2.718x10^{-6}cm for holes and electrons respectively. We can show that the diffusion constant as noticed is inversely proportional to the effective mass of hole and electron. Our results are in good agreement with each other, since the mobility of holes is smaller compared with that of electrons, and its effective mass is larger than that of electrons. Its relaxation time will be larger than that of electrons.

Figure 4 depicts the dependence of the TEP on the natural logarithm of the charge carriers concentration. The main conclusion from this curve is that α decreases sharply and linearly as the concentration increase as suggested from the following formula

$$\alpha = \frac{k}{e}\left[A + \ln\frac{2\left(2\pi m_p^* kT\right)^{3/2}}{\left(2\pi h\right)^3}\right] - \frac{k}{e}\ln p$$

Figure 5 illustrates the dependence of the thermoelectric power coefficient on the natural logarithm of the electric conductivity.

The following relation can be applied[15]

$$\alpha = \frac{k}{e}\left[A + \ln\frac{2\left(2\pi m_p^* kT\right)^{3/2} e\mu}{\left(2\pi h\right)} - \ln\sigma\right]$$

This behaviour which governs the relation between the electrical conductivity and TEP is similar behaviour of figure 4 & 5 predicts that the variation of α is mainly due to the carrier's concentration variation with temperature.

The choice of materials for thermoelectric generation, refrigerators and thermocouples is base on the efficiency parameters, defined by the relation

$$z = \alpha^2\sigma / \kappa$$

Where α is the Seebeck coefficient, σ is the electric conductivity, κ is the thermal conductivity. However, the term figure of merit is a measure of both performance and efficiency of a certain thermoelectric element. For our best $TlBiTe_2$ samples the obtained value z =3.5418x10^{-11}K^{-1} which permits the practical application as thermoelectric element. The proposed treatment of the experimental data sheds new light on the main physical parameters in $TlBiTe_2$ single crystal. The pronounced parameters obtained from TEP data gave evidence for practical applications.

4. Conclusion

In the present paper, measurements of thermoelectric power in a wide range of temperature for $TlBiTe_2$ single crystals grown by modified Bridgman technique were reported. The experimental data, gives us the chance to determine the following pronounced parameters, conductivity type of charge carriers, mobility, effective masses of charge carriers, diffusion coefficient and diffusion length as well as the relaxation time of both types of charge carriers. Also the efficiency of the material as thermoelement was checked.

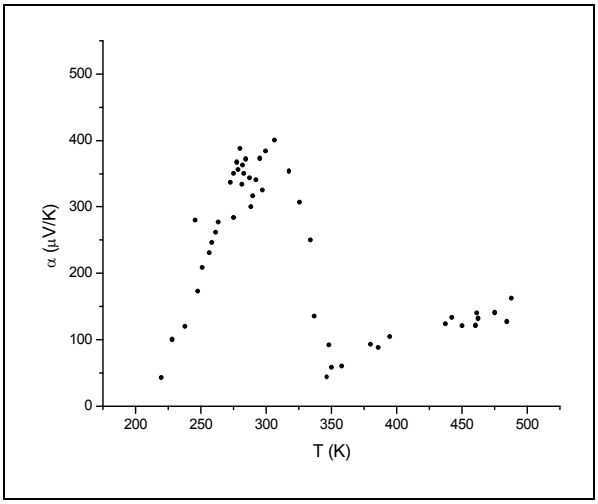

Fig. 1 Temperature dependence on thermoelectric power for $TlBiTe_2$ single crystal.

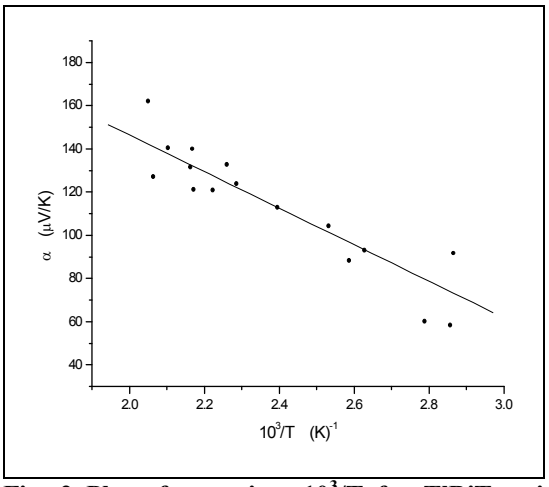

Fig. 2 Plot of α against $10^3/T$ for $TlBiTe_2$ single crystal.

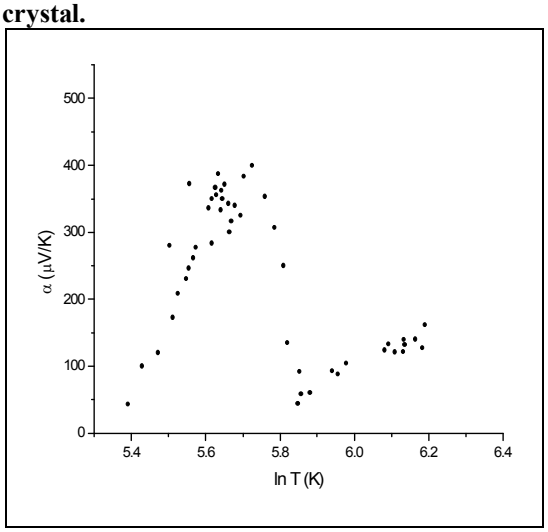

Fig. 3 Variation of α with t l*n* T for $TlBiTe_2$ single crystal.

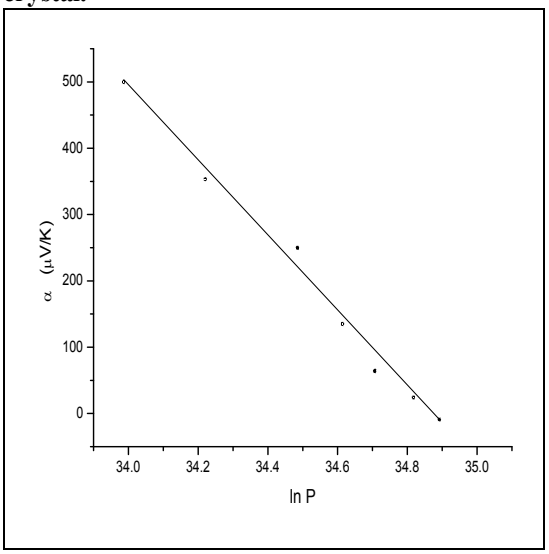

Fig. 4 The relation between thermoelectric power α and the concentration of holes for $TlBiTe_2$.

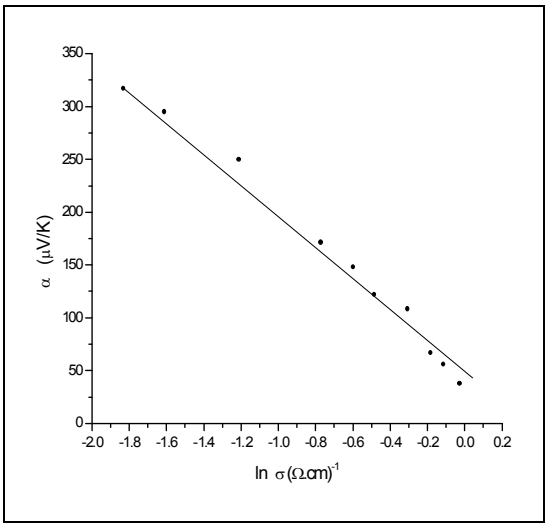

Fig. 5 Dependence of thermoelectric power of $TlBiTe_2$ on electrical conductivity.

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4/22/2013