

# Investigation of Thermoelectric Properties of Thallium Bismuth Diselenide Crystals

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Thermoelectric materials, which can be used in high-efficiency cooling and refrigeration, as well as energy scavenging, sensing, and thermo-power systems, can help to solve the global energy issue by providing a long-term energy solution. Our study sheds light on the thermoelectric power measurements of thallium bismuth diselenide crystals. A modified Bridgman technique was used to make TlBiSe<sub>2</sub> crystals. TlBiSe<sub>2</sub> crystals are particularly engaging in the quest for more effective thermoelectric materials that can change thermal energy to electrical energy and vice versa. The properties of thermal transport were studied. Thermoelectric power measurements were performed at temperatures ranging from 211 to 504 K. Based on these measurements, the conductivity of the crystals was determined to be n-type. The mobilities of the charge carriers, i.e., holes and electrons, were calculated to be 0.0115 cm<sup>2</sup>/(V s) and 0.0229 cm<sup>2</sup>/(V s), respectively. The effective masses of the majority and minority carriers were determined to be  $4.3 \times 10^{-33}$  kg and  $1.6 \times 10^{-31}$  kg, respectively. In addition, the relaxation times, diffusion coefficients, and diffusion lengths of both majority and minority carriers were checked. All the obtained parameters revealed that this semiconducting compound can be used in the fields of energy conversion, semiconducting devices, and electronic engineering.

topics: characterization of crystals, TlBiSe<sub>2</sub>, thermoelectric power

## 1. Introduction

TlBiSe<sub>2</sub>, TlBiS<sub>2</sub>, and TlBiTe<sub>2</sub> belong to the family of ternary compounds III–V–VI, which are characterized by narrow-gap semiconductors [1]. In recent years, thallium compounds have attracted interest as promising thermoelectric materials [2]. Thermoelectric materials are employed in a variety of technical applications. Even at low temperatures, thermoelectric (TE) materials transform thermal energy directly into electrical power. The advancement of steady, high-performance TE materials has drawn the attention of scientists due to their various potential applications. In the past thirty years, a huge expansion in chalcogenide semiconductors has appeared because of their fascinating physical properties as well as their wide innovative applications [3]. Thermoelectric materials made of thallium compounds have recently sparked interest [4]. Thallium chalcogenides have piqued interest in the thermoelectrics field due to their low heat conductivity. In the Tl<sub>2</sub>SnSe<sub>3</sub>–Tl<sub>4</sub>SnSe<sub>4</sub>–TlBiSe<sub>2</sub> subsystem, research into ternary compounds, limited solid solutions, and eutectic complex alloys is an essential step in the discovery of new semiconductor substances [2]. The thermoelectric power measurements of thallium bismuth diselenide crystals may be improved as a result of our research. TlBiSe<sub>2</sub> has been considered a semiconducting ternary

compound [5–9]. To the best of our knowledge, there are no good experimental findings in the literature regarding the thermoelectric power of TlBiSe<sub>2</sub>. The goal of this research is to investigate thermoelectric power (TEP) in the temperature range of 211–504 K. Thermal transport properties were investigated. Temperatures ranging from 211 to 504 K were used to measure thermoelectric power. Based on these tests, the crystals' conductivity was judged to be n-type. The mobilities of charge carriers (holes and electrons) were calculated. The majority and minority carriers' effective masses were calculated. In addition, both majority and minority carriers' relaxation periods, diffusion coefficients, and diffusion lengths were examined. Since the published literature does not provide significant information for the TEP of TlBiSe<sub>2</sub>, we can report on this work. This paper provides an account of a previous endeavor in the design of materials for thermoelectric force production.

## 2. Experimental methodology and materials

### 2.1. Preparation of TlBiSe<sub>2</sub>

The modified Bridgman method was used to develop the TlBiSe<sub>2</sub> crystals. TlBiSe<sub>2</sub> crystals were grown by a modification of the Bridgman technique by using the Travelling Solvent Method (TSM). Details of the three-zone furnace and the new hydraulic

pulling system have been previously published [10]. The current samples were formed by combining the necessary components in their stoichiometric proportions. Starting ingredients for the growth studies included 99.9999% pure thulium (Aldrich), bismuth, and selenium of the same purity and brand. The necessary composition consists of 15.2853 g of Tl (representing 30.5706% of the sample), 15.6291 g of Bi (representing 31.2581%), and 19.0857 g of Se (representing 38.1714%). The ingredients were placed in a silica ampoule and evacuated down to  $10^{-5}$  Torr. The silica tube features a restricted pointed end at the rim to make seeding simpler. The description of the effective sample preparation has been published by us [11].

## 2.2. Measuring technique

The thermoelectric power (TEP) of the bulk specimen was measured at different temperatures. The strain contact type of sample holder was chosen. A vacuum working chamber was locally developed for the current work and is designed [12, 13] to permit measurements at a broad range of temperatures. Thermoelectric performance was measured using a vacuum calorimeter ( $10^{-3}$  Torr). This protected the sample from oxidation and water vapor condensation at high and low temperatures, respectively. In the calorimeter, there are two heaters. The heat from the outer heater (the external source) is progressively released into the specimen's environment. The inner heater (attached to the crystal's lower end) was designed specifically to manage the temperature and gradient along the specimen, as without it, the temperature gradient ran parallel to the natural cleavage planes. The TEP is calculated by multiplying the thermal voltage differential across the crystal by the temperature difference between the hot and cold ends at different temperatures. Except for generating a noticeable current using a Tinsley potentiometer, this work uses a compensation technique for reading voltages (U33E). The potentiometer was used to measure the thermo-e.m.f. (thermo-electromotive force), while T1 and T2 were measured using a digital multimeter (HC-5010). More details regarding the equipment and measuring approach have been published [14]. The thermoelectric power of the investigated TlBiSe<sub>2</sub> was measured in the temperature range of 211 to 504 K.

## 3. Results and discussion

The results of the temperature dependence of thermoelectric power (TEP) of TlBiSe<sub>2</sub> single crystals are shown in Fig. 1. The compound behaves similarly to a Cu compound [15]. The following points are highlighted in the results and figure:

- Over the entire temperature range of examination, our sample exhibits n-type conductivity with no polarity charges, which is

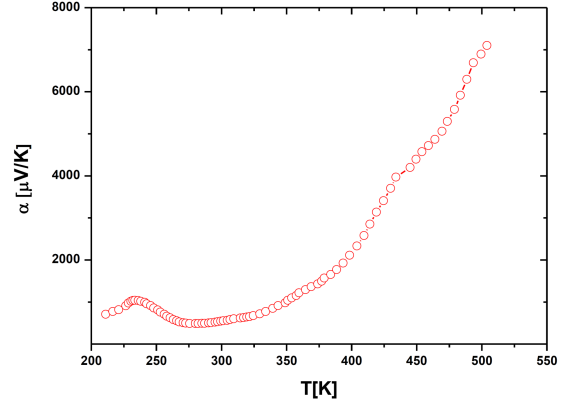


Fig. 1. The dependence of  $\alpha$  against the temperature for TlBiSe<sub>2</sub> crystal.

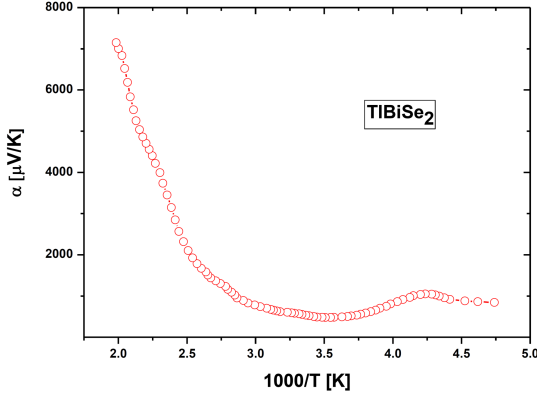
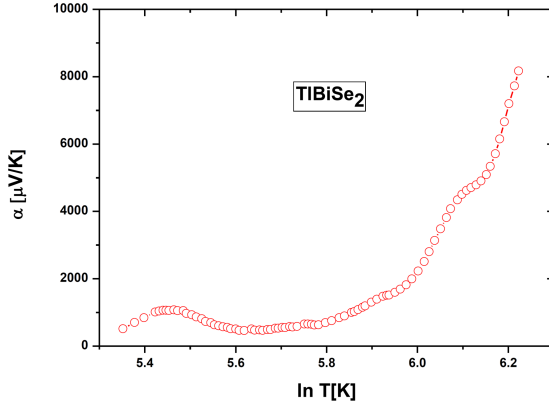
consistent with our previous Hall coefficient data [11] and is consistent with the data in this study [16].

- The value of the thermoelectric power  $\alpha$  for TlBiSe<sub>2</sub> at room temperature was set to 624  $\mu\text{V/K}$ , which is greater than the value in [17] for K<sub>2</sub>Cu<sub>2</sub>GeS<sub>4</sub> chalcogenide.
- The TEP increased with temperature at the start of the curve, reaching a maximum value of 1048  $\mu\text{V/K}$  at 236 K. This behavior led to the conclusion that more electrons are produced and contribute to the increase in the values as the temperature rises because of the thermal generation of free charge carriers.
- After 236 K, TEP started to fall until it reached a minimum of 470  $\mu\text{V/K}$  at 275 K. This decrease indicates that the compensation process takes place in this temperature range, as well as the presence of specific crystal defects and trapping centers in the carrier flow direction.
- In the same figure, a third section is visible, where TEP rises sharply at an increasing temperature above 334 K. The increase in  $\alpha$  is perceived as a function of the charge carrier thermal generation as the temperature rises. Such behavior is predicted in this intrinsic range, where all carriers (electrons and holes) contribute to the increment of the value.

This discussion may concern two segments, namely intrinsic and extrinsic regions. This allowed us to evaluate several physical parameters. As can be seen from the following, the TEP of the semiconductor in the intrinsic place is expressed as [18]

$$\alpha = \frac{k_B}{e} \left[ \frac{b-1}{b+1} \left( \frac{\Delta E_g}{2k_B T} + 2 \right) \right] - \frac{3}{4} \ln \left( \frac{m_n^*}{m_p^*} \right), \quad (1)$$

where  $k_B$  is the Boltzmann constant;  $b = \frac{\mu_n}{\mu_p}$ ;  $\mu_n$  and  $\mu_p$  are the mobility of electrons and holes, respectively; and  $\Delta E_g$  is the forbidden bandwidth. The effective masses of electrons and holes are  $m_n^*$

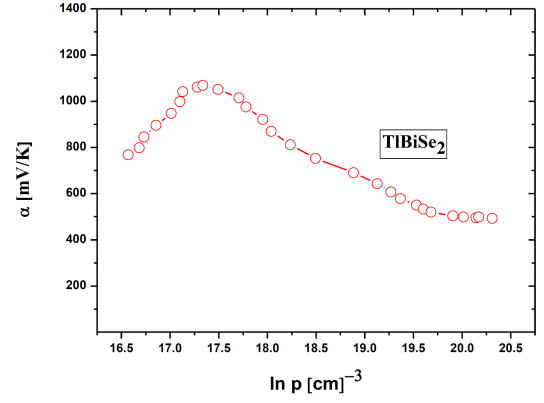

 Fig. 2. Plot of  $\alpha$  for TlBiSe<sub>2</sub> crystal vs  $10^3/T$ .

 Fig. 3. The relationship between  $\alpha$  and  $\ln(T)$  for TlBiSe<sub>2</sub> crystal.

and  $m_p^*$ , respectively. It is implied by (1) that a plot of a function of the reciprocal of temperature will be a straight line in the intrinsic range. Figure 2 outlines the relationship between  $\alpha$  and  $10^3/T$ . The common view of the variety of  $\alpha$  vs  $T$  decreases linearly and rapidly with temperature, as shown in the graph.

The electron and hole mobilities were found to have a ratio of  $b \approx 2$ . Taking the value of  $\mu_p = 0.0115 \text{ cm}^2/(\text{V s})$ , which was collected from the Hall measurement results, into consideration, the value of the electron mobility calculations was found to be  $\mu_n = 0.0229 \text{ cm}^2/(\text{V s})$ . In addition, the ratio of the effective masses of electrons and holes can be calculated as  $m_n^*/m_p^* = 0.0717$ , indicating that the hole's effective mass is bigger than the electron's effective mass. Wilson [19] offered another equation for use in the extrinsic region, i.e.,

$$\alpha = \frac{k_B}{e} \left[ 2 - \ln \left( \frac{p h^3}{2 (2\pi m_p^* k_B T)^{\frac{3}{2}}} \right) \right]. \quad (2)$$

Figure 3 is obtained by plotting the above-mentioned relationship (2) between  $\alpha$  and duration  $\ln(T)$ . The results show that  $\alpha$  increases linearly with increasing temperature in the temperature range corresponding to the impurity region.


 Fig. 4. The dependence of  $\alpha$  on the natural logarithm of charge carrier concentration for TlBiSe<sub>2</sub> crystal.

We obtained  $m_n^* = 4.3 \times 10^{-33} \text{ kg}$  from the intersection of the line with the  $\alpha$ -axis. This value can be combined with the maintenance results for the  $m_n^*/m_p^*$  ratio above to determine the effective mass of the holes, which is  $m_p^* = 1.6 \times 10^{-31} \text{ kg}$ . The relaxation time for both current carriers can be estimated using the calculated effective masses of both minority and majority carriers, and the value of it for electrons is equal to  $\tau_n = 1.86 \times 10^{-18} \text{ s}$  and for holes  $\tau_p = 6.9 \times 10^{-17} \text{ s}$ . The Einstein relation ( $D = k_B T \mu / e$ ) can be used to derive another important parameter — using the resulting  $\mu_p$  and  $\mu_n$  values, the diffusion coefficients of both carriers (electrons and holes) can be evaluated and are  $D_p = 6.8 \times 10^{-23} \text{ cm}^2/\text{s}$  and  $D_n = 3.6 \times 10^{-24} \text{ cm}^2/\text{s}$ .

As we have observed, the diffusion coefficient is inversely proportional to the effective mass of holes and electrons. The determined electron mobility is much higher than the hole mobility. However, because the hole's effective mass is greater than the electron's, this result is appropriate. The diffusion length of free carriers,  $L_p = 1.01 \times 10^{-16} \text{ cm}$  and  $L_n = 5.652 \times 10^{-18} \text{ cm}$  for holes and electrons, respectively, can be calculated by combining diffusion and relaxation time values.

We demonstrate that the diffusion constant is inversely proportional to the effective mass of the hole and electron, as previously stated. Because the mobility of holes is lower than that of electrons and their effective mass is greater than that of electrons, our findings are in strong agreement. The holes would have a longer relaxation time than the electrons.

The dependence of TEP on the normal logarithm of the charge-carrier concentration is shown in Fig. 4. The key inference from this curve is that as the concentration increases,  $\alpha$  decreases sharply and linearly, as shown by the following formula [19]

$$\alpha = \frac{k_B}{e} \left[ A + \ln \left( \frac{2e\mu (2\pi m_p^* k_B T)^{\frac{3}{2}}}{(2\pi h)^3} \right) \right] - \frac{k_B}{e} \ln(p). \quad (3)$$

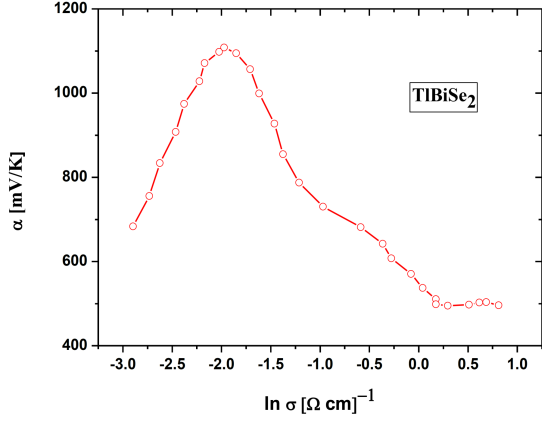


Fig. 5. The dependence of the thermoelectric power coefficient on the natural logarithm of the electrical conductivity for TlBiSe<sub>2</sub> crystal.

The thermoelectric power coefficient is shown in Fig. 5 as a function of the normal logarithm of the electrical conductivity. The following formula can be used [20]

$$\alpha = \frac{k_B}{e} \left[ A + \ln \left( \frac{2e\mu (2\pi m_p^* k_B T)^{\frac{3}{2}}}{(2\pi h)^3} \right) \right] - \frac{k_B}{e} \ln(\sigma). \quad (4)$$

This behavior, which regulates the relationship between electrical conductivity and TEP, is similar to the behavior shown in Figs. 4 and 5, and indicates that the variance of  $\alpha$  is primarily due to the carrier's concentration changing with temperature. The electrical and lattice parameters described in the figure of merit ZT govern the performance of thermoelectric materials. Low thermal conductivity  $\kappa$ , which consists of a lattice component  $\kappa_{lat}$  and an electronic component  $\kappa_{el}$ , is ideal because of its high electrical conductivity and Seebeck coefficient  $\alpha$ . Because all these variables are interconnected, adjusting them is difficult. The following equation describes the efficiency parameters that guide material selection for thermoelectric generators, refrigerators, and thermocouples, i.e.,

$$z = \frac{\alpha^2 \sigma}{\kappa}, \quad (5)$$

where  $\kappa$  is the thermal conductivity,  $\sigma$  is the electrical conductivity, and  $\alpha$  is the Seebeck coefficient. TlBiSe<sub>2</sub> has a thermal conductivity of 0.85 W/(m K) [21]. A dimensionless quantity ZT is used in the thermoelectric material evaluation and is calculated by multiplying the figure of merit by the temperature. On the other hand, the term "figure of merit" refers to the output and efficiency of a thermoelectric element. Our TlBiSe<sub>2</sub> samples have a  $z = 0.426 \times 10^{-6} \text{ K}^{-1}$  value, greater than the  $z$  value of the compound TlBiTe<sub>2</sub> [22], which enables the practical implementation of TlBiSe<sub>2</sub> as a thermoelectric element. The proposed experimental data treatment sheds fresh light on the TlBiSe<sub>2</sub>

crystals' important physical properties. The TEP data revealed a number of distinct parameters that may be employed in real-world scenarios.

#### 4. Conclusion

In this study, the thermoelectric power of TlBiSe<sub>2</sub> crystals grown using the modified Bridgman technique was measured over a broad temperature range. The experimental data allowed us to establish the following significant parameters: charge carrier conductivity type, mobility, effective masses of charge carriers, diffusion coefficient, diffusion length, and relaxation time of both types of charge carriers. The performance of the material as a thermoelement was also tested.

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