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Study of thermoelectric parameters of Bi_2Te_3 semiconductors

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The investigation of the thermoelectric properties of semiconductors is of paramount importance in contemporary scientific research, particularly in relation to the direct conversion of thermal energy into electrical energy and vice versa. This area of study constitutes a fundamental component of semiconductor physics and significantly contributes to the advancement of related scientific disciplines. Thermoelectric semiconductors are already extensively employed, and their potential applications are anticipated to broaden in the foreseeable future. These semiconductors are essential to a diverse array of systems, including space technology and household appliances. Research in this domain is continuously evolving and expanding, primarily due to the rapid transfer of foundational knowledge to industry, resulting in substantial economic benefits. Consequently, a considerable portion of research is focused on the thermoelectric properties of semiconductors and the development of thermoelectric technologies. In this study, we examined the thermoelectric parameters of P-type Bi_2Te_3 semiconductors within the temperature range of 291–373 K.

This study examines and compares the thermo-electromotive force (thermoemf), electrical conductivity, thermal conductivity, and Z parameter behavior at elevated temperatures of two types of P-type semiconductors, each synthesized through distinct methodologies, with theoretical predictions. Additionally, the band gap of the semiconductors is calculated based on the temperature-dependent variation of electrical conductivity and is subsequently compared with theoretical values. The findings indicate that the experimental results align with the theoretical data available in the literature, within the established error margins.

Keywords: P-type Bi_2Te_3 semiconductors, thermoelectric parameters.

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Introduction

The translation of fundamental scientific discoveries into novel products and technologies has precipitated the emergence of new scientific challenges. Addressing these challenges continues to propel technological advancements globally. It is well-established that solid-state physics, particularly semiconductor physics, is experiencing rapid development. This is attributed to the superior properties of semiconductors, which are integral to all electronic materials, rendering semiconductor technology one of the most pivotal technologies of the 21st century. From the acquisition of semiconductors to the exploration of their diverse properties, the construction and enhancement of various devices and systems utilizing

these properties, and their subsequent introduction to industry, semiconductor technology, which significantly contributes to numerous scientific fields, is extensively researched worldwide [1-5]. Semiconductors exhibit a wide array of types and properties, with applications so extensive that there is virtually no domain devoid of semiconductor utilization. Currently, global research is concentrated on the thermoelectric properties of semiconductors, addressing issues such as the direct conversion of thermal energy into electrical energy and vice versa. Furthermore, the investigation of the thermoelectric properties of semiconductors constitutes a fundamental area of research in semiconductor physics and is crucial for the advancement of related scientific disciplines. Thermoelectric semiconductors are already recognized for their broad range of applications, and it is anticipated that their use will expand into diverse fields in

the near future. Systems composed of thermoelectric semiconductors are employed in a wide spectrum of fields, from space technology to consumer electronics. Research into these systems continues to deepen and expand, as the foundational knowledge acquired is transferred to industry more rapidly than other technologies, resulting in cost savings. Consequently, significant research efforts have been concentrated on the thermoelectric properties of semiconductors and thermoelectric technology. In this study, the thermoelectric parameters of P-type $(\text{Bi}_2\text{Te}_3)\text{Sb}_2$ semiconductors within the temperature range of 291-373K are examined. The behavior of the thermoelectric, electrical conductivity, thermal conductivity, and Z parameter of two types of P-type semiconductors, obtained through two different methods at TES Ltd, has been investigated and compared with theoretical findings. Additionally, by analyzing the variation of electrical conductivity with temperature, the forbidden energy gap in the semiconductors' energy bands has been calculated separately and compared with theoretical predictions. The experimental results obtained were found to be in close agreement with the theoretical findings [6-10].

I. Methods

In this study, two distinct P-type semiconductors, produced via the Travelling Heater Method (THM) and the pressing method, were utilized. Each semiconductor sample was individually examined, and the resulting parameters were analyzed. The electrical conductivity (σ) and thermoelectability (α) of all samples were measured ten times at intervals of 10°C , ranging from room temperature (18°C) to an ambient temperature of 100°C , and the average values were calculated.

Consequently, the variation of the average α and σ values of P-type melted (Er) and P-type pressed (Pr) semiconductors with respect to temperature was determined. Utilizing these values, the variation of thermal conductivity (χ) and $Z = \frac{\alpha^2 \sigma}{\chi}$ parameters with temperature was ascertained.

Additionally, by calculating the slope of the function (where $T=273^\circ\text{C} + t^\circ\text{C}$ is temperature in Kelvin), the forbidden region value $E_g(\text{eV})$ was determined separately for each semiconductor.

For P-type semiconductors obtained via the zone melting (THM) method, a composition of 74% $\text{Bi}_2\text{Te}_3 + 26\% \text{Sb}_2\text{Te}_3$ was employed. The cross-sections of the alloys obtained can vary according to the inner diameter of the quartz tubes. Semiconductors with a diameter of 8 mm were used in the experiment. While the melting temperature of N-type semiconductors is 706°C , that of P-type is 711°C . The pressing method is based on the powder metallurgy technique. A powdered mixture of 80% $\text{Bi}_2\text{Te}_3 + 20\% \text{Bi}_2\text{Se}_3$ is placed in a flat square prism-shaped mold surrounded by a heater. The mold is heated to 400°C and subjected to a pressure of $7 \text{ atm} = 7.105 \text{ Pa}$ by means of a press. The thickness of the semiconductors produced varies according to the dimensions of the mold. In the experiment, a powder mixture consisting of 74% $\text{Bi}_2\text{Te}_3 + 26\% \text{Sb}_2\text{Te}_3$ was used for P-type pressed semiconductors

with a square cross-section and a side of 7 mm (area 49 mm^2) [11-13].

The shapes of the semiconductors used in the study vary according to the method of their production. The samples obtained by the zone melting method are in the form of a cylinder with a height of 2 cm and a diameter of 8 mm, while the pressed samples are in the form of a flat square prism consisting of a square with a height of 2 cm and a base of $7 \text{ mm} \times 7 \text{ mm}$. To categorize semiconductors into groups according to their type, a specialized N-P type determination intelligent system was employed, which was developed at Ltd [14]. The general image of this device is provided in Figure 1.

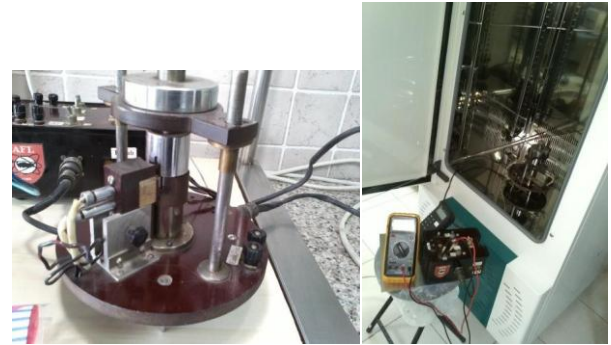


Fig. 1. N-P Type Device and Samples.

In this study, the T.C. Harman method was employed to examine the conductivity-temperature and thermoelectric-temperature variations of two samples. To achieve this, a measuring instrument was designed and constructed. The entire experimental setup comprises one measuring instrument, one adjustment unit, and three digital multimeters. The measuring instrument is depicted in the accompanying figure. It consists of a fixed base with two mounted steel supports, a heater capable of moving along the supports, and a movable system with two electrodes spanning a range of 1 cm. Positioned between the supports is a perforated anvil with a diameter of 4 cm. The heater, of identical diameter, is constructed from wire wound around a thin tube. The ends of the thermocouples, composed of copper (Cu) and a conduit (60% Cu + 40% Ni), were threaded through the perforations in the anvil and heater to ensure contact with the upper and lower surfaces of the semiconductor samples.



Fig. 2. $\alpha - \sigma$ Measuring instrument and air conditioning cabinet fixed with screw top caps.

To ensure the semiconductor sample remains stationary on the anvil and to facilitate the measurement of potential difference, a holder was constructed from ebonite, designed as a lid with an open aperture on the top and one side. Once the holder is affixed to the anvil, the sample is positioned within it, and the heater is gradually moved and lowered to achieve complete contact with the semiconductor. The base of the steel component of the heater is circularly hollowed to maximize contact. Needle-shaped, spring-loaded, and movable electrodes are employed to measure the voltage on the semiconductor. After positioning the semiconductor within the device, the electrodes are brought into full contact and secured using a side screw. The input wires of the heater, along with the output ends of the thermocouples and electrodes, are soldered to the input-output jack located at the base. An identical jack is installed on the adjustment unit, and multiple cables are utilized to interconnect them. The tuning unit facilitates the measurement of α and σ of semiconductors using a single system. The α of the semiconductor is measured when the " " switch on the unit is set to the " " position and the "Emk - V" switch is in the "V-(voltage)" position. To measure the α of the semiconductor, the "Emk - V" switch must be adjusted to the "E" position, and the " " switch must be set to the " α - σ " position. A 0.01Ω standard resistor is connected to the "Rs" output on the unit, an ammeter is connected to the "A" output, and a DC voltmeter is connected to the "mV" output. To maintain the current flowing through the semiconductor (maximum $I = 1A$), the temperature difference between the semiconductor's ends, and to regulate the voltage applied to the heater, the entire system is powered by a variac. To examine the parameters concerning ambient temperature, the measuring instrument, along with the semiconductor sample, is placed in a temperature-controlled air conditioning unit. After setting the device's temperature, stabilization is awaited before conducting measurements. The SFL Advanced High Temperature & Environmental Systems air conditioning was employed in the experiment. Measurements commenced at room temperature ($18^\circ C$) and increased by $10^\circ C$ increments up to $100^\circ C$. Three Fluke 45 Dual Display multimeters were utilized to measure the AC current through the semiconductors, V_s on the standard resistor, V_x voltages on the sample, and the voltage generated by the thermocouples or thermocouples formed by the semiconductor. The α - σ measuring instrument and the air conditioning device are depicted in Figure 2.

In accordance with contemporary semiconductor theory, the physical properties of both intrinsic and P-type semiconductors are contingent upon the charge concentration (n) within the semiconductor. The value of n in semiconductors is influenced by temperature, band structure, and the interaction mechanism of carriers with the crystal lattice, specifically scattering on phonons. Given that the σ and χ of a semiconductor are dependent on n , a correlation exists among these parameters. In P-type semiconductors, the conductivity coefficient (σ) at elevated temperatures, including room temperature and above, exhibits variation with temperature,

$$\sigma = \sigma_0 e^{\frac{-E_g}{2kT}} \quad (1)$$

the changes are as follows. Here, σ_0 is a constant that is independent of temperature, and T approaches infinity; that is, when all charge carriers are in conduction, it refers to σ . The approximate value of is 10^5 .

If we take the natural logarithm of both sides of this equation,

$$\ln \sigma = \ln \sigma_0 - \frac{E_g}{2kT} \quad (2)$$

we obtain the equation. Here $k = 10^{-4} \text{ eV / K}$ is the Boltzman constant, T is the temperature in Kelvin. It is clear that $\ln \sigma$ here is a linear function with respect to $1/T$ ($\ln \sigma \sim 1/T$) (see Figure 3).

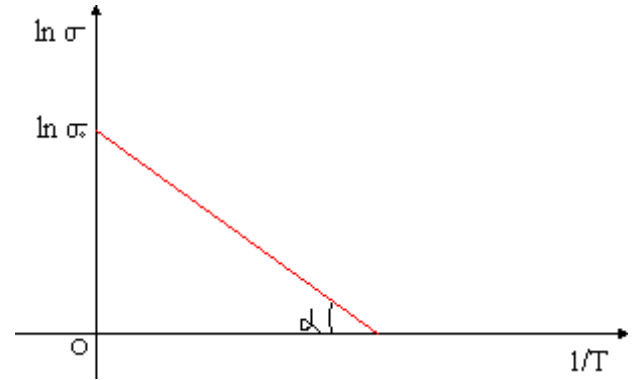


Fig. 3. Graph of function $\ln \sigma = f\left(\frac{1}{T}\right)$.

The graph of this function is a line and its slope is $(\tan \alpha) \frac{E_g}{2k}$. This means that. The expression

$$\text{slope} = \frac{E_g}{2k} \quad (3)$$

can be written.

So if the function and slope of a semiconductor $\ln \sigma = f\left(\frac{1}{T}\right)$ are obtained, then

$$E_g = 2k \tan \alpha \quad (4)$$

The value of the forbidden region, denoted as E_g , can be determined using the specified formula. In this study, the E_g of melted and pressed P-type semiconductors was calculated utilizing this method. Heat conduction in a semiconductor arises from the contributions of charge carriers and phonons. In P-type semiconductors, the contribution of electrons or holes to heat conduction remains constant at medium and high temperatures. Consequently, the parameters and are invariant. For the thermoelectric semiconductors under investigation, the thermal conductivity is W/cmK . According to theoretical analyses, the value of cm^{-1} in N-type or P-type semiconductors is consistent

$$\chi = 9.8 \cdot 10^{-3} + \frac{2k^2}{e^2} \cdot \sigma T \quad (5)$$

$$\sigma > 3.5 \cdot 10^{-3} \cdot \Omega^{-1} \text{ cm}^{-1} \text{ for}$$

$$\chi = 9.8 \cdot 10^{-3} + \frac{3k^2}{e^2} \cdot \sigma T \quad (6)$$

formulas can be used. Here $e = -1.6 \cdot 10^{-19} \text{ C}$ is the electron charge. Here, since all semiconductors used are $\sigma < 2500 \Omega^{-1} \text{ cm}^{-1}$, to calculate the thermal conductivity $\chi = 9.8 \cdot 10^{-3} + \frac{2k^2}{e^2} \cdot \sigma T$ or $\chi = 9.8 \cdot 10^{-3} + 0.7 \cdot 10^{-8} \sigma T$ formula was used.

Using directly measured α , σ and calculated χ values, the Z parameters characterizing the quality of semiconductors was calculated;

$$Z = \frac{\alpha^2 \sigma}{\chi} \quad (8)$$

For each semiconductor sample, the variations in the parameters σ , α , χ , and Z were graphically represented across the temperature range of 18°C to 100°C (291 K to 373 K). Additionally, the E_g parameter of the semiconductors was determined from the function. Consequently, utilizing the developed measurement system, five parameters (σ , α , χ , Z , and E_g) of P-type thermoelectric semiconductors, obtained through two distinct methods, were investigated and compared with both theoretical and experimental results available in the literature.

After measuring the relevant parameters of each sample at room temperature (18°C), the samples, along with the measuring instrument, were placed into the dry air device manufactured by SFL Advanced High Temperature & Environmental Systems. The temperature was then adjusted to 18°C, 30°C, and subsequently increased to 100°C environmental conditions were assessed, with the temperature being set and monitored via

a digital display. It was anticipated that the temperature would stabilize. Measurements were conducted once the temperature differential within the device had stabilized. It was noted that the stabilization period was approximately 20 to 30 minutes.

II. Results and discussion

In this study, a P-type semiconductor with a cylindrical shape, a radius of $r = 4 \text{ mm}$ (cross-sectional area $A = \pi r^2 = 3.14 \cdot 0.4^2 = 5 \cdot 10^{-3} \text{ cm}^2$), and a length of 3 cm was utilized. Pressed semiconductors of the same dimensions were configured as flat square prisms, with a cross-sectional area of $A = a^2 = 0.7 \text{ cm} \times 0.7 \text{ cm} = 0.49 \text{ cm}^2$. The voltage drop (V_x) across the semiconductors was measured between two fixed points at a distance determined by the electrodes of the measuring instrument, with a length of 1 cm assumed for the samples. The samples were divided into two groups, and each group was measured ten times at varying temperatures, with average values subsequently calculated. This approach minimized potential measurement errors and ensured the accuracy of the measurements. The tables and graphs depicting the average values of χ and Z , as well as the variations in E_g and Z values with respect to temperature, are presented separately in Figure 4 and Figure 5 for each sample. Additionally, the value of E_g is calculated and displayed in the tables.

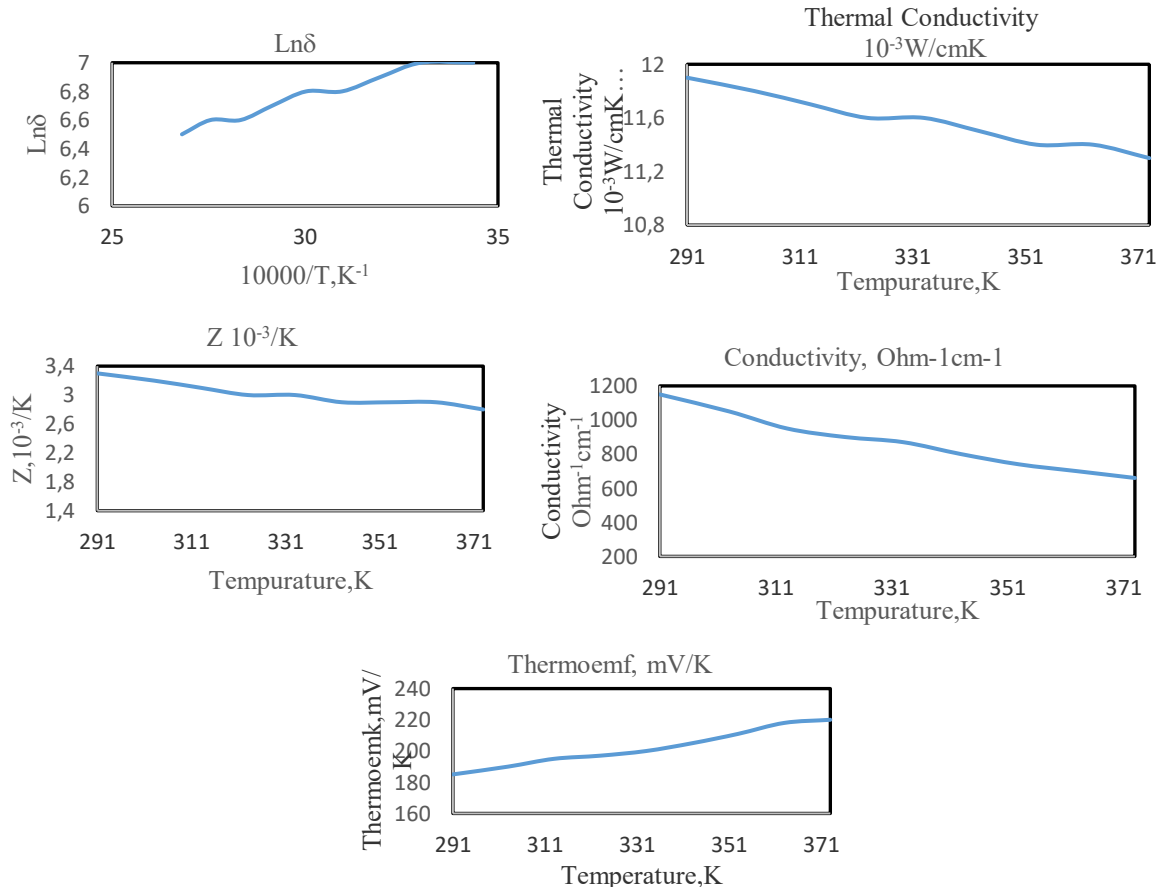


Fig. 4. Characteristics of P-type Pressed Semiconductor.

Table 1.

P -Type Pressed								
Temperature	10000/T,	Conductivity	Thermoe	Thermal	Z	Lnσ	Slope	Eg,
K	1/K	Ohm ⁻¹ cm ⁻¹	mk,	conductivity,	10 /K ⁻³			eV
			ΔV/K	10 ⁻³ W/cmK				
291	34.36	1150	185	11.9	3.3	7.0	0.07	0.13
303	33.00	1050	190	11.8	3.2	7.0		
313	31.95	950	195	11.7	3.1	6.9		
323	30.96	900	197	11.6	3.0	6.8		
333	30.03	870	200	11.6	3.0	6.8		
343	29.15	800	205	11.5	2.9	6.7		
353	28.33	740	211	11.4	2.9	6.6		
363	27.55	700	218	11.4	2.9	6.6		
373	26.81	660	220	11.3	2.8	6.5		

Table 2.

P-Type Melted								
Temperatur	10000/T,	Conducti	Thermoemf,	Thermal	Z	Lnσ	Slope	Eg ,
e	1/K	vity		conductivity,	10 /K ⁻³			eV
K		Ohm ⁻¹ cm ⁻¹	ΔV/K	10 ⁻³ W/cmK				
291	34.36	1350	192	12.3	4.0	7.2	0.07	0.11
303	33.00	1245	195	12.2	3.9	7.1		
313	31.95	1200	197	12.2	3.8	7.1		
323	30.96	1170	200	12.2	3.8	7.1		
333	30.03	1100	200	12.2	3.6	7.0		
343	29.15	980	210	12.0	3.6	6.9		
353	28.33	970	210	12.0	3.6	6.9		
363	27.55	880	215	11.8	3.4	6.8		
373	26.81	840	220	11.8	3.4	6.7		

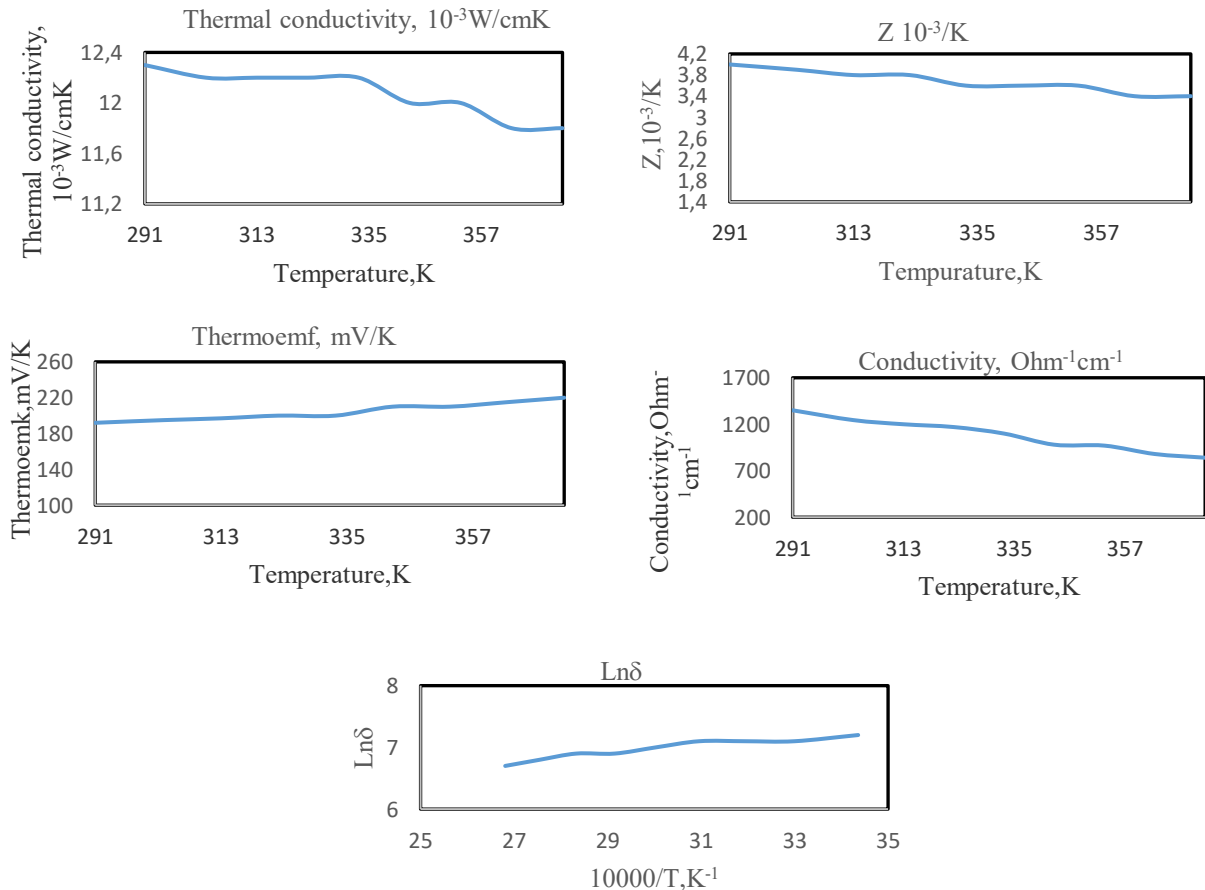


Fig. 5. Characteristics of P-type Fused Semiconductor.

Table 3.

Conductivity-Temperature Variation

Temperature, K	P-type melted (<i>Er</i>),	P-type pressed (<i>Pr</i>),
291	1350	1150
303	1245	1050
313	1200	950
323	1170	900
333	1100	870
343	980	800
353	970	740
363	880	700
373	840	660

Table 4.

Thermoemf - Temperature Variation

Temperature, K	P-type melted (<i>Er</i>),	P-type pressed (<i>Pr</i>),
291	192	185
303	195	190
313	197	195
323	200	197
333	200	200
343	210	205
353	210	211
363	215	218
373	220	220

Table 5.

Thermal Conductivity-Temperature Variation

Temperature, K	P-type melted (<i>Er</i>),	P-type pressed (<i>Pr</i>),
291	12.3	11.9
303	12.2	11.8
313	12.2	11.7
323	12.2	11.6
333	12.2	11.6
343	12.0	11.5
353	12.0	11.4
363	11.8	11.4
373	11.8	11.3

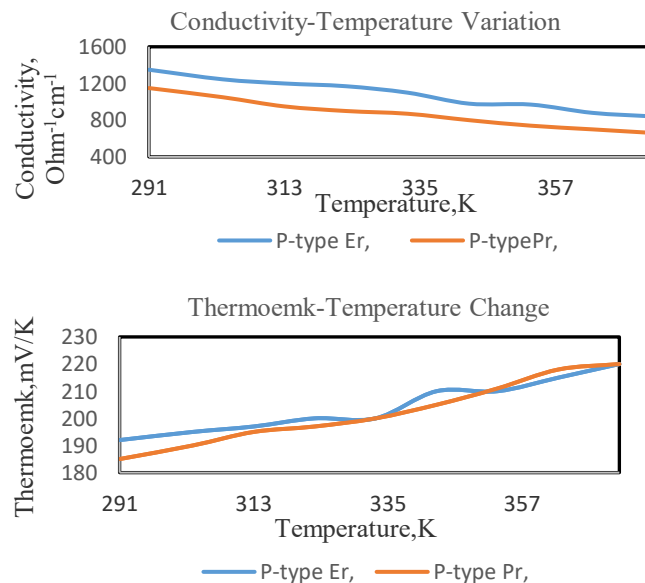
Table 6.

Z - Temperature Variation

Temperature, K	P-type melted (<i>Er</i>),	P-type pressed (<i>Pr</i>),
291	4	3.3
303	3.9	3.2
313	3.8	3.1
323	3.8	3
333	3.6	3
343	3.6	2.9
353	3.6	2.9
363	3.4	2.9
373	3.4	2.8

Figures 6 and 7 present the variation of the parameters α , c , and Z with respect to temperature for all samples, displayed separately as a single table and f-graph. The findings of this study indicate that the behavior of the parameters α , c , and Z across two groups, as a function of temperature, aligns with the experimental results reported by researchers such as A.F. Ioffe, T. Caillat, C. Lahalle-Gravier, and B. Lendir [15-21] for analogous thermoelectric materials. Furthermore, the calculated E_g values in this study ranged from 0.11 eV to 0.13 eV for type P, which is consistent with the literature range of 0.10 eV to 0.12 eV. Consequently, the results obtained demonstrate a relative error of 10% when compared to those found by international researchers. These findings substantiate the project's success, both theoretically and experimentally.

Upon examining the groups independently, it is evident that all parameters, particularly Z , of the melted crystals exceed those of the pressed semiconductors within the temperature range of 18°C to 100°C. Consequently, it appears more suitable to employ semiconductors produced via the region melting method (THM) in the fabrication of thermoelectric modules. Given that the coolers or generators constructed from these modules are anticipated to function across diverse climates and temperatures, the utilization of melted semiconductors is likely to be more cost-effective.

**Fig. 6.** Change in The Properties of Different Semiconductors

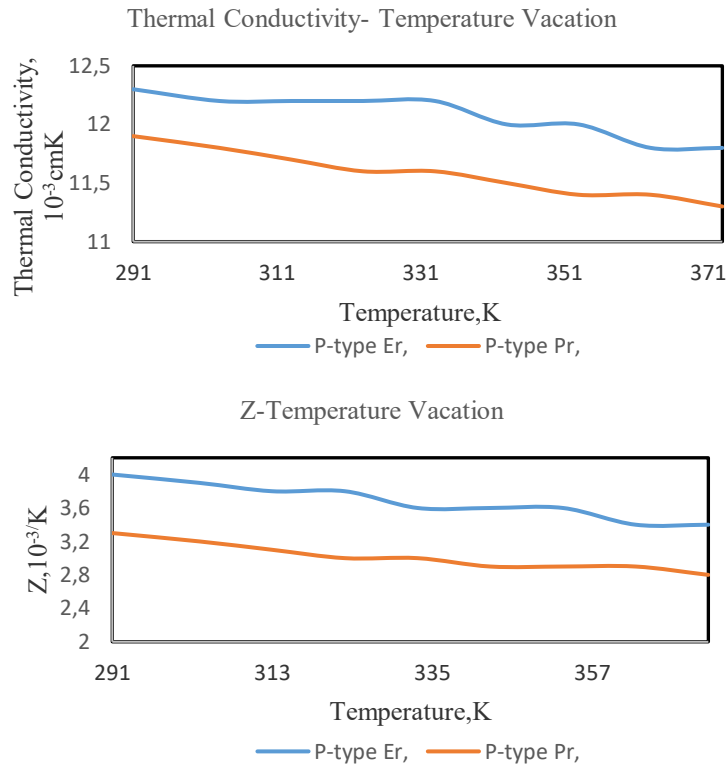


Fig. 7. Change in The Properties of Different Semiconductors

Conclusion

Upon evaluating the results based on the type of semiconductors, it is observed that P-type melted semiconductors exhibit smaller and larger α and Z values compared to P-type pressed semiconductors. The study found that the Z value, which characterizes the thermoelectric quality of the semiconductor, decreased by 40% to 20% in P-type melted semiconductors and by 15% in P-type pressed semiconductors within the temperature range of 18°C to 100°C. The theoretical and experimental findings presented in this article are of significant

importance to solid-state physics, particularly in the investigation of the thermoelectric properties of semiconductors. The developed measurement system is demonstrated to be applicable for assessing the parameters of various semiconductors at both high and low temperatures, as necessary. In light of the current state of semiconductor technology in Turkey, this study is poised to not only advance semiconductor physics within the country but also serve as a milestone in this field.

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Гюнай Омер

Дослідження термоелектричних параметрів напівпровідників р- Bi_2Te_3 у температурному діапазоні 291-373 К

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Дослідження термоелектричних властивостей напівпровідників має першорядне значення в сучасних наукових дослідженнях, особливо щодо прямого перетворення теплової енергії в електричну і навпаки. Ця галузь дослідження є фундаментальним компонентом фізики напівпровідників і значною мірою сприяє розвитку суміжних наукових дисциплін. Термоелектричні напівпровідники широко використовуються, і очікується, що їх потенційне застосування розшириться в найближчому майбутньому. Ці напівпровідники є важливими для різноманітних систем, включаючи космічні технології та побутову техніку. Дослідження в цій галузі постійно розвиваються головним чином завдяки швидкій передачі фундаментальних знань у промисловість, що призводить до значних економічних вигод. Отже, значна частина досліджень зосереджена на термоелектричних властивостях напівпровідників та розвитку термоелектричних технологій. У цьому дослідженні ми розглянули термоелектричні параметри напівпровідників р-типу Bi_2Te_3 у діапазоні температур 291–373 К.

Детально розглядається та порівнюється поведінка термоелектрорушійної сили (термоЕРС), електропровідності, теплопровідності та параметра Z при підвищених температурах двох типів напівпровідників р-типу, кожен із яких синтезовано за допомогою різних методів, з теоретичними прогнозами. Крім того, ширина забороненої зони напівпровідників розраховується на основі температурно-залежної зміни електропровідності та згодом порівнюється з теоретичними значеннями. Отримані результати показують, що експериментальні результати узгоджуються з теоретичними даними, доступними в літературі, в межах встановлених похибок.

Ключові слова: напівпровідники р- Bi_2Te_3 , термоелектричні параметри.