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# PART I: WHAT MAKES A GOOD THERMOELECTRIC

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#### Abstract

Starting from spectroscopy pure materials, a monocrystal sample of p type,  $Bi_2Te_{2.8}Se_{0.2}$ , was synthesized by the Bridgman method at the Serbian Academy of Sciences and Arts in Belgrade (SANU). The transport properties of single crystals were investigated. Transport properties have shown that with current increasing, mobility and Hall coefficient increase. Positive values of the Hall coefficient confirm that the material is of the p type with a high concentration of charge carriers,  $n_b = 10^{18}$  cm<sup>-3</sup>. **Keywords:** Bridgman technique, Hall and Van der Pauw method, doping

#### **3. RESULTS AND DISCUSSION**

The calculated data from the measurement results of the transport quantities for sample 6/4 ( $_{\perp}$ ) with a Schottky diode at room temperature (25 ° C) and magnetic induction of the permanent magnet B = 0.370 T are given in Table 1 and Table 2. Measurements were performed at currents of 0.1 and 0.5 mA.

# **1 INTRODUCTION**

Based on the thermoelectric effect, waste thermal energy generated as a by-product of industrial processes can be converted into electricity. Known as "Peltier", "Seebeck" or "Thomson" effect, the thermoelectric effect is seen in semiconductor devices that generate voltage when a different temperature is present on each side, or create a temperature difference between the two sides when the voltage is on the device. The thermoelectric materials development is conditioned by finding materials with a high figure of merit. The parameter that evaluates the quality of thermoelectric materials, the Figure of merit (Z), is determined by the dimensionless quantity, ZT, [1,2] which is defined as:

$$ZT = \frac{\alpha^2 \cdot \sigma \cdot T}{k} = \frac{\alpha^2 \cdot T}{k \cdot \rho} = \frac{\alpha^2 \cdot T}{(k_e + k_l) \cdot \rho}$$
(1)

where:  $\alpha$  - Sebek coefficient,  $\sigma$  - electrical conductivity, k - thermal conductivity, T - absolute temperature,  $\rho$  - electrical resistance.

Thermal conductivity has two components: electronic conductivity,  $k_e$  and lattice conductivity,  $k_l$ . The ratio  $\alpha^2/\rho$  is defined as the power factor and determines the electrical properties. The combination of material properties required for thermoelectric materials to have quality and usable properties is also a challenge for scientists. The basic foundation in the research of thermoelectric materials is to satisfy properties that are in contradiction with each other, as can be seen from Equation 1. In order to maximize the quality factor (obtaining the highest possible thermal current, which is the absolute value of the Sebek coefficient), it must have high electrical conductivity and low thermal conductivity. In order to get as much thermal current as possible, we need only one type of charge carrier. Semiconductors are materials that are relatively easy to change the type of charge carrier (electrons and holes).

Best bulk thermoelectric materials at room temperature are  $Bi_2Te_3/Sb_2Te_3$ .

If doping is increased, the electrical conductivity increases but the Seebeck coefficient is reduced for almost all typical thermoelectric materials. Namely low gap semiconductors, almost all typical thermoelectric materials best compromise and still highly doped semiconductors are in charge concentrations range of 10<sup>18</sup>-10<sup>19</sup>cm<sup>3</sup> (Figure 1).

Table 1. Results for sample 6/4 ( $_{\perp}$ ) at a current of 0.1 mA

Measured size	Symbol	Result	Measuerment unit
Bulk carrier concentration	n <sub>b</sub>	5.511x10 <sup>18</sup>	/cm <sup>3</sup>
Mobility	μ	7.237x10 <sup>1</sup>	cm²/Vs
Specific resistivity	ρ	1.565x10 <sup>-2</sup>	Ωcm
Average Hall Coefficient	R <sub>H</sub>	1.133x10 <sup>0</sup>	cm <sup>3</sup> /C
A-C Cross Hall Coefficient	R <sub>H1</sub>	-1.784x10 <sup>0</sup>	cm <sup>3</sup> /C
B-D Cross Hall Coefficient	R <sub>H2</sub>	4.050x10 <sup>0</sup>	cm <sup>3</sup> /C
Sheet carrier concentration	n <sub>s</sub>	9.920x10 <sup>17</sup>	/cm <sup>2</sup>
Specific conductivity	σ	6.389x10 <sup>1</sup>	1/Ωcm
Magneto resistance	ΔR	8.315x10 <sup>-3</sup>	Ω
Vertical/Horizontal ratio of resistivity	α	4.807x10 <sup>-1</sup>	

#### **Table 2.** Results for sample 6/4 ( $_{\perp}$ ) at a current of 0.5 mA

Measured size	Symbol	Result	Measuerment unit
Bulk concentration	n <sub>b</sub>	4.150x10 <sup>18</sup>	/cm <sup>3</sup>
Mobility	μ	1.594x10 <sup>2</sup>	cm²/Vs
Specific resistivity	ρ	9.435x10 <sup>-3</sup>	Ωcm
Average Hall Coefficient	R <sub>H</sub>	1.504x10 <sup>0</sup>	cm <sup>3</sup> /C
A-C Cross Hall Coefficient	R <sub>H1</sub>	1.173x10 <sup>0</sup>	cm <sup>3</sup> /C
B-D Cross Hall Coefficient	R <sub>H2</sub>	1.836x10 <sup>0</sup>	cm <sup>3</sup> /C
Sheet concentration	n <sub>s</sub>	7.469x10 <sup>17</sup>	/cm <sup>2</sup>
Specific conductivity	σ	1.060x10 <sup>2</sup>	1/Ωcm
Magneto resistance	ΔR	2.968x10 <sup>-3</sup>	Ω



The Thermoelectric Figure of Merit (ZT)

Figure 1. Best compromise of thermoelectric [3]

Best compromise of thermoelectric is marked with a red rectangle on the Figure 1. With special techniques and advances in modern material synthesis, especially in nano materials, a new time for complex thermoelectric materials is approaching.

The significant contribution of our research is reflected primarily in the domain of materials science [4,5,6], especially in the field of thermoelectric materials. Successful synthesis of p type single crystal  $Bi_2Te_{2.8}Se_{0.2}$  by the Bridgman process obtained at the Serbian Academy of Sciences and Arts (SANU) in Belgrade was performed. A significant scientific contribution has been made in the application field of bismuth telluride as a thermoelectric material and selenium as its dopant. In this way, the conducted research enriched the set of data relevant for further research and for possible practical application.

## 2. EXPERIMENTAL

Vertical/Horizontal ratio of resistivity	α	1.079x10 <sup>-1</sup>	

Mobility increases with current increasing. The Hall coefficient values are positive. This indicates that the samples are of p type and that the charge carriers majority are holes. That the samples are of p type was also confirmed by the hot point method. The mobility of most charge carriers decreases with increasing current, which indicates that the temperature of the samples increases, which affects on the mobility. For our sample the mobility value is increase from  $\mu = 7.237 \times 10^1 \text{ cm}^2/\text{Vs}$  at current intensity of 0.1 mA to  $\mu = 1.594 \times 10^2 \text{ cm}^2/\text{Vs}$  at current intensity of 0.5 mA.

#### 4. CONCLUSION

This paper was the result of the selenium doped bismuth telluride monocrystal semiconductor compound properties testing. Hall's and Van der Pauw's methods were used for material characterization.

The electrical properties of this crystal were measured and the mobility, concentration of the charge carriers majority and Hall coefficient were observed. On the basis of the Hall coefficient, it was determined that the majority carriers are holes in the monocrystal. The measured holes mobility was less than the holes mobility in pure bismuth telluride.

The results of these studies show that the selenium doped bismuth and tellurium monocrystal was successfully synthesized by the Bridgman method, and significantly complement existing bismuth telluride single crystals knowledge.

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The sample tested by the Hall and Van der Pauw method was cut from the ingot normally to the crystallization direction ( $_{\perp}$ ). In the following, these sample will be referred to as 6/4 ( $_{\perp}$ ). Before the measurement starting, the sample was prepared to be in the form of thin disc. The samples on which the measurements were performed had a uniform thickness of 1.8 mm (Table). Sample did not have any irregularities on them. All measurements were carried out at room temperature (T =300 K). The source of magnetic field applied perpendicular to the Hall element was a permanent magnet of 0.37 T. Hall Effect measurements were done to obtain transport properties.

For resistance measure, voltage and current contacts were attached to 4 fixed contact terminals located at the sample ends and at different current intensities. Schottky contacts were used for tests performed at room temperature. The change of transport and electrical parameters with increasing current intensity was also monitored.

## REFERENCES

- [1] H. J., Goldsmid, R.W. Douglas, Br. J. Appl. Phys. 5 (1954) 386 390.
- [2] Tritt, T. M. Ed. Semiconductors and Semimetals, Recent Trends in Thermoelectric Materials
  - Research: Part One to Three (Academic, San Diego, CA, 69 to 71, 2001, p. 352.

[3] <u>https://www.fzu.cz/~knizek/pdf/ThermoelectricMaterials.pdf</u>

- [4] E. Požega, Sinteza i karakterizacija monokristala bizmuta i telura dopiranih selenom, cirkonijumom i arsenom (Doktorska disretacija), Univerzitet u Beogradu, Tehnički fakultet u Boru, Bor, 2018, p. 82.
- [5] E. Požega, S. Ivanov, Z. Stević, Lj. Karanović, R. Tomanec, L. Gomidželović, A. Kostov, Trans. Nonferrous Met. Soc. China 25 (2015) 3279 - 3285
- [6] E. Požega, P. Nikolić, S. Bernik, L. Gomidželović, N. Labus, M. Radovanović, S. Marjanović, Synthesis and investigation of BiSbTeSe single crystal doped with Zr produced using Bridgman method, Revista de Metalurgia 53 (3) (2017)