SYNTHESIS AND THERMOELECTRIC PROPERTIES OF SnSe BASED ALLOYS

[1]František MIHOK, [2]Karel SAKSL

[1]*Institute of Material Research of Slovak Academy of Sciences, Košice, Slovakia, EU, fmihok@saske.sk*

[2]*Faculty of Materials Metallurgy and Recycling, Technical University in Košice, Košice, Slovakia, EU*

https://doi.org/10.37904/metal.2023.4665

Abstract

Thermoelectric generators represent a unique way for recovering waste heat. Modules are made from specialized materials with thermoelectric properties. They represent cost-effective, simple, easy to maintain and reversible solution to handling any wasteful energy in the form of heat. Modules consist of many N and P semiconductor pairs connected in a series. These devices are very flexible and can be used as heaters, coolers or generators based on Peltier's and Seebeck's effects. With careful material selection it is possible to enforce or reduce the desired effect. The main disadvantage of thermoelectric modules is their low conversion efficiency. However, novel materials with significantly improved efficiency sparked renewed interest in these materials from scientific and commercial sectors. New and reliable procedure to measure thermoelectric properties, mainly Seebeck's coefficient and electrical conductivity, is introduced in this submission. Our solution is cost-effective and easily reproducible because it is made from readily available and 3D printed parts. Our method uses a significant amount of calibration materials to achieve accuracy in wide range values for room temperature measurements. Materials based on SnSe alloy represent an ideal material for constructing thermoelectric modules and are characterized in this submission. Even low amounts of other elements used as dopants can significantly change physical properties of these alloys. It is even possible to get N and P type semiconductors using the same dopant with varying concentration. Both materials therefore have similar mechanical properties in a wide temperature range. Efficiency of these materials is adequate for typical thermoelectric materials.

Keywords: Seebeck's coefficient, electrical conductivity, thermoelectric generator, semiconductor

1. INTRODUCTION

With a growing population, its energy demands are gradually increasing. At the same time, the energy consumption of modern society is rising. Renewable energy sources and efficient energy management are necessary to meet the energy demands without further damaging our planet's environment. Thermoelectric materials represent a significant component for harnessing surplus thermal energy in manufacturing, transportation, and other processes. Thermoelectric generators made from these materials can be installed almost anywhere a temperature gradient exists. However, the efficiency of thermoelectric generators currently ranges from around 5% to 20%. Additionally, high-efficiency devices often rely on expensive, scarce, and toxic metals. Therefore, it is necessary for material research in this field to continue evolving and searching for new, more efficient, and cost-effective materials. Materials capable of functioning within broader temperature gradients will also enable more effective operation of new processes. The resulting thermoelectric devices are very easy to operate and maintain.

2. THEORY

The thermoelectric effect was first described by Thomas Johann Seebeck in the 19th century. The Seebeck's coefficient(α), or thermopower, describes the relationship between a temperature gradient(T_h - T_c) and the resulting electrical potential(V).

$$V = \alpha(T_h - T_c) \tag{1}$$

A few years later, J.C.A. Peltier observed that when an electric current passed through a system consisting of two dissimilar metals, one side would heat up while the other side would cool down. The relationship between these two observations was later explained and comprehensively described by Lord Kelvin. Currently available thermoelectric materials achieve only low conversion efficiencies: 5-20% (solar cells ~40%). The efficiency of thermoelectric materials can be defined using the dimensionless figure of merit, ZT, according to the equation:

$$ZT = \frac{\alpha^2\sigma}{\kappa}T \tag{2}$$

From this equation, we can determine that an ideal thermoelectric material has high values of the Seebeck's coefficient(α) and electrical conductivity(σ), and low values of thermal conductivity(κ). Typically, these conditions are met best by semiconductors.

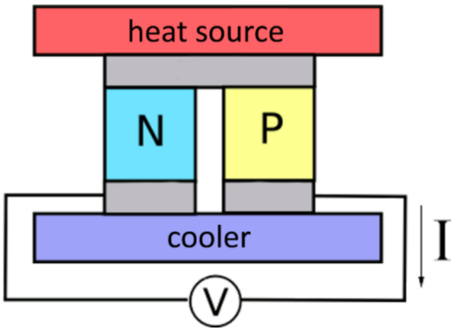

Figure 1 Working principle of thermoelectric cell

A typical thermoelectric device consists of two semiconductors: one N-type and the other being P-type. These semiconductors are connected in series (**Figure 1**). When a temperature gradient is applied to the device, electrons move between the semiconductors, resulting in the generation of an electric current.

The typical potential difference generated in a single N-P junction ranges from millivolts to microvolts. Therefore, commercial thermoelectric cells require dozens to hundreds of pairs to obtain a common working potential of 3.33, 5 or 12 volts (**Figure 2**).

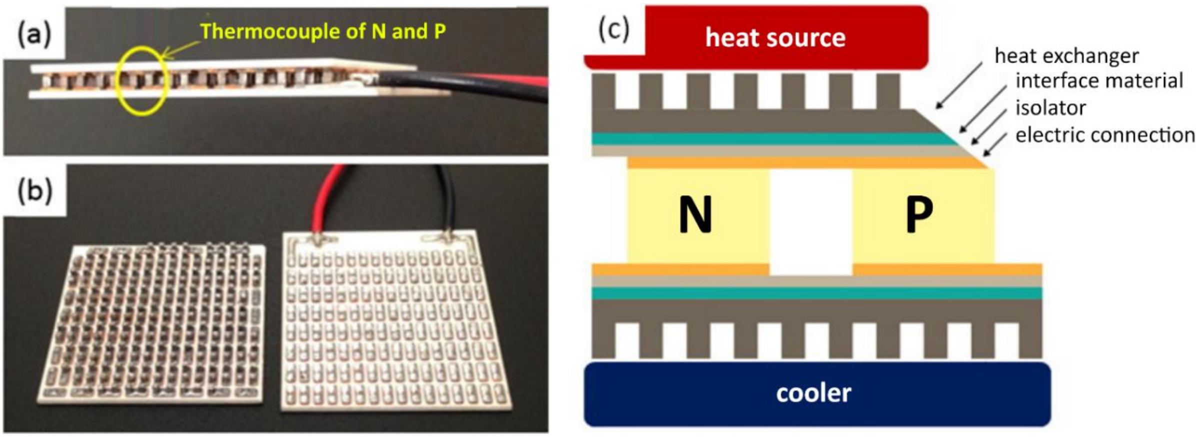

Figure 2 Scheme of commercial thermoelectric module; a) thermocouple of N and P; b) disassembled module; c) scheme of commercial thermoelectric device [2]

Thermoelectric materials have been used for many years in Radioisotope Thermoelectric Generators (RTGs), which are the power source of various space probes. Their simplicity and maintenance-free operation make them ideal for this application. Automotive manufacturers are experimenting with the addition of thermoelectric generators to the exhaust systems of cars. Small amounts of electrical energy can also be generated from the temperature gradient between the human body and the surroundings, which is sufficient to power simple sensor devices or watches. Solar energy can also be used as a heat source for eco-friendly electricity generation. In addition to thermal and electrical conversions, thermoelectrics can be used for precise temperature measurement [1].

3. EXPERIMENTAL

As deduced from **Equation 2**, the Seebeck's coefficient and electrical conductivity are essential parameters for the qualitative evaluation of a thermoelectric material. When measuring the Seebeck's coefficient, the material needs to be connected in an electrical circuit at two, as far away from each other as possible, points. For electrical conductivity measurements, connection at four points is required for higher accuracy. This is not a problem when using materials in the form of rods. However, many thermoelectric materials need to be prepared using various pressing methods, resulting in disk-shaped materials. These disks can be cut into rod-like shapes, but this process is time-consuming and often unsuitable due to the brittleness of many thermoelectric materials. Thermoelectric materials are also commonly prepared in the form of thin films, which require special methods with precise temperature control, such as TPS (Transient Plane Source) "hot disk" technique. This method is typically available only in commercial equipment and not easily replicable.

J. de Boor and colleagues proposed a system for measuring electrical conductivity that can also be used with disk-shaped samples. However, to determine the actual conductivity ρ of the material from the measured conductivity *R*, a geometric correction factor (*GCF*) must be taken into account:

$$\rho = R \cdot GCF \tag{3}$$

In case rod or wires are used we can assume *GCF* to be:

$$GCF_{rod} = \frac{A}{s} \tag{4}$$

where *A* stands for cross-section area and ***s*** is the distance between measuring points. When disk are used the equation is as follows:

$$\frac{GCF}{t} = \frac{1+A_1 \ln D + A_2 \ln s}{A_3 + A_4 \ln D + A_5 \ln s} \tag{5}$$

where ***t*** strands for disk thickness, *D* disk diameter, and $A_{1\text{-}5}$ are parameters. The ideal parameters for disk with diameter 10 – 25.4 mm are the following: A_1 = 0.7403; A_2 = 1.0390; A_3 = 1.1228; A_4 = -0.2955; A_5 = 0.1622 [3].

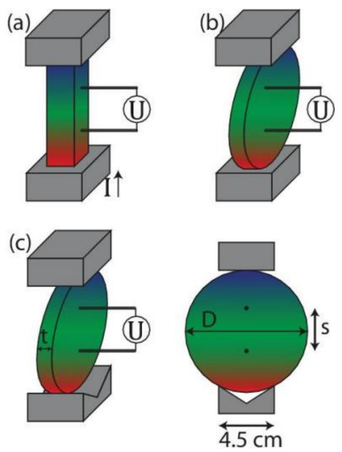

Figure 3 Scheme of system for measuring electrical conductivity based on the work of J. de Boor; a) measured sample – rod; b) c) measured sample – disk [3]

The system proposed by J. de Boor (**Figure 3**) being our base, we have prepared our measuring system. The entire system was designed using CAD software. CAD models were produced using a 3D printer, and standard metric hardware was used to assemble the modules. The system was designed to be modular, allowing for easy customization. One advantage of this modular approach is the ability to directly measure the Seebeck's coefficient in addition to electrical conductivity. Different measurement probes can be attached to the sample in the upper and lower positions and on the circular surfaces from both sides. Thanks to the modularity of the system, various heat sources such as soldering iron tips, thermoelectric generators, power resistors, and other heating elements can be used for the heating required in Seebeck's coefficient measurements. In addition to disk-shaped samples, the system can also work with rod-shaped samples, which are the most typical form of thermoelectric materials. Switching between the measured quantities requires making several changes to the system since the sample mounting is different. The system allows for more precise measurements over a longer period and with greater temperature control. The overall modularity makes it easy to incorporate new shapes of measured samples while saving on the total amount of material required. The main drawback of the system is the material used for production. PLA-type plastic undergoes drastic changes in mechanical properties at around 65 °C. Therefore, the system cannot be used for measurements at surrounding temperatures higher than 55 °C.

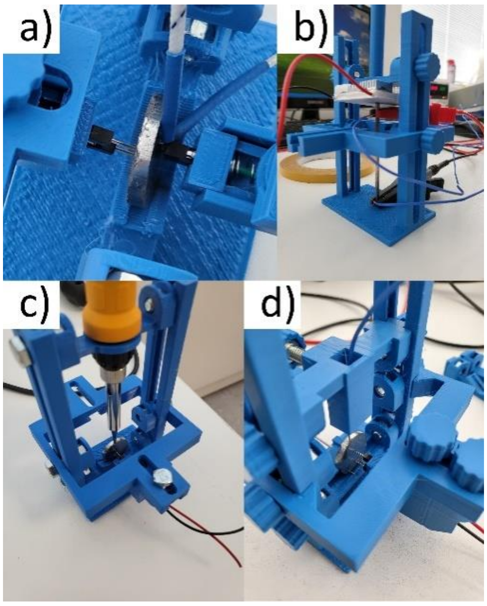

Figure 4 3D printed apparatus for measuring thermoelectric parameters; a) Seebeck's coefficient mode; b) measuring rods; c) soldering iron as heat source; d) electrical conductivity mode

4. RESULTS AND DISCUSSION

Based on the knowledge and experience gained during measurements on the apparatus, we have prepared an improved version called THEMA (THermoElectric Measuring Apparatus). This version has reduced the overall modularity of the system in favor of a more stable sample mounting and simplified manipulation and operation. In this version, cooling was also directly incorporated in addition to heating. This proved to be necessary for measurement stability and repeatability. The new version allows for much easier manipulation of the samples while still accommodating samples of various shapes. This is facilitated by a new type of sample holder, which also collects data about the potential and temperature (**Figure 5**). Temperature is traditionally measured using K-type thermocouples, although other types of thermocouples, thermistors, or thermal imaging methods can also be used, similar to the original apparatus. Temperature data collection is done using a data logger (Pico Technology TC-08, UK), while potential data is recorded using a multimeter (Keithley 2100, USA). For monitoring, data integration, and initial data analysis, we have developed our own Python program.

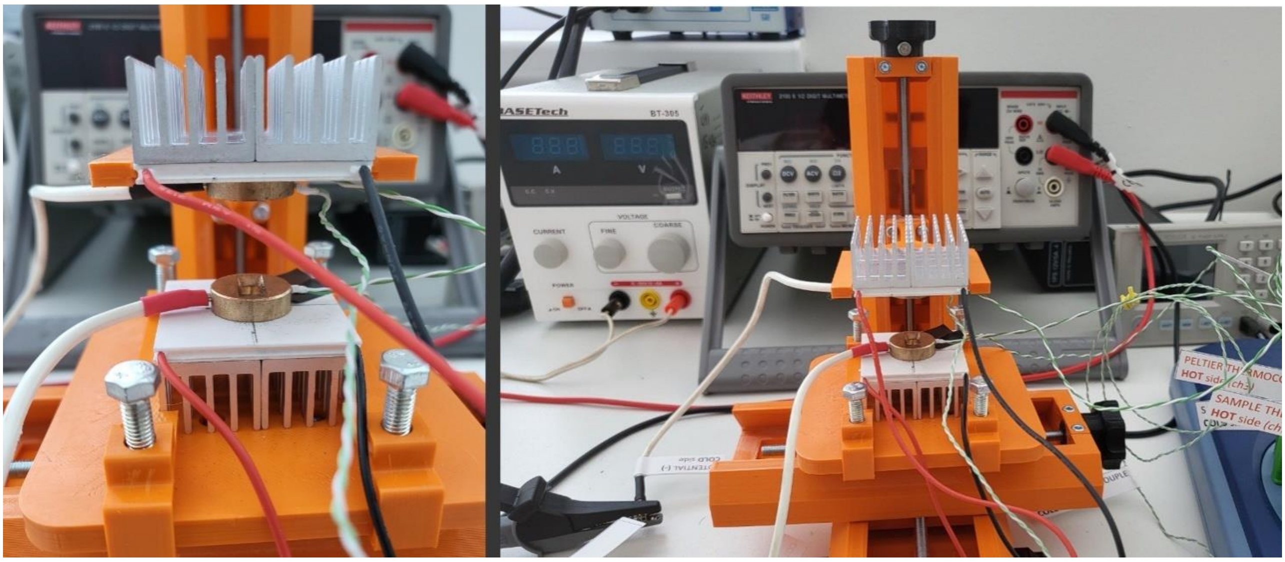

Figure 5 Apparatus THEMA; sample holders visible on the right

The calibration of the entire apparatus was performed using materials with known Seebeck's coefficient values (**Figure 6**). Initially, we prepared these materials ourselves, but we observed high deviations in some cases. After acquiring highly pure materials in disk form, we recalibrated the apparatus and obtained consistent results. Based on this, we questioned the accuracy of tabulated values for certain materials, which may exist in different forms depending on the preparation method, such as silicon. Materials with weak electrical conductivity proved to be problematic for measuring the Seebeck's coefficient due to limitations of our multimeter. For some poorly conductive materials, we were able to measure the coefficient by applying an external voltage to the system. However, selenium and molybdenum remained unmeasurable even with this approach. When measuring the investigated materials, correction is applied to the data based on measurements of reference materials. This linear correction accounts for the specific characteristics of our measurement method and our apparatus, including transition resistances, thermal capacities of the holders, heat dissipation through the probes, and other factors.

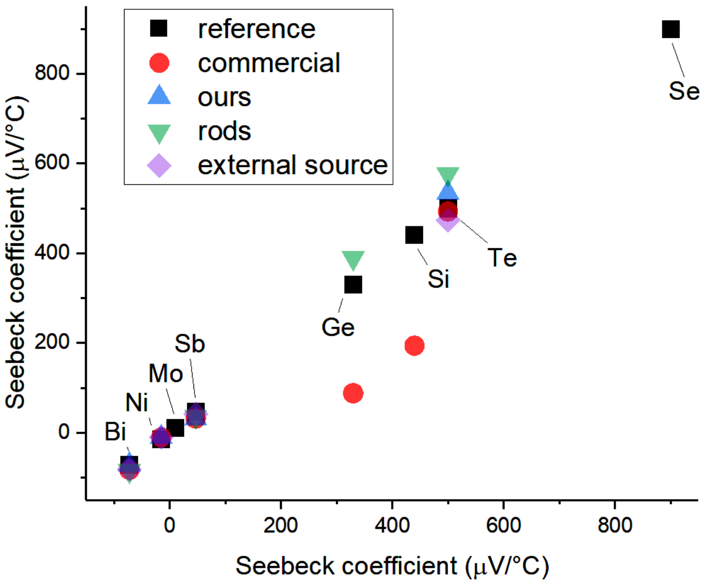

Figure 6 Comparison of reference and THEMA determined values for samples: disks (commercial, ours); rods and with external power source

We chose SnSe alloy as the initial thermoelectric material for our investigation. It was found that low amounts of Sb dopant change the alloy from its original P-type to an N-type semiconductor[4]. Based on this fact, we decided to prepare these alloys($Sn_{1-X}Sb_XSe_1$). The alloys were prepared by mixing pure elements in the desired proportions and melting them at 500°C for 12 hours. The obtained melts were crushed, and using Spark Plasma Sintering (SPS), disks with a diameter of 20 mm were pressed. We attempted to measure the Seebeck's coefficients on these disks, but we obtained values that differed by orders of magnitude. However, the polarities of the materials were the same as in the original article. This prompted us to develop our own advanced procedure for measuring thermoelectric properties. Using the latest version of the THEMA apparatus, we obtained Seebeck's coefficient values in the correct range, but the polarity on the N-type samples changed to P-type. This can be seen in **Figure 7**. Synthesized samples follow the reference pattern but even the sample with 4.6 wt% Sb that is in the supposed N region behaved as a P type albeit a weak one. We attribute this mainly to the different sample structures. Reference materials were grown monocrystals while ours are polycrystalsas a result of modified synthesis method which is simpler and more time efficient while still providing samples with Seebeck's coefficient in the same range.

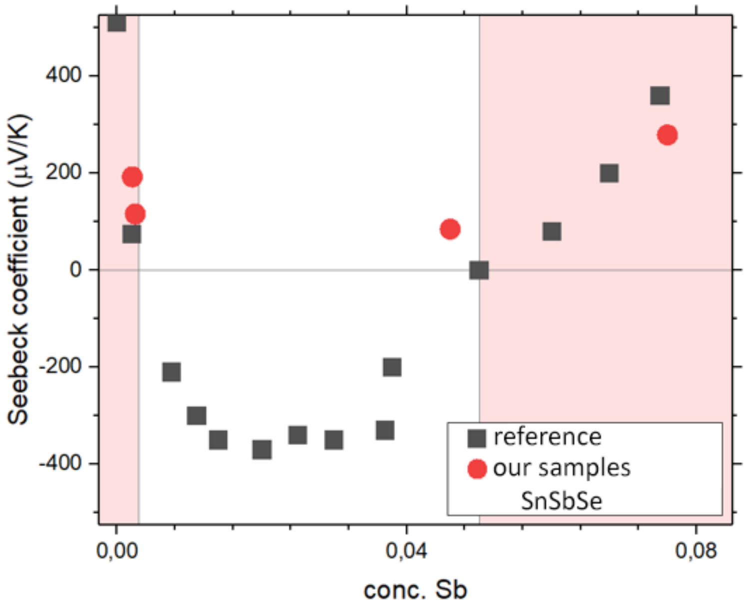

Figure 7 Comparison of Seebeck's coefficient based on Sb amount ofour samples with reference values from work of Yamamoto et al. [4]; region highlighted in red is P type zone and white region is N type zone

5. CONCLUSION

The systems described in this work enable efficient, fast, and accurate determination of the Seebeck's coefficient and electrical conductivity. Both systems are cost-effective and material-efficient because of 3D printing. Both apparatuses can operate up to temperatures of ~100°C, and with the use of technical plastics, temperatures of ~150°C can be achieved comfortably. We verified the measurement accuracy using 8 reference materials, although due to technical limitations, we were able to reliably work with only 4 of them. Other apparatuses described in the literature commonly use only 1 material, typically Cu, with a very low Seebeck's coefficient value, for calibration. Our calibration method covers a wide range of Seebeck's coefficients in both positive and negative regions. After designing a suitable methodology for reliable measurement of low-conductivity materials, modifications can be made to incorporate these procedures into the apparatus. In other respects, we consider the apparatus to be complete and reliable.

Thanks to the ability to measure the properties of thermoelectric materials, we could once again focus on the preparation of thermoelectric materials. The prepared materials based on doped SnSe alloy appeared to be an ideal material for the preparation of thermoelectric modules according to initial measurements. However, after measuring them on the THEMA apparatus, it was revealed that the expected N-type semiconductors behaved as weak P-type semiconductors. Doping the alloy with Bi resulted in confirming N-type semiconductor in a similar region when compared to Sb doping ratio. Our main objective for future work is looking for another dopants to achieve a higher efficiency N-type semiconductor and to increase the values of the Seebeck's coefficient and electrical conductivity of synthesized materials without significantly increasing their cost.

ACKNOWLEDGEMENTS

This work was financially supported by project VEGA 2/0039/22 and APVV project SK-PL-21-0022.

REFERENCES

[1] FEJERČÁK, M. *Development and research of novel thermoelectric materials*. Dissertation thesis. Pavol Jozef Šafárik University in Košice, Košice, 2019.

[2] LEBLANC, S. Thermoelectric generators: Linking material properties and systems engineering for waste heat recovery applications. *Sustainable Materials and Technologies*. [online]. Dec. 2014, vol. 1-2, pp. 26-35. Available from: https://doi.org/10.1016/j.susmat.2014.11.002.

[3] DE BOOR, J., ZABROCKI, K., FROHRING, J., MÜLLER, E. Electrical conductivity measurements on disk-shaped samples. *Review of Scientific Instruments*. [online]. Jul. 2014, vol. 85, no. 7, p. 075104. Available from: https://doi.org/10.1063/1.4886812.

[4] YAMAMOTO, C. *et al.* Double charge polarity switching in Sb-doped SnSe with switchable substitution sites. *Adv. Funct. Mater.* [online]. Feb. 2021, vol. 31, no. 8, p. 2008092. Available from: https://doi.org/10.1002/adfm.202008092.