

L.I. Anatyshuk, *Acad. NAS Ukraine*^{1,2}

M.V. Havryliuk,¹

V.V. Lysko, *Cand.Sc (Phys-Math)*^{1,2}

¹Institute of Thermoelectricity of the NAS and MES of Ukraine,
1, Nauky str., Chernivtsi, 58029, Ukraine;

²Yuriy Fedkovych Chernivtsi National University,
2, Kotsiubynsky str., Chernivtsi, 58012, Ukraine

e-mail: anatysh@gmail.com

EQUIPMENT FOR DETERMINING THERMOELECTRIC PROPERTIES OF MATERIAL BY MODIFIED HARMAN'S METHOD

The results of the development of equipment for determining the thermoelectric properties of materials – electrical conductivity, thermal conductivity, the Seebeck coefficient and thermoelectric figure of merit in the temperature range of 30 – 500 °C using modified Harman's method are presented. Measurement errors are estimated and reduction methods are described. The results of measurements of material samples based on Bi_2Te_3 obtained using the described equipment are shown.

Key words: Harman's method, thermoelectric figure, absolute method.

Introduction

General characterization of the problem. Thermoelectric energy converters find more and more applications in various fields of science and technology, in particular in medicine, metrology, space and military technology, electronics, household and computer technology, etc.

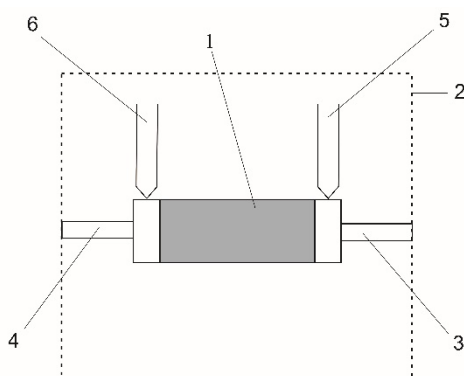
Recent years have seen increasing interest in the creation of thermoelectric generators, which are used for the conversion of heat from industry and internal combustion engines, which opens up new opportunities for "green" technologies. Special attention is drawn to the creation of TEGs on vehicles, primarily cars. The use of such thermoelectric generators allows you to get a fuel economy of 5 – 10 %. Such works are being intensively developed in the USA, Japan, and Western Europe. In doing so, the typical operating temperature range for thermoelectric energy converters is 50 – 300 °C. For this interval, materials based on *Bi-Te* are most suitable, and an additional improvement in efficiency can be achieved by using materials with programmable heterogeneity, namely functionally graded materials.

One of the main factors affecting the quality of thermoelectric energy converters is the figure of merit of thermoelectric materials they are made of. Advances in the technology of obtaining materials are directly related to the accuracy of determining their parameters, since further improvement of the quality of materials is possible only if a clear connection is established between the technological actions during the obtaining of the material and its properties.

Analysis of the literature. The most attractive for the creation of high-precision measuring equipment for determining the thermoelectric properties of materials are the use of the absolute method and Harman's method. The main disadvantages of the absolute method [1, 2] are the complexity of the design of the sample holder, and, therefore, the process of setting up the sample for measurement, and

the need for a long time to reach stationary mode by the system, which makes the measurement process quite long. In addition, in order to increase the accuracy of the measurements, the samples used in the measurements are quite large – with a diameter of about 6 – 8 mm and a length of 8 – 15 mm, which, when examining a large number of samples, leads to significant losses of material, in addition, reduces the speed of reaching stationary mode by the system. Harman's method is devoid of such shortcomings of the absolute method [3, 4]. Much smaller samples are used to determine thermoelectric properties by this method, and the structure of the sample holder itself is simple and convenient to use.

The essence of Harman's method is as follows. A sample of thermoelectric material is fixed in the thermostat on two current leads (Fig. 1).



*Fig. 1. Schematic of Harman's method. 1 – sample, 2 – thermostat,
 3, 4 – current leads, 5, 6 – thermocouples.*

The values of the thermoelectric figure of merit, as well as the thermal conductivity, electrical conductivity, and the Seebeck coefficient, are determined by the resistances of the sample and the voltage drops on the sample, measured when passing direct and alternating current therethrough:

$$Z = \frac{1}{T_{av}} \left(\frac{R_{\approx}}{R_{=}} - 1 \right) \left(1 + \sum_i \gamma_i \right),$$

$$\alpha = \frac{U_{=} - U_{\approx}}{\Delta T}, \quad \sigma = \frac{1}{R_{\approx}} \frac{l}{S}, \quad \kappa = \frac{\alpha^2 \sigma}{Z},$$

where R_{\approx} , U_{\approx} are the resistance of the sample and the voltage drop on it when alternating current is passed, $R_{=}$, $U_{=}$ are the resistance of the sample and the voltage drop on it when direct current is passed, T_{av} is the average temperature of the sample, l , S are the length and area of the sample cross-section, γ_i are correction factors that take into account the heat exchange of the sample and current leads with the thermostat. These factors depend on a large number of parameters, namely the radiation coefficients of the sample, contact plates and current leads, their temperature dependences, as well as the exact values of electrical conductivity and thermal conductivity of wire materials, the radiation coefficient of chamber walls and its temperature dependence, exact geometric dimensions of current leads, etc.

Work [5] presents an analysis of the errors in measuring the figure of merit using Harman's method and shows that the main source of errors when using Harman's method is the heat exchange of the sample with the environment through current leads and radiation. To minimize these errors, the technique of modified Harman's method is proposed, which makes it possible to measure the properties of the thermoelectric material with a high speed of response, and at the same time take into consideration the heat exchange of the sample with the thermostat, measuring all the necessary values for this during one experiment.

The purpose of the work is to develop high-speed, high-precision equipment for determining the thermoelectric properties of a material using modified Harman's method in the temperature range of 30 – 500 °C, which takes into consideration possible measurement errors, and the equipment itself is made on a modern element basis, using computer processing of measurement results.

1. Description of experimental installation

Installation for measuring the properties of parameters of TEM samples using modified Harman's method is schematically shown in Fig. 2.

The installation consists of a measuring unit, a control unit and a pumping vacuum post. The control unit includes sources of direct and alternating current with appropriate ammeters, voltage and temperature meters, and a thermoregulation system.

The main unit of the installation is a measuring unit with a TEM sample holder. The design of the measuring unit is shown in Fig. 3.

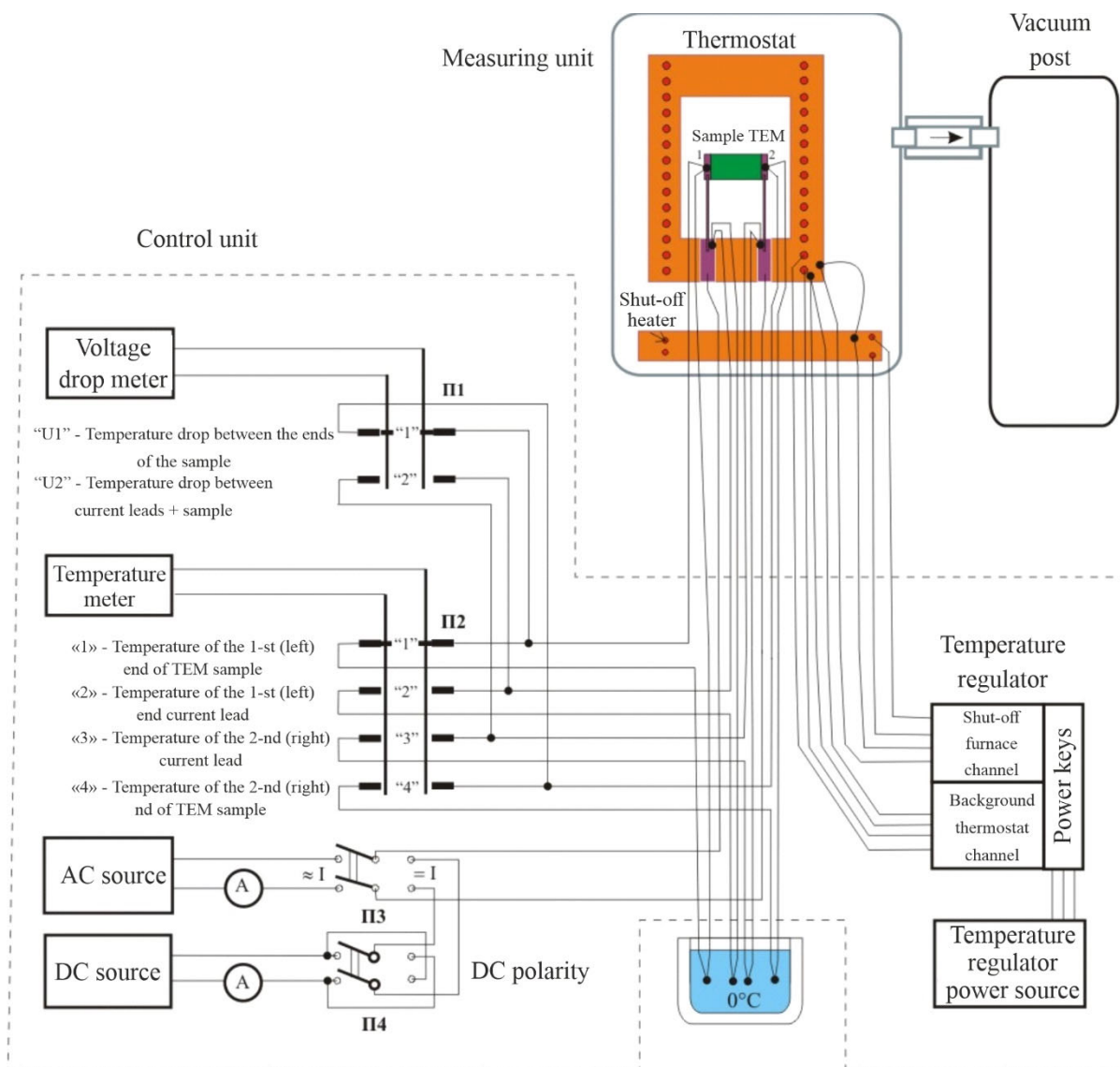


Fig. 2. Schematic of the installation for measuring parameters of TEM samples.

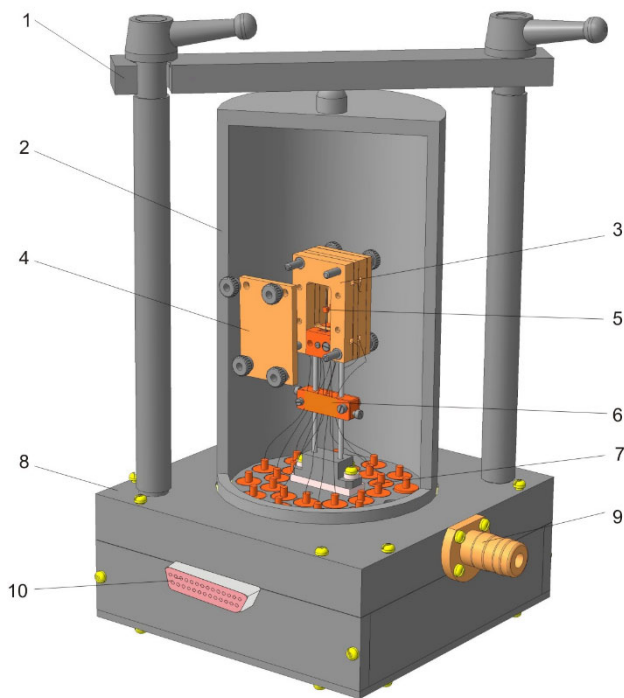


Fig. 3. Design of the measuring unit.

- 1 – vacuum cap clamp,*
- 2 – vacuum cap,*
- 3 – thermostat,*
- 4 – removable cover of the thermostat,*
- 5 – sample holder probes,*
- 6 – shut-off heater,*
- 7 – pressure leads,*
- 8 – the base of the measuring unit,*
- 9 – vacuum fitting,*
- 10 – connector.*

A TEM sample holder is fixed on the base of the measuring unit body, on thin stainless legs (Fig. 4). The holder itself is a metal collapsible thermostat, in the middle of which there is a niche with two pads on thin, elastic stainless racks. These pads are used as TEM sample holders, as well as current leads and contact elements of potential and temperature sensors. The racks themselves are mounted in heat spreader plates, which have good thermal contact with the base of the thermostat, but are electrically isolated from it. The pads, which in their area are comparable to the area of the ends of the TEM sample, are parallel to each other and are located at a distance from each other that is comparable to the length of the TEM sample. The pads are capable of holding the sample in suspension due to friction and elasticity of the racks. Pads and heat spreader plates, each having one measuring thermocouple and together with the current leads being one whole, form the probes. The probes in the installation are replaceable. This makes it possible to easily change them during routine or repair work, or to install others – for different sizes of samples. For measurement, the TEM sample is inserted between the probe pads through the removable side covers of the thermostat and soldered to them for better thermal and electrical contact.

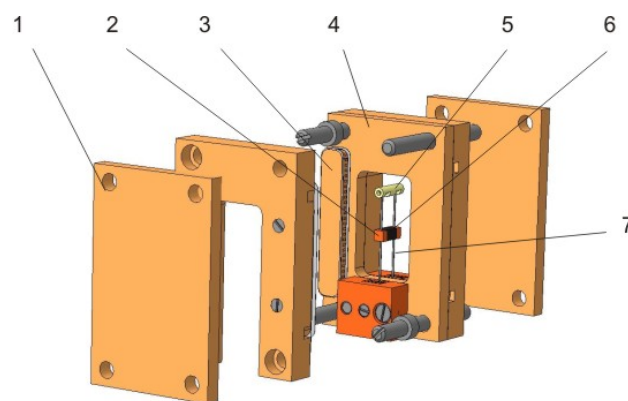


Fig. 4. Sample arrangement in the holder. 1 – Thermostat cover, 2 – probe pads, 3 – heating element, 4 – thermostat base, 5 – ceramic screed, 6 – TEM sample, 7 – probe rack.

The thermostat is active. Resistive heating elements and thermocouples are mounted in its walls and the required temperature is maintained with the help of a thermoregulator. To prevent thermal distortions in the thermostat, a shut-off heater is attached to its legs, the temperature of which is maintained by the thermoregulator at a given level. Moreover, all conductors leaving the thermostat are in contact with the shut-off heater and, thus, acquire the same temperature as it. This significantly reduces heat loss from the thermostat through the conductors. The conductors themselves are connected through sealed leads to the connector and further, through the measuring cable, to the control unit. The thermostat is covered with a cap, from under which air can be pumped out with the help of a vacuum post, or the air can be replaced with an inert gas. Measuring TEM samples in a vacuum or in an inert atmosphere reduces measurement errors, and also protects the TEM sample and the surface of the thermostat from oxidation during high-temperature measurements. The vacuum cap has clamping structural elements for better tightness.

2. Description of the measurement technique

Determination of the thermoelectric properties of the material by modified Harman's method is carried out as follows. A sample of thermoelectric material is fixed between two contact plates with high thermal and electrical conductivity on the current conductors in the thermostat. The side surface of the sample and contact plates is covered with a thin, uniform layer of material with a low emissivity. To further increase the accuracy, the measurement process is carried out consecutively twice at two different temperatures, and the magnitude of errors caused by radiation from the surface of the sample and contact plates is experimentally determined. In doing so, the temperature of the thermostat at which the first measurement is made is lower than the temperature at which the second measurement is made and is such that the errors caused by radiation from the surface of the sample and contact plates are insignificant and can be neglected. Since at the first temperature the contribution of radiation is insignificant, it is believed that all the heat is transferred through the current leads to the thermostat by thermal conductivity, therefore it is possible to determine the heat transfer coefficient K_2 along the current leads by thermal conductivity by passing an alternating current through the sample and measuring the magnitude of the voltage drops on the sample U_1 and on the current leads U_2 :

$$K_2 = \frac{1}{2} \frac{Q_1 + Q_2}{(T_{av} - T_0)} \quad (1)$$

where: $Q_1 = IU_1$ is the Joule heat released in the sample, $Q_2 = IU_2$ is the Joule heat released in each of the current leads, $T_{av} = (T_1 + T_2)/2$ is the average value of temperatures measured on the sample ends, T_0 is thermostat temperature.

At the second temperature value, voltage drops on the sample and current leads are measured, as well as temperatures at the ends of the sample and the thermostat when alternating current is passed through the sample, voltage drop on the sample, voltage drops on the current leads to the sample, temperatures at the ends of the sample and the thermostat when direct current is passed therethrough. The ohmic voltage drop on the sample $U\sigma$ is determined when alternating current is passed or at the moment direct current is turned on, and thermoEMF $U\alpha$ is determined when direct current is passed. The value of thermoelectric figure of merit, the Seebeck coefficient and electrical conductivity, as well as thermal conductivity are found, with account of heat transfer through current leads and radiation.

To do this, based on the Wiedemann-Franz law, by the results of measurements of temperatures and voltage drops on the sample and current leads at two temperatures T' and T'' of the thermostat, the heat transfer coefficient along the current leads at temperature T''' is determined

$$K_2(T''') = K_2(T') \frac{U_2(T') T''}{U_2(T'') T'} \quad (2)$$

Thus, the total heat flow at a higher temperature is divided into heat flow by thermal conduction through current leads and heat flow by radiation. Since the surfaces of the sample and the contact plates are covered with the same coating, the effective radiation heat transfer coefficient K_{eff} can be used at temperature T'''

$$K_{eff} = \frac{Q_1 - (2K_2 \cdot (T_{av} - T_0) - Q_2)}{(T_{av} - T_0)} \quad (3)$$

Analysis of the accuracy of the proposed method of determining the thermoelectric properties of materials is given in [5]. The distributions of electric potential and temperature in the sample, contact plates, and current leads were obtained by computer simulation, which made it possible to optimize the measurement scheme and obtain the values of possible errors in the determination of the thermoelectric figure of merit associated with heat transfer by radiation. Errors in determining the thermoelectric figure of merit by the proposed method, associated with heat transfer through current leads and radiation, in the temperature range of 30 – 500 °C should not exceed 2 %.

Typical results of measuring the temperature dependences of parameters of the sample of n -type Bi_2Te_3 thermoelectric material are presented in Fig. 5.

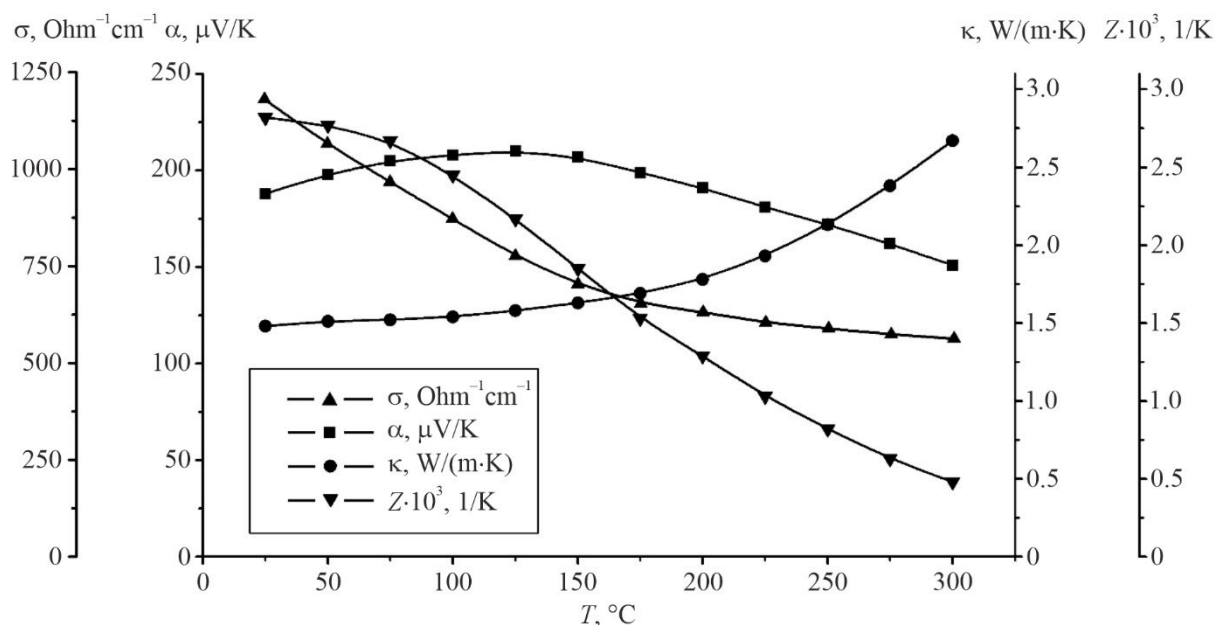


Fig. 5. Temperature dependences of the properties of n -type thermoelectric material sample based on Bi_2Te_3 .

An experimental comparison of the results obtained by modified Harman's method on the equipment described above with the results obtained on the installation for measuring the properties of thermoelectric materials, built on the absolute method, was carried out [6 – 7]. It was established that deviations in the results increase with a rise in temperature and are within 6 – 7 % in the temperature range of 200 ÷ 300 °C.

Conclusions

1. High-speed, high-precision equipment has been developed for determining the thermoelectric properties of a material by modified Harman's method in the temperature range of 30 – 500 °C using computer processing of measurement results, which takes into account and eliminates possible measurement errors.
2. It has been established that the errors in determining the thermoelectric figure of merit by the proposed method, related to heat transfer by radiation, in the temperature range of 30 – 500 °C will not exceed 2 %.
3. A comparison of the results obtained by modified Harman's method with the results obtained at the installation for measuring the properties of thermoelectric materials by the absolute method was carried out.
4. It was established that deviations in the results increase with a rise in temperature and are within 6 – 7 % in the range of 200 ÷ 300 °C.

References

1. Anatyshuk L.I., Lysko V.V. (2014). On improvement of the accuracy and speed in the process of measuring characteristics of thermoelectric materials. *Journal of Electronic Materials*, 43 (10), 3863 – 3869. <https://doi.org/10.1007/s11664-014-3300-5>.
2. Anatyshuk L.I., Havryliuk M.V., Lysko V.V. (2015). Absolute method for measuring of thermoelectric properties of materials. *Materials Today: Proceedings*, 2 (2), 737 – 743. <https://doi.org/10.1016/j.matpr.2015.05.110>.
3. Harman T.C., Cahn J.H., and Logan M.J. (1959). Measurement of thermal conductivity by utilization of the Peltier effect. *Journal of Applied Physics*, 30(9), 1351 – 1359.
4. Buist R.J. (1992). A new methodology for testing thermoelectric materials and devices. *Proc. of the 11th Intern. Conf. on Thermoelectrics*, Arlington, Texas, 1992, p. 196-209.
5. Anatyshuk L.I., Lysko V.V. (2012). Modified Harman's method. *AIP Conf. Proc.* №1449, 373 – 376.
6. Anatyshuk L.I., Lysko V.V. (2020). *Thermoelectricity: Vol. 5. Metrology of Thermoelectric Materials*. – Chernivtsi: Bukrek. ISBN 978-617-7770-40-3.
7. Anatyshuk L.I., Havryliuk M.V., Lysko V.V. (2018). Ways for quality improvement in the measurement of thermoelectric material properties by the absolute method. *J. Thermoelectricity*, 2, 90 – 100.
8. Anatyshuk L.I., Havryliuk M.V., Lysko V.V., Tiumentsev V.A. (2018). Automation and computerization of measurements of thermoelectric parameters of materials. *J. Thermoelectricity*, 3, 80 – 100.

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Анатичук Л.І., *акад. НАН України*^{1,2}

Гаврилюк М.В.¹

Лисько В.В., *канд. фіз.-мат. наук*^{1,2}

¹ Інститут термоелектрики НАН та МОН України,
вул. Науки, 1, Чернівці, 58029, Україна;

² Чернівецький національний університет імені Юрія Федьковича,
вул. Коцюбинського 2, Чернівці, 58012, Україна
e-mail: anatysh@gmail.com

ОБЛАДНАННЯ ДЛЯ ВИЗНАЧЕННЯ ТЕРМОЕЛЕКТРИЧНИХ ВЛАСТИВОСТЕЙ МАТЕРІАЛУ МОДИФІКОВАНИМ МЕТОДОМ ХАРМАНА

Наведено результати розробки обладнання для визначення термоелектричних властивостей матеріалів – електропровідності, теплопровідності, коефіцієнту термоЕРС та термоелектричної добротності в інтервалі температур 30 – 500 °С з використанням модифікованого методу Хармана. Оцінено похибки вимірювань та описано методи їх зниження. Показано результати вимірювань зразків матеріалів на основі Bi_2Te_3 , отримані за допомогою описаного обладнання.

Ключові слова: метод Хармана, термоелектрична добротність, абсолютний метод.

Література

1. Anatyshuk L.I., Lysko V.V. (2014). On improvement of the accuracy and speed in the process of measuring characteristics of thermoelectric materials. *Journal of Electronic Materials*, 43 (10), 3863 – 3869. <https://doi.org/10.1007/s11664-014-3300-5>.
2. Anatyshuk L.I., Havryliuk M.V., Lysko V.V. (2015). Absolute method for measuring of thermoelectric properties of materials. *Materials Today: Proceedings*, 2 (2), 737 – 743. <https://doi.org/10.1016/j.matpr.2015.05.110>.
3. Harman T.C., Cahn J.H., and Logan M.J. (1959). Measurement of thermal conductivity by utilization of the Peltier effect. *Journal of Applied Physics*, 30(9), 1351 – 1359.
4. Buist R.J. (1992). A new methodology for testing thermoelectric materials and devices. *Proc. of the 11th Intern. Conf. on Thermoelectrics*, Arlington, Texas, 1992, p. 196-209.
5. Anatyshuk L.I., Lysko V.V. (2012). Modified Harman's method. *AIP Conf. Proc.* №1449, 373 – 376.
6. Anatyshuk L.I., Lysko V.V. (2020). *Thermoelectricity: Vol. 5. Metrology of Thermoelectric Materials*. – Chernivtsi: Bukrek. ISBN 978-617-7770-40-3.
7. Anatyshuk L.I., Havryliuk M.V., Lysko V.V. (2018). Ways for quality improvement in the measurement of thermoelectric material properties by the absolute method. *J. Thermoelectricity*, 2, 90 – 100.
8. Anatyshuk L.I., Havryliuk M.V., Lysko V.V., Tiumentsev V.A. (2018). Automation and computerization of measurements of thermoelectric parameters of materials. *J. Thermoelectricity*, 3, 80 – 100.

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