PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 19, № 4 (2018) P. 297-302
DOI: 10.15330/pcss.19.4.297-302

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 19, № 4 (2018) С. 297-302

UDK: 608.1

ISSN 1729-4428

O.V. Nitsovich[1,2], M.V. Serbyn[1,2]

Fragments From the History of the Invention of Bi_2Te_3 and its First Practical Uses

[1]Institute of Thermoelectricity of the NAS and MES of Ukraine, Chernivtsi, Ukraine
[2]Yuriy Fedkovych Chernivtsi National University, Chernivtsi, Ukraine

The paper presents an analysis of information on the research and use of materials on the basis of Bi_2Te_3, as a thermoelectric material. It was established that Bi_2Te_3, as a thermoelectric material, was first investigated in 1905, and was practically applied in thermoelectric devices in the 1950s. The main tendencies of the current state of thermoelectric material science are determined.

Key words: bismuth telluride, thermoelectricity, thermoelectric efficiency.

Article acted received 02.12.2018; accepted for publication 15.12.2018.

Introduction

The history of thermoelectricity goes back to a period of over 200 years ago. Thousands of scientists have devoted their research to the study of thermoelectric phenomena.

For a proper understanding of the process of development of science, the study of the history of science, trends of its development, its links to the history of society is of great importance. For this reason, the study of the main stages of thermoelectricity development remains topical nowadays. Important information essential for sufficient prognosis of the ways of further development of thermoelectricity, in particular, thermoelectric materials science, determination of both significance of the trend in question and its prospectsin the future can be provided by studying the features of the development of this trend in the past as well as its current state. In addition, the historical analysis of thermoelectric materials science, the development of which is a complex, multifaceted process of human cognition, reveals important details of it, traces the mechanism for discovering new patterns, and also protects researchers and developers from repeating their predecessors' mistakes.

It is well-known that a lot of ideas and scientific data find practical application only on condition that technical progress reaches a level at which their realization becomes possible. The study of specific situations in thermoelectricity, analysis of theoretical concepts and technical solutions of the past serve as the basis for their revision, identifying the possibilities of their renovated use under modern conditions.

Thermoelectric materials science is one of the most important areas in thermoelectricity,since the achievements in this field in general determine the possibilities and versatility of practical applications of thermoelectric energy conversion.

The first researcher of a variety of thermoelectric materials was, certainly, Thomas Seebeck. He conducted research into the thermoelectric properties of various solid and liquid conductors, minerals and semiconductors [1].

For a long time, materials for thermoelectric devices were developed by an empirical selection of components. The main requirements to them were first formulated by J. Rayleigh [2]. In his opinion, materials, effective for practical use, should have the highest possible thermoelectric coefficient α and electrical conductivity σ, as well as the lowest possible thermal conductivity κ:

$$\eta \sim \alpha, \sigma, \frac{1}{\kappa}, \quad (1)$$

In the works of A.F. Ioffe, these requirements were combined into the concept of thermoelectric figure of merit Z, which was given a mathematical record and which was analyzed in detail from the point of view of achieving optimal parameters by influencing the microscopic characteristics of the material, such as mobility, effective mass, carrier concentration, etc. . [3]:

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

Currently, the practical use of thermoelectricity is implemented in three directions: thermoelectric generators, cooling devices and measuring equipment. For all these areas, the main thermoelectric material used is Bi-Te-based solid solutions, which show optimal thermoelectric properties in the temperature range of 200-400K. Therefore, this work is focused on the review, systematization and analysis of the data on the study and application of Bi_2Te_3 as a thermoelectric material from the time of its first discovery until the present moment.

I. History of the discovery of bismuth telluride

The first known natural compounds of tellurium and bismuth were taken by Ignaz von Born in 1790for compounds of silver with molybdenum. In 1795, Martin Heinrich *Klaproth*, even before his discovery of tellurium (1798.), found only bismuth and sulfur in these compounds. The correct composition of the studied compounds was determined in 1822 by G. Rose and,nearly simultaneously, by J. Berzelius [4].

The prevailing formula for describing minerals at that time was obtained on the basis of analysis of rocks quarried in the BanskaStiavnica (Slovakia) area, conducted by A. Wehrle. Among the 39 samples of natural compounds of bismuth telluride, 23 had the composition Bi_2Te_2S, the rest showed a higher content of bismuth and either a smaller amount or complete absence of sulfur, as well as the presence of other elements in the composition [5].

Among the variety of natural minerals studied by Seebeck in 1895, there were also samples studied by J. Berzelius. In his works they were called vismutin (German: Wismuthglanzes) they had bismuth-tellurium compounds poor in selenium, sulfur, antimony, and silver [1]. Thus, T. Zeebeck was the first to study the thermoelectric properties of Bi-Te-based compounds. He also demonstrated the connection of the thermoelectric properties of substances with their crystal structure for the first time.

II. Investigation of the properties of Bi_2Te_3

One of the pioneers in the study of the synthesis of tellurium and bismuth was K. Mönkemeyer. In 1905, he constructed a state diagram of the Bi-Te binary system alloy (Fig. 1), which he obtained from the cooling curves of Bi + Te alloys [6]. He determined the melting points of Bi, Te, and Bi_2Te_3:

Bi………………267 ºC,
Te……….........428 ºC,
Bi_2Te_3………….573 ºC,

and found the following eutectics points:

Eutectics	T,ºC	at.% Bi
$Bi+Bi_2Te_3$	261	98.5
Bi_2Te_3+Te	388	9

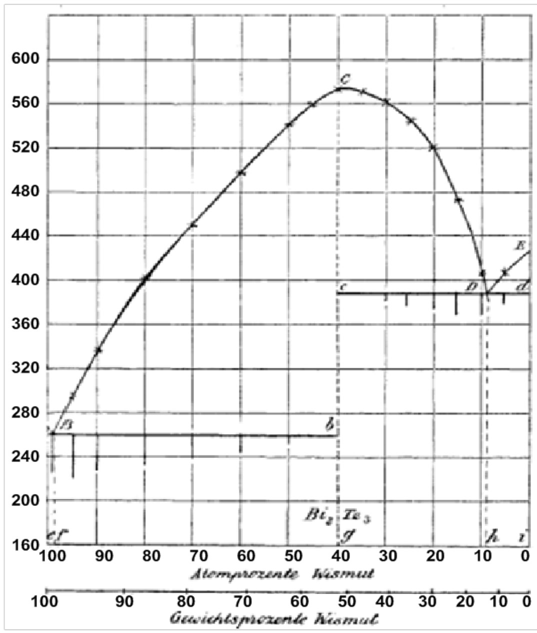

Fig. 1. Diagram of equilibrium of Bi-Te [6].

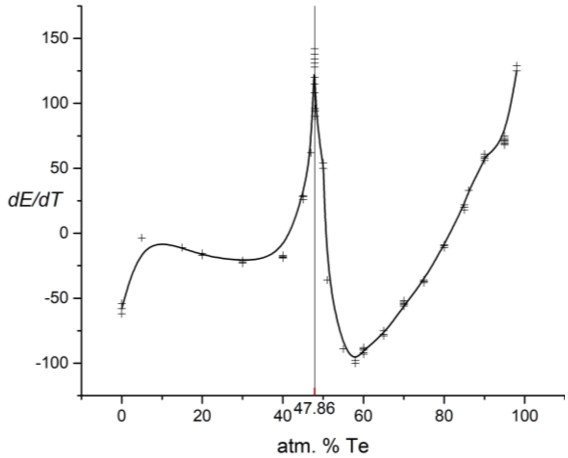

Fig. 2. Dependency of thermo-EMF of Bi-Te alloy fromTe concentration in it.

The maximum on the state diagram and 2 eutectic horizontals indicate the presence of a compound, which Mönkemeyer discovered at the point corresponding to 47.86% Te and this compound is Bi_2Te_3.

In 1910 Werner Hacken quantitatively determined the Seebeck coefficient and the electrical conductivity of many elements, alloys and compounds, including Sb_2Te_3 and Bi_2Te_3, in order to find a good thermoelectric material [7]. ThermoEMF values obtained by Haken for different concentrations of Te are shown in Fig.2 (thermoEMF was compared to the copper electrolyte values).

As can be seen from the figure, with the increase in the amount of bismuth, the value of thermoEMF decreases sharply, and the more bismuth is present in the alloy, the more negative the thermoEMF becomes, which at 58 at.%Tereaches -100 mV. The thermopower value further increases sharply and reaches a maximum of 140 mV at 47.86 at.%Te, then drops sharply again and at 47at.% Te is 62 mV, and at 40 at.% Te again shows negative values. The thermoEMF curve clearly shows the chemical compound Bi_2Te_3, which corresponds to a concentration of 47 at.%Te.

The study of electrical resistance as a function of the concentration Te showed that with an increase in the amount of bismuth, the resistance increases, but after 60at.% it begins to decrease and reaches a minimum at the concentration of Bi_2Te_3compound and then rises again to the values characteristic to the pure bismuth [7].

III. Application of bismuth telluride in thermoelectricity

The German physicist and mathematician Edmund Altenkirch was the first to calculate in 1911 the potential efficiency of thermoelectric generators and the performance of Peltier coolers [8]. He showed that the voltage developed by a thermopile is directly proportional to the square of the thermoEMF coefficient, and also found that the most effective materials for thermoelectric conversion should be those for which the Wiedemann-Franz law is not satisfied. However, based on the usual for the beginning of the XIX century assertions that metals are the best materials for thermocouple legs, and also considering that only for such materials their thermoelectric parameters were studied, the researchers of that time came to the false conclusion that thermoelectric converters cannot be used in practice, because the calculated values of thermoelectric power converter efficiency based on metals were very small.

In 1933, in [9], E. Schlegel showed that for efficient use of thermoelectric coolers, it is necessary to achieve a temperature difference of 30 °C. To achieve the established temperature difference, it is necessary that the coefficient of thermoEMF α is> 170 mV / °C. The metal thermocouples known at that time did not satisfy this requirement.The author analyzed the possibilities of using a number of materials in thermoelectric refrigerators that, due to their high thermoEMF, were considered the most appropriate. Among these materials were Bi, Te, Si, Sb, Sb-Cd and Bi-Te. E. Schlegel obtained the following results: an alloy with Bi and Te with a content of Te of 48% had a thermEMF of 140 mV, with a content of Te of 47% thermoEMF was 62 mV, which is almost less by half. Thus, it was found that a change in the structure of the material leads to a significant change in the thermoEMF of the alloy.

Analyzing the research results, the author came to the conclusion that the use of the Peltier effect for cooling is almost hopeless for the following reasons:

1. Thermoelectric materials have a high electrical resistance, and due to their poor soldering ability, they also have high contact resistances, so the resulting Joule heat is higher than Peltier cooling;

2. Poor processibillityof materials with high thermoEMF values;

3. Irregularity of thermopower due to the high sensitivity of materials with regard to the method of their manufacture, the degree of chemical purity and the aging of metals.

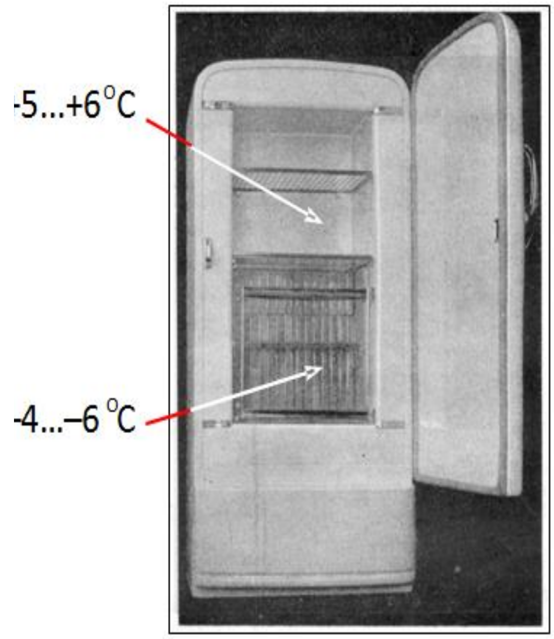

Fig. 3. Cooler based on the Peltier effect [12].

Although Schlegel noted that further research was needed within the frames of both the theory and production of thermoelectric coolers, until the 1950s, however, bismuth telluride was not used to develop thermoelectric cooling systems. Intense research and implementation ofBi_2Te_3 and solid solutions based on it started on the initiative and under the guidance of A.Ioffe, who developed the theory of the use of semiconductor thermoelements. He showed that semiconductor cooler can compete in terms of efficiency with any refrigeration machines of the time. [10-12].

Ioffe's research and development led to the emergence of the first commercial thermoelectric devices for power generation and cooling. Thermoelements used heavily doped semiconductors; the most famous of those are antimony telluride, bismuth and lead. In 1949. I. Shmelev synthesized p-type thermoelectric material based on Bi_2Te_3-Sb_2Te_3 solid solution [16-19]. In 1952. L.S.Stilbans and colleagues made a cooler model where PbTe was used as the n-leg, whereas Bi_2Te_3 was used for the p-leg. They were able to achieve $\Delta T_{max}= 30°C$ [12]. However, the use of such a thermopile still did not allow for the heat removal from its hot junction with air, therefore it was carried out with running water. The following model of the cooler was developed, in which PbTe was used for the n-leg of the thermoelement, and the p-leg was made of the Bi_2Te_3-Sb_2Te_3 triple alloy. Such a thermoelement provided the maximum temperature drop $\Delta T_{max}=40°C$. The heat removal from the hot junctions of a thermopile was carried out by convection of water in a tank with a ribbed surface [11–12]. A refrigerated cabinet with a chamber volume of 55 liters was developed. Here, for the n-leg of the thermoelement, the PbTe-PbSe solid solution was used, and the p-leg was still made of Bi_2Te_3-Sb_2Te_3. Such thermoelements provided the maximum temperature drop $\Delta T_{max}= 60°C$. This allowed the researchers further proceeding to cooling the hot junctions of thermopiles using a system of radiators with direct use of ambient convection.

Simultaneously, in 1954 British scientists J. Goldsmid and R. Douglas conducted a research into the physical properties of thermoelectric materials. They found that for thermoelectric cooling, semiconductors with high average atomic mass and thermoelectric power (thermoEMF coefficient) should be selected, from the range of 200 to 300 mV $°C^{-1}$ [13]. Considering this fact, they conducted a search for semiconductor compounds with the required characteristics that would be easy to manufacture. Bi_2Te_3, which was obtained by direct fusion of elements, turned out to be one of such materials. The authors found that it is possible to obtain p-type Bi_2Te_3 samples with the following properties:

- thermoEMF coefficient - 220 mV $°C^{-1}$;
- electrical conductivity - 4.0 · 102 $Ohm^{-1} \cdot cm^{-1}$;
- thermal conductivity - $2.1 \cdot 10^{-2}$ W · $cm^{-1} \cdot °C^{-1}$.

Goldsmid and Douglas suggested that if n-type samples with similar properties were obtained, then a temperature difference of at least 33 ° C should be achievable for such a thermoelement. However, a similar n-type material was not yet available at that time, so they built a thermocouple using a p-type leg with Bi_2Te_3, pure-bismuth n-legs and obtained the temperature difference $\Delta T_{max}= 26°C$. In 1955. J. Goldsmid managed to create a material of n-type conductivity based on Bi_2Te_3, which allowed obtaining on the thermoelement temperature differences $\Delta T_{max}= 40°C$[14]. At that time, an intensive study of the physical properties of materials based on Bi_2Te_3 and methods for their production began [15-16, 20-28]. In 1956 Sinani and his colleagues [15] synthesized and studied a thermoelectric material for an n-leg thermoelement based on Bi_2Te_3-Bi_2Se_3. The best thermoelectric properties were shown by a solid solution of 80 mol.% Bi_2Te_3 + 20 mol.% Bi_2Se_3. Thus, starting from 1956. solid solutions Bi_2Te3-Sb_2Te_3 and Bi_2Te_3-Bi_2Se_3 became the main materials for thermoelectric cooling thermoelements.

In 1957, at the Institute of Semiconductors of the Academy of Sciences of the USSR, a household cooler with a capacity of 91 litres (Fig. 3), was developed under the guidance of A.Joffe. In the upper chamber the temperature was equal to + 5 ... + 6 °C and in the lower section - 4 ... - 6 °C. Bi_2Te_3-Bi_2Se_3 and Bi_2Te_3-Sb_2Te_3-based materials were used to manufacture the cascade thermopile legs.

In the same year, T. Schilliday (USA) studied a thermoelectric cooler, in which ring-shaped thermoelements made of p-and n-type Bi_2Te_3-based materials were used [27]. Using this device, $\Delta T_{max} = 49^{\circ}C$ was achieved. The author developed a theory for calculating the performance of such Peltier coolers. It was shown that experiment-based data of the efficiency of the device were consistent with theoretical predictions within the limits of experimental error.

The investigation of the coefficients of thermoEMF α, electrical conductivity σ and thermal conductivity κ of n- and p-type Bi-Te-based materials in the range of 150-300 K and the determination of the efficiency of such materials in 1958 [29] showed that ZT of those materials reached a maximum value of approximately 0.76 at 290K, and the coefficient of electrical conductivity for both n- and p-legs should be equal to $\sigma = 1000\, Ohm^{-1}cm^{-1}$. Also, the author indicated the possibility of achieving$\Delta T_{max} = 65^{\circ}C$ for thermoelectric coolers based on the materials under study. Also, the efficiency of thermoelectric generators made of the above mentioned TEM, which was equal to $\eta = 1\%$ at $\Delta T = 25^{\circ}C$, was calculated.

The research on the creation of thermoelectric converters made of the materials based on bismuth telluride was also carried out in Japan [30-33]. In the works of the Japanese scientist, M. Aoki [30-32], 1959, the electrical conductivity, the Hall coefficient, the thermal conductivity and the thermoelectric power of Bi_2Te_3 semiconductor materials were studied in the temperature range from 100 to 650 °K. P-type samples were made of Bi_2Te_3, n-type of Bi_2Te_3 + excess Te. The thermoelectric cooler was made of materials with the following properties: $\rho_p = 0.6 \cdot 10^{-3} Ohm \cdot cm$, $\alpha_p = 142\, \mu V/K$, $\kappa_p = 1.9 \cdot 10^{-2}\, W/(cm \cdot K)$, $\rho_n = 0.78 \cdot 10^{-3} Ohm \cdot cm$, $\alpha_n = -179\, \mu V/K$, $\kappa_n = 2.0 \cdot 10^{-2} W/(cm \cdot K)$, showing $\Delta T_{max} = 67^{\circ}C$ at an average temperature of 17 °C [31].

In the 1960s, a variety of thermoelectric generators was developed in France, the USA and the USSR, for the manufacture of which thermoelements of Bi_2Te_3-based materials were used [34]. The efficiency of such thermogenerators reached 5% max.

By optimizing the composition of Bi_2Te_3-based materials, selecting doping impurities for n-legs, as well as improving the technology for obtaining such materials, it became possible to raise their dimensionless figure of merit ZT only to 1.2 [35-36]. Moreover, ΔT_{max} of the thermoelectric coolers based on modern materials does not exceed $75^{\circ}C$.

Recently, the possibility of increasing the efficiency of thermoelectric energy conversion is associated with the use of nanomaterials [37]. However, at the early stages of the research of such materials, the values of ZT were ~ 10 and more, but detailed studies of more realistic models showed the possibility of achieving ZT of ~ 2-2.5. Such materials require further technological research to develop industrial power converters.

Conclusions

Despite the optimistic forecasts made by many researchers in the 1950s of the possibilities of achieving in the next two or three decades, the $Z = (10 - 20) \cdot 10^{-3} K^{-1}$ thermoelectric quality factor most thermoelectric materials used today does not exceed $3{,}7 \cdot 10^{-3} K^{-1}$. At the same time, the main material for practical applications of thermoelectric energy conversion in the range of 200-400 K remains the Bi-Te based alloys.

Thus, one of the most important challenges of the thermoelectric material science is the development of the technology of material production, optimization of composition and doping agents, as well as the search for and the creation of fundamentally new high-efficient thermoelectric materials.

Nitsovich O.V. - candidate of physical and mathematical sciences, researcher;
Serbin M.V. - laboratory assistant..

[1] T. J. Seebeck, Magnetische Polarisation der Metalle und Erze durch Temperatur-Differenz. Leipzig (W. Engelmann, 1895).
[2] J. Rayleigh, J.Rus. Phys.-Chem. Soc. 18(1), 3 (1886).
[3] L. I. Anatychuk. Thermocouples and thermoelectric devices. Directory (Naukova Dumka, Kyiv, 1979).
[4] Berzelius, Akad. Stockh. Handl. (1823).
[5] F. Slavik, Handbuch der Mineralchemie: Band IV Erste Hälfte: Schwefel-Verbindungen. (Springer-Verlag Berlin Heidelberg, Berlin, 1926).
[6] K. Mönkemeyer, Zeitschrift für anorganische Chemie 46, 415 (1905).
[7] W. Haken, Annalen der Physik 832, 291 (1910).
[8] E. Altenkirch, Phyzikalische Zeitschrift 10(16), 560 (1909).
[9] E. Schlegele, Zeitschrift für die gesamte Kälte-Industrie 40(1), 2 (1933).
[10] A. F. Ioffe, Semiconductors in modern physics (Pub. AN USSR, Moskow, 1954).
[11] A. F. Ioffe, L. S. Stilbans, E. K. Iordanishvili, T. S. Stavitskaya, Thermoelectric cooling (Pub. AN USSR, Moskow, 1956).
[12] A. F. Ioffe, Semiconductor thermoelements (Pub. AN USSR, Moskow, 1960).
[13] H. J. Goldsmid, R. W. Douglas, British Journal of Applied Physics 5(11), 386 (1954) (doi:10.1088/0508-3443/5/11/303).
[14] H. J. Goldsmid, J. Electronics. 1, 218 (1955) (doi:10.1080/00207215508961410).
[15] S. S. Sinani, G. N. Gordyakova, J. Tech. Phys. 26(10), 2398 (1956).
[16] G. I. Shmelev, Physics of solid state 1, 63 (1959).
[17] G. I. Shmelev, Alloys based on three-component compounds for thermocouples, Diss. (1949).
[18] L. P. Bulat, E. K. Iordanishvili, A. A.Pustovalov, M. I. Fedorov, Journal of Thermoelectricity 4, 7 (2009).
[19] Pat. No 109343 USSR. Thermocouple and method of connecting its branches. G. I. Shmelev (1952).
[20] G. V. Kokosh, S. S. Sinani, Physics of solid state 1, 89 (1959).
[21] S. V. Ayrapetyants, B. A. Efremova, J. Tech. Phys. 28(8), 1768 (1958).
[22] G. V. Kokosh, S. S. Sinani, Physics of solid state 2(6), 1118 (1960).
[23] S.B. Satterthwaite, R.W.Ure, Physical review 108(5), 1164 (1957) (doi:10.1103/PhysRev.108.1164).
[24] H. Benel, Compt. Rend. Acad. Sci. Paris 247(5), 584 (1958).
[25] U. Birkholz, Zeitschrift für Naturforschung 13A, 780 (1958).
[26] T.C.Harman, B.Paris, S.E.Miller, H.L.Goering, Journal of Physics and Chemistry of Solids 2(3), 181 (1957) (doi:10.1016/0022-3697(57)90081-1).
[27] T.S. Schilliday, J.Appl. Phys. 28(9), 1035 (1957) (doi:10.1063/1.1722903).
[28] B. M. Goltsman, V. A. Kudinov, I. A. Smirnov, Semiconductor thermoelectric materials based on bismuth telluride(Bi2Te3) (Nauka, Moskow, 1972).
[29] H. J. Goldsmid, A.R. Sheard, D.A. Wright, Br. J. Appl. Phys. 9, 365 (1958) (doi:10.1088/0508-3443/9/9/306).
[30] M. Aoki, Japan J. of Applied Physics 28(2), 77 (1959).
[31] M. Aoki, Z.P.Chang, Japan J. of Applied Physics 28(2), 82 (1959).
[32] M. Kikuchi, T. Iizuka, Bulletin of the electrotechnical laboratory 23, 671 (1959).
[33] A. S. Okhotin, A. A. Efremov, V. S. Okhotin, A. S. Pushkarskiy. Ed. by A. R. Regel. Thermoelectric generators (Atomizdat, Moscow, 1976).
[34] H. J. Goldsmid, Materials. 7, 2577 (2014) (doi:10.3390/ma7042577).
[35] L. I. Anatychuk, Journal of Thermoelectricity, 2, 7 (2007).
[36] D.M. Rowe, Thermoelectric Handbook. Macro to Nano (CRC Press, Taylor and Francis Group, Boca Raton, London, New York, 2006).

O.V. Nitsovich, M.V. Serbyn

О.В. Ніцович[1,2], М.В. Сербин[1,2]

Фрагменти з історії винайдення Bi_2Te_3 та його перших практичних використань

[1]Інститут термоелектрики НАН та МОН України, 58029, Україна, м. Чернівці, вул. Науки, 1,
e-mail: anatych@gmail.com
[2]Чернівецький національний університет ім. Ю. Федьковича, 58012, Україна, Чернівці,
вул. Коцюбинського, 2, e-mail: office@chnu.edu.ua

У роботі наведено аналіз інформації по дослідженню та використанню матеріалів на основі Bi_2Te_3, в якості термоелектричного матеріалу. Встановлено, що Bi_2Te_3, як термоелектричний матеріал, вперше був досліджений в 1905 році, а практичне застосування в термоелектричних приладах отримав у 1950-х роках. Визначено основні тенденції сучасного стану термоелектричного матеріалознавства.

Ключові слова: телурид вісмуту, термоелектрика, термоелектрична ефективність.