V.V. Lysko

V.V. Lysko, *Cand.Sc (Phys-Math)* [1,2]
O.V. Nitsovich, *Cand.Sc (Phys-Math)* [1,2]

[1]Institute of Thermoelectricity of the NAS
and MES of Ukraine,
1, Nauky str., Chernivtsi, 58029, Ukraine;
[2]Yuriy Fedkovych Chernivtsi National University,
2, Kotsiubynsky str., Chernivtsi, 58012, Ukraine
e-mail: anatych@gmail.com

O.V. Nitsovich

COMPUTER SIMULATION OF THE PROCESS OF MANUFACTURING FLAT INGOTS OF THERMOELECTRIC MATERIALS BASED ON Bi_2Te_3 BY VERTICAL ZONE MELTING METHOD

The results of the development of a computer model for optimizing the process of manufacturing flat ingots of thermoelectric materials based on Bi_2Te_3 using the vertical zone melting method are presented. The created model allows one to study the dependence of the crystallization front shape on various technological parameters – the geometric dimensions of the heater and coolers, their temperatures, speed of movement, etc. This makes it possible to carry out multifactorial optimization of technological modes and equipment design, significantly reducing the material costs and time required for conducting similar experimental studies. Bibl. 19, Figs. 3.

Key words: simulation, vertical zone melting, thermoelectric material, bismuth telluride.

Introduction

The practical use of thermoelectricity today is implemented in three main directions - cooling devices, thermoelectric generators and measuring equipment. For all these areas, the main thermoelectric materials used are alloys based on Bi_2Te_3, since it is solid solutions based on bismuth telluride that have the best thermoelectric properties in the temperature range of 200 – 600°K [1 – 6]. A lot of attention is paid to the improvement of methods of obtaining such materials [7 – 14].

One of the most common industrial methods of growing polycrystalline thermoelectric materials based on Bi-Te is the method of vertical zone melting. The quality of the obtained material is affected by various factors, for example: impurity distribution coefficient; length of the molten zone; zone movement speed; degree of mixing of the molten zone; heater temperature, etc. A structurally homogeneous crystal can be obtained only by selecting the optimal growing conditions. The curvature of the crystallization front, which is the main technological characteristic of growth, has a great influence on the quality of the obtained thermoelectric material. The shape of the crystallization front can be convex in the liquid phase, flat or concave in the solid phase. The most favourable for growing single crystals with a low density of defects is a flat crystallization front. The shape of the crystallization front is determined by the radial and axial temperature gradients in the ingot during growth.

Computer simulation of the process of growing thermoelectric materials allows one to study the dependence of the crystallization front shape on various technological parameters, significantly reducing material costs and research time required to ensure the growth of crystals of the required quality.

The papers [15, 16] present the results of computer simulation of the process of vertical zone melting of thermoelectric material in the form of rods with a round cross-section; in particular, the influence of the temperature and dimensions of the heater, the growth rate and other process parameters on the shape of the crystallization front is investigated. The paper [17] examines the possibility of growing single crystals of thermoelectric materials by the method of vertical zone melting in the presence of electric current passing through the ingot.

An interesting opportunity to improve the structure of the material and reduce technological defects when cutting ingots into thermoelements is the production of ingots in the form of flat rods. The creation of technology for the production of such ingots requires multi-parameter optimization of controlled parameters of the growing process.

Therefore, *the purpose of this work* is to create a computer model of the process of manufacturing flat ingots of thermoelectric materials based on Bi_2Te_3 by the method of vertical zone melting.

1. Physical model of vertical zone melting process

The physical model of growing flat ingots of thermoelectric materials based on Bi_2Te_3 by the method of vertical zone melting is shown in Fig. 1.

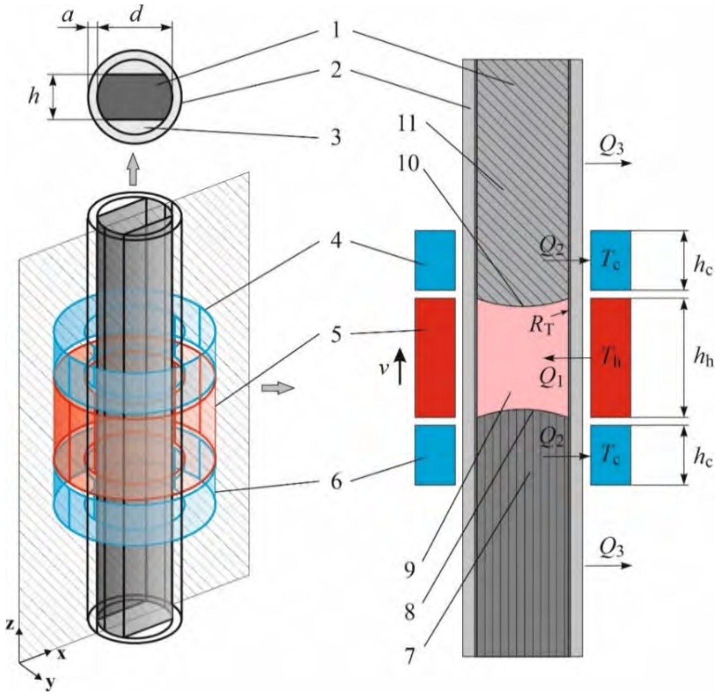

Fig. 1. Physical model of growing thermoelectric materials by vertical zone melting: 1 – thermoelectric material; 2 – container; 3 – quartz inserts; 4, 6 – coolers; 5 – heater; 7 – material in the solid phase (structurally oriented crystal); 8 – crystallization front; 9 – melt zone; 10 – melt front; 11 – material in the solid phase (polycrystal).

The figure shows a fragment of an ingot, which includes polycrystalline material 11, a molten zone 9 and a single crystal 7. The ingot is placed in a container 2. With the help of a heater 5 and a system of coolers 4 and 6, a molten zone 9 is formed, which, moving together with the heater along the ingot, ensures the melting of the polycrystal and the crystallization of the melt below the boundary 8, which is called the crystallization front.

In Fig. 1: T_h is heater temperature; T_c is the temperature of coolers; Q_1 is heat flow transferred from the heater to the container; Q_2 is heat flow transferred from the container to the coolers; Q_3 is heat flow transferred from the container to the environment; R_T is contact thermal resistance between the walls of the container and the thermoelectric material; *v* is the speed of movement of the thermal unit; *d* is ingot diameter; *a* is the thickness of the container wall. To improve the structure of the material, it is proposed to add special quartz inserts to the container, which will form a flat rod of thermoelectric material with a thickness of *h*.

2. Mathematical and computer models of vertical zone melting process

The COMSOL Multiphysics package of application programs [18] was used for computer simulation of the process of growing the thermoelectric material Bi_2Te_3 [18], which allows simulating almost all physical processes described by algebraic and partial differential equations. For this, it is sufficient to use ready-made modules of the corresponding physical phenomenon. If necessary, the researcher can change the equation built into the COMSOL module, or set his own. The numerical calculation is carried out using the finite element method [19].

The simulation of the movement of the heater and coolers in the COMSOL Multiphysics system was carried out by using the Moving Mesh module, which allows changing the mesh during calculations of non-stationary processes.

The temperature distribution in the studied sample was found from the solution of the differential equation of thermal conductivity, supplemented by the dependences of the physical properties of the studied material, as a function of the phase state at a given point at a given temperature:

$$\rho\, C_p \frac{\partial T}{\partial t} + \rho\, C_p u\, \nabla T + \nabla q = Q, \tag{1}$$

$$q = -\kappa \nabla T, \tag{2}$$

$$\rho = \theta\rho_{phase1} + (1-\theta)\rho_{phase2}, \tag{3}$$

$$C_p = \frac{1}{2}\left(\theta\rho_{phase1}\, C_{p_{phase1}} + (1-\theta)\rho_{phase2}\, C_{p_{phase2}}\right) + L\frac{d\alpha_m}{dT}, \tag{4}$$

$$\alpha_m = \frac{1}{2}\cdot\frac{(1-\theta)\rho_{phase2} - \theta\rho_{phase1}}{\theta\rho_{phase1} + (1-\theta)\rho_{phase2}}, \tag{5}$$

$$\kappa = \theta\kappa_{phase1} + (1-\theta)\kappa_{phase2}, \tag{6}$$

where ρ is the density, C_p is the heat capacity of the material, κ is the thermal conductivity, u is the velocity of the medium which is zero in the problem under study, T is the temperature, θ is the phase ratio at a given temperature, α_m is the mass ratio between the phases, L is the latent heat of the phase transition, Q is the external heat flow. The $phase1$ and $phase2$ indices indicate which phase the properties belong to, the solid phase or the liquid phase, respectively.

To account for radiation heat transfer, a Surface-to-Surface Radiation boundary condition is added to the Heat Transfer in Solids physics interface in COMSOL Multiphysics by selecting the outer boundaries of the container and thermal unit:

$$-n(-\kappa\nabla T) = \varepsilon\sigma_b(T_{ext}^4 - T^4), \tag{7}$$

where T_{ext} is the wall temperature of the thermal unit; T is the temperature of the container wall, n is the vector directed along the normal to the surface of the cylinder (container); $\varepsilon = \left(\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1\right)^{-1}$ is the reduced radiation coefficient of the system, ε_1 is the radiation coefficient of the thermal unit, $\varepsilon_2$is the radiation coefficient of the container; σ_b is the Stefan-Boltzmann constant.

Convection and mass transfer of molten Bi_2Te_3 are not taken into account.

To carry out calculations, the geometric dimensions of the system elements, the initial temperatures of the heater and coolers, the liquidus and solidus temperatures of the thermoelectric material based on Bi_2Te_3, as well as the temperature dependence of the properties of the grown material are specified in the created computer model.

3. Results of computer simulation

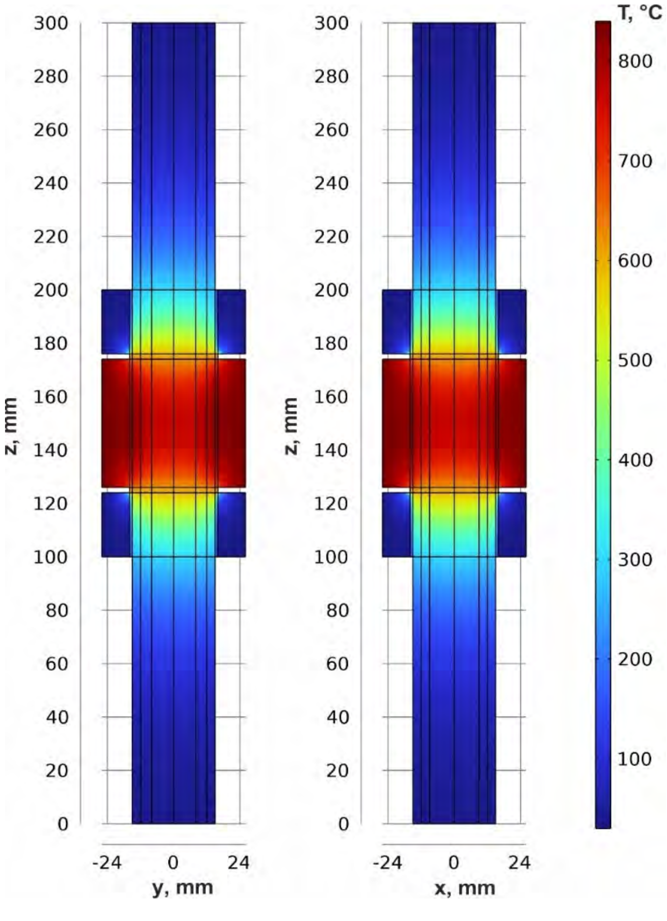

Fig. 2. Typical temperature distribution in a setup for growing thermoelectric materials using the vertical zone melting method. (h = 16 mm; d = 24 mm; a = 3 mm; h_h = 2d; h_c = 1d; T_h = 840℃; T_c = 30℃; v = 0.5 cm/h).

An example of temperature distribution in the sections YZ (x = 0) and XZ (y = 0) for given growing conditions and geometric dimensions (h = 16 mm; d= 24 mm; a = 3 mm; h_h = 2d; h_c = 1d; T_h = 840°C; T_c = 30°C; v = 0.5 cm/h) is given in Fig. 2, an example of crystallization front shape in these sections at different heater temperatures (h = 16 mm; d = 24 mm; a = 3 mm; h_h = 2d; h_c = 1d; T_c = 30°C; v = 0.5 cm/h) – in Fig. 3.

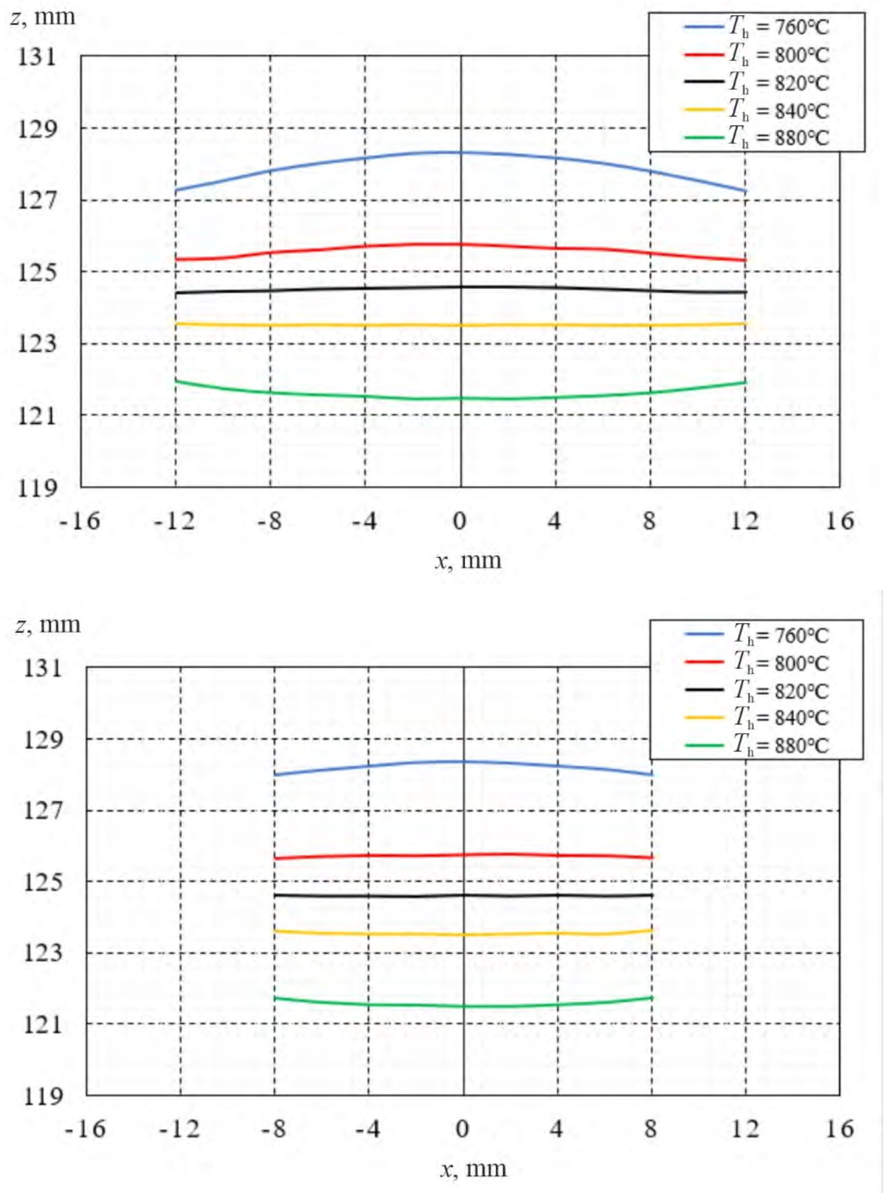

Fig. 3. The shape of the crystallization front in sections XZ (y = 0) and YZ (x = 0) for different temperatures of the heater T_h *(h = 16 mm; d = 24 mm; a = 3 mm;* $h_h = 2d$; $h_c = 1d$; $T_c = 30℃$; *v = 0.5 cm/h).*

The created computer model allows one to determine the optimal geometry of the container, the dimensions of the heater and coolers, their temperatures, the speed of movement of the heating unit and other technological parameters and to develop the technology of growing flat ingots of thermoelectric materials based on Bi_2Te_3 without significant costs for the production of a large number of parts of different geometries. and experimental studies.

Conclusions

1. A computer model has been developed to optimize the process of manufacturing flat ingots of thermoelectric materials based on Bi_2Te_3 using the vertical zone melting method.
2. The created computer model allows one to study the dependence of the crystallization front shape on various process parameters (geometric dimensions of the heater and refrigerators, their temperatures, speed of movement, etc.) and thus carry out multifactorial optimization of

technological modes and equipment design, significantly reducing material costs and time, which are necessary for conducting similar experimental studies.

References

1. Cao T., Shi X.L., Li M., Hu B., Chen W., Liu W.Di, W. Lyu, MacLeod J., Chen Z.G. (2023). Advances in bismuth-telluride-based thermoelectric devices: progress and challenges. *EScience,* 3 (3), Article 100122. https://doi.org/0.1016/j.esci.2023.100122.
2. Goldsmid H.J. (2014). Bismuth telluride and its alloys as materials for thermoelectric generation. *Materials*, 7, 2577-2592. https://doi.org/10.3390/ma7042577.
3. Kuo Chia-Hung, Hwang Chii-Shyang, Jeng Ming-Shan, Su Wei-Sheng, Chou Ya-Wen, Ku Jie-Ren (2010). Thermoelectric transport properties of bismuth telluride bulk materials fabricated by ball milling and spark plasma sintering. *Journal of Alloys and Compounds*, 496 (1 – 2), 687 – 690. https://doi.org/10.1016/j.jallcom.2010.02.171.
4. Anatychuk L.I., Hwang Jenn-Dong, Lysko V.V., Prybyla A.V. (2013). Thermoelectric heat recuperators for cement kilns. *J. Thermoelectricity*, 5, 36 – 42.
5. Anatychuk L.I., Lysko V.V., Kravtsov S.O. (2019). Design of thermoelectric generator for transport high-power starting preheater. *J. Thermoelectricity,* 5, 17 – 36.
6. Anatychuk L.I., Lysko V.V. (2021). Computer design of a thermoelectric generator for heat and electricity supply to heavy-duty vehicles. *J. Thermoelectricity,* 2, 79 – 88.
7. Tritt T. (2000). *Recent trends in thermoelectric materials research, Part Two* (Semiconductors and semimetals, Vol. 70). Academic Press, 2000. 320 p. ISBN-13: 978-0127521794.
8. Zhai R.S., Zhu T.J. (2022). Improved thermoelectric properties of zone-melted *p*-type bismuth-telluride-based alloys for power generation. *Rare Met.* 41, 1490 – 1495. https://doi.org/10.1007/s12598-021-01901-2.
9. Saberi Y., Sajjadi S.A. (2022). A comprehensive review on the effects of doping process on the thermoelectric properties of Bi_2Te_3 based alloys. *Journal of Alloys and Compounds,* 904, Article 163918. https://doi.org/10.1016/j.jallcom.2022.163918.
10. Saleemi M., Toprak M.S., Li S., Johnsson M., Muhammed M. (2012). Synthesis, processing, and thermoelectric properties of bulk nanostructured bismuth telluride (Bi_2Te_3). *J. Mater. Chem.* 2, 725 – 730. https://doi.org/10.1039/C1JM13880D.
11. Lysko V.V., Tudoroi P.F. (2019). Computer simulation of extrusion process of Bi_2Te_3 based tape thermoelectric materials. *J. Thermoelectricity,* 2, 58 – 65.
12. Anatychuk L.I., Lysko V.V. (2020). *Thermoelectricity: Vol. 5. Metrology of thermoelectric materials.* Chernivtsi: Bukrek ISBN 978-617-7770-40-3.
13. Anatychuk 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.
14. Anatychuk L.I., Havrylyuk N.V., Lysko V.V. (2012). Methods and equipment for quality control of thermoelectric materials. *Journal of Electronic Materials,* 41(6), 1680 – 1685. https://doi.org/10.1007/s11664-012-1973-1.
15. Nitsovich O.V. (2018). Research on the conditions of forming a flat crystallization front when growing Bi_2Te_3 based thermoelectric material by vertical zone melting method. *J. Thermoelectricity*. 3, 76 – 82.
16. Anatychuk L.I., Nitsovich O.V. (2018). Simulation of the effect of thermal unit velocity on the

process of growing Bi_2Te_3 based materials by vertical zone melting method. *J. Thermoelectricity,* 3, 76 – 82.

17. Nitsovich O.V. (2018). Computer simulation of Bi_2Te_3 crystallization process in the presence of electrical current. *J. Thermoelectricity,* 5, 12 – 21.
18. COMSOL Multiphysics, v. 6.0. www.comsol.com. COMSOL AB, Stockholm, Sweden. 2021.
19. Reddy J.N. (2006). *An introduction to the finite element method* (Third ed.). McGraw-Hill. ISBN 9780071267618.

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Лисько В.В., *канд. фіз.-мат. наук* [1,2]
Ніцович О.В., *канд. фіз.-мат. наук* [1]

[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: anatych@gmail.com

КОМП’ЮТЕРНЕ МОДЕЛЮВАННЯ ПРОЦЕСУ ВИГОТОВЛЕННЯ ПЛОСКИХ ЗЛИТКІВ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ НА ОСНОВІ Bi_2Te_3 МЕТОДОМ ВЕРТИКАЛЬНОЇ ЗОННОЇ ПЛАВКИ

Представлено результати розробки комп’ютерної моделі для оптимізації процесу виготовлення плоских злитків термоелектричних матеріалів на основі Bi_2Te_3 методом вертикальної зонної плавки. Створена модель дозволяє досліджувати залежності форми фронту кристалізації від різних технологічних параметрів – геометричних розмірів нагрівника та холодильників, їх температур, швидкості руху тощо. Це дає можливість проводити багатофакторну оптимізацію технологічних режимів та конструкції обладнання, суттєво знизивши матеріальні витрати і час, що необхідні для проведення аналогічних експериментальних досліджень. Бібл. 19, рис. 3.

Ключові слова: моделювання, вертикальна зонна плавка, термоелектричний матеріал, телурид вісмуту.

Література

1. Cao T., Shi X.L., Li M., Hu B., Chen W., Liu W.Di, W. Lyu, MacLeod J., Chen Z.G. (2023). Advances in bismuth-telluride-based thermoelectric devices: progress and challenges. *EScience,* 3 (3), Article 100122. https://doi.org/0.1016/j.esci.2023.100122.
2. Goldsmid H.J. (2014). Bismuth telluride and its alloys as materials for thermoelectric generation. *Materials,* 7, 2577-2592. https://doi.org/10.3390/ma7042577.
3. Kuo Chia-Hung, Hwang Chii-Shyang, Jeng Ming-Shan, Su Wei-Sheng, Chou Ya-Wen, Ku Jie-Ren (2010). Thermoelectric transport properties of bismuth telluride bulk materials fabricated by ball milling and spark plasma sintering. *Journal of Alloys and Compounds,* 496 (1 – 2), 687 – 690. https://doi.org/10.1016/j.jallcom.2010.02.171.
4. Anatychuk L.I., Hwang Jenn-Dong, Lysko V.V., Prybyla A.V. (2013). Thermoelectric heat

recuperators for cement kilns. *J. Thermoelectricity,* 5, 36 – 42.

5. Anatychuk L.I., Lysko V.V., Kravtsov S.O. (2019). Design of thermoelectric generator for transport high-power starting preheater. *J. Thermoelectricity,* 5, 17 – 36.
6. Anatychuk L.I., Lysko V.V. (2021). Computer design of a thermoelectric generator for heat and electricity supply to heavy-duty vehicles. *J. Thermoelectricity,* 2, 79 – 88.
7. Tritt T. (2000). *Recent trends in thermoelectric materials research, Part Two* (Semiconductors and semimetals, Vol. 70). Academic Press, 2000. 320 p. ISBN-13: 978-0127521794.
8. Zhai R.S., Zhu T.J. (2022). Improved thermoelectric properties of zone-melted *p*-type bismuth-telluride-based alloys for power generation. *Rare Met.* 41, 1490 – 1495. https://doi.org/10.1007/s12598-021-01901-2.
9. Saberi Y., Sajjadi S.A. (2022). A comprehensive review on the effects of doping process on the thermoelectric properties of Bi_2Te_3 based alloys. *Journal of Alloys and Compounds,*904, Article 163918. https://doi.org/10.1016/j.jallcom.2022.163918.
10. Saleemi M., Toprak M.S., Li S., Johnsson M., Muhammed M. (2012). Synthesis, processing, and thermoelectric properties of bulk nanostructured bismuth telluride (Bi_2Te_3). *J. Mater. Chem.* 2, 725 – 730. https://doi.org/10.1039/C1JM13880D.
11. Lysko V.V., Tudoroi P.F. (2019). Computer simulation of extrusion process of Bi_2Te_3 based tape thermoelectric materials. *J. Thermoelectricity,* 2, 58 – 65.
12. Anatychuk L.I., Lysko V.V. (2020). *Thermoelectricity: Vol. 5. Metrology of thermoelectric materials.* Chernivtsi: Bukrek ISBN 978-617-7770-40-3.
13. Anatychuk 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.
14. Anatychuk L.I., Havrylyuk N.V., Lysko V.V. (2012). Methods and equipment for quality control of thermoelectric materials. *Journal of Electronic Materials,* 41 (6), 1680 – 1685. https://doi.org/10.1007/s11664-012-1973-1.
15. Nitsovich O.V. (2018). Research on the conditions of forming a flat crystallization front when growing Bi_2Te_3 based thermoelectric material by vertical zone melting method. *J. Thermoelectricity*. 3, 76 – 82.
16. Anatychuk L.I., Nitsovich O.V. (2018). Simulation of the effect of thermal unit velocity on the process of growing Bi_2Te_3 based materials by vertical zone melting method. *J. Thermoelectricity,* 3, 76 – 82.
17. Nitsovich O.V. (2018). Computer simulation of Bi_2Te_3 crystallization process in the presence of electrical current. *J. Thermoelectricity,* 5, 12 – 21.
18. COMSOL Multiphysics, v. 6.0. www.comsol.com. COMSOL AB, Stockholm, Sweden. 2021.
19. Reddy J.N. (2006). *An introduction to the finite element method* (Third ed.). McGraw-Hill. ISBN 9780071267618.

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