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COMPUTER RESEARCH ON THE INFLUENCE OF THE PELTIER EFFECT ON THE CRYSTALLIZATION PROCESS OF Bi_2Te_3 BASED THERMOELECTRIC MATERIALS

The article presents the results of computer simulation of the process of growing Bi_2Te_3 based thermoelectric materials by the vertical zone melting method with regard to the Peltier effect occurring at the interface between solid and liquid phases of the grown material when electric current is passed through an ingot. Bibl. 7, Fig. 6, Tabl. 1.

Key words: simulation, vertical zone melting, thermoelectric material, growing in electric field.

Introduction

Bismuth telluride-based solid solutions are unique commercially available thermoelectric materials (TEM) for solid-state cooling and generation of electrical energy. Therefore, much attention is paid to the improvement of Bi_2Te_3 based TEM production methods.

Zone melting is one of the most used methods for the production of semiconductor materials, in particular thermoelectric. However, the production of thermoelectric materials with the necessary properties is possible only under the conditions of a controlled crystallization process, since when TEM is obtained by this method, the crystallization front curvature, the temperature gradient at the interface between the solid and liquid phases, the melt zone geometry, and the velocity have a great influence on the single crystal growth stability and homogeneity.

In [1-3], the possibility of growing single crystals of thermoelectric materials by the method of vertical zone melting in the presence of electric current passing through an ingot was considered. It is known that when passing an electric current, at the interface between the solid and liquid phases of the same semiconductor, just as at the interface between two different materials, the Peltier heat will be released or absorbed. This amount of heat is sufficient to affect the course of crystallization. However, studies of temperature distributions and geometry of the crystallization front cause considerable experimental difficulties, so simulation of the TEM growth process is relevant, which makes it possible to optimize the choice of technological parameters of the setup and the modes of material growth.

So, *the purpose of this work* is computer research on the influence of the Peltier effect that occurs at the interface between the solid and liquid phases when growing Bi_2Te_3 based thermoelectric materials by the vertical zone melting when passing electric current through the molten zone, on growing process, specifically, on the shape of crystallization front and temperature gradients.

Physical model of vertical zone melting process with current

The physical model of the process of growing single crystals based on Bi_2Te_3 by the method of vertical zone melting is shown in Fig.1.

The figure shows an ingot fragment, including polycrystalline material 2, molten zone 6 and single crystal 3. The ingot is placed in quartz ampoule 1. With the help of heater 7 and cooler system 8, molten zone 6 is formed, which, moving with the heater along the sample, provides melting of polycrystal and melt crystallization below boundary 5, which is called the crystallization front.

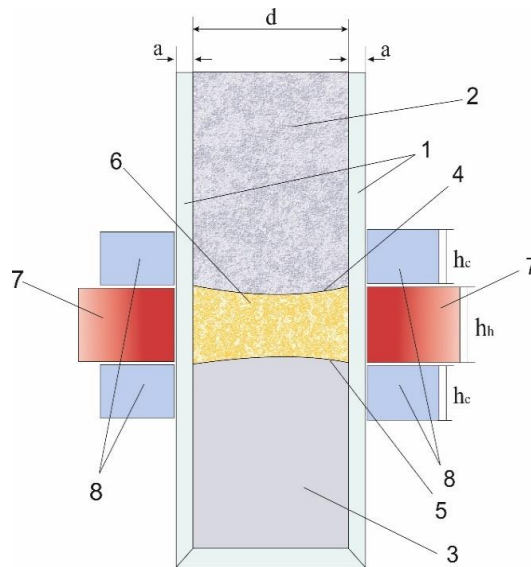


Fig.1. Physical model of installation for growing TEM by vertical zone melting method:

1 – quartz ampoule, 2 – material in solid phase (polycrystal), 3 – material in solid phase (single crystal),
4 – melt front boundary, 5 – crystallization front boundary, 6 – material in liquid phase (melt zone),
7 – heater, 8 – coolers.

When simulating zone growth, the stationary mode was considered, that is, the movement of the heat unit, including heater 7 and coolers 8, was not taken into account. It is known that crystals based on bismuth telluride are grown at a velocity of 1.5-2.5 cm/h. Estimating the time required for the system to achieve thermal equilibrium, which, even with rough calculations, was 40 s, it was determined that during this time the furnace will only move 0.2 mm. The heat loss in this area will be two orders of magnitude less than the heat that is transferred from the thermal unit to the ampoule. Thus, these losses can be neglected in computer simulation, since they will have little effect on the overall temperature distribution.

Mathematical model of TEM growing process by vertical zone melting method with current

When simulating the heat conduction process in a homogeneous medium with a phase transition in the COMSOL Multiphysics software package, the classical system of nonstationary differential heat conduction equations is solved, supplemented by the dependences of the physical properties of the solid under study as a function of the phase state at a given point at a specified temperature with regard to the Joule-Lenz heat and thermoelectric effects:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p u \nabla T + \nabla q = Q + Q_s \quad (1)$$

$$q = -\kappa \nabla T + Pj, \quad (2)$$

$$Q_s = jE \quad (3)$$

here

$$j = \sigma E + j_s, \quad (4)$$

$$j_s = -\sigma \alpha \nabla T, \quad (5)$$

$$P = \alpha T, \quad (6)$$

$$E = -\nabla U, \quad (7)$$

$$\rho = \theta \rho_{phase1} + (1 - \theta) \rho_{phase2}, \quad (8)$$

$$C_p = \frac{1}{2} \left(\theta \rho_{phase1} C_{p_{phase1}} + (1 - \theta) \rho_{phase2} C_{p_{phase2}} \right) + L \frac{d\alpha_m}{dT}, \quad (9)$$

$$\alpha_m = \frac{1}{2} \cdot \frac{(1-\theta) \rho_{phase2} - \theta \rho_{phase1}}{\theta \rho_{phase1} + (1-\theta) \rho_{phase2}}, \quad (10)$$

$$\kappa = \theta \kappa_{phase1} + (1 - \theta) \kappa_{phase2}. \quad (11)$$

де ρ is the density, kg/m³; C_p is heat capacity of material at constant pressure, J/(kg·K); κ is thermal conductivity, W/(cm·K), u is medium velocity, m/s, in the investigated problem is zero; T is temperature, K; t is time, s; θ is the phase ratio at a given temperature; α_m is mass ratio between phases; L is the latent heat of phase transition, J/kg; Q is external heat flux, W. The indices phase1 and phase2 indicate to what phase the properties, solid phase or liquid, respectively, are related. To simulate the effect of the electrical field on the growing process, the following boundary conditions are set at the upper and lower boundaries of the ingot:

$$U|_{z=0} = U_0, U|_{z=l} = 0. \quad (11)$$

The condition of thermal insulation was set on all external walls of the heater and coolers:

$$-n \cdot (-\kappa \nabla T) = 0. \quad (12)$$

On the outer wall of the quartz ampoule the boundary condition is set as a function of:

$$-n(-\kappa \nabla T) = h(T_{ext} - T) + \varepsilon \sigma_b (T_{ext}^4 - T^4), \quad (13)$$

where T_{ext} is the ambient temperature, K; T is the temperature of the wall of the quartz ampoule, K; n is vector directed along the normal to the surface of the cylinder (ampoule); ε is quartz emissivity; σ_b is Stephan-Boltzmann constant, W/(m²·K⁴); h is the heat transfer coefficient, W/(m²·K), which is expressed by the formula [4]:

$$h = \begin{cases} \frac{k}{l} \left(0,68 + \frac{0,67 Ra_l^{1/4}}{\left(1 + \left(\frac{0,492 k}{\mu C_p}\right)^{9/16}\right)^{4/9}} \right), \text{ якщо } Ra_l \leq 10^9 \\ \frac{k}{l} \left(0,825 + \frac{0,38 Ra_l^{1/6}}{\left(1 + \left(\frac{0,492 k}{\mu C_p}\right)^{9/16}\right)^{8/27}} \right), \text{ якщо } Ra_l > 10^9 \end{cases},$$

here, Ra_l is the Raleigh number which is defined by the following expression:

$$Ra_l = \frac{g \alpha_p \rho^2 C_p (T - T_{ext}) l^3}{\mu \kappa},$$

where g is the acceleration of gravity, m/s^2 ; α_p is the temperature coefficient of volumetric expansion, K^{-1} ; l is the length of the air layer, m ; μ is the dynamic viscosity, $(Pa \cdot S)$.

In order to take into account the features of phase transitions during heating – cooling of Bi_2Te_3 , the thermoelectric properties of TEM are set depending on temperature, according to the data obtained in [5]. Convection and mass transfer of molten Bi_2Te_3 were not taken into account in this model.

Computer simulation results

Below are the results of computer simulation of the influence of the Peltier effect on the crystallization of bismuth telluride by vertical zone melting in the presence of electric current, in accordance with the physical model shown in Fig. 1. Table 1 shows some input parameters of the model.

Table 1.

Input data used in simulation

	$T, ^\circ C$	ε	$C_p, J/(mole \cdot K)$	$\rho, g/cm^3$	<i>Liquidus and solidus, $^\circ C$</i>
Bi_2Te_3	-	-	59.73-126.19	7.74	585-530
Quartz	-	0.9-0.41	-	-	-
Heater	700-820	0.8	-	7.0	-
Cooler	30	-	-	-	-

The diameter d of the grown crystal was taken to be 24 mm, the height of the heater was chosen optimal and, as noted in [6], should be equal to $h_h = 3d$. The height of the coolers $h_c = 1/2d$, the distance between the quartz tube, as well as between the heater and coolers was 2 mm. To simulate the effect of the electric field on the growing process, a potential difference was set at the upper and lower boundaries of the material.

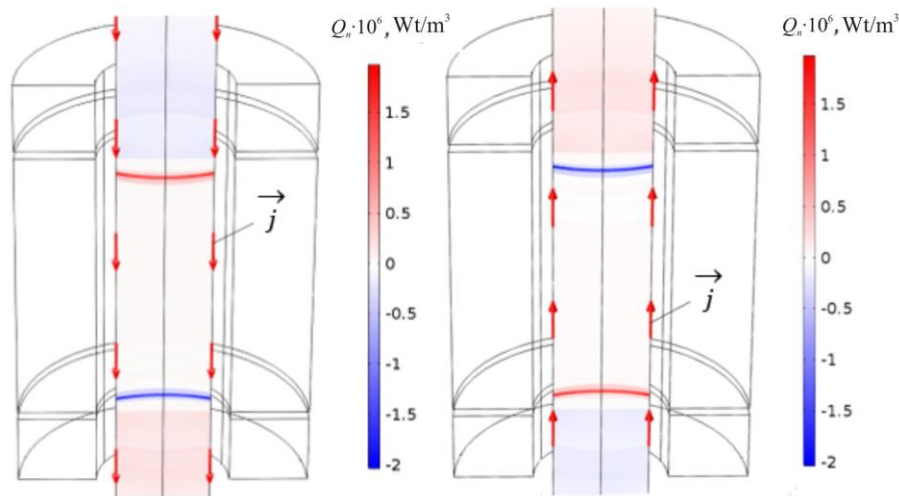
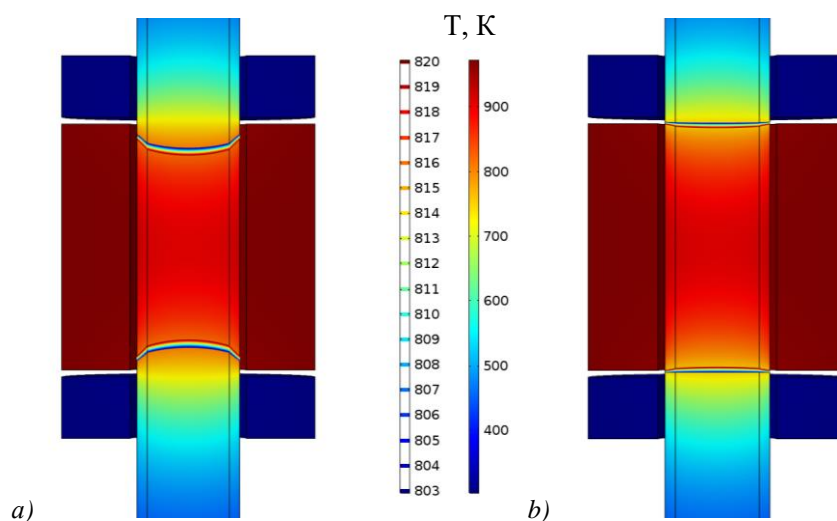


Fig.2. Release and absorption of the Peltier heat at the interfaces between solid and liquid phases depending on the direction of current passage

As can be seen from Fig. 2, the Peltier heat is a positive value, when current passes from the solid to liquid phase and, on the contrary, when current flows from the liquid to solid phase, the Peltier heat is absorbed.

The shape of the crystallization front, which can be concave, flat, or convex, is of great importance for the formation of a structurally homogeneous crystal during growth [6–7]. On a concave surface in the melt, near the walls of the container, parasitic nuclei easily appear. This form of the front contributes to stresses, shrinkage shells and uneven distribution of impurities over the cross section of the grown crystal. The convex interface prevents the growth of random nuclei formed near the walls of the container, but the higher the growth rate, the more likely the formation of parasitic nuclei and the smaller the radius of curvature of the interface. A flat interface minimizes the occurrence of stresses in the crystal and promotes a uniform distribution of impurities over the cross section of the crystal. Therefore, it is important to create a flat crystallization front (Fig. 3, b).



*Fig.3. Crystallization front view for different heater temperatures at $j=0.5 \cdot 10^5$:
a) $T_h=700^\circ\text{C}$; b) $T_h=790^\circ\text{C}$*

Fig.4 shows the dependence of the curvature value k of the crystallization front on the heater temperature at different densities of current passed through the molten zone. The curvature was calculated as $k = z_{\max} - z_{\min}$ along the front.

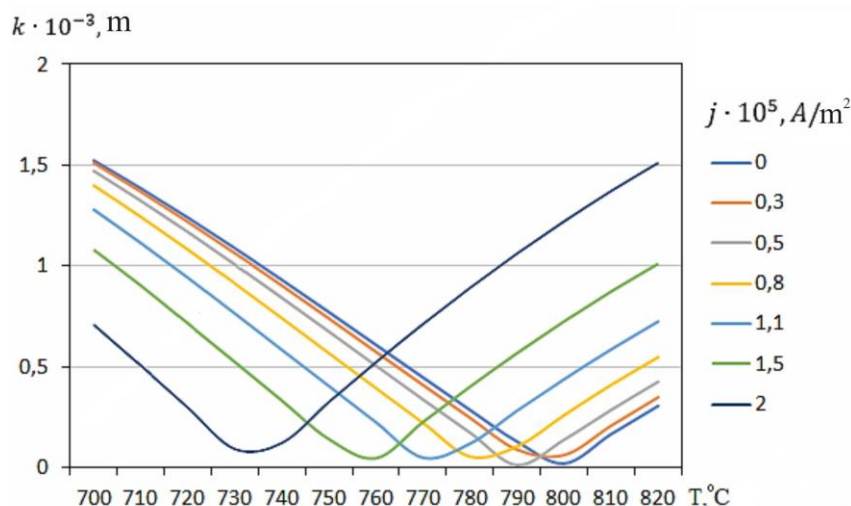


Fig.4. Dependence of the curvature value k of the crystallization front on the heater temperature at different densities of current

As can be seen from Fig. 4, for a given installation configuration, without passing an electric current, a flat crystallization front was achieved at temperatures of 790-800 °C. By varying the current density from 0.3 до $2 \cdot 10^5 \text{ A/m}^2$, a flat front can be achieved at lower heater temperatures.

The dependence of the temperature gradient along the crystallization front on the direction of current passage is shown in Fig.5. In this case the temperature of the heater is $T_h = 785^\circ\text{C}$, the current density $j = 0.5 \cdot 10^5 \text{ A/m}^2$.

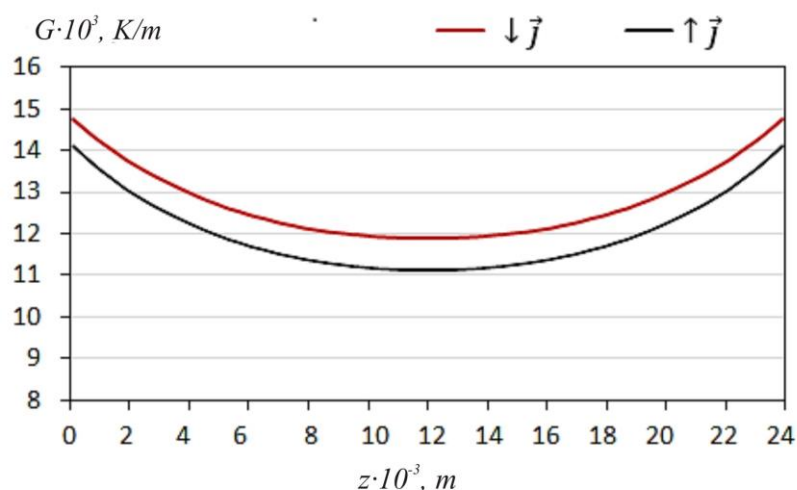


Fig.5. Dependence of the radial temperature gradient G on the direction of current passage

The use of the Peltier effect for zone growing with the passage of direct electric current is complicated by the fact that the Joule-Lenz heat is simultaneously released in the solid and liquid phases, which enhances the Peltier effect at the melt front and weakens it at the crystallization front.

Fig.6. shows the dependence of the radial temperature gradient G on the heater temperatures for different densities of current which is passed through the molten zone.

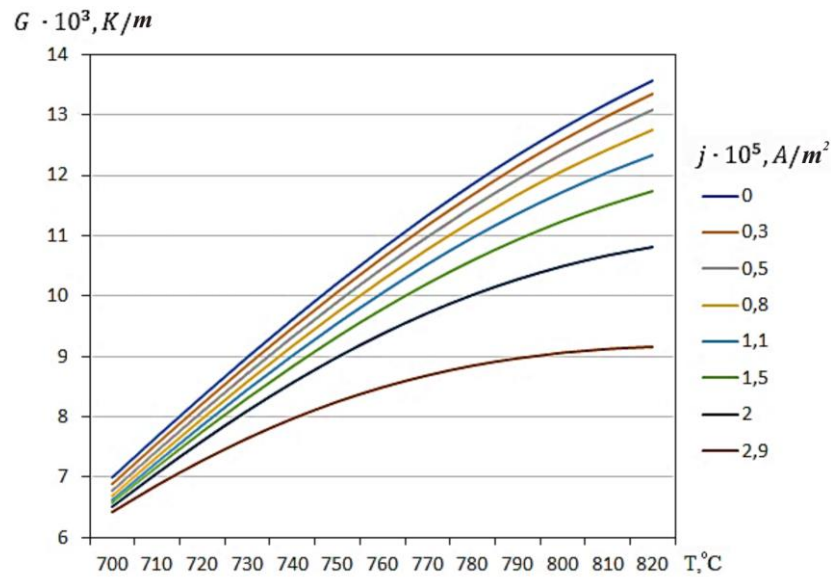


Fig.5. Dependence of the radial temperature gradient G on the heater temperatures for different current densities

From these results it follows that due to an increase in the Joule-Lenz heat, the temperature gradient at the crystallization front decreases with increasing current.

Conclusions

1. A technique was developed for computer simulation of the process of growing TEM based on Bi_2Te_3 by the method of vertical zone recrystallization with the passage of electric current through the sample.
2. The possibility of controlling the temperature distribution in the ingot during TEM growth by vertical zone melting method by passing electric current through the molten zone and the origination of the Peltier effect at the interface between the solid and liquid phases was confirmed.

The optimal values of the heater temperatures and current values were determined which ensure the formation of a flat crystallization front.

References

1. Pfann U.G. (1970). *Zonnaya plavka [Zone melting]*. V.N.Vigdorovich (Ed.). Moscow: Mir [in Russian].
2. Goltsman B.M., Liaschenok V.I., Strekopytova N.I. (1986). Kristallizatsiia v elektricheskom pole termoelektricheskikh materialov na osnove telluride vismuta [Crystallization in electrical field of thermoelectric materials based on bismuth telluride]. In: *Termoelektricheskie istochniki toka: materailly, konstruktsiia, primeneniie. Tezisy dokladov vsesoiuznogo soveshchaniia - Thermoelectric current sources: materials, design, application. Abstracts of All-Union Conference reports*. Ashgabad [in Russian].
3. Liaschenok V.I., Strekopytova N.I. (1995). Influence of electric current flow during crystallization process on thermoelectric properties of materials. *Proc. of XIV International Conference of Thermoelectrics (1995)*, 112-114.
4. Incropera F.P., DeWitt D.P., Bergman T.L., Lavine A.S. (2007). *Fundamentals of heat and mass transfer*. 6th Ed. New York: John Wiley & Sons Ltd.

5. Nitsovykh O.V. (2018). Computer simulation of Bi_2Te_3 crystallization process in the presence of electric current. *J. Thermoelectricity*, 5, 12-21.
6. Nitsovykh 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.
7. Vilke K.T. (1977). *Metody vyrashchivaniia kristallov [Methods of crystal growth]*. Leningrad: Nedra [in Russian].

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КОМП'ЮТЕРНЕ ДОСЛІДЖЕННЯ ВПЛИВУ ЕФЕКТУ ПЕЛЬТЬЄ НА ПРОЦЕС КРИСТАЛІЗАЦІЇ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ НА ОСНОВІ Bi_2Te_3

У статті наведено результати комп'ютерного моделювання процесу вирощування термоелектричних матеріалів на основі Bi_2Te_3 методом вертикальної зонної плавки з врахуванням ефекту Пельтьє, що виникає на межі розділу твердої та рідкої фаз вирощуваного матеріалу при пропусканні через злиток електричного струму. . Бібл. 7, рис. 5, табл. 1.

Ключові слова: моделювання, вертикальна зонна плавка, термоелектричний матеріал, вирощування в електричному полі.

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КОМПЬЮТЕРНОЕ ИССЛЕДОВАНИЕ ВЛИЯНИЯ ЭФФЕКТА ПЕЛЬТЬЕ НА ПРОЦЕСС КРИСТАЛЛИЗАЦИИ ТЕРМОЭЛЕКТРИЧЕСКИХ МАТЕРИАЛОВ НА ОСНОВЕ Bi₂Te₃

В статье приведены результаты компьютерного моделирования процесса выращивания термоэлектрических материалов на основе Bi₂Te₃ методом вертикальной зонной плавки с учетом эффекта Пельтье, который возникает на границе раздела твердой и жидкой фаз выращиваемого материала при пропускании через слиток электрического тока. Библ. 7, рис. 6, табл. 1.

Ключевые слова: моделирование, вертикальная зонная плавка, термоэлектрический материал, выращивание в электрическом поле.

References

1. Pfann U.G. (1970). *Zonnaya plavka [Zone melting]*. V.N.Vigdorovich (Ed.). Moscow: Mir [in Russian].
2. Goltsman B.M., Liaschenok V.I., Strekopytova N.I. (1986). Kristallizatsiia v elektricheskom pole termoelektricheskikh materialov na osnove telluride vismuta [Crystallization in electrical field of thermoelectric materials based on bismuth telluride]. In: *Termoelektricheskie istochniki toka: materaily, konstruksii, primeneniie. Tezisy dokladov vsesoiuznogo soveshchaniia - Thermoelectric current sources: materials, design, application. Abstracts of All-Union Conference reports*. Ashgabad [in Russian].
3. Liaschenok V.I., Strekopytova N.I. (1995). Influence of electric current flow during crystallization process on thermoelectric properties of materials. *Proc. of XIV International Conference of Thermoelectrics (1995)*, 112-114.
4. Incropera F.P., DeWitt D.P., Bergman T.L., Lavine A.S. (2007). *Fundamentals of heat and mass transfer*. 6th Ed. New York: John Wiley & Sons Ltd.
5. Nitsovych O.V. (2018). Computer simulation of Bi₂Te₃ crystallization process in the presence of electric current. *J.Thermoelectricity*, 5, 12-21.
6. Nitsovych O.V. (2018). Research on the conditions of forming a flat crystallization front when growing Bi₂Te₃ based thermoelectric material by vertical zone melting method. *J.Thermoelectricity*, 3, 76-82.
7. Vilke K.T. (1977). *Metody vyrashchivaniia kristallov [Methods of crystal growth]*. Leningrad: Nedra [in Russian].

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