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VIBRATION EFFECT ON THE HOMOGENEITY OF Bi_2Te_3 BASED THERMOELECTRIC MATERIALS GROWN BY VERTICAL ZONE MELTING TECHNIQUE

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• *The results of studying vibration effect on the homogeneity of thermoelectric materials grown by vertical zone melting technique are given. It is shown that vibration of ampoule during growth contributes to leveling of crystallization front and mixing of melt components. Owing to vibration effect on the melt, the distribution of impurities becomes more uniform, the radial and axial homogeneities of materials are increased.*

Introduction

Vertical zone melting technique is widely used to obtain low-temperature Bi_2Te_3 based thermoelectric materials, but not always yields homogeneous crystals along the length and over the cross-section of ingot, especially of large diameter. The weak point of this technique is a non-uniform temperature distribution due to different heat removal at crystallization in the crystal centre and on its periphery. This brings about a convex (towards solid phase) shape of crystallization front and high inhomogeneity of component distribution in the ingot.

Research on impurity distribution as a function of thermal and dynamic effects, in particular, convection, rotation, magnetic field, vibration and others is widely used to improve the figure of merit of Bi_2Te_3 based thermoelectric materials.

There are different explanations of vibration influence on the shape and growth rate of crystals, their structural perfection and impurity composition. Thus, the authors of [1] attribute vibration effect to leveling of crystallization conditions at the interface of two phases, periodic temperature change at crystallization front, which leads to equilibrium crystal shapes and a change in the energy state of liquid phase under the influence of vibrations. A change in vibration intensity affects the relation between growth rates of different faces.

In Ref. [2] it is shown that under the influence of vibrations the density of dislocations is reduced. It is explained by a number of factors, namely: increase of heat transfer efficiency, mutual annihilation of dislocations, migration thereof beyond the blocks and to crystal surface.

Vibrations can reduce the thickness of boundary layers near crystallization front, which is of basic importance when growing single crystals. Using vibration effect on the melt, one can change the value of temperature gradient at crystallization front, that is change the kinetics and rate of crystal growth [3]. The degree of vibration effect on the boundary layer depends on the amplitude and frequency of vibration. It is also assumed that vibrations change the melt structure, affect the kinetic (mobility of particles) and thermodynamic factors (supercooling values). Acceleration of crystal growth due to vibration is attributable to a reduction of diffusion layer thickness close to crystallization front and increase in diffusion rate [4-6].

Convective fluxes arising in the melt can result in the inhomogeneous distribution of impurities in grown crystals. Therefore, vibration allows control over convective fluxes and change in the shape of crystallization front. Under the influence of vibrations the melt components are mixed close to crystallization front, which leads to radial and longitudinal homogeneity in a crystal grown by zone melting technique due to crystallization front leveling [7, 8]. Experimentally established [7] is a change in the amount of impurity in crystal lattice with different vibration amplitudes which is explained by a change in coefficient of impurity distribution at acceleration (retardation) of crystal growth due to vibrations.

Exposure to vibration is also caused by the possibility of "cluster" ("block") crystal growth mechanism related to structural reconstruction of melt close to crystallization front [9], which is comparable to the effect of vibrocompaction on granular bodies. Compaction and ordering of blocks near the crystal surface results, on the one hand, in crystal growth acceleration, and, on the other hand, in their structure improvement.

It should be noted that the influence of vibration is generally investigated on Czochralski growth units, and the literature practically lacks information on the effect of vibration on the homogeneity of thermoelectric material grown by vertical zone melting technique. As long as this technique is widely used in practice, investigations of the effect produced by vibrations on the properties of materials grown by vertical zone melting technique are relevant.

The purpose of this work is to determine the effect of vibration on the homogeneity of impurity distribution and structural perfection of Bi_2Te_3 based thermoelectric materials grown by vertical zone melting technique.

Experimental procedure

Thermoelectric materials based on Bi_2Te_3-Bi_2Se_3 and Bi_2Te_3-Sb_2Te_3 solid solutions were synthesized of elementary *Bi*, *Te*, *Sb* and *Se* of 5*N* purity in graphitized quartz ampoules of diameter 28 mm at temperature 1050 K for 1 hour on agitation in synthesis furnace. Growth of thermoelectric material with the use of vibration took place in the same ampoules filled with argon on the vertical zone melting unit schematically shown in Fig. 1.

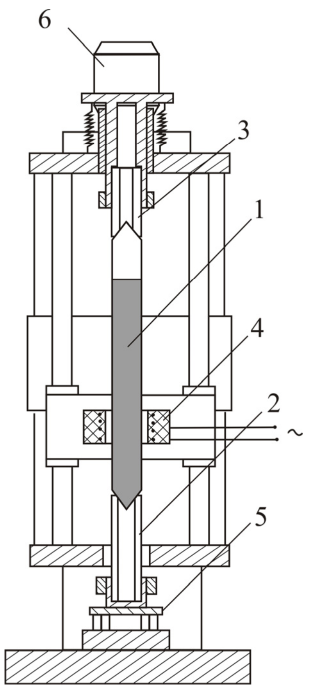


Fig. 1. Vertical zone melting unit with vibration: 1 – ampoule with thermoelectric material; 2, 3 – clutches; 4 – electric heater; 5 – vibrating plate; 6 – electric motor.

Vertical zone melting unit with vibration comprises quartz cylinder ampoule 1 with thermoelectric material vertically arranged between clutches 2 and 3 of the vibrating and hold-down devices, respectively. With the use of electric heater 4, in ampoule 1 a melt zone with temperature 730 – 780 °C is created which moves slowly at the velocity of υ = 15 – 22 mm/hour, as the heater travels from the bottom to upper end of the ampoule. Vibrator 5 starts working simultaneously with switching on the heater's vertical travel. Vibration frequency is 50 – 100 Hz, vibration amplitude is 100 – 150 μm. Vibrations are transferred from vibrating plate 5 to thermoelectric material which is in ampoule 1. After a single pass of molten zone from the lower ampoule end to the upper, the electric power supplied to vibrator, heater and travel device is switched off and the heater by means of electric motor 6 and reversing mechanism moves to the bottom (initial) position for the next growth procedure.

Grown thermoelectric material (ingot) is removed from the ampoule, and is subject to further treatment after the measurement of thermoelectric parameters.

Such a unit was used to grow multi-component thermoelectric material of *n*-and *p*-type based on Bi_2Te_3-Bi_2Se_3 and Bi_2Te_3-Sb_2Te_3 solid solutions. Thermoelectric parameters (the Seebeck coefficient α and the electric conductivity σ) were measured along the ingot axis at room temperature. Along the ingot, thin sections were provided beforehand, located in a circle at an angle of 120°. The results of measurement on three thin sections were averaged. The electric conductivity of samples was measured by double-probe method, the Seebeck coefficient – by hot probe method (at $\Delta T = 10$ K). The temperature of the probe and heater in the growth unit was maintained by means of temperature controller with an accuracy of ± 0.1 K.

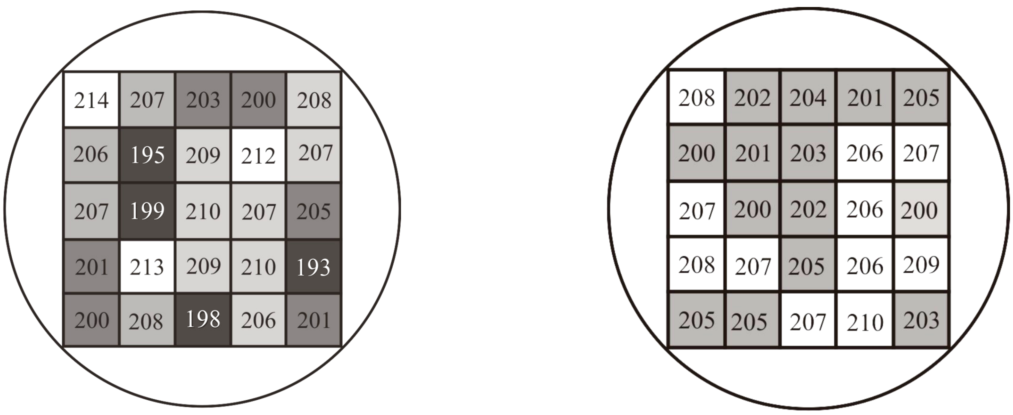
Radial homogeneity of samples was determined by measuring thermoelectric parameters (α, σ) on material legs of size 2 × 2 mm cut of discs. The accuracy of measuring the Seebeck coefficient was ± 1.5%, the accuracy of measuring the electric conductivity – ± 2.2%.

The structure of grown crystals was controlled by metallographic method on MIM-7 microscope with a 500-fold magnification. For this purpose, discs 8 mm thick were cut of the ingot, ground, polished and subject to metallographic analysis. For a better etch of dislocations, polished samples were etched with aqueous solution HNO_3:HCl: $K_2S_2O_8$ (1:1:2) for 1 – 1.5 min at temperature of 25 °C. Etching solution causes selective dissolution and oxidation of some phases and colouring of the others. After etching, the surface of samples was again investigated on the metallographic microscope.

Discussion of the results

The use of vibration in the process of material growth on vertical zone melting unit results in crystallization front leveling. Owing to the effect of vibration on the melt, the distribution of impurities becomes more uniform, the radial and axial homogeneity of materials are increased.

The radial homogeneity of samples of thermoelectric material grown by vertical zone melting method with the use of vibration was estimated by the distribution of thermoelectric parameters (α, σ) over the cross-section of ingot. Figs. 2 and 3 show the distributions of the Seebeck coefficient α and electric conductivity σ over the cross section of ingot obtained on the samples grown with and without vibration.

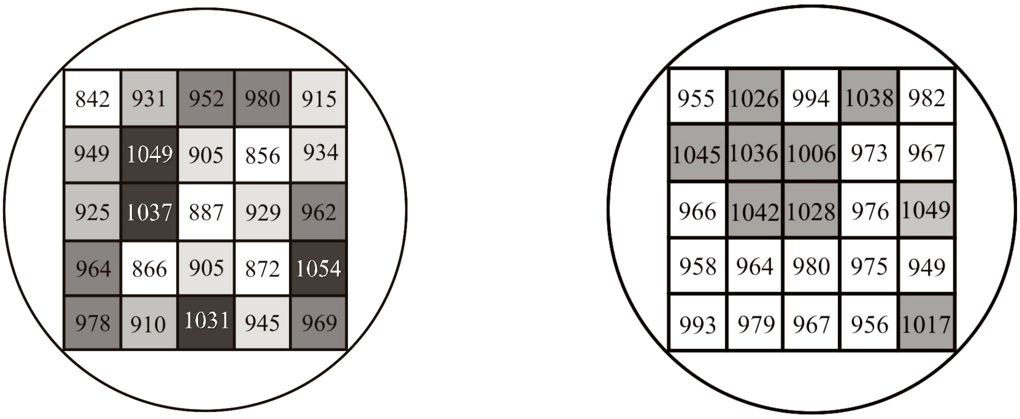


a) *b)*

Fig. 2. Distribution of the Seebeck coefficient α *(μV/K) over the cross-section of ingot:*
a) – sample grown without vibration, b) – sample grown with vibration.

Measurement of the Seebeck coefficient on thermoelectric material legs showed the best homogeneity on the samples grown by zone melting with vibration. From the analysis of these measurements it follows that deviation of parameter α from the average value in this case is ± 2.4%, whereas without vibration the deviation is α ± 5%.

The electric conductivity proved to be even more sensitive to vibration (Fig. 3). Thus, without vibration a deviation of parameter σ from the average value is ± 15%, with vibration – ± 5%, i.e. homogeneity is improved by a factor about 3. Improved homogeneity of the electric conductivity testifies to uniform distribution of components over the cross section of ingot, which results from crystallization front leveling and mixing of the melt due to vibration.



a) *b)*

Fig. 3. Distribution of the electric conductivity σ ($\Omega^{-1}\cdot cm^{-1}$) over the cross-section of ingot:
a) – sample grown without vibration, b) – sample grown with vibration.

Metallographic method of dislocation etching is based on the fact that the rate of crystal dissolution by etchant at points of damaged crystal lattice is higher than at the undamaged points [10]. Study of samples structure on the metallographic microscope showed that a fine crystalline material structure is formed due to vibration. The pictures of samples grown with the use of vibration prior to and after etching are given in Fig. 4.

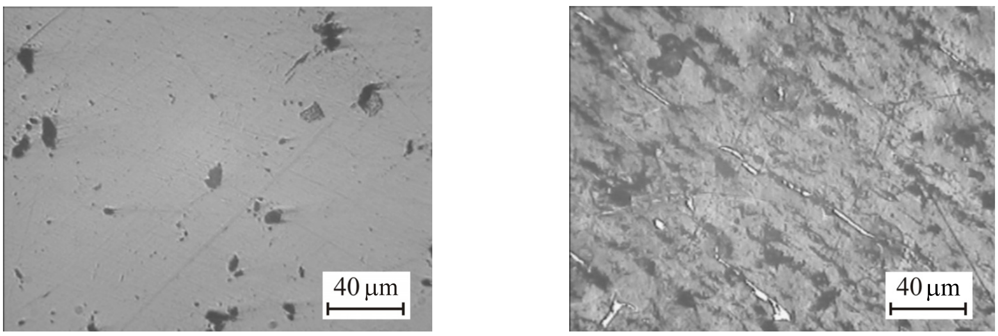


Fig. 4. Pictures of samples grown with the use of vibration prior to and after etching.

Analysis of crystallization conditions and thorough selection of growth conditions, possibility of selection and control in the process of growth enabled ingots with a high homogeneity of distribution of α, σ values both along the ingot axis and over its cross section. Figs. 5 – 8 show the results of measuring the temperature dependences of thermoelectric parameters of samples obtained with the use of vibration. Measurements were performed by the absolute method on automatic installation in the temperature range of 20 – 300 °C. The accuracy of measuring α, σ was 0.7 – 0.8% and the accuracy of measuring thermal conductivity was 2.4%.

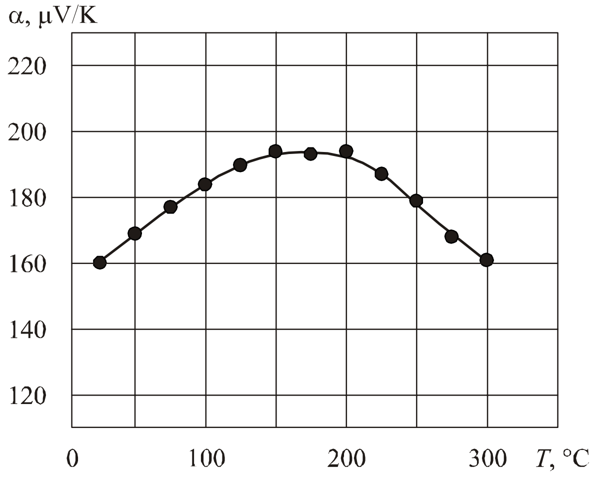


Fig. 5. Temperature dependence of the Seebeck coefficient for p-type material based on Bi_2Te_3-Sb_2Te_3 solid solution.

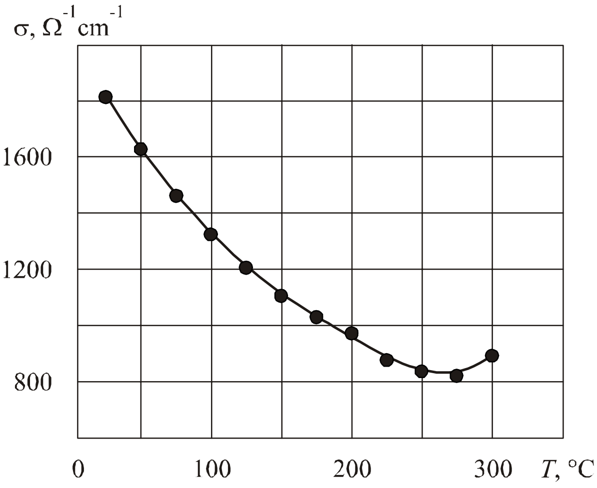


Fig. 6. Temperature dependence of electric conductivity for p-type material based on Bi_2Te_3-Sb_2Te_3 solid solution.

It is seen that in the operating range from room temperature to 300 °C the Seebeck coefficient has maximum 195 – 185 μV/K at 125 – 225 °C (Fig. 5). Accordingly, the dimensionless figure of merit *ZT* reaches maximum close to 1 in the same temperature range (Fig. 8). The electric conductivity is monotonically reduced from 1800 to 800 $\Omega^{-1}\cdot cm^{-1}$ (Fig. 6) and thermal conductivity grows over the entire temperature range (Fig. 7).

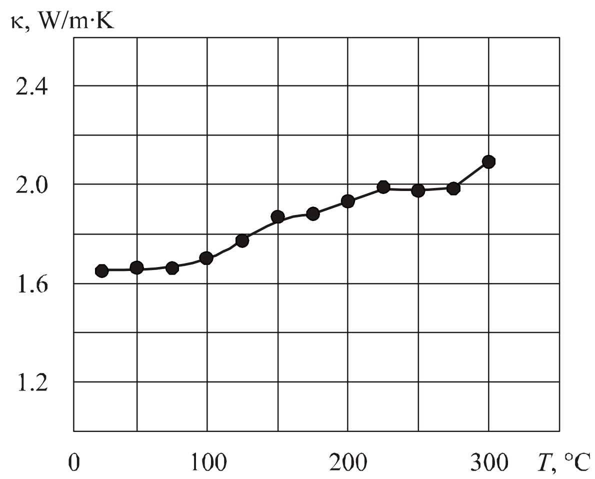


Fig. 7.Temperature dependence of thermal conductivity for p-type material based on Bi_2Te_3-Sb_2Te_3 solid solution.

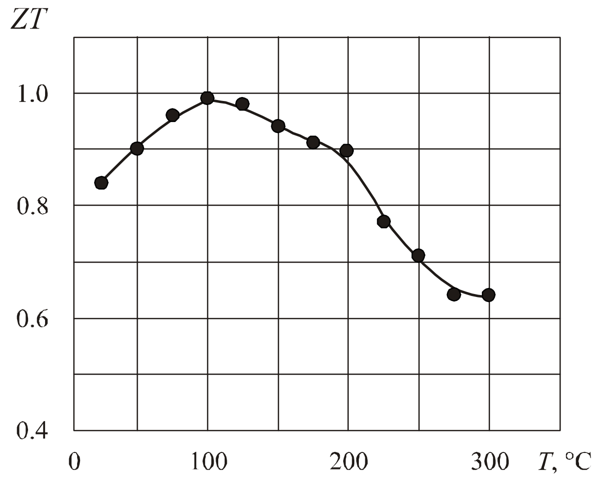


Fig. 8. Temperature dependence of the dimensionless figure of merit for p-type material based on Bi_2Te_3-Sb_2Te_3 solid solution.

Conclusions

An efficient method for improving the homogeneity and structure of Bi_2Te_3 based thermoelectric material grown by vertical zone melting technique with the use of vibration of rate 50 – 100 Hz and amplitude 100 – 150 μm has been developed. The use of vibration improves thermoelectric material homogeneity as regards the Seebeck coefficient by a factor of 2, and electric conductivity – by a factor of 3.

Vibration is an efficient method of affecting hydrodynamics, heat and mass-exchange, the distribution of impurities and kinetics of growth of Bi_2Te_3 based thermoelectric materials using vertical zone melting technique.

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