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**OPTIMIZATION OF MATERIALS BASED ON  
*Bi-Te* POWDERS FOR THERMOELECTRIC  
ENERGY CONVERTERS**

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*Proceeding from the temperature and concentration dependences of the kinetic coefficients of thermoelectric material (TEM), the concentration dependences of thermoelectric figure of merit of powder based TEM were determined under the conditions of miniaturization for thermoelectric cooling and generation modes with different mean radii of powder particles. In so doing, the microscopic parameters of TEM necessary for taking into account the impact of size effects were directly determined on the basis of approximation models of their kinetic coefficients. The impact of size effects on the electrical conductivity of TEM was taken into account in the approximation of constant with respect to energy mean free path of charge carriers, and their impact on the lattice thermal conductivity – with regard to frequency dependence of the relaxation time of phonons scattered on each other due to anharmonicity of lattice thermal vibrations. In the latter case, both Umklapp and normal processes were considered capable of modifying scattering of electrons at layer boundaries. It was shown that with the use of TEM powder with the mean particle radius  $50\ \mu\text{m}$  a gain in the figure of merit as compared to single crystal does not exceed 2 – 11 %. For smaller particle radii a gain can be greater. In particular, with the use of submicron TEM powders with the mean particle radius  $0.1\ \mu\text{m}$  the maximum thermoelectric figure of merit is increased by a factor of 1.18 – 2.15 as compared to single crystal. In so doing, the use of TEM powders with the mean particle radius  $50\ \mu\text{m}$  and more scarcely affects the optimal concentration of doping single-charge impurities, whereas transition to smaller mean radii of powder particles reduces it. For instance, with the mean particle radius  $0.1\ \mu\text{m}$  it is reduced by a factor of 1.04 – 1.57 as compared to single crystal.*

**Key words:** electrical conductivity, thermoEMF, thermal conductivity, phonons, charge carriers, relaxation time, normal processes, Umklapp processes, mean free path, thermoelectric figure of merit.

## Introduction

Enhancement of the figure of merit of thermoelectric materials and thus, improvement of the output parameters and characteristics of thermoelectric energy converters with a simultaneous simplification and cheapening of their manufacturing process is one of the relevant tasks of up-to-date functional electronics. Theoretical and experimental investigations of powder based

thermoelectric materials pursued by various authors [1 – 5] give certain grounds to believe that the use of powders with the proper selection of the mean radius of their component particles will not only yield purely technological advantages in the manufacture of thermoelectric modules, but also improve their qualitative characteristics as compared to those of modules based on bulk single crystals.

It is common knowledge that the figure of merit of TEM depends on the concentration of charge carriers, hence, of doping impurities [6]. Moreover, for each temperature there exists such optimal charge carrier concentration whereby the figure of merit is maximal. However, when passing from single crystals to powder based materials, the effects related to charge carrier and phonon scattering at powder particle boundaries become apparent. In so doing, the kinetic coefficients of TEM are changed, hence, the maximum figure of merit and the corresponding optimal concentration of charge carriers can vary. Therefore, the purpose of this paper is optimization of powder based TEM for charge carrier concentration under the conditions of the impact of mean radius of particles constituting this material on its kinetic coefficients.

### Method of estimation of the figure of merit of powder based TEM versus mean particle radius and charge carrier concentration

Taking into consideration that powder boundary scattering has no impact on thermoEMF, and electron thermal conductivity and electrical conductivity in case of energy independence of electron mean free path depend on mean radius of powder particles through the same multiplier [7, 8], one can readily derive the following expression for thermoelectric figure of merit  $Z$  of thin layer with respect to single crystal  $Z_{mono}$ :

$$Z/Z_{mono} = \frac{1 + \kappa_{n,p(mono)}/\kappa_{l(mono)}}{Z_a^{-1} + \kappa_{n,p(mono)}/\kappa_{l(mono)}}. \quad (1)$$

In this formula

$$Z_a = \left[ \int_0^1 \int_{-1}^1 y^2 \frac{k_{n,p}^* \sqrt{y^2 - 2zy + 1}}{k_{n,p}^* \sqrt{y^2 - 2zy + 1} + 1} dz dy \right] \left[ \int_0^1 \int_0^1 \int_{-1}^1 \frac{x^4 \exp(x/\theta) y^2}{[\exp(x/\theta) - 1]^2} \times \right. \\ \left. \times \left( \frac{k_{\parallel}^* \sqrt{y^2 - 2zy + 1}}{1 + k_{\parallel}^* Q_{\parallel}(x) \sqrt{y^2 - 2zy + 1}} + \frac{2k_{\parallel}^* \sqrt{y^2 - 2zy + 1}}{1 + k_{\parallel}^* Q_{\parallel}(x) \sqrt{y^2 - 2zy + 1}} \right) dz dy dx \right]^{-1} \times \\ \times \left\{ \int_0^1 \frac{x^4 \exp(x/\theta)}{[\exp(x/\theta) - 1]^2} \left( \frac{1}{Q_{\parallel}(x)} + \frac{2}{Q_{\parallel}(x)} \right) dx \right\}. \quad (2)$$

In formulae (1–2), the following notations are introduced:  $\kappa_{n,p(mono)}$  – electron or hole components of full thermal conductivity of single crystal,  $\kappa_{l(mono)}$  – its lattice component,  $k_{n,p} = r_0/l_{n,p}$   $r_0$  – mean radius of powder particles,  $l_{n,p}$  – mean free path of electrons (holes) in single crystal,  $k_{\parallel}^* = (r_0 \gamma^2 \theta / \rho) (k_B T_D / \hbar v_{\parallel})^4 (k_B T_D / \rho v_{\parallel}^2)$ ,  $\theta = T/T_D$ ,  $T$  – absolute temperature,  $T_D$  – the

Debye temperature of material,  $\gamma$ ,  $\rho$  and  $v_{||}$  – the Gruneisen parameter, the density and velocity of sound in TEM, respectively,  $k_B$  – the Boltzmann constant, the rest of notations are commonly accepted. Index "||" means that the corresponding parameter is taken in a direction parallel to layer plane of TEM. Frequency polynomials  $Q_{||}(x)$  and  $Q_{\perp}(x)$ , accordingly, are given below:

$$Q_{||}(x) = x^4 + \mu x, \quad (3)$$

$$Q_{\perp}(x) = (\mu + 3.125\theta^3)x. \quad (4)$$

Formulae (3) and (4) take into account both normal and Umklapp processes for the longitudinal ( $l$ ) and transverse ( $t$ ) phonon modes. Component  $\mu x$  is responsible for Umklapp processes. It is also taken into account that phonon scattering due to normal processes takes place differently for the longitudinal and transverse modes, which is adequately described by other components in (3) and (4).

Relation (2) with regard to (3) and (4) was derived with the use of approaches developed in [7, 8] for the cases of spherical particles and contacts between them.

Thus, from relations (1 – 4) we see that for the calculation of thermoelectric figure of merit and efficiency of powder based TEM one must, using the experimental data, previously divide full thermal conductivity of single crystal into a component caused by electrons (holes) and lattice thermal conductivity. Also, based on the experimental data of the dependences of electrical conductivity, thermoEMF and thermal conductivity of single crystal on the temperature and charge carrier concentration, it is necessary to determine the temperature and concentration dependences of mean free path of electrons (holes)  $l_{n,p}$  and parameter  $\mu$  which is responsible for phonon scattering and, hence, for the value of TEM lattice thermal conductivity.

### **Determination of the microscopic parameters of TEM based on the approximation of their kinetic coefficients**

To determine the above microscopic parameters, the approximation models of experimental dependences of the kinetic coefficients of TEM are used that are built, for instance, by least-squares method [9]. On the basis of these models the microscopic parameters of TEM are determined as follows.

At first, on the assumption of energy independence of the mean free path of charge carriers, by the concentration and temperature-dependent thermoEMF from Eq. [10]

$$\alpha = \frac{k_B}{e} \left[ \frac{2F_1(\eta)}{F_0(\eta)} - \eta \right] \quad (5)$$

the reduced chemical potential  $\eta = \zeta/k_B T$  is determined. Following that, on the assumption of impurity conductivity, from the equation of constancy of the number of particles [10]

$$n_0 = \frac{4(2\pi m_{n,p}^* k_B T)^{3/2}}{\sqrt{\pi} h^3} F_{1/2}(\eta) \quad (6)$$

by the known density-of-state mass of electrons (holes)  $m_{n,p}^*$ , for instance, at temperature 300 K, charge carrier concentration  $n_0$  is determined. Then, at each fixed concentration  $n_0$  the temperature dependence of density-of-state effective mass  $m_{n,p}^*$  is found. There is another method which is realized with the availability of data on charge carrier mobility. At first, charge carrier concentration is determined by the conductivity and mobility, and then from Eq. (6) – the density-of-state effective mass.

Following that, by the experimental temperature and concentration dependences of the electrical conductivity the mean free path of electrons (holes)  $l_{n,p}$  on the temperature and charge carrier concentration is determined. For this purpose we employ the relation for the case of energy-independent mean free path of electrons (holes) [4]:

$$\sigma_{mono} = \frac{4n_0 e^2 l_{n,p} F_0(\eta)}{\sqrt{2m_{e,h}^* k_B T} F_{1/2}(\eta)}. \quad (7)$$

In formulae (5) – (7),  $F_r(\eta)$  – the Fermi integrals of corresponding indices determined by the relation:

$$F_r(\eta) = \int_0^\infty \frac{x^r dx}{\exp(x - \eta) + 1}. \quad (8)$$

Concerning the use of relation (6) for the determination of carrier concentration it should be noted that density-of-state effective mass of electrons (holes) is a function of not only temperature, but also charge carrier concentration. However, in case of materials for coolers an argument of approximation models is not charge carrier concentration, but the electrical conductivity at 300 K. For this case a simplifying assumption that at 300 K the effective mass does not depend on charge carrier concentration was invoked.

With a knowledge of  $\eta$ , one can use the Wiedemann-Franz relation to determine crystal thermal conductivity component due to free charge carriers:

$$\kappa_{n,p(mono)} = L\sigma T. \quad (9)$$

In so doing, the Lorentz number is equal to:

$$L = \left(\frac{k_B}{e}\right)^2 \left[ \frac{3F_2(\eta)}{F_0(\eta)} - \frac{4F_1^2(\eta)}{F_0^2(\eta)} \right]. \quad (10)$$

Knowing the thermal conductivity due to free carriers, as well as the experimental thermal conductivity of TEM described by the corresponding approximation model, one can readily determine its lattice component. Knowing the temperature and concentration dependence of the lattice component of the thermal conductivity of TEM, it is easy, using the method developed in

[8] with regard to relations given in [11], to determine coefficient  $\mu$  of polynomials (3), (4) characterizing frequency dependence of phonon-phonon scattering probability.

### Results of optimization of materials for coolers

Calculation of dependences of the figure of merit of powder based materials on the concentration of charge carriers was performed for *n*-type materials  $Bi_2Te_{2.7}Se_{0.3} + (0.09 \dots 0.03) \% CdCl_2$  and *p*-type materials  $Bi_{0.5}Sb_{1.5}Te_3 + 4 \% Te$  which are used for cooling modules. We employed the averaged experimental dependences given in [6, 9] of the kinetic coefficients  $\alpha_{mono}$ ,  $\sigma_{mono}$ ,  $\kappa_{mono}$  of these materials on the temperature and electrical conductivity values at 300 K, proportional to charge carrier concentration. The calculations used parameters of phonon spectra and density-of-state effective masses of electrons and holes given in [12]. The calculations were performed on the basis of relations (1) – (4) by computer methods in the Mathcad-14 environment.

The concentration dependences of the figure of merit *ZT* of powder based materials obtained for various temperatures and particle radii are given in Fig. 1 – 4.

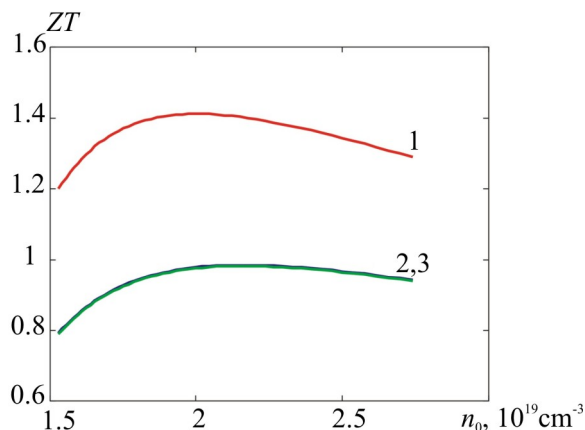


Fig. 1. Concentration dependences of *ZT* of *n*-type TEM powders based on  $Bi_2Te_{2.7}Se_{0.3}$  at temperature 300 K and mean particle radii,  $\mu\text{m}$ : 1 – 0.1; 2 – 50; 3 – bulk crystal.

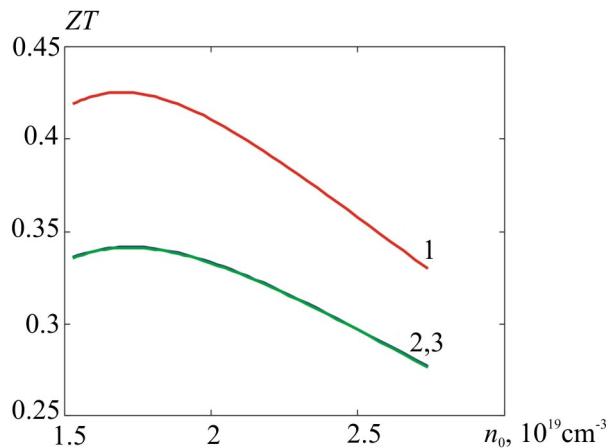


Fig. 2. Concentration dependences of *ZT* of *n*-type TEM powders based on  $Bi_2Te_{2.7}Se_{0.3}$  at temperature 150 K and mean particle radii,  $\mu\text{m}$ : 1 – 0.1; 2 – 50; 3 – bulk crystal.

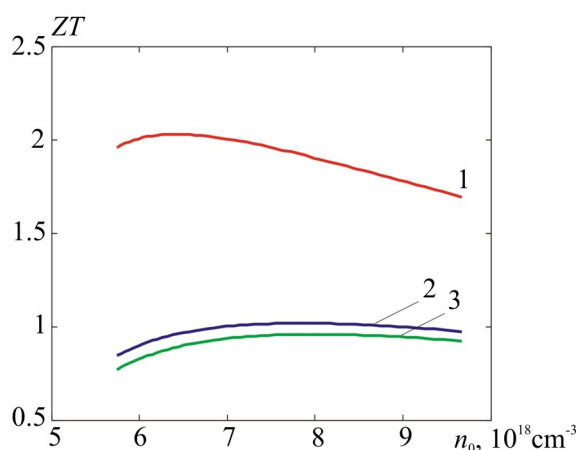


Fig. 3. Concentration dependences of ZT of p-type TEM powders based on  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  at temperature 300 K and mean particle radii,  $\mu\text{m}$ : 1 – 0.1; 2 – 50; 3 – bulk crystal.

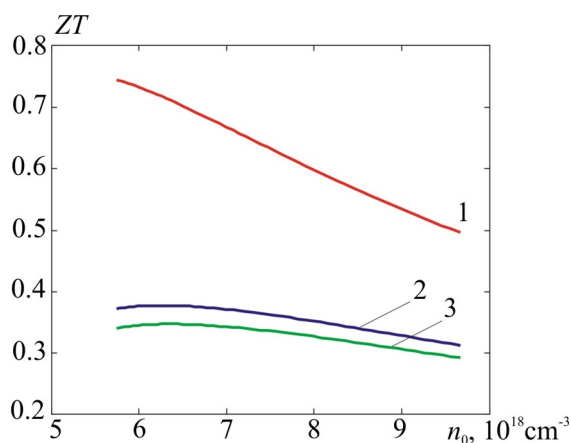


Fig. 4. Concentration dependences of ZT of p-type TEM powders based on  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  at temperature 150 K and mean particle radii,  $\mu\text{m}$ : 1 – 0.1; 2 – 50; 3 – bulk crystal.

From the figures it is seen that for the above materials at all temperatures when passing from single crystal to TEM powders there is a gain in the figure of merit. The figure of merit enhancement is attributable to the impact of size effects related to compatibility of charge carrier and phonon mean free paths to particle radius. In all cases there is radius-dependent optimal concentration of charge carriers whereby maximum thermoelectric figure of merit is achieved. However, as long as charge carrier and phonon mean free paths are measured by nanometers, there is no essential gain in the thermoelectric figure of merit when passing from single crystal to TEM powders with mean particle radii 50  $\mu\text{m}$  and more. Essential gain, namely by a factor of 1.25 – 2.15 as compared to single crystal, is obtained with the use of TEM powders with the mean particle radius 0.1  $\mu\text{m}$ . Nevertheless, the results imply that transition from a single crystal to TEM powders can be done without degrading the output parameters of coolers, and hence, one can achieve substantial simplification and cheapening of the process of manufacturing thermoelectric modules, including miniature-sized. More detailed information on the impact of mean radius of

TEM powder particles on the thermoelectric figure of merit and efficiency of materials for coolers is given in Table 1.

*Table 1*

*Predicted figures of merit of powder based materials for coolers*

Mean particle radius, $\mu\text{m}$	Optimal concentration at 300 K	Conductivity at 300 K, S/cm	Thermoelectric figure of merit $ZT$ at operating temperature	Gain as compared to single crystal, %
<i>n</i> -type cooling material at 300 K				
0.1	$2 \cdot 10^{19}$	824	1.299	42
1	$2.1 \cdot 10^{19}$	872	1.006	10
5	$2.1 \cdot 10^{19}$	884	0.940	2.6
10	$2.1 \cdot 10^{19}$	884	0.929	1.4
50	$2.1 \cdot 10^{19}$	884	0.919	0.3
Single crystal		884	0.916	0
<i>n</i> -type cooling material at 150 K				
0.1	$1.6 \cdot 10^{19}$	596	0.425	25
1	$1.7 \cdot 10^{19}$	632	0.358	5
5	$1.67 \cdot 10^{19}$	620	0.345	1.2
10	$1.67 \cdot 10^{19}$	620	0.343	0.6
50	$1.67 \cdot 10^{19}$	620	0.341	0
Single crystal	$1.67 \cdot 10^{19}$	620	0.341	0
<i>p</i> -type cooling material at 300 K				
0.1	$6.31 \cdot 10^{18}$	744	2.031	111
1	$6.92 \cdot 10^{18}$	840	1.508	57
5	$7.30 \cdot 10^{18}$	900	1.224	27
10	$7.38 \cdot 10^{18}$	912	1.138	18
50	$7.81 \cdot 10^{18}$	972	1.085	11
Single crystal	$7.89 \cdot 10^{18}$	984	0.961	0
<i>p</i> -type cooling material at 150 K				
0.1	$5.74 \cdot 10^{18}$	600	0.744	115
1	$5.79 \cdot 10^{18}$	612	0.548	58
5	$5.93 \cdot 10^{18}$	648	0.443	28
10	$5.98 \cdot 10^{18}$	660	0.414	20
50	$6.14 \cdot 10^{18}$	696	0.377	9
Single crystal	$6.14 \cdot 10^{18}$	696	0.346	0

From the table, among other issues, it is seen that in the case of materials for coolers a transition from single crystal to TEM powders has little effect on the optimal concentration of charge carriers, and, hence, of  $n$ -type doping impurities, in  $n$ -type materials, and a much stronger effect – in  $p$ -type materials.

### Results of optimization of materials for generators

Calculation of dependences of the figure of merit of powder TEM on the concentration of charge carriers was performed for  $n$ -type materials  $(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$  and  $p$ -type materials  $(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$  which are used for generator modules. The averaged experimental dependences given in [9] of the kinetic coefficients  $\alpha_{mono}$ ,  $\sigma_{mono}$ ,  $\kappa_{mono}$  of these materials on the temperature and electrical conductivity values at 300 K were employed. The calculations used parameters of phonon spectra and density-of-state effective masses of electrons and holes given in [10, 13].

The concentration dependences of the figure of merit  $ZT$  of powders of these materials obtained for various particle radii and temperatures are given in Fig. 5 – 8.

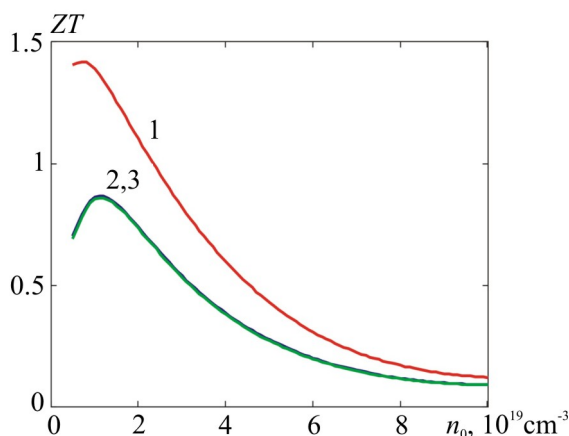


Fig. 5. Concentration dependences of  $ZT$  of  $n$ -type TEM powder  $(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$  at temperature 300 K and mean particle radii,  $\mu\text{m}$ : 1 – 0.1; 2 – 50; 3 – bulk crystal.

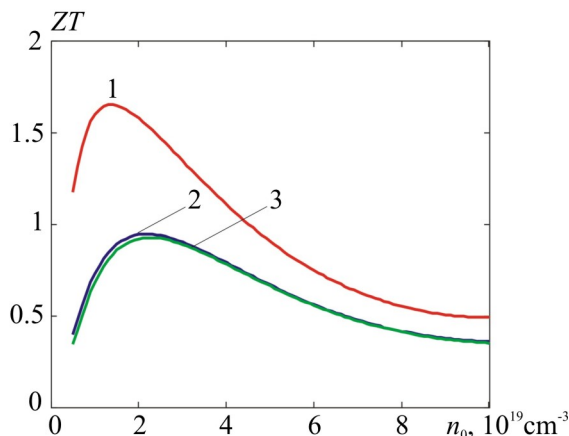


Fig. 6. Concentration dependences of  $ZT$  of  $n$ -type TEM powder  $(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$  at temperature 450 K and mean particle radii,  $\mu\text{m}$ : 1 – 0.1; 2 – 50; 3 – bulk crystal.



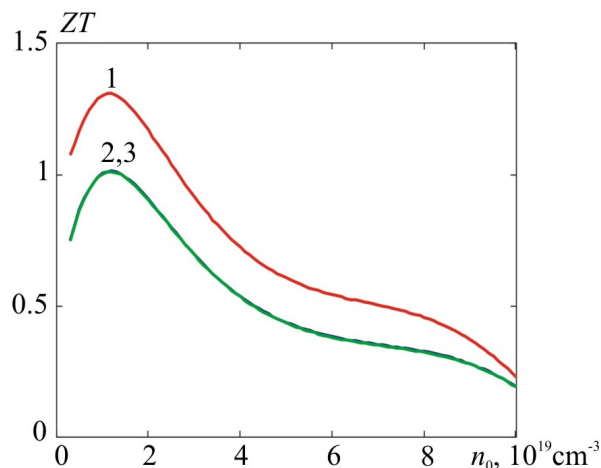


Fig. 7. Concentration dependences of ZT of p-type TEM powder  $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.72}(\text{Sb}_2\text{Se}_3)_{0.03}$  at temperature 300 K and mean particle radii,  $\mu\text{m}$ : 1 – 0.1; 2 – 50; 3 – bulk crystal.

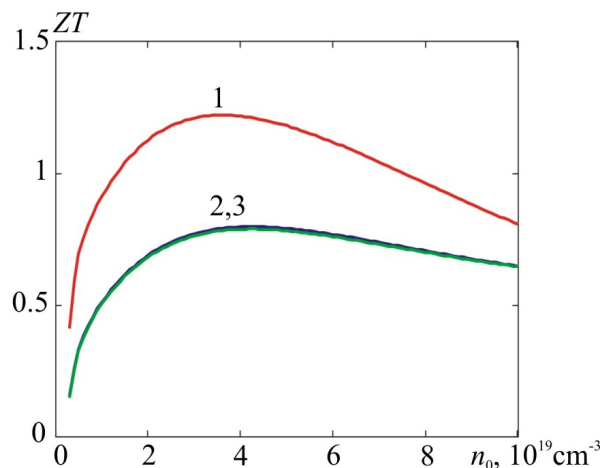


Fig. 8. Concentration dependences of ZT of p-type TEM powder  $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.72}(\text{Sb}_2\text{Se}_3)_{0.03}$  at temperature 450 K and mean particle radii,  $\mu\text{m}$ : 1 – 0.1; 2 – 50; 3 – bulk crystal.

Just as in the case of materials for coolers, for each mean radius of powder particle there is optimal concentration of charge carriers whereby maximum thermoelectric figure of merit is achieved, and in the case of materials for generators it is expressed stronger than in the case of materials for coolers. Essential gain in the thermoelectric figure of merit, namely by a factor of 1.30 – 1.78 as compared to single crystal is obtained at mean particle radius 0.1  $\mu\text{m}$ . More detailed information on the impact of mean radius of SPS-TEM particles on the thermoelectric figure of merit and efficiency of materials for coolers is given in Table 2.

From the table, among other issues, it is seen that with a decrease in the mean radius of TEM powder particles, the optimal concentration of charge carriers necessary for achieving maximum thermoelectric figure of merit is reduced. For instance, at the mean particle radius 0.1  $\mu\text{m}$  it is reduced by a factor of 1.09 – 1.57 as compared to single crystal.

Table 2

*Predicted figures of merit of powder based materials for generators*

Mean particle radius, $\mu\text{m}$	Optimal concentration at 300 K	Conductivity at 300 K, S/cm	Thermoelectric figure of merit $ZT$ at operating temperature	Gain as compared to single crystal, %
<i>n</i> -type generator material at 300 K				
0.1	$7.0 \cdot 10^{18}$	857	1.424	66
1	$1.0 \cdot 10^{19}$	1128	1.011	18
5	$1.1 \cdot 10^{19}$	1203	0.909	5.8
10	$1.1 \cdot 10^{19}$	1203	0.887	3.3
50	$1.1 \cdot 10^{19}$	1203	0.865	0.7
Single crystal	$1.1 \cdot 10^{19}$	1203	0.859	0
<i>n</i> -type generator material at 450 K				
0.1	$1.4 \cdot 10^{19}$	1402	1.653	78
1	$1.6 \cdot 10^{19}$	1517	1.243	34
5	$1.9 \cdot 10^{19}$	1674	1.051	13
10	$2.0 \cdot 10^{19}$	1723	1.003	8
50	$2.2 \cdot 10^{19}$	1817	0.948	2
Single crystal	$2.2 \cdot 10^{19}$	1817	0.928	0
<i>p</i> -type generator material at 300 K				
0.1	$1.1 \cdot 10^{19}$	704	1.308	30
1	$1.2 \cdot 10^{19}$	743	1.083	7.2
5	$1.2 \cdot 10^{19}$	743	1.024	1.4
10	$1.2 \cdot 10^{19}$	743	1.019	0.9
50	$1.2 \cdot 10^{19}$	743	1.011	0.1
Single crystal	$1.2 \cdot 10^{19}$	743	1.010	0
<i>p</i> -type generator material at 450 K				
0.1	$3.5 \cdot 10^{19}$	1593	1.220	55
1	$4.0 \cdot 10^{19}$	1758	0.956	21
5	$4.0 \cdot 10^{19}$	1758	0.847	7.5
10	$4.1 \cdot 10^{19}$	1790	0.824	4.6
50	$4.1 \cdot 10^{19}$	1790	0.797	1.1
Single crystal	$4.1 \cdot 10^{19}$	1790	0.788	0

## **Comment on the role of phonon tunneling through vacuum gaps in thermoelectricity**

Concerning the term used in the name of this section it should be noted that no phonon tunneling proper, i.e. acoustic vibration quanta through vacuum can exist, because classical experiment with a bell placed under the globe has not been refuted by anybody from classical or quantum standpoint. Then how should this term be understood? In Wikipedia, the free encyclopedia, one can come across a statement that it is a kind of “slang” which actually means tunneling of free charge carriers under the influence of their interaction with surface phonons in solids located on both sides of vacuum gap. However, this interpretation is inconsistent, because wave-particle nature of electrons (holes), and thus the possibility in principle of their passage through vacuum gap is unrelated to their interaction with phonons, either surface or bulk. It is more to the point to assert that this interaction under certain conditions can change in one direction or another possibility of passage of charge carriers through the gap. Nevertheless, the term “phonon tunneling” has a right to exist, if it is considered in the light of physical mechanism of heat transfer through vacuum gap between two piezoelectric, but not necessarily electrically conductive bodies. This mechanism was theoretically analyzed by the authors of [14] who, by the way, coined this term. The essence of this mechanism is as follows. Let there be two piezoelectric bodies 1 and 2, divided by vacuum gap. Lattice thermal vibrations in body 1 due to direct piezoelectric effect generate charge-density waves of alternating sign. Time- and space-varying charge, induced on the surface of body 1 adjacent to vacuum gap, generates in this gap an evanescent with the distance alternating electrical field, which, in turn, also induces time-and space-varying charge on the surface, hence, by induction, in the bulk of body 2. This charge, by virtue of inverse piezoelectric effect generates time- and space-variable deformations, i.e. vibrations, in the bulk of body 2. Thus, it turns out that phonons would “overflow” or “tunnel” through vacuum gap from body 1 to body 2. If these bodies are at different temperatures, such “overflow” is accompanied by heat transfer through vacuum gap which results in deviations from the Stephan-Boltzmann law. It is believed that if piezoelectric moduli of the bodies are rather great, the difference in temperatures is also great, and vacuum gap is small as compared to the wavelength of thermal phonon in a solid, then heat transfer through such gap can be great. This mechanism may act when one of the bodies is a piezoelectric (necessarily!), and another is a conductor, even metal. Then the field created in vacuum gap by the induced charge generates in the subsurface layer of conductor an alternating current. The latter, due to interaction of free charge carriers with phonons, leads to deformation, i.e. excitation of vibrations in the subsurface conductor layer, i.e. we again deal with a kind of “phonon tunneling”. Apparently, exactly this variant of the above mechanism action generated its peculiar interpretation cited in Wikipedia. However, the author of this paper is not aware (at least among commonly used!) of such semiconductor thermoelectric materials which simultaneously would be strongly marked piezoelectrics. Therefore, there is no reason to be apprehensive about a drastic growth of thermal conductivity, hence of a drop in thermoelectric figure of merit and efficiency of powder based TEM due to an abnormally large

heat transfer through the pores. There is also no need in some radical revision of the existing theoretical concepts set forth, for instance, in [15] on the generalized conductivities and thermoEMF of nanostructured TEM, including spark plasma sintered SPS-TEM.

## Conclusions

1. The impact of phonon and charge carrier scattering at the boundaries of particles constituting SPS-TEM on the electrical conductivity and lattice thermal conductivity is the most essential factor which accounts for maintenance of thermoelectric figure of merit when passing from single crystal to SPS-TEM with the mean particle radius from 50  $\mu\text{m}$ . Figure of merit improvement can be expected at smaller mean particle radii.
2. The use of powder based TEM instead of single crystals allows simplification and cheapening of the process of manufacturing thermoelectric modules without sacrificing their output parameters and characteristics.
3. A greater reduction of lattice thermal conductivity as compared to electrical conductivity creates conditions for improvement of the figure of merit of TEM when passing from the bulk single crystals to SPS-TEM.
4. The greatest gain in the figure of merit, namely a factor of 2.15 in the case of materials for coolers and by a factor of 1.78 for generator materials is achieved at particle radius 0.1  $\mu\text{m}$ .
5. At particle radii exceeding 50  $\mu\text{m}$  and temperatures 150 – 450 K the expected figure of merit improvement of considered materials with respect to corresponding single crystals does not exceed 11 % in the case of materials for coolers and 1.1 % in the case of generator materials.
6. There is no reason to be apprehensive about a drastic drop in the thermoelectric figure of merit and efficiency of SPS-TEM due to an abnormally large heat transfer through the pores.

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Submitted 03.09.2015