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## **IMPACT OF SIZE EFFECTS ON THE PROPERTIES OF THERMOELECTRIC MATERIALS**

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*Size effects capable of influencing the properties of thermoelectric materials are divided into classical and quantum ones. The former take place when the size of material particle at least along one of coordinate axes is comparable to mean free path of charge or phonon carriers. The latter occur when this size is comparable to the de Broglie wavelength of electrons (holes). This paper deals exclusively with classical size effects. Here, the shape-forming structural elements in the form of small spherical particles and in the form of semi-spheres contacting in a round area (spot) of a radius which is small against the radius of semi-spheres have been analyzed. The impact of size effects on the electric conductivity of material is considered in the approximation of constant (with respect to energy) mean free path of electrons (holes), since exactly this approximation is valid for  $\text{Bi}_2\text{Te}_3$  with charge carrier scattering on the deformation potential of acoustic phonons in the relevant for thermoelectricity temperature region. The impact of size effects on the lattice thermal conductivity of material is considered in two approximations, namely that of constant mean free path of phonons and the mean free path depending on frequency due to N- and U-processes of phonon collisions which are relevant in the temperature range of 300 K and higher and are capable of modifying scattering on the boundaries. From the results of approximation it follows that in the approximation of constant mean free paths of electrons and phonons there is no gain in the thermoelectric figure of merit when passing from single-crystal to nanostructured, extruded or powder-based SPS-material. However, with regard to frequency dependence of the mean free path of phonons it turns out that in passing from single-crystal to powder-based material, the thermoelectric figure of merit can increase approximately twice with an oriented arrangement of cleavage planes of shape-forming elements or approximately by 20 % with a random arrangement of these planes. In so doing, the sizes of spherical particles of nanostructured material or nanocontacts between micro semi-spheres should lie within 10 to 40 nm.*

**Key words:** nanostructured material, thermoelectric figure of merit, phonons, electrons, scattering, relaxation time, normal processes, Umklapp processes, Rayleigh distribution.

### **Introduction**

Bismuth telluride  $\text{Bi}_2\text{Te}_3$  is thermoelectric material most commonly used for the manufacture of working elements of various thermoelectric instruments and devices, in particular, generators and coolers [1, 2]. Its specific feature is a pronounced electric conductivity and thermal conductivity anisotropy. This crystal possesses  $R3m$  group symmetry and a layered structure. Its thermal conductivity and electric conductivity tensors have two independent components each. In particular, in the absence of a magnetic field, electric conductivity tensor has component  $\sigma_{11}$  in layers plane and component  $\sigma_{33}$  in a perpendicular direction, with  $\sigma_{11} > \sigma_{33}$ . The same inequality is valid for thermal conductivity components:  $\chi_{11} > \chi_{33}$ . Therefore, thermoelectric modules of a single crystal are made so that temperature gradient and electric current are parallel to cleavage planes, owing to which the

dimensionless thermoelectric figure of merit  $ZT$  at 300 K reaches 1. This direction of temperature gradient and electric current can be also retained when passing from single-crystal to powder-based materials prepared by hot pressing, extrusion or spark plasma sintering methods, if cleavage planes of powder particles are parallel to each other. However, it is much more common when cleavage planes of individual particles that coincide with planes of crystal layers are randomly oriented (nonparallel).

As a result, the figure of merit of material in conformity with the Odelevsky formula with regard to the ratios between components of thermal and electric conductivity tensors should have reduced by a factor of about from  $\sqrt{2}$  to  $\sqrt{3}$ , i.e. by 30 to 40 %, however, in practice such a reduction is not observed. On the other hand, there are many theoretical works, for instance [3-5], where it is shown that transition from single-crystal material to bulk nanostructured material should increase the dimensionless thermoelectric figure of merit. As the mechanisms for such increase, on the one hand, phonon scattering on the boundaries of nanoparticles [3], leading to lattice thermal conductivity reduction is considered, on the other hand – quantum tunneling of charge carriers through vacuum or dielectric gaps between particles, leading to increase in electric conductivity and thermoEMF, hence, in power factor [4, 5]. In these papers it is shown that the best values of dimensionless thermoelectric figure of merit of bulk nanostructured material based on bismuth telluride should have achieved  $3.5 \div 3.6$ , but in practice no such increase takes place. The discrepancy between theory and experiment is generally related to stronger reduction of electric conductivity when passing from single-crystal material to bulk nanostructured material than it is predicted by theory. This factor forces the experimenters to employ combined materials based on powders, consisting of a nanocomponent with particle size  $5 \div 20$  nm, and a microcomponent with particle size  $40 \div 70\mu\text{m}$  [6]. Such materials possess power factor typical of single-crystal material, but their thermal conductivity is reduced due to additional phonon scattering on the boundaries of nanoparticles. Relative mass fractions of nano- and microcomponents in powder are selected so as to assure maximum value of thermoelectric figure of merit.

Among the weak points of [3-5] and some other theoretical papers covering this problem, is a modeling character of tunneling effects calculations caused by the absence of valid knowledge on the shape and height of potential barriers between nanoparticles, as well as ignoring the frequency dependence of phonon relaxation time when considering their scattering on nanoparticle boundaries.

With regard to the foregoing, the purpose of this paper is to consider the mechanism of thermoelectric figure of merit variation when passing from single-crystal to bulk nanostructured material due to charge carrier and phonon scattering on the boundaries of spherical nanoparticles in the approximation of relaxation time for electrons and phonons.

### **Thermoelectric figure of merit calculation in the approximation of constant electron and phonon mean free paths**

Consider the problem of thermoelectric figure of merit calculation in the approximation of constant electron and phonon mean free paths. It can be shown that in the framework of this approximation thermoEMF is not changed, as long as both thermal diffusion flux and electric current are proportional to relaxation time. Therefore, a change in thermoelectric figure of merit in this case is completely determined by a change in electric conductivity to thermal conductivity ratio. If electron and phonon mean free paths are  $l_e$  and  $l_{ph}$ , respectively, then the ratio of figure of merit  $Z_n$  of the bulk nanostructured material consisting of identical nanoparticles of radius  $r$  to figure of merit  $Z_m$  of single-crystal material in conformity with the rule of summation of the inverse mean free paths will make [7-9]:

$$Z_n / Z_m = \left[ \int_0^1 \int_{-1}^1 \frac{(r/l_e) \sqrt{y^2 + 2zy + 1} y^2 dz dy}{(r/l_e) \sqrt{y^2 + 2zy + 1} + 1} \right] \left[ \int_0^1 \int_{-1}^1 \frac{(r/l_p) \sqrt{y^2 + 2zy + 1} y^2 dz dy}{(r/l_p) \sqrt{y^2 + 2zy + 1} + 1} \right]^{-1}. \quad (1)$$

Double integrals over dimensionless variables  $z$  and  $y$  in this formula appear due to averaging of expressions for thermal conductivity and electric conductivity over the mean free paths inside the sphere.

### Consideration of frequency dependence of phonon relaxation time

We now consider the problem of calculation of thermoelectric figure of merit with regard to frequency dependence of relaxation time of mutually scattered phonons. For this purpose, we first write a general expression for lattice thermal conductivity component parallel to layers (cleavage planes), taking into account that in the temperature region relevant for thermoelectric applications it is determined by Umklapp processes, as well as by normal processes, capable of modifying scattering on sample boundaries by virtue of scattering probabilities redistribution according to frequencies [10, 11]. This expression is of the form:

$$\chi_{||} = \frac{3\hbar\rho v_{||}^4 k_B}{32\gamma^2 (k_B T_D)^2 \theta^3 \pi_0} \int_0^1 \frac{x^4 \exp(x/\theta)}{[\exp(x/\theta) - 1]^2} \left( \frac{1}{Q_{||}(x)} + \frac{2}{Q_{\perp}(x)} \right) dx. \quad (2)$$

In this formula, index  $||$  refers to lattice thermal conductivity in the direction parallel to layers (cleavage planes),  $\rho$  is crystal density,  $v$  is sound velocity in it,  $\gamma$  is the Gruneisen parameter,  $T_D$  is the Debye temperature,  $\theta = T/T_D$ ,  $Q_{||}(x)$  and  $Q_{\perp}(x)$  are frequency polynomials determined by the mechanisms of scattering the longitudinal and transverse phonons, respectively, and having in this case the form:

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

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

With regard to thermal conductivity dependence on material density, we note that formula (2) in this respect is precise for a simple cubic lattice with one atom in a unit cell. The real  $Bi_2Te_3$  lattice is not of that kind, but we have to replace it by such, provided the real material density is maintained. Coefficient  $\mu$  was approximately calculated for a simple cubic lattice by Leibfried and Shleman [10], but, according to experimental data given in [10], even for materials with such lattice it is not universal. Therefore, we will derive coefficient  $\mu_{||}$  from the real value of the respective component of  $Bi_2Te_3$  thermal conductivity tensor [1], assuming that the latter coincides with the theoretical value (2) with regard to (3) and (4). At  $\chi_{||} = 1.45$  W/m·K,  $\rho = 7859$  kg/m<sup>3</sup>,  $\gamma = 1.5$ ,  $v_{||} = 2952$  m/s,  $T_D = 155$  K and  $T = 300$  K we obtain  $\mu_{||} = 0.022$ .

The ratio of nanoparticle thermal conductivity to single crystal thermal conductivity in this case is:

$$\chi_l^{(nano)} / \chi_{||m} = 1.5 \int_0^1 \int_{-1}^1 \int_{-1}^1 \frac{z^2 x^4 \exp(x/\theta)}{[\exp(x/\theta) - 1]^2} \left( \frac{(r/L^*) \sqrt{z^2 - 2zy + 1}}{1 + (r/L^*) Q_{||}(x) \sqrt{z^2 - 2zy + 1}} + \frac{2(r/L^*) \sqrt{z^2 - 2zy + 1}}{1 + (r/L^*) Q_{\perp}(x) \sqrt{z^2 - 2zy + 1}} \right) dy dz dx \left\{ \int_0^1 \frac{x^4 \exp(x/\theta)}{[\exp(x/\theta) - 1]^2} \left( \frac{1}{Q_{||}(x)} + \frac{2}{Q_{\perp}(x)} \right) dx \right\}^{-1}. \quad (5)$$

In formula (5)  $L^* = \rho \hbar^4 v_{||}^6 / \gamma^2 (k_B T_D)^5$ .

In this case, the ratio of the figure of merit of bulk nanostructured material to that of single-crystal material will be:

$$Z_n / Z_m = 1.5 \left[ \int_0^1 \int_{-1}^1 \frac{(r/l_e) \sqrt{y^2 + 2zy + 1} y^2 dz dy}{(r/l_e) \sqrt{y^2 + 2zy + 1} + 1} \right] \left[ \chi_i^{(nano)} / \chi_{ilm} \right]^{-1}. \quad (6)$$

In the case of micro semi-spheres contacting in a round area (spot) of radius  $r$ , formulae (5) and (6) take on the form [12]:

$$\begin{aligned} \chi_i^{(nano)} / \chi_{ilm} = \pi^{-1} \int_0^1 \int_0^{2\pi} \int_0^1 \frac{zx^4 \exp(x/\theta)}{[\exp(x/\theta) - 1]^2} & \left( \frac{(r/L^*) \sqrt{z^2 - 2z \cos \phi + 1}}{1 + (r/L^*) Q_{||}(x) \sqrt{z^2 - 2z \cos \phi + 1}} + \right. \\ & \left. + \frac{2(r/L^*) \sqrt{z^2 - 2z \cos \phi + 1}}{1 + (r/L^*) Q_{||}(x) \sqrt{z^2 - 2z \cos \phi + 1}} \right) d\phi dz dx \left\{ \int_0^1 \frac{x^4 \exp(x/\theta)}{[\exp(x/\theta) - 1]^2} \left( \frac{1}{Q_{||}(x)} + \frac{2}{Q_{\perp}(x)} \right) dx \right\}^{-1}. \end{aligned} \quad (7)$$

$$Z_n / Z_m = \pi^{-1} \left[ \int_0^1 \int_{-1}^1 \frac{(r/l_e) \sqrt{y^2 + 2y \cos \phi + 1} y dz dy}{(r/l_e) \sqrt{y^2 + 2y \cos \phi + 1} + 1} \right] \left[ \chi_i^{(nano)} / \chi_{ilm} \right]^{-1}. \quad (8)$$

Dependence of the ratio of thermoelectric figure of merit of bulk nanostructured material to that of single-crystal material based on  $Bi_2Te_3$   $(ZT)_{nano}/(ZT)_{mono}$  on the radius of nanoparticles is shown in Fig 1.

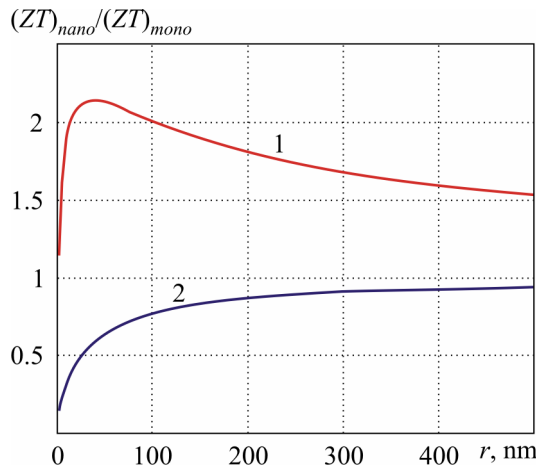


Fig. 1. Dependences of the ratio of thermoelectric figure of merit of bulk nanostructured material to that of single-crystal material  $(ZT)_{nano}/(ZT)_{mono}$  on nanoparticle radius: 1) – with regard to frequency dependence of phonon relaxation time; 2) – in the approximation of constant mean free paths of electrons and phonons.

In the calculations, based on the reference data [1] it was assumed that  $l_{ph} = 4.16$  nm,  $l_e = 38.6$  nm at a temperature of 300 K. In connection with Fig.1, a question may arise as to the validity of transferring the properties of an individual nanoparticle to the properties of material as a whole. Therefore, we note that if pores in material structure are vacuum and separated from each other, and no tunneling of charge carriers takes place, then material porosity, both in the framework of percolation theory, and within the approach set forth, for instance, in [5], enters into the expressions for thermal conductivity and electric conductivity through the same multiplier, hence, it does not produce a direct effect on the thermoelectric figure of merit. Thus, abstracting from the size distribution of nanoparticles, the thermoelectric figure of merit of material as a whole is unambiguously determined through the kinetic coefficients of an individual particle.

From Fig. 1 it is evident that with regard to frequency dependence of phonon relaxation time the thermoelectric figure of merit of bulk nanostructured material in the range of nanoparticle radii  $35 \div 40$  nm achieves a maximum which exceeds the thermoelectric figure of merit of single-crystal material by a factor of 2.14. However, such maximum is possible only with parallel cleavage planes of individual nanoparticles. With randomly oriented cleavage planes, the thermoelectric figure of merit of  $Bi_2Te_3$  based bulk nanostructured material will be a factor of  $\sqrt{3}$  lower, i.e. it will remain at a level of about 23 % higher than the thermoelectric figure of merit of single-crystal material. Even with nanoparticle radius of the order of 5nm with correction for random orientation of cleavage planes, the thermoelectric figure of merit of bulk nanostructured material should remain at a level of at least 97 % of the thermoelectric figure of merit of a single crystal. These results are in qualitative, as well as quantitative agreement with the results of experimental works [13, 14], but contradict to the results of paper [6] according to which the thermoelectric figure of merit of  $Bi_2Te_3$  based bulk nanostructured material of nanoparticles with the radius  $5 \div 20$  nm at 300 K is as low as 82 % of the thermoelectric figure of merit of a single crystal. Thus, when passing from single-crystal material to bulk nanostructured material, power factor is scarcely ever retained, which permits calling in question the presence of energy filtration of current carriers that should have resulted in thermoEMF increase. Even if such filtration occurs, then, apparently, it does not always contribute to power factor retention, since electric conductivity reduction is not compensated by increase in squared thermoEMF. However, in the approximation of constant mean free paths of electrons and phonons the thermoelectric figure of merit values of the bulk nanostructured materials exceeding unity are mainly attributable to tunneling effects.

The results for a circular contact are identical, but slightly different in the numerical values.

Consider now the impact on these results of temperature and size distribution of the bulk nanostructured material particles. The impact of temperature on the scattering of electrons and phonons on the boundaries will be taken into account through temperature dependences of parameters  $L^*$  and  $l_e$  according to formulae [1, 10]:

$$L^* = \rho \hbar^4 \nu_{\parallel}^6 / \gamma^2 \theta (k_B T_D)^5, \quad (9)$$

$$l_e = l_e (300) \frac{300}{T}. \quad (10)$$

According to the definition, adjustable parameter  $\mu_{\parallel}$  does not depend on temperature, since on evidence derived from [1] the Leibfried-Shleman evaluation formula reflects correctly the temperature dependence of  $Bi_2Te_3$  lattice conductivity in the range from nitrogen to room temperatures and higher. The size distribution of particles will be taken into account based on the Rayleigh distribution for which the dependence of probability density  $w(r)$  on particle radius  $r$  is given by:

$$w(r) = \frac{r}{r_0^2} \exp\left(-\frac{r^2}{r_0^2}\right). \quad (11)$$

In this case the generally effective material parameters  $\sigma_{ef}$  and  $\chi_{lef}$  are determined by two methods. The first method lies in solving phenomenological equations for the distributions of temperature and electric potential in an individual particle based on simulation of its geometry. The second method lies in using the Odelevsky relations with averaging the equations for  $\sigma_{ef}$  and  $\chi_{lef}$  over the volumetric share of “phases”, i.e. in this case, particles of various sizes [5]. However, our analysis shows that the latter case of determination of the effective electric conductivity and thermal conductivity of material with a high degree of precision is equivalent to their simple averaging over

the volumetric share of particles of various sizes. There is no need in conversion of thermoEMF value, since in the approximation of constant (with respect to energy) mean free path of charge carriers it does not depend on the boundary scattering. Based on this, we have determined the temperature dependence of optimal most probable radius  $R_{opt}$  of powder nanoparticle in the temperature range of 75 to 600 K and the temperature dependence of maximum thermoelectric figure of merit at these temperatures. The most probable nanoparticle radius was taken to be optimal when the ratio of thermoelectric figure of merit of bulk nanostructured material to that of single-crystal material at each investigated temperature reaches its maximum. The corresponding dependences are depicted in Fig. 2.

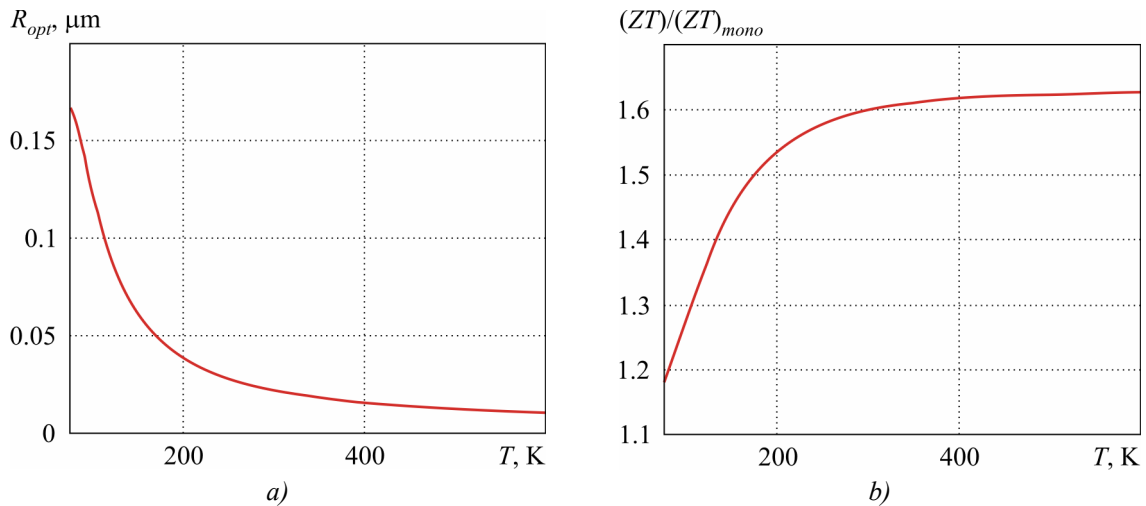


Fig. 2. Temperature dependences in the range of 75 to 600 K: a) – optimal most probable nanoparticle radius; b) – the ratio of thermoelectric figure of merit of bulk nanostructured material to that of single-crystal material.

From Fig. 2 it is seen that with temperature increase from 75 to 600 K, the optimal most probable nanoparticle radius decreases from 0.17  $\mu\text{m}$  to 0.01  $\mu\text{m}$ , and the ratio of thermoelectric figure of merit of bulk nanostructured material to that of single-crystal material (on condition of optimality of the most probable nanoparticle radius) increases from 1.19 to 1.63.

## Conclusions and recommendations

1. In the approximation of constant mean free paths of charge carriers and phonons the thermoelectric figure of merit of bulk nanostructured material based on  $\text{Bi}_2\text{Te}_3$ , calculated with regard to classical size effects does not exceed the thermoelectric figure of merit of single-crystal material.
2. With regard to frequency dependence of the relaxation time of mutually scattered phonons it turns out that in the range of nanoparticle radii 40  $\div$  500 nm the thermoelectric figure of merit of bulk nanostructured material based on  $\text{Bi}_2\text{Te}_3$  can exceed by a factor of 1.5  $\div$  2.1 the thermoelectric figure of merit of single-crystal material. It is true, if cleavage planes of individual crystallites are oriented parallel to temperature gradient and electric current directions. However, if cleavage planes are randomly oriented, the thermoelectric figure of merit of such nanostructured material will remain on the level of 0.88  $\div$  1.23 of that of single-crystal material.
3. The lower values of thermoelectric figure of merit of bulk nanostructured materials are attributable to a drop in power factor due to thermoEMF reduction in these materials with respect to single-crystal material.

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