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**ON THE ISSUE OF THE MECHANISM FOR
INCREASING THE THERMOELECTRIC
FIGURE OF MERIT OF THE BULK
NANOSTRUCTURED MATERIALS**



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Charge carrier and phonon scattering on the boundaries of spherical powder particle has been considered as the mechanism for increasing the figure of merit of the bulk nanostructured material as compared to a single crystal. In so doing, charge carrier scattering is considered in the approximation of constant mean free path, and phonon scattering – within two approaches, namely constant mean free path and with account of frequency dependence of phonon relaxation time. It is shown that with constant mean free paths of electrons and phonons the thermoelectric figure of merit of nanostructured material is considerably lower than that of a single crystal. However, with account of frequency dependence of phonon relaxation time it turns out that with a proper selection of nanopowder size, namely if its particles have the radius of the order of 30 – 40 nm, the figure of merit of Bi_2Te_3 based material can be increased by a factor of 2.1 as compared to a single crystal under oriented pressing and retained at a level of $0.87 \div 1.23$ of its value for a single crystal under conventional pressing, when cleavage planes of individual particles are randomly oriented.

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

Introduction

Bismuth telluride Bi_2Te_3 is thermoelectric material most commonly used for the manufacture of working elements of various thermoelectric instruments and devices [1]. Its specific feature is a pronounced electric conductivity and thermal conductivity anisotropy. Taking into account that this crystal possesses $R3m$ group symmetry and cleavage planes along which it easily splits, 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 σ_{11} in cleavage plane and component σ_{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 can be also retained when passing from a single crystal to powder based materials prepared by hot pressing, extrusion or spark plasma sintering methods, if oriented pressing is used. However, non-oriented pressing, whereby cleavage planes of individual particles are randomly oriented, is much more common.

As a result, the figure of merit of material in conformity with the Odelevsky formula with regard to thermal and electric conductivity anisotropy factors should have reduced by a factor of about $\sqrt{2} - \sqrt{3}$, i.e. by 30 to 40 %, however, in practice such reduction is not observed. On the other hand, there are many theoretical works, for instance, [2-4], where it is shown that transition from a single

crystal to the bulk nanostructured material should increase the thermoelectric figure of merit. As the mechanisms for such increase, on the one hand, phonon scattering on the boundaries of nanoparticles [2], 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 [3, 4]. In these papers it is shown that the best values of dimensionless thermoelectric figure of merit of bismuth telluride based bulk nanostructured material should have achieved $3.5 \div 3.6$, but in practice no such increase is observed. The discrepancy between theory and experiment is generally related to stronger restrictions on thermoEMF and electric conductivity when passing from a single crystal 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 $40 \div 70$ μ m [5]. The function of microcomponent is to retain power factor typical of a single crystal, the function of a nanocomponent is to reduce lattice thermal conductivity due to additional phonon scattering on the boundaries of nanoparticles. Mass ratio between nano- and microcomponents is selected so as to assure the maximum value of the dimensionless thermoelectric figure of merit.

Among the weak points of [2-4] 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, our purpose in this paper is to consider the mechanism of thermoelectric figure of merit variation when passing from a single crystal to bulk nanostructured material due to charge carrier and phonon scattering on the boundaries of spherical nanoparticles in the drift approximation.

Consideration of the problem in the approximation of constant electron and phonon mean free paths

Consider this problem 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 bulk nanostructured material consisting of equal particles of radius r to figure of merit Z_m of a single crystal in conformity with the rule of summation of the inverse mean free paths will make by analogy with [6]:

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

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

Problem consideration with regard to frequency dependence of phonon relaxation time

We now consider this problem with regard to frequency dependence of phonon relaxation time. For this purpose we first write a general expression for the larger component of lattice thermal

conductivity, 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 [7, 8]. This expression is of the form [9]:

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

In this formula, index || refers to lattice thermal conductivity in the direction parallel to layers (cleavage planes), ρ is crystal density, v is sound velocity in it, k_B is the Boltzmann constant; γ 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 longitudinal and transverse phonons, respectively, and having in this case the form:

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

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

In these formulae, $\mu_{||}$ is certain coefficient depending in the simplest case of cubic lattice on its geometry.

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 μ was approximately calculated for a simple cubic lattice by Leibfried and Shleman [7], but, according to experimental data given in [6], 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/m³, $\gamma = 1.5$, $v_{||} = 2952$ 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 [9]:

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

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

In this case the ratio of bulk nanostructured material figure of merit to single crystal figure of merit is determined as:

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

Dependence of a relative thermoelectric figure of merit of Bi_2Te_3 based bulk nanostructured material on the radius of nanoparticles is shown in Fig. 1.

In the construction of curve 2 in this figure, 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 this figure 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, there is no tunneling of charge carriers, and the pores are not communicating, then material porosity, both in the framework of percolation theory, and within the approach set forth, for instance, in [4], 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 bulk nanostructured material as a whole is completely determined by the kinetic coefficients of an individual particle.

From the figure it is evident that with regard to frequency dependence of phonon relaxation time the relative thermoelectric figure of merit has a maximum 2.14 which is achieved in the range of nanoparticle radii $35 \div 40$ nm. However, it is possible only with oriented pressing. Whereas with a random orientation of cleavage planes, the relative 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 a single crystal. 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 [10, 11], but contradict to the results of paper [5] 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 a single crystal 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 the electric conductivity is decreased stronger than squared thermoEMF is increased. However, in the approximation of constant mean free paths of electrons and phonons, with increase in nanoparticle radius, the thermoelectric figure of merit monotonously increases from a low value to 1. Therefore, in such approximation the thermoelectric figure of merit values of the bulk nanostructured material exceeding unity with regard to a single crystal are mainly attributable to tunneling effects.

Conclusions and recommendations

1. In the approximation of constant mean free paths of charge carriers and phonons the thermoelectric figure of merit of Bi_2Te_3 based bulk nanostructured material, calculated without regard to possible

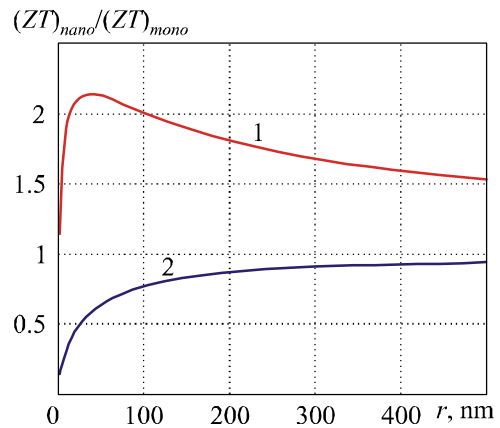


Fig. 1. Dependence of a relative thermoelectric figure of merit of bulk nanostructured material on nanoparticle radius: 1) – with regard to frequency dependence of phonon relaxation time; 2) – in the approximation of constant mean free paths of electrons and phonons.

increase of power factor due to tunnelling effects, in the range of nanoparticle radii $5 \div 500$ nm at 300 K does not exceed 1, even if cleavage planes of individual crystallites are oriented parallel to temperature gradient and electric current directions.

2. With regard to frequency dependence of phonon-phonon relaxation time, even in the drift approximation it turns out that in the range of nanoparticle radii $40 \div 500$ nm the thermoelectric figure of merit of Bi_2Te_3 based bulk nanostructured material can reach $1.5 \div 2.1$ with regard to a single crystal, if cleavage planes of individual crystallites are oriented parallel to temperature gradient and electric current directions. If, however, cleavage planes are randomly oriented, then the thermoelectric figure of merit of such nanostructured material is retained at a level of $0.88 \div 1.23$ of single crystal thermoelectric figure of merit.
3. The experimentally observed in a number of cases lower values of thermoelectric figure of merit of bulk nanostructured material are attributable to a drop in power factor as a result of incomplete recovery of thermoEMF and electric conductivity in these materials with respect to single crystals.

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