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METHOD FOR KINETIC COEFFICIENTS AVERAGING OVER THE SIZE OF PARTICLES AND ITS IMPACT ON PREDICTED FIGURE OF MERIT OF NANOSTRUCTURED THERMOELECTRIC MATERIAL

This paper deals with the four methods for averaging the electric conductivity and lattice thermal conductivity of nanostructured thermoelectric material over the size of particles, namely effective medium method with regard to the volume share of various-size particles, effective medium method with regard to the fraction of various-size particles, simple averaging of kinetic coefficients with regard to the volume share of various-size particles and simple averaging of kinetic coefficients with regard to the fraction of various-size particles. These methods are used for the calculation of dimensionless thermoelectric figure of merit of material with respect to a single crystal depending on the most probable radius of its particle based on the model Rayleigh distribution. Moreover, for comparison, dimensionless thermoelectric figure of merit of material is calculated on the assumption of equal size of its particles. Calculations have been made for the case of Bi_2Te_3 It is shown that despite the difference in the results obtained by these methods, in all the cases there is an optimal radius of thermoelectric material particle, whereby its dimensionless thermoelectric figure of merit is maximum. This radius lies in the range of 0.02 – 0.04 μm, and its respective dimensionless thermoelectric figure of merit at 300 K is of the order of 2.08 ÷ 2.12 with respect to a single crystal on condition that cleavage planes of individual particles are oriented parallel to temperature gradient and electric current, and there are no thermopower losses when passing from a single crystal to nanostructured thermoelectric material.

Key words: nanostructured material, thermoelectric figure of merit, phonons, electrons, scattering, relaxation time, normal processes, Umklapp processes, Rayleigh distribution, effective medium method, averaging over size.

Introduction

Methods for determination of the effective kinetic coefficients of thermoelectric material produced by hot pressing, extrusion or spark plasma sintering techniques via the kinetic coefficients of its component particles or, in other words, its shape-forming elements, have been considered in a variety of theoretical papers [1-4]. These methods can be divided into two big classes, namely the methods based on solving phenomenological equations of electric and thermal conductivity for shape-forming elements and the methods based on constructing from shape-forming elements of the so-called "effective thermoelectric medium". The former in the strict sense of the word is applicable only when the characteristic sizes of shape-forming elements of material structure are much in excess of the characteristic mean free paths of charge carriers and phonons, and, hence, their application to nanostructured thermoelectric materials based on Bi_2Te_3 provokes certain objections from the authors of this paper. These objections are as follows. First, the mean free path, for instance, of electrons in Bi_2Te_3 at 300 K is of the order of 36 nm [5], hence, phenomenological equations for electric potential distribution are hardly applicable to particles of

comparable or, the more so, smaller dimensions. Second, the lattice conductivity of Bi_2Te_3 at 300 K and higher temperature is mainly caused by phonon Umklapp processes [6]. If such processes are available, the relaxation time of phonons with their mutual scattering is a function of frequency ω, and, hence, introduction of phonon mean free path in the usual sense of this concept is hardly possible, though some formal parameter having dimensions of length and depending on scattering mechanisms, namely $l_p(\omega) = \nu\tau(\omega)$, where ν – average sound velocity in material, $\tau(\omega)$ – phonon relaxation time, can be introduced. The disadvantage of this method is also the fact that the analytical solution of phenomenological equations for arbitrary-shaped particles, the more so with account of thermoelectric effects, is difficult or impossible, and one has to resort to somewhat artificial simulation of this shape. On the other hand, the effective medium method also requires certain modification with regard to thermoelectric phenomena. Some aspects of this problem have been considered in [4].

Taking into account the foregoing, our purpose in this paper is to consider and compare a number of methods for determination of the effective kinetic coefficients of nanostructured thermoelectric material with regard to size distribution of its particles. The methods in hand do not call for solution of phenomenological equations of thermal conductivity and thermal conductivity for an individual nanoparticle.

Kinetic coefficients of a nanoparticle as a function of its size

We first will determine the electric conductivity of an individual nanoparticle as a function of its size. To simplify the calculations, the nanoparticle will be considered to be spherical. Moreover, we will take into account that the electric conductivity of Bi_2Te_3 at temperatures 300 K and higher is determined by the acoustic phonon deformation potential scattering charge carriers. And for this case the approximation of constant mean free path is valid. Therefore, the ratio between the electric conductivity $\sigma_n(r)$ of a nanoparticle of radius r and the electric conductivity σ_0 of a single crystal will give:

$$\sigma_n(r)/\sigma_0 = 1.5\int_0^1\int_{-1}^1 \frac{(r/l_e)\sqrt{y^2+2zy+1}\,y^2\,dz\,dy}{(r/l_e)\sqrt{y^2+2zy+1}+1}. \tag{1}$$

In this formula, l_e is the electron mean free path. Double integral here results from averaging the expression for the electric conductivity over the mean free paths inside the sphere. It can be shown that within this approximation the thermopower 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 governed by a change in the electric conductivity – thermal conductivity ratio.

We now turn to determination of lattice thermal conductivity of a nanoparticle with regard to both phonon Umklapp processes and normal processes. The ratio between the thermal conductivity κ_n of a nanoparticle of radius r and the thermal conductivity κ_0 of a single crystal, provided its cleavage planes oriented in parallel to temperature gradient in conformity with the results of [7-9] is determined by the expression:

$$\kappa_n/\kappa_0 = 1.5\int_0^1\int_0^1\int_{-1}^1 \frac{z^2x^4\exp(x/\theta)}{\left[\exp(x/\theta)-1\right]^2}\left(\frac{(r/L^*)\sqrt{z^2-2zy+1}}{1+(r/L^*)Q_{l\|}(x)\sqrt{z^2-2zy+1}}+\right.$$
$$\left.+\frac{2(r/L^*)\sqrt{z^2-2zy+1}}{1+(r/L^*)Q_{t\|}(x)\sqrt{z^2-2zy+1}}\right)dy\,dz\,dx\left\{\int_0^1\frac{x^4\exp(x/\theta)}{\left[\exp(x/\theta)-1\right]^2}\left(\frac{1}{Q_{l\|}(x)}+\frac{2}{Q_{t\|}(x)}\right)dx\right\}^{-1}. \tag{2}$$

In so doing, $L^* = \rho\hbar^4\nu_{\|}^6/\gamma^2(k_BT_D)^5$, where ρ is the material density, $\nu_{\|}$ is the sound velocity in it along the direction of cleavage planes, γ is the Gruneisen parameter, k_B is the Boltzmann constant, T_D is the Debye temperature, $\theta = T/T_D$, the rest of designations are generally accepted. Frequency polynomials $Q_{l\|}(x)$ and $Q_{t\|}(x)$ are of the form:

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

$$Q_{t\|,\perp} = \left(\mu_{\|} + 3.125\theta^3\right)x. \tag{4}$$

where $\mu_{\|} = 0.022$ for Bi_2Te_3 [7-9].

Determination of the effective kinetic coefficients of material as a whole

In the determination of the effective kinetic coefficients of nanostructured thermoelectric material as a whole, for simplicity of calculations we will ignore the influence of material pores on these coefficients, i.e. we will not consider the effects of tunnelling or charge carrier emission, as well as convective and radiation mechanisms of energy transfer and the effects related to intercommunication of pores. Then, with account of particle size distribution function $w(r)$, these coefficients can be determined by the four different methods.

The first method consists in using the Odelevsky formula [1] with regard to the volume share of various-size particles. In this case the effective electric conductivity σ_{ef} and thermal conductivity κ_{ef} of material as a whole are determined as solutions of the following equations:

$$\int_0^\infty \frac{\sigma_{ef} - \sigma_n(r)}{2\sigma_{ef} + \sigma_n(r)} r^3 w(r)\,\mathrm{d}r = 0, \tag{5}$$

$$\int_0^\infty \frac{\kappa_{ef} - \kappa_n(r)}{2\kappa_{ef} + \kappa_n(r)} r^3 w(r)\,\mathrm{d}r = 0. \tag{6}$$

The second method consists in using the Odelevsky formula with regard to the fraction of various-size particles. In this case equations (5) and (6) acquire the form:

$$\int_0^\infty \frac{\sigma_{ef} - \sigma_n(r)}{2\sigma_{ef} + \sigma_n(r)} w(r)\,\mathrm{d}r = 0, \tag{7}$$

$$\int_0^\infty \frac{\kappa_{ef} - \kappa_n(r)}{2\kappa_{ef} + \kappa_n(r)} w(r)\,\mathrm{d}r = 0. \tag{8}$$

The third method consists in averaging the electric conductivity and lattice thermal conductivity over the volume share of various-size particles. In this case the effective kinetic coefficients of nanostructured material are determined directly:

$$\begin{pmatrix}\sigma_{ef}\\ \kappa_{ef}\end{pmatrix} = \int_0^\infty \begin{pmatrix}\sigma_n(r)\\ \kappa_n(r)\end{pmatrix} r^3 w(r)\mathrm{d}r. \tag{9}$$

The fourth method consists in averaging the electric conductivity and lattice thermal conductivity over the fraction of various-size particles. In this case the ratio (9) acquires the form:

$$\begin{pmatrix}\sigma_{ef}\\ \kappa_{ef}\end{pmatrix} = \int_0^\infty \begin{pmatrix}\sigma_n(r)\\ \kappa_n(r)\end{pmatrix} w(r)\mathrm{d}r. \tag{10}$$

In Eqs. (5) – (8) normalization factors are omitted because they have no effect on the results of calculation of the effective kinetic coefficients, as well as in Eqs. (9) and (10), because they have no effect on the dimensionless thermoelectric figure of merit of nanostructured material with respect to a single crystal whose calculation in the framework of the outlined methods is the purpose of this paper.

For concrete calculations we take particle size distribution function $w(r)$ as follows:

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

This particle size distribution function is called the Rayleigh distribution, which has been assumed because it is the simplest single-parameter distribution. Parameter r_0 is the most probable particle radius. This function, as it must be, satisfies normalization condition $\int_0^\infty w(r)\,\mathrm{d}r = 1$.

With regard to (11), the relations (5) – (10) acquire the form as follows:

$$\int_0^\infty \frac{\sigma_{ef} - \sigma_n\left(r_0\sqrt{2t}\right)}{2\sigma_{ef} + \sigma_n\left(r_0\sqrt{2t}\right)}\sqrt{t^3}\exp(-t)\,\mathrm{d}t = 0, \tag{12}$$

$$\int_0^\infty \frac{\kappa_{ef} - \kappa_n\left(r_0\sqrt{2t}\right)}{2\kappa_{ef} + \kappa_n\left(r_0\sqrt{2t}\right)}\sqrt{t^3}\exp(-t)\,\mathrm{d}t = 0, \tag{13}$$

$$\int_0^\infty \frac{\sigma_{ef} - \sigma_n\left(r_0\sqrt{2t}\right)}{2\sigma_{ef} + \sigma_n\left(r_0\sqrt{2t}\right)}\exp(-t)\,\mathrm{d}t = 0\,, \tag{14}$$

$$\int_0^\infty \frac{\kappa_{ef} - \kappa_n\left(r_0\sqrt{2t}\right)}{2\kappa_{ef} + \kappa_n\left(r_0\sqrt{2t}\right)}\exp(-t)\,\mathrm{d}t = 0, \tag{15}$$

$$\begin{pmatrix}\sigma_{ef}\\ \kappa_{ef}\end{pmatrix} = \int_0^\infty \begin{pmatrix}\sigma_n\left(r_0\sqrt{2t}\right)\\ \kappa_n\left(r_0\sqrt{2t}\right)\end{pmatrix}\sqrt{t^3}\exp(-t)\,\mathrm{d}t, \tag{16}$$

$$\begin{pmatrix}\sigma_{ef}\\ \kappa_{ef}\end{pmatrix} = \int_0^\infty \begin{pmatrix}\sigma_n\left(r_0\sqrt{2t}\right)\\ \kappa_n\left(r_0\sqrt{2t}\right)\end{pmatrix}\exp(-t)\,\mathrm{d}t. \tag{17}$$

The results of calculation of the dimensionless thermoelectric figure of merit of the bulk nanostructured material based on Bi_2Te_3 with respect to a single crystal using different methods of determination of the effective kinetic coefficients are shown in Fig. 1.

It is seen from the figure that curves 1 and 3 coincide to a high degree of accuracy. This would imply that in determining the effective kinetic coefficients of thermoelectric material via the kinetic coefficients of shape-forming elements, instead of the Odelevsky formulae on condition of α = const one can employ the usual averaging over the volume share of particles with regard to size distribution function. In so doing, the maximum dimensionless thermoelectric figure of merit of the bulk nanostructured thermoelectric material, on condition that particle cleavage planes are oriented parallel to electric current and thermal flux, is a factor of $2.06 \div 2.1$ larger than the dimensionless thermoelectric figure of merit of a single crystal and is achieved with the most probable particle radius 0.02 μm. Curves

2 and 4 are also close to each other which means that in determining the effective kinetic coefficients of thermoelectric material by the fraction of particles with regard to size distribution function, instead of the Odelevsky formulae with a reasonable degree of accuracy one can also use the usual averaging of the kinetic coefficients by the fraction of various-size particles. With such method of averaging, the maximum dimensionless thermoelectric figure of merit of the bulk nanostructured thermoelectric material is a factor of 1.076 ÷ 2.082 greater than the dimensionless thermoelectric figure of merit of a single crystal and is achieved with the most probable nanoparticle radius 0.02 ÷ 0.03 μm. Curve 5 has been constructed on the assumption of equal size of all nanoparticles. In this case the maximum dimensionless thermoelectric figure of merit of the bulk nanostructured thermoelectric material is a factor of 2.12 greater than the thermoelectric figure of merit of a single crystal and is achieved with nanoparticle radius 0.03 μm. Hence it follows that the method of averaging in determining the effective kinetic coefficients of the bulk nanostructured thermoelectric material scarcely affects the predicted value of its dimensionless thermoelectric figure of merit, but markedly affects the estimation of the optimal value of the most probable particle radius.

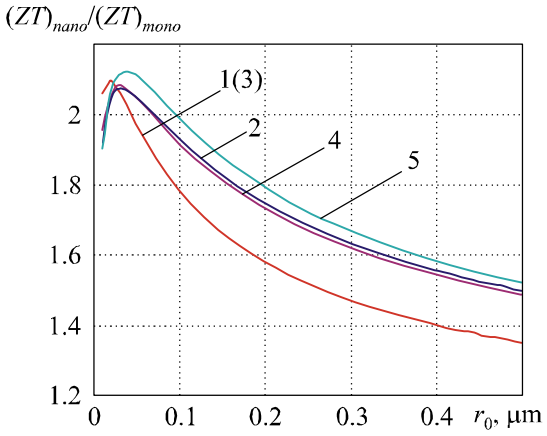

Fig. 1. Dependence of the dimensionless thermoelectric figure of merit of the bulk nanostructured thermoelectric material based on Bi_2Te_3 on the most probable particle radius with different methods of determination of the effective kinetic coefficients. Curve numbers 1 – 4 correspond to conventional serial numbers of averaging methods described in the text. Curve 5 corresponds to the case of zero particle size dispersion, where there is no need in averaging.

If equivalent-result methods for averaging over the volume share of particles with regard to size distribution function are assumed to be most correct, then the optimal value of the most probable particle radius of the bulk nanostructured thermoelectric material is 0.02 μm.

Conclusions and recommendations

1. This paper is concerned with the four methods of taking into account the size distribution of the bulk nanostructured thermoelectric material particles in determining its dimensionless thermoelecric figure of merit with respect to a single crystal.
2. The most correct are equivalent-result methods for determination of the effective kinetic coefficients of the bulk nanostructured thermoelectric material as a whole via the kinetic coefficients of shape-forming elements using the Odelevsky formulae with regard to the volume share of various-size particles and by simple averaging the electric conductivity and lattice thermal conductivity over the volume share of various-size particles. In this case, the maximum thermoelectric figure of merit of the bulk nanostructured material is about 2.1 times greater than the

thermoelectric figure of merit of a single crystal and is achieved with the most probable particle radius equal to 0.02 μm.

3. Determination of the effective kinetic coefficients of the bulk nanostructured thermoelectric material using the Odelevsky formulae with regard to the fraction of various-size particles and by simple averaging the electric conductivity and lattice thermal conductivity over the fraction of various-size particles yields the dimensionless thermoelectric figure of merit of the bulk nanostructure material which is about $2.076 \div 2.082$ times greater than the thermoelectric figure of merit of a single crystal, this value being achieved with the most probable particle radius equal to 0.03 μm.
4. Determination of the effective kinetic coefficients of the bulk nanostructured material with neglect of size particle distribution yields the dimensionless thermoelectric figure of merit of the bulk nanostructured material 2.12 times greater than the thermoelectric figure of merit of a single crystal which is achieved at particle radius equal to 0.04 μm.
5. Thus, the method of averaging over particle size in determining the effective kinetic coefficients of the bulk nanostructured material with neglecting the influence of pores and tunneling effects scarcely affects the predicted maximum value of the dimensionless thermoelectric figure of merit of the bulk nanostructured material, but markedly affects the optimal value of the most probable radius of its particle that should be approached. Therefore, the most probable radius equal to 0.02 μm should be considered optimal on condition that size distribution of material particles is the Rayleigh distribution.

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