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OPTIMIZATION OF *Bi-Te* BASED MATERIALS FOR THERMOELECTRIC ENERGY CONVERTERS UNDER THE CONDITIONS OF MINIATURIZATION

Based on the temperature and concentration dependences of the kinetic coefficients of thermoelectric material (TEM), the concentration dependences of thermoelectric figure of merit of TEM were determined under the conditions of miniaturization for thermoelectric cooling and generation modes with different layer thicknesses. 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 reduction of TEM layer thickness to 50 μm a gain in the figure of merit as compared to single crystal is 1 – 4 %. For lower thicknesses a gain can be greater. In particular, with reduction of TEM layer thickness to 0.1 μm, maximum thermoelectric figure of merit is increased by a factor of 1.7 – 3.2 against single crystal. In so doing, reduction of TEM layer thickness to 50 μm scarcely affects the optimal concentration of doping single-charge impurities, whereas transition to lower thicknesses reduces it. For instance, with the layer thickness 0.1 μm it is reduced by a factor of 1.1 – 2.2 as compared to single crystal.

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

Introduction

Miniaturization of thermoelectric energy converters is a relevant task of up-to-date functional electronics. The need for miniaturization is primarily dictated by considerations of reduced consumption of thermoelectric material which is the most expensive part of these converters. Moreover, earlier studies pursued by various authors on the powders, films and wires of thermoelectric materials [1 – 5] give certain grounds to believe that miniaturization will not degrade the output characteristics of thermoelectric energy converters, and even will improve them as compared to characteristics of converters based on the 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 thin layers, the effects related to charge carrier and phonon scattering at layer 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 TEM for charge carrier concentration under the conditions of the impact of TEM layer thickness on its kinetic coefficients.

Method of estimation of the figure of merit of TEM thin layers versus their thickness and charge carrier concentration

Taking into consideration that layer 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 layer thickness through the same multiplier [7, 8], one can readily derive the following expression for the figure of merit Z of thin layer with respect to single crystal Z_{mono}:

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

In this formula

$$Z_a = \left\{d_0 l_{n,p}^{-1}\ln\left[1+l_{n,p}d_0^{-1}\right]\right\}^{-1}\left[\int_0^1\int_0^1 \frac{x^4\exp(x/\theta)}{\left[\exp(x/\theta)-1\right]^2}\left(\frac{k_{||}^* z}{1+k_{||}^* Q_{l||}(x)z}+\frac{2k_{||}^* z}{1+k_{||}^* Q_{t||}(x)z}\right)dzdx\right]^{-1}\left\{\int_0^1 \frac{x^4\exp(x/\theta)}{\left[\exp(x/\theta)-1\right]^2}\left(\frac{1}{Q_{l||}(x)}+\frac{2}{Q_{t||}(x)}\right)dx\right\}. \tag{2}$$

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, d_0 – layer thickness, $l_{n,p}$ – mean free path of electrons (holes) in single crystal, $k_{||}^* = \left(d_0\gamma^2\theta/\rho\right)\left(k_B T_D/\hbar v_{||}\right)^4\left(k_B T_D/\rho v_{||}^2\right)$, $\theta = T/T_D$, T – absolute temperature, T_D – the Debye temperature of material, γ, ρ 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 $Q_{l||}(x)$ and $Q_{t||}(x)$, accordingly, are given below:

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

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

Formulae (3) and (4) take into account both normal and Umklapp processes for the longitudinal (*l*) and transverse (*t*) phonon modes. Component μx 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, however, these approaches were modified with regard to specific geometry of charge carriers and phonons in a thin TEM layer.

Thus, from relations (1 – 4) we see that for the calculation of thermoelectric figure of merit and efficiency of thin layers one must, using the experimental data, preliminarily 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 μ 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]

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

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]

$$n_0 = \frac{4\left(2\pi m^*_{n,p} k_B T\right)^{3/2}}{\sqrt{\pi} h^3} F_{1/2}(\eta) \tag{6}$$

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]:

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

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

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

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 electric 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 η, one can use the Wiedemann-Franz relation to determine crystal thermal conductivity component due to free charge carriers:

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

In so doing, the Lorentz number is equal to:

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

Knowing the thermal conductivity due to free carriers, as well as the experimental thermal conductivity of TEM described by 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 μ of polynomials (3), (4) characterizing frequency dependence of phonon-phonon scattering probability.

The results of optimization of materials for coolers

Calculation of dependences of the figure of merit of microlayers on the concentration of charge carriers was performed for *n*-type materials $Bi_2Te_{2.7}Se_{0.3}$ + (0.09…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 α_{mono}, σ_{mono}, κ_{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 thin layers obtained for various thicknesses and temperatures are given in Fig. 1 – 6.

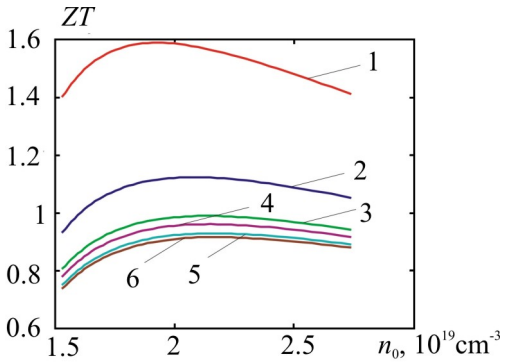

Fig. 1. Concentration dependences of ZT of thin layers of n-type TEM $Bi_2Te_{2.7}Se_{0.3}$ at temperature 300 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

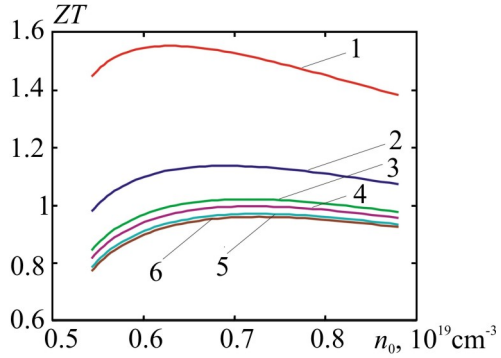

Fig. 2. Concentration dependences of ZT of thin layers of p-type TEM $Bi_{0.5}Sb_{1.5}Te_3$ at temperature 300 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

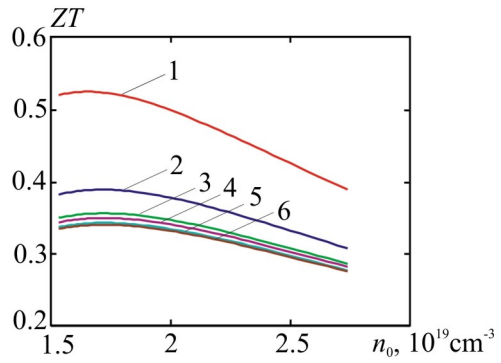

Fig. 3. Concentration dependences of ZT of thin layers of n-type TEM $Bi_2Te_{2.7}Se_{0.3}$ at temperature 150 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

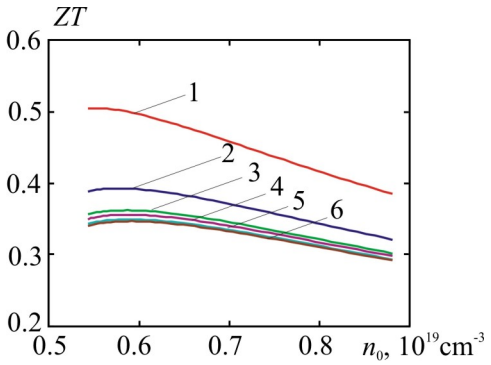

Fig. 4. Concentration dependences of ZT of thin layers of p-type TEM $Bi_{0.5}Sb_{1.5}Te_3$ at temperature 150 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

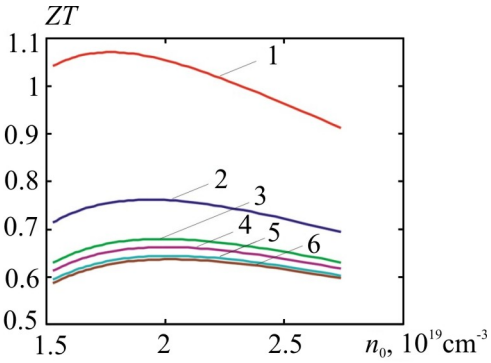

Fig. 5. Concentration dependences of ZT of thin layers of n-type TEM $Bi_2Te_{2.7}Se_{0.3}$ at temperature 225 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

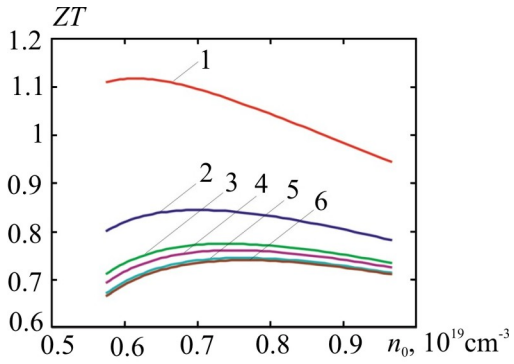

Fig. 6. Concentration dependences of ZT of thin layers of p-type TEM $Bi_{0.5}Sb_{1.5}Te_3$ at temperature 225 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

From the figures it is seen that for the above materials at all temperatures when passing from single crystal to thin TEM layers 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 layer thicknesses. In all cases there is thickness-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 layers 50 μm thick. Essential gain, namely by a factor of 1.2 – 2 as compared to single crystal, is

obtained in the range of thicknesses 0.1 – 1 μm. Nevertheless, the results imply that transition from a single crystal to thin layers can be done without degrading the output parameters of coolers, and hence, one can achieve substantial saving of TEM. To achieve a more essential gain in the figure of merit, one must pass to still thinner, e.g. submicron layers or nanolayers. However, a gain in the figure of merit with such thin TEM can be assured and maintained only using special technology of creating TEM-metal contacts providing possibly lower values of contact resistances.

Results of optimization of materials for generators

Calculation of dependences of the figure of merit of microlayers on the concentration of charge carriers was performed for *n*-type materials $(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sbi_2Se_3)_{0.05}$ 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 α_{mono}, σ_{mono}, κ_{mono} of these materials on temperature and the 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 thin layers of these materials obtained for various thicknesses and temperatures are given in Fig. 7 – 12.

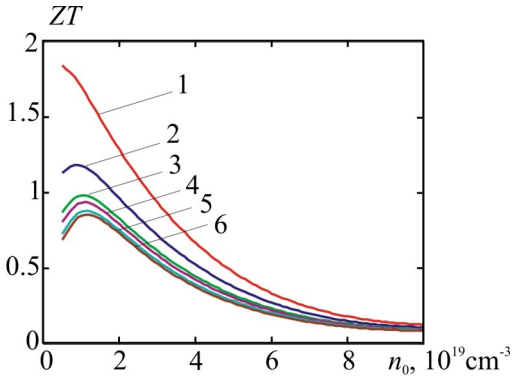

Fig. 7. Concentration dependences of ZT of thin layers of n-type TEM $(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ at temperature 300 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

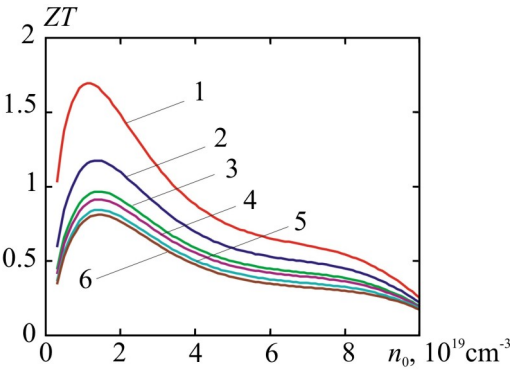

Fig. 8. Concentration dependences of ZT of thin layers of p-type TEM $(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ at temperature 300 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

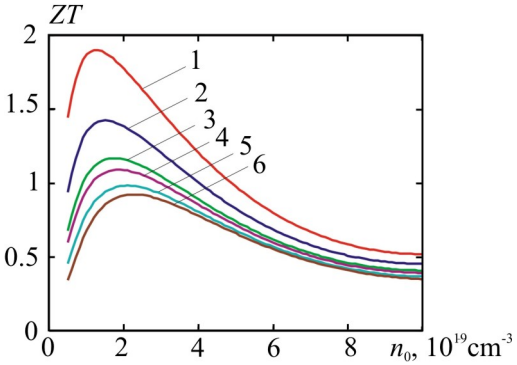

Fig. 9. Concentration dependences of ZT of thin layers of n-type TEM $(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ at temperature 450 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

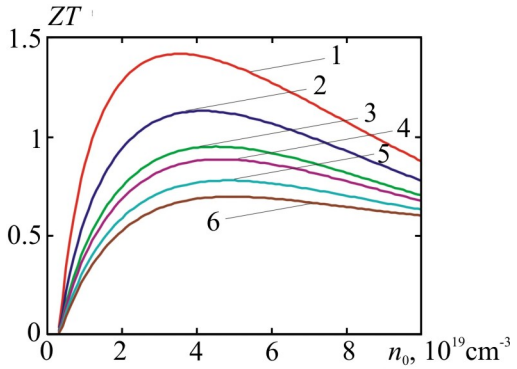

Fig. 10. Concentration dependences of ZT of thin layers of p-type TEM $(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ at temperature 450 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

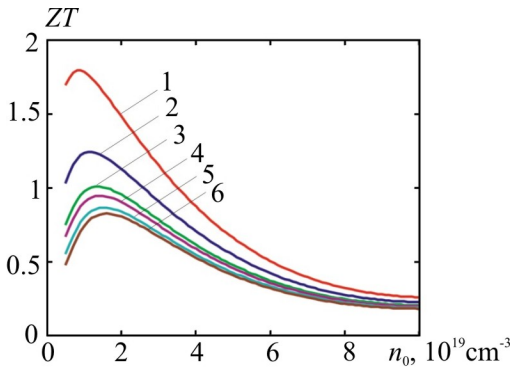

Fig. 11. Concentration dependences of ZT of thin layers of m-type TEM $(Bi_2Te_3)_{0.9}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ at temperature 375 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

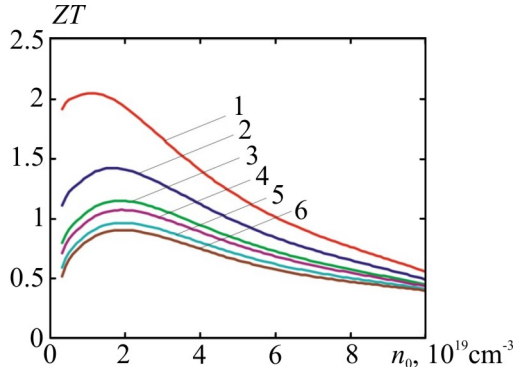

Fig. 12. Concentration dependences of ZT of thin layers of p-type TEM $(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ at temperature 225 K and layer thicknesses, μm: 1 – 0.1; 2 – 1; 3 – 5; 4 – 10; 5 – 50; 6 – bulk crystal.

Just as in the case of materials for coolers, for each thickness of TEM layer 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 1.6 – 3.2 as compared to single crystal is obtained in the range of thicknesses 0.1 – 1 μm. At thicknesses 1 – 50 μm the gain is reduced, though it makes about 4 % as compared to single crystal.

There is no need in additional optimization of the figure of merit of materials for the concentration of doping impurities as compared to single crystal in the range of thicknesses 5 – 50 μm. Some change in concentration is required only at thicknesses 0.1 μm. In particular, it must be reduced by a factor of 1.14 – 2.2 as compared to single crystal. The strongest change is required for *n*-type generator materials.

Conclusions

1. The impact of phonon and charge carrier scattering at the boundaries of microminiature TEM layers on the electrical conductivity and lattice thermal conductivity is the most essential factor assuring thermoelectric figure of merit when passing from single crystal to layers of thickness from 50 μm. The figure of merit improvement can be expected at lower layer thicknesses.
2. The use of thin TEM layers instead of single crystals allows for essential saving of TEM without sacrificing the output parameters and characteristics of thermoelectric coolers and generators.
3. A stronger reduction of lattice thermal conductivity as compared to electrical conductivity creates opportunities for TEM figure of merit improvement when passing from the bulk single crystals to microminiature layers.
4. The greatest gain in the figure of merit, namely 1.7 – fold for cooling materials and 3.15 – fold for generator materials is achieved at layer thickness 0.1 μm.
5. At thicknesses over 50 μm and temperatures 150 – 300 K the expected improvement of the figure of merit of considered materials with respect to corresponding single crystals does not exceed 4 %.

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