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ON THE FUNDAMENTAL DIFFERENCE BETWEEN THERMOELECTRIC COMPOSITES AND DOPED THERMOELECTRIC MATERIALS AND THE CONSEQUENCES IT IMPLIES

It is shown that if the effect of doping impurities on a thermoelectric material is reduced only to a change in the concentration of free charge carriers in it, then, for example, for a material based on bismuth telluride even at a temperature of 400 K, it is impossible to obtain a value of the dimensionless thermoelectric figure of merit, which would be far in excess of 1. On the other hand, the dimensionless thermoelectric figure of merit of thermoelectric composites based on semiconductor materials with metal nanoclusters or nanoparticles can significantly exceed 1, if they are indeed composites, that is, materials, each component of which, having entered the composition of the composite, retains its inherent macroscopic values of kinetic coefficients and their temperature dependences. In this case, the increase in the figure of merit of such a thermoelectric composite is reduced to optimizing its composition and solving the problem of the technological possibilities of manufacturing this particular composite. However, it should be borne in mind that the answer to the question about the practical application of such composites, even if they are created and their parameters are stably reproducible, depends on the possibility of creating devices in which they are used, that should have not only high consumer characteristics, but also the corresponding stability, reliability, durability and service life. Bibl. 6, Fig. 6.

Key words: thermoelectric material, doping, dimensionless thermoelectric figure of merit, percolation threshold, composite, nanoparticles, optimal composition of the composite.

Introduction

Today, significant efforts of specialists in the field of thermoelectric materials science are aimed at solving both theoretical and practical problems related to finding ways to increase the dimensionless thermoelectric figure of merit of both doped thermoelectric materials and composites. However, despite these efforts, significant progress in this direction has either not been achieved, or some high results are not consistently reproducible. From this point of view, efforts aimed, for example, at creating superlattices or quantum well materials, deserve a separate analysis. But the purpose of this paper is an unbiased analysis of the situation in the field of creation and application of TEM based on "traditional" alloys of *Bi* (*Sb*) - *Te* (*Se*) system.

About the limited potential of doped TEM

To prove this limitation by calculation, we investigate the effect of the concentration of doping impurities on the dimensionless thermoelectric figure of merit of TEM under the following model assumptions:

1) the band spectrum of charge carriers in TEM is parabolic and isotropic with the temperature-independent effective mass;
2) quasi-elastic scattering of charge carriers in the relevant temperature area occurs on a deformation potential of acoustic phonons with the energy-independent cross-section and mean free path inversely proportional to temperature;
3) the lattice thermal conductivity of semiconductor is determined by phonon-phonon scattering with Umklapp and is inversely proportional to temperature, obeying the Leibfried-Schlemann law [1, 2];
4) doping impurities do not affect anything except the concentration of free charge carriers in material.

Given the validity of these assumptions, the scattering index of charge carriers $r = -0.5$.

For further calculations, we assume that at a certain temperature T_0 we know the thermoelectric parameters of the undoped TEM, namely its thermoEMF α_{s0}, electrical conductivity σ_{s0} and thermal conductivity κ_{s0}. Assume also that the relative increase in the concentration of free charge carriers in the TEM after the introduction of a doping impurity is equal to x.

The construction of the necessary temperature dependences and concentration dependences of the characteristics of the doped TEM on the basis of known general relations [1] is carried out in the following order.

From the relation for thermoEMF

$$\alpha_{s0} = \frac{k}{e}\left[\frac{2F_1(\eta_0)}{F_0(\eta_0)} - \eta_0\right] \tag{1}$$

we find a reduced chemical potential η_0 of charge carrier gas in the undoped material at a temperature of T_0.

Then from equation

$$\frac{T^{1.5}F_{0.5}(\eta)}{(1+x)T_0^{1.5}F_{0.5}(\eta_0)} = 1 \tag{2}$$

we determine the temperature dependence of reduced chemical potential η of charge carrier gas on temperature T in given temperature range at an arbitrary concentration of doping impurities.

From the relation

$$\alpha_s = \frac{k}{e}\left[\frac{2F_1(\eta)}{F_0(\eta)} - \eta\right] \tag{3}$$

we determine the temperature dependence of the thermoEMF of doped TEM.

From the relation

$$L_s(\eta)=\left(\frac{k}{e}\right)^2\left[\frac{3F_2(\eta)}{F_0(\eta)}-\frac{4F_1^2(\eta)}{F_0^2(\eta)}\right] \tag{4}$$

we determine the temperature dependence of the Lorentz number of doped TEM.

The temperature dependence of the electrical conductivity of doped TEM under the above model assumptions is determined as follows:

$$\sigma_s=\sigma_{s0}\cdot(1+x)\left(\frac{T_0}{T}\right)^{1.5}\frac{F_0(\eta)F_{0.5}(\eta_0)}{F_{0.5}(\eta)F_0(\eta_0)}\,. \tag{5}$$

The temperature dependence of the electrical conductivity of doped TEM with regard to everything said above is determined as:

$$\kappa_s=\sigma_s L_s(\eta)T+\left[\kappa_{s0}-\sigma_{s0}L_s(\eta_0)T_0\right]\frac{T_0}{T}\,. \tag{6}$$

In formulae (1) – (5), $F_m(\eta)$ denote the Fermi integrals which are determined by the following relation:

$$F_m(\eta)=\int_0^\infty x^m\left[\exp(x-\eta)+1\right]^{-1}dx\,. \tag{7}$$

Relations (1) – (7) fully determine the temperature dependences of the thermoEMF, electrical conductivity and thermal conductivity of doped TEM.

The calculated concentration dependences of the dimensional thermoelectric figure of merit of doped TEM at temperatures 200 and 400 K are shown in Fig. 1.

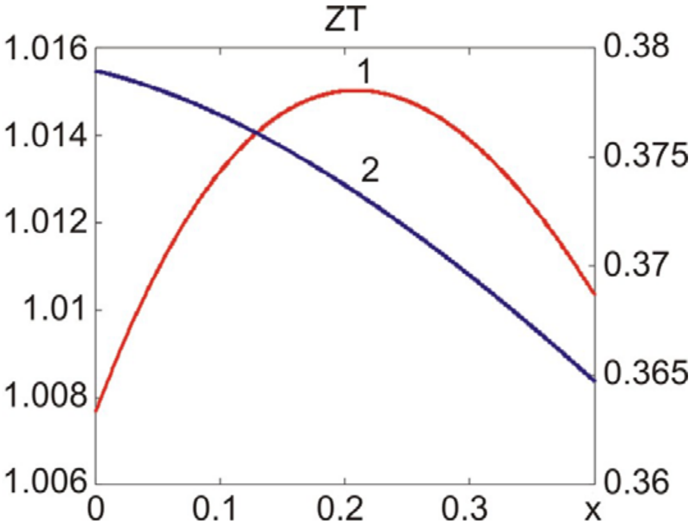

Fig. 1.Concentration dependences of the dimensional thermoelectric figure of merit of doped TEM at temperatures:1 – 400 K (left axis), 2 – 200 K (right axis)

When constructing plots, the following parameters of TEM were taken: $\alpha_{s0} = 200\ \mu$ V/K, $\sigma_{s0} = 800$ S/cm, $\kappa_{s0} = 1.4$ W/(m·K) [1].

The plots show that at a temperature of 400 K even the highest value of the dimensionless thermoelectric figure of merit of the doped material, which corresponds to its "optimal" composition near $x = 0.2$, is only about 0.01, i.e. less than 1 % higher than the value of the thermoelectric figure of merit of the source material. The existence of the optimum in this case is explained by two competing factors: an increase in electrical conductivity and a decrease in thermoEMF with increasing concentration of charge carriers. At lower temperature, when the gas of free charge carriers is quite degenerate, the concentration dependence of the dimensionless thermoelectric figure of merit is also weak (the highest value differs from the lowest in the considered range of concentrations of charge carrier by about 5.5%), but this dependence is entirely determined by the decrease in thermoEMF.

Thus, we clearly see the limited potential of doped TEM. The best results are achieved when doping simultaneously reduces the lattice thermal conductivity. Moreover, doping of TEM by isovalent impurities is effective, because in this case the electrical conductivity, the electron (hole) part of thermal conductivity and thermoEMF of the material change relatively little, and the lattice thermal conductivity changes to a greater extent, quite often in the direction of decrease.

On the fundamental difference between thermoelectric composites and doped TEM and their potential

Thus, we have seen that the fundamental role of doping impurities in the traditional sense of the term is that they, changing their state, either "supply" free charge carriers of this or other sign, or do not supply carriers, but affect the scattering or spectrum of phonons in TEM, changing in this or other direction the lattice thermal conductivity and even the nature of its temperature dependence, on which we will also dwell later. It is clear that in this case the characteristics of the doped material cannot be described in any way due to the macroscopic characteristics of its components. The principal feature of the composite, in contrast to the doped material, is the ability to determine at least its kinetic coefficients, namely electrical conductivity, thermal conductivity and thermoEMF due to the relevant characteristics of individual components (phases) and the composition of the composite without going deep into the microscopic mechanisms of these characteristics. That is why the theory of composites is quite often identified with the theory of the "effective medium", which is understood as a purely macroscopic object. It is clear that in this case only that material can be called a composite whose components (phases), when incorporated into the composite, regardless of its composition, retain their inherent macroscopic properties and their temperature dependences. The "rules of mixing" macroscopic characteristics, according to which the characteristics of the composite as a whole are determined, depend on the concept of "effective environment" followed by the researcher. For example, if we follow the concept, according to which the percolation effect is insignificant, then for a two-phase system the TEM - metal kinetic coefficients are defined as follows [2]:

$$\sigma_c = \sigma_m \nu_m + \sigma_s \left(1 - \nu_m\right), \tag{8}$$

$$\kappa_c = \kappa_m \nu_m + \kappa_s \left(1 - \nu_m\right). \tag{9}$$

The indices “s” and “m” refer to TEM and metal, respectively, ν_m – the volume fraction of metal. The thermoEMF of composite is determined as [3]:

$$\alpha_c = \frac{(\alpha_m/\kappa_m)\nu_m + (\alpha_s/\kappa_s)(1-\nu_m)}{\kappa_m^{-1}\nu_m + \kappa_s^{-1}(1-\nu_m)}. \tag{10}$$

However, if percolation effect is essential, formulae (8) and (9), respectively, acquire the form [3, 4]:

$$\sigma_c = 0.25\left\{\sigma_s(2-3\nu_m) + \sigma_m(3\nu_m-1) + \sqrt{[\sigma_s(2-3\nu_m) + \sigma_m(3\nu_m-1)]^2 + 8\sigma_m\sigma_s}\right\}, \tag{11}$$

$$\kappa_c = 0.25\left\{\kappa_s(2-3\nu_m) + \kappa_m(3\nu_m-1) + \sqrt{[\kappa_s(2-3\nu_m) + \kappa_m(3\nu_m-1)]^2 + 8\kappa_m\kappa_s}\right\}, \tag{12}$$

and formula (10) remains unchanged.

Consider the difference between these two concepts using an example of composite, even though hypothetical, which consists of bismuth telluride and nickel. The plot of the electrical conductivity of the composite depending on the volume fraction of the metal $\nu_m \equiv \nu$ in accordance with formulae (8) and (11) is shown in Fig. 2. In this case, the electrical conductivity of nickel is taken equal to $1.3 \cdot 10^5$ S/cm.

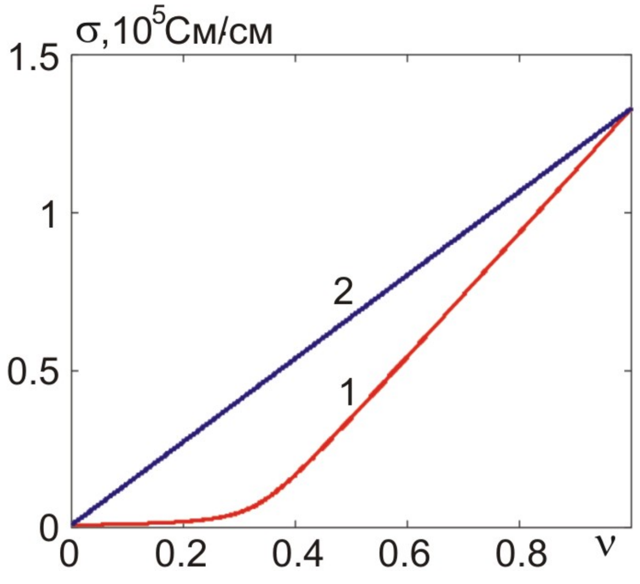

Fig. 2.Dependence of the electrical conductivity of “bismuth telluride-nickel” composite on the volume fraction of nickel: 1 – in the presence of percolation; 2 – in the absence of percolation

The figure shows that in the presence of percolation, as the content of nickel particles in the composite increases, the electrical conductivity of the composite increases first more slowly and then faster than in its absence.

Let us consider the question of what size of the nickel fraction can be considered macroscopic. If we consider, for example, a cluster with a radius of 35 nm, then taking into account that the nickel lattice constant is equal to 0.5 nm [5] and this lattice is body-centered, we obtain that such a cluster can accommodate approximately 2.9×10^6 atoms, which means that the relative deviation of the macroscopic parameters of the cluster from their average values is less than 0.1%, that is, this or larger clusters can be considered macroscopic and one can ascribe to them the conductivity of nickel. Based on the conductivity of nickel and the concentration of electrons in it [5], we can find that the free path of electrons in nickel at 300 K is 4.18 nm. Then at an arbitrary temperature the electrical conductivity of the metal cluster is approximately equal to:

$$\sigma_{cl} = \sigma_0 \left(T_0 / T \right) \frac{r_c}{r_c + l_0 \left(T_0 / T \right)}. \tag{13}$$

In this formula, σ_0 – electrical conductivity of the bulk nickel sample at a temperature of T_0, r_c – cluster radius, l_0 – mean free path of electron in the bulk nickel sample at 300 K.

Fig.3 shows the dependences of the thermoelectric figure of merit of TEM-nickel clusters composite on its composition with regard to the percolation effect at temperatures 200 and 400 K.

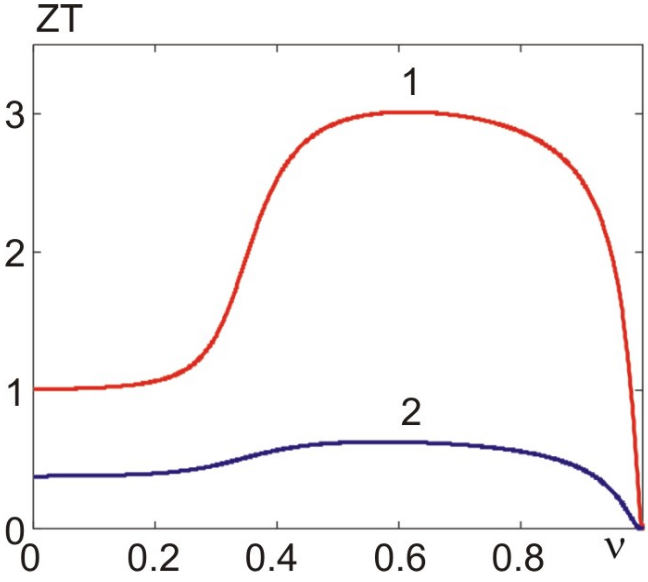

Fig. 3. Thermoelectric figure of merit of composite with regard to the percolation effect at temperatures: 1 – 400 K, 2 – 200 K.

It was assumed that the thermal conductivity of nickel is 90 W/(m·K) and by virtue of the Wiedemann-Franz law does not depend on temperature. The thermoEMF of nickel was considered to be equal to 23 μV/K and temperature independent.

From the figure it is seen that up to nickel content almost 30% by volume, i.e. within the percolation threshold, the thermoelectric figure of merit of the composite at 400 K retains a value equal to 1, but after this threshold increases rapidly, reaching a value of almost 3 at about 60 volume % of nickel, goes to the "plateau", and then rapidly decreases to the value inherent in pure nickel.

Fig.4 shows the same dependences as in Fig.3, but without regard to percolation effect.

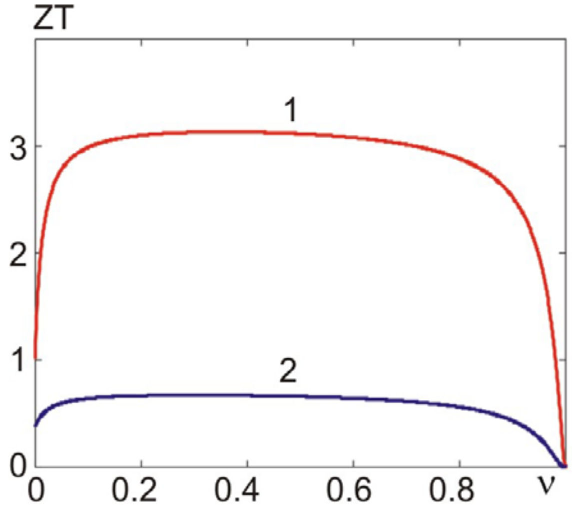

Fig. 4. Thermoelectric figure of merit of the composite without regard to the percolation effect at temperatures:1 – 400 K, 2 – 200 K.

The figure shows that neglect of the percolation has little effect on the maximum thermoelectric figure of merit of the composite, although it significantly affects the rate of reaching this maximum, the length of the "plateau" and the rate of further decline to a small value inherent in pure nickel. Note that Figs. 3 and 4 correctly reflect the physical situation if the temperature dependence of the lattice thermal conductivity of TEM is subject to the Leibfried-Schlemman formula. Instead, the following plots in Figs. 5 and 6 are constructed for the case when this formula is violated in such a way that the lattice thermal conductivity increases approximately linearly with temperature [6].

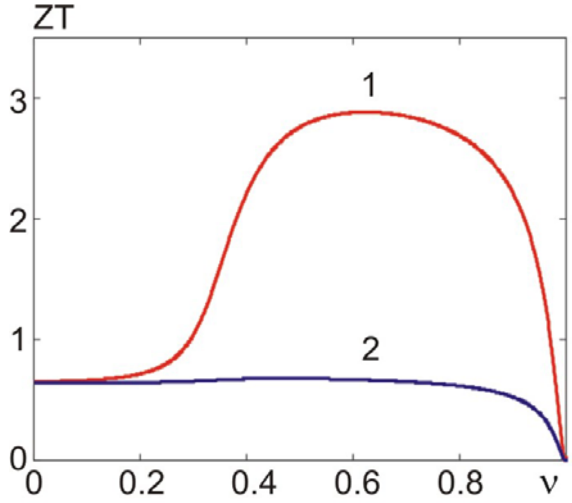

Fig. 5. Thermoelectric figure of merit of the composite with regard to the percolation effect and a deviation of TEM lattice thermal conductivity from the Leibfried-Schlemann formula at temperatures: 1 – 400 K, 2 – 400 K.

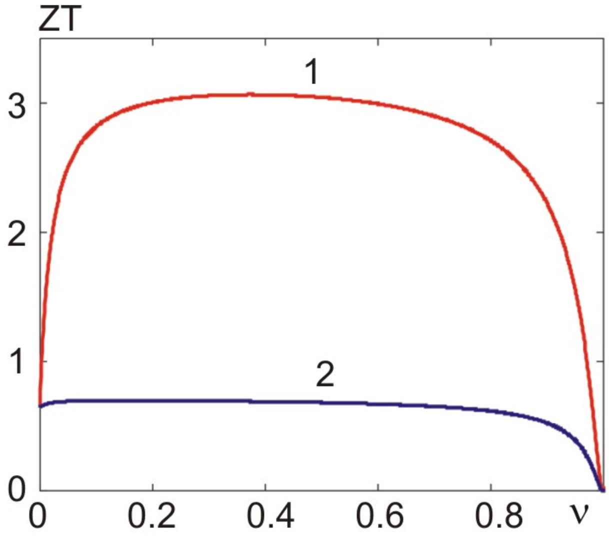

Fig. 6. Thermoelectric figure of merit of the composite without regard to the percolation effect, but with regard to a deviation of TEM lattice thermal conductivity from the Leibfried-Schlemann formula at temperatures: 1 – 400 K, 2 – 200 K.

The figures show that even the linear increase in the lattice thermal conductivity of TEM with temperature does not affect the maximum value of the thermoelectric figure of merit of the composite. From this we conclude that such a significant advantage of composites over doped materials, at least in principle, is achievable precisely because the components that make up the composites retain their macroscopic characteristics. If this does not happen, then such an advantage will not be obtained. Therefore, those materials that have a relatively low thermoelectric efficiency should be considered as specially doped materials rather than the composites, despite the fact that the authors consider them to be the composites. Consider from this point of view, for example, the results of [6]. Its authors report that they obtained for the graphite/ $Bi_{0.5}Sb_{1.5}Te_3$ composite an increase in thermoelectric figure of merit to 1.05 or 35 % compared to the "pure" TEM with a graphite content of 0.05 mol.%. And such an increase in the composite is impossible if the percolation effect occurs (Fig. 5), but it is possible if the percolation effect is absent (Fig. 6). However, since this effect occurs, and according to [6] the electrical conductivity of the material with the addition of graphite generally decreases, although insignificantly, thermoEMF increases slightly, and the lattice thermal conductivity decreases by more than 1.5 times, it should be assumed that we are dealing not with a composite, and with a specially doped material, the main role of graphite in which is the rearrangement of the phonon spectrum of TEM and phonon scattering mechanisms in it, which leads to a significant decrease in lattice thermal conductivity and changes in the nature of its temperature dependence.

However, it should be noted that we do not consider in this paper either the technological aspects of the manufacture of the composite thermoelectric materials, taking into account the above requirements for them, or their strength characteristics and service life. And these aspects are no less, if not more important than the actual thermoelectric figure of merit. Therefore, the trend in the development of thermoelectric materials and devices, albeit very slowly, is shifting towards the development of a kind of "compromise" materials and structures, in which, with given consumer characteristics, minimum mechanical stresses, and, consequently, maximum reliability, durability and service life of both materials and devices would be achieved.

Conclusions

1. It is shown that the dimensionless thermoelectric figure of merit of materials based on bismuth telluride cannot increase by more than 1%, if the role of the doping impurity is only to increase the concentration of charge carriers.
2. Unlike doped thermoelectric materials, the composites that contain highly conductive, such as metal, clusters with a diameter of 70 nm or more, have significantly greater thermoelectric capabilities making it possible to obtain at 400 K the dimensionless thermoelectric figure of merit about 3. This value is not affected by the percolation or possible increase of lattice thermal conductivity of TEM with temperature. This is possible primarily because in the composites, in contrast to doped materials, their components retain the thermoelectric characteristics, including their temperature dependences, which were inherent in these components before entering the composite. This feature for the composite is fundamental. If the preservation of the characteristics of the components does not take place, then we are not dealing with a composite, but with a special doped material, which cannot offer such significant advantages.
3. From this point of view, it is important to dope TEM primarily with such impurities and in such quantities that little change the electrical conductivity and thermoEMF of TEM, but significantly reduce its lattice thermal conductivity, even if changing the nature of its temperature dependence.

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ПРО ПРИНЦИПОВУ ВІДМІННІСТЬ ТЕРМОЕЛЕКТРИЧНИХ КОМПОЗИТІВ ВІД ЛЕГОВАНИХ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ ТА НАСЛІДКИ З НЕЇ

Показано, що якщо вплив легуючих домішок на термоелектричний матеріал зводиться лише до зміни концентрації вільних носіїв заряду у ньому, то, наприклад, для матеріалу на основі телуриду вісмуту навіть за температури 400 К неможливо отримати значення безрозмірної термоелектричної ефективності, яке б істотно перевищувало 1. З іншого боку безрозмірна термоелектрична ефективність термоелектричних композитів на основі напівпровідникових матеріалів з металевими нанокластерами або наночастинками може істотно перевищувати 1, якщо вони справді є композитами, тобто матеріалами, кожна складова яких, увійшовши до складу композиту, зберігає притаманні їй макроскопічні значення кінетичних коефіцієнтів та їх температурні залежності . В цьому разі підвищення добротності такого термоелектричного композиту зводиться до оптимізації його складу і вирішення питання про технологічні можливості виготовлення саме цього композиту. Однак слід мати на увазі, що відповідь на питання про практичне застосування таких композитів, якщо вони навіть будуть створені і їх параметри будуть стабільно відтворюваними, залежить від можливості створення з їх застосуванням пристроїв, які б мали не лише високі споживчі характеристики, а й відповідну стабільність,надійність, довговічність та ресурсну стійкість. Бібл. 6, рис. 6.

Ключові слова: термоелектричний матеріал, легування, безрозмірна термоелектрична ефективність, поріг перколяції, композит, наночастинки, оптимальний склад композиту.

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О ПРИНЦИПИАЛЬНОМ ОТЛИЧИИ ТЕРМОЭЛЕКТРИЧЕСКИХ КОМПОЗИТОВ ОТ ЛЕГИРОВАННЫХ ТЕРМОЭЛЕКТРИЧЕСКИХ МАТЕРИАЛОВ И СЛЕДСТВИЯХ ИЗ НЕГО

Показано, что если влияние легирующих примесей на термоэлектрический материал (ТЭМ) сводится только к изменению концентрации свободных носителей заряда в нем, то, например, для материала на основе теллурида висмута даже при температуре 400 К невозможно получить значение безразмерной термоэлектрической эффективности, которое бы существенно превышало 1. С другой стороны, безразмерная термоэлектрическая эффективность термоэлектрических композитов на основе полупроводниковых материалов с металлическими нанокластерами либо наночастицами может существенно превышать 1, если они действительно являются композитами, т.е. материалами, каждая составляющая которых, войдя в состав композита, сохраняет присущие ей макроскопические значения кинетических коэффициентов и их температурные зависимости. В этом случае повышение добротности такого термоэлектрического композита сводится к оптимизации его состава и решении вопроса о технологических возможностях изготовления именно этого композита. Однако следует иметь в виду, что ответ на вопрос о практическом применении таких композитов, если они даже будут созданы и их параметры будут стабильно воспроизводимыми, зависит от возможности создания с их применением устройств, которые должны иметь не только высокие потребительские характеристики, но и соответствующую стабильность, надежность, долговечность и ресурсную устойчивость. Библ. 6, рис. 6.

Ключевые слова: термоэлектрический материал, легирование, безразмерная термоэлектрическая эффективность, порог перколяции, композит, наночастицы, оптимальный состав композита.

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