# ON THE EFFECTIVE KINETIC COEFFICIENTS OF THERMOELECTRIC NANOCOMPOSITES

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**Introduction**

Increasing the figure of merit is the main challenge in thermoelectric instrumentation technologies and in thermoelectric energy conversion. Apparently highly efficient thermoelectric elements based on plane-laminated nanostructures such as quantum well (QW) superlattices are not stable; and to date no laboratory in the world can repeat the best achieved results. The heat diffusion processes most likely reduce the lifetime of such systems. The other challenge is very high fabrication cost of the thermoelectric QW-superlattices. Against to QW and QD thermoelectrics bulk crystalline nanostructured composites are probably prospective thermoelectric materials [1-4].

Really there are at least two mechanisms that can increase the thermoelectric figure of merit

$$Z=\frac{\sigma}{\kappa}\alpha^2 \qquad (1)$$

in such nanocomposites ($\sigma$ – is the electric conductivity, $\alpha$ – coefficient of thermo-e.m.f., $\kappa$ – heat conductivity): (i) electrons tunneling through interfaces between nanoparticles in the composite; and (ii) additional phonons scattering on the interfaces between nanoparticles.

Influence of electrons tunneling on increase of the efficiency of thermoelectrics with flat vacuum gaps where the phonons heat conductivity is negligible, has been studied in [1]. In the theoretical paper [2] detail and all-round investigation of thermionic structure (difference between thermoelectric and thermionic processes disappears in nanostructures) with flat vacuum gaps was fulfilled; the possibility of significant increase of the thermoelectric figure of merit was found. A percolation structures below the threshold of course can be a perspective good thermoelectric with electrons tunneling; this idea was stated in [3]. Also usage of ball milling of a crystalline thermoelectric to nanopowder state and then hot pressing of the powder to bulk nanocomposites was suggested in [3].

In the recent paper [4] the value ZT = 1.4 at 100°C and ZT about 1.2 at room temperature (T – absolute temperature) was achieved in p-type nanocrystalline bismuth antimony telluride bulk alloy. These nanocrystalline bulk materials were made by hotpressing nanopowders ball-milled from crystalline ingots. Authors [4] explained increase of ZT as the result of low thermal conductivity caused by the increased phonon scattering by grain boundaries and defects.

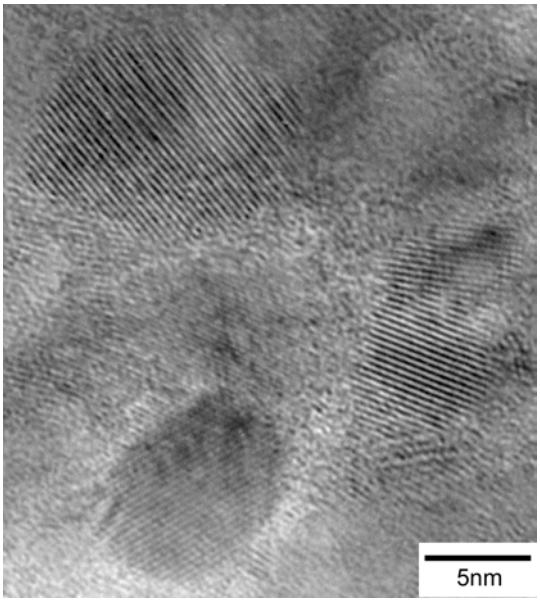
Our preparation of thermoelectric bulk nanocomposites, mechanisms of improvement of the figure of merit, problem of calculation of effective kinetic coefficient of composite medium including percolation nanostructures below the threshold of course and theoretical problems which should be solved are discussed in the present paper.

**Preparation of thermoelectric nanocomposites**

We used the following technological process for creation of bulk thermoelectric nanocomposites:

a. Fine crushing and clearing of initial material. The material should be a good traditional crystalline thermoelectric (such as solid solutions based on bismuth telluride). We used as the initial material the p-type of $Bi_{0,5}Sb_{1,5}Te_3$ polycrystalline solid solution.

A

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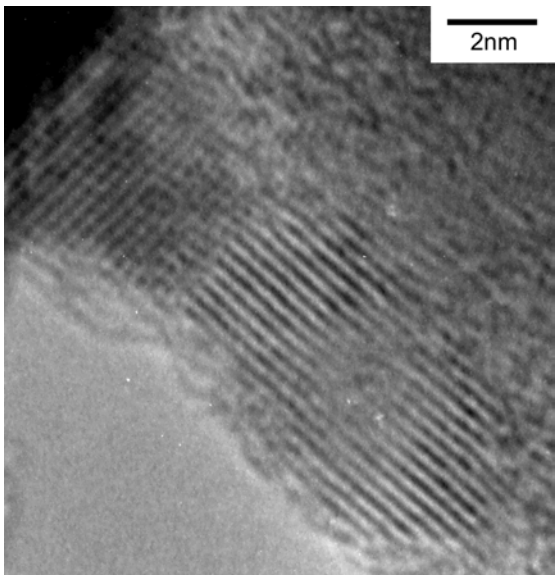


Fig.1. HRTEM images of p-$Bi_{0,5}Sb_{1,5}Te_3$ powder after 2 hours mechanic-activation processing

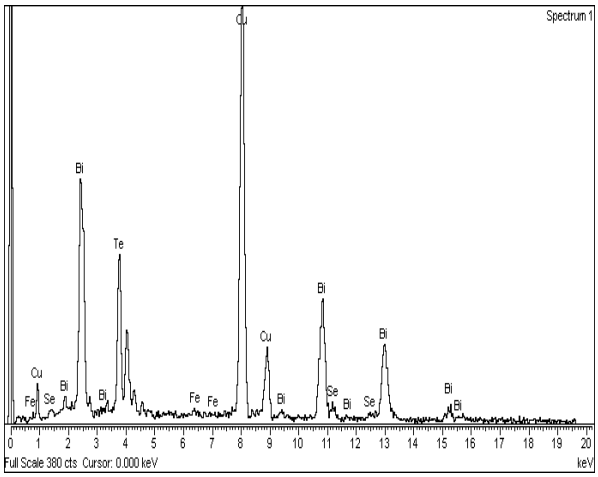


Fig.2. EDS spectrum of bismuth telluride powder after ball milling

b. Weigh and high energy ball milling. We used the so called mechanic-activation processing – the processes of fine crushing and homogenization was carried out in a high-power and a high-speed planetary mill which provides the effective crushing and hashing of powders at impact of working bodies with acceleration up to 20g. To exclude pollution all operations with nanostructured powder were carried out in the argon atmosphere. HRTEM images and EDS spectrum of the nanopowder are presented at Fig.1 and Fig.2 accordingly.

c. Extraction of the activated mixed powders from drums of mechanical activator in the argon atmosphere.

d. Assembly of high pressure containers.

e. Consolidation under pressure of the activated powder mixes. Sintering of the powder at high temperature and high pressure to form bulk nanocomposites. The powder mix was exposed to simultaneous influence of high pressures (P=1,5GPa) and high temperature (up to $350^0$C); see Fig.3.

We see from Fig.1, that the average size of nanoparticles after ball milling is 10 nm, the minimal size – 2 nm and the greatest (very seldom) – 40 nm. Surfaces of the nanoparticles are clean (Fig. 1B).

The lines of Cu in the Fig. 2 connect with the supporting grid; the trace of Fe was caused by the steel balls and the steel container.

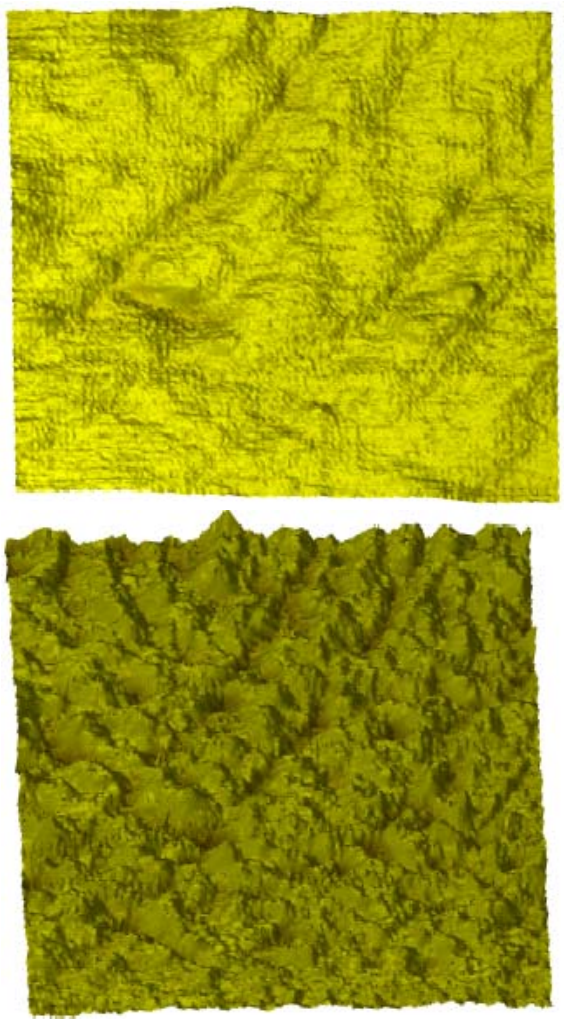

Fig.3. Surfaces of bulk nanocomposite («NanoScan» microscope). The area of scanning is (5.8 * 5.8) mcm$^2$. The upper image – the surface are polished, the lower – the same surface after pickling by feeble hydrochloric acid solution.

Traces of polishing are visible on a surface (Fig. 3.); pinholes and borders of grains are not looked through. The structure is homogeneous and isotropic. After pickling «structural elements» are visible; the sizes are (50 – 200) nm. These elements consist of finer formations.

The given method for fabrication of bulk nanostructured thermoelectric materials is cheap enough in comparison with preparation of quantum wells and quantum dots thermoelectric nanostructures. Moreover there exist ways to make such bulk structures to be stable and to have good mechanical characteristics.

**Effective kinetic coefficients**

To study the electron tunneling the correspondent coefficient of transparence of a potential barrier should be calculated as the function of the barrier's width and the work function of a material. If we have vacuum gap between nanoparticles the work function is equal to few eV, and at the room temperature the gap should be less then 5-10 nm for effective tunneling. However such gap is still large comparing with interatomic distance, therefore phonons can not move through the gap. Then the total heat conductivity ($\kappa = \kappa_e + \kappa_p$ – the sum of electrons and phonons heat conductivities) will reduce in comparison with the initial bulk material. So the figure of merit (1) will increase. If the gaps between nanoparticles filled by solid layers (semiconductor or oxide) the work function will be reduced up to few tenth of eV [5,6]. In this case phonons will take part in the heat conductivity but the contribution of phonon heat transport will be less than the phonon heat conductivity of the initial bulk material.

Additional phonons scattering on the interfaces between the nanoparticles will also reduce the phonon heat conductivity; the contribution of this mechanism hardly gives in exact calculation.

The structure of the nanocomposites can be simulated as a set of elementary identical cells – structural elements. The kinetic coefficients of each cell should be calculated taking into consideration the quantum tunneling and the additional phonon scattering. Then the effective kinetic coefficients (EKC) of thermoelectric nanocomposites of the bulk sample can be calculated.

Properties of macroscopic inhomogeneous medium in whole are described by EKC. According to definition EKC relate among themselves average on volume the thermodynamic flows and the generalized forces [7].

The thermoelectric effects is an example of the physical phenomena, when two thermodynamic flows ( $\mathbf{j}$ – density of an electric current and $\mathbf{q}$ – density of heat flow) are created simultaneously by two thermodynamic fields: $\mathbf{E}$ - electric field and $\nabla T$ – temperature gradient

$$\begin{cases} \mathbf{j} = \sigma\mathbf{E} + \sigma\alpha\left(-\nabla T\right), \\ \dfrac{\mathbf{q}}{T} = \sigma\alpha\mathbf{E} + \kappa\left(1+ZT\right)\left(-\nabla T\right) \end{cases} \qquad (2)$$

Then EKC can be determined as coefficients that connect the volume average of thermodynamic fields and flows.

$$\begin{cases} \langle \mathbf{j} \rangle = s^* \langle \mathbf{E} \rangle + s^* a^* \langle -\nabla T \rangle, \\ \dfrac{\langle \mathbf{q} \rangle}{T} = s^* a^* \langle \mathbf{E} \rangle + k^* (1+Z^*T) \langle -\nabla T \rangle \end{cases} \qquad (3)$$

$$Z^*T = \frac{s^* a^{*2}}{k^*} T$$

the asterisk means EKC of a composite.

As we see the figure of merit of composites determines by EKC, and there correct calculation is the key problem to investigate the efficiency of composites.

Calculation of EKC represents rather a challenge problem which in not solved till now in a general form [7,8]. The solution of the problem of determining of EKC strongly depends on a form of inhomogeneities. The task appears especially difficult if we deal with double-flow system as in thermoelectricity. In some cases the method [9] can be used that allows to reduce double-flow problem with cross composed to single-flow problem, for example to calculation of conductivity. So this method allows establishing exact conformity (isomorphism) between problems on finding EKC for system with the thermoelectric phenomena and the effective electric conductivity in a media without thermoelectric phenomena (see also [7]).

**EKC of percolation structures**

One of variants of macroscopic inhomogeneous medium is the percolation structure. Such structures are very interest for our porpoises because they give a basic possibility of significant increasing the figure of merit of nanocomposites. Really, let us create a composite material with the percolation structure below the threshold of course. It is known that the number of so called single disconnected bonds below the threshold of course increase with oncoming to the threshold of course $p_c$ as $N = \left(p_c - p\right)^{-a}$, where parameter $a$ has the order of one. It is known also that the role of single disconnected bonds can play tunnel junctions.

It is known also that effective electric conductivity $\sigma^*$ above and below of the threshold of course $p_c$ is a degree function on affinity to the threshold of course $\tau = \left(p - p_c\right)/p_c$ as a first approximation:

$$\frac{\sigma^*}{\sigma_1} \approx \tau^t, \quad \tau > 0, \quad \frac{\sigma^*}{\sigma_1} \approx \frac{\sigma_2}{\sigma_1}\left|\tau\right|^{-q}, \quad \tau < 0,$$

where $t$ and $q$ - critical indexes of conductivity higher and lower then $p_c$; in practically interesting, three-dimensional case, they gave values: $t = 2.0$, $q = 0.73$.

The behavior of effective thermo-e.m.f $\alpha^*$ at the cases $\kappa_1 \approx \kappa_2$ and $\kappa_1 \ll \kappa_2$ are qualitatively differs (the indexes "1" and "2" – are numbers of phases in a composite). In the case $\kappa_1 \approx \kappa_2$ and when the inequalities $\left(\dfrac{\sigma_2}{\sigma_1}\right)^{\frac{t}{t+q}} \ll \dfrac{\alpha_2\sigma_2}{\alpha_1\sigma_1} \ll 1$ take place, the coefficient $\alpha^*$ essentially changes in the critical area (Fig. 4):

(I) $a^* \gg a_1, p > p_c, t^t \ll a_2 s_2 / a_1 s_1, t \ll \Delta$

(II) $a^* = a_2 \dfrac{s_2}{s_1} t^{-t}, p > p_c, \Delta \ll t \ll \left(\dfrac{a_2}{a_1}\dfrac{s_2}{s_1}\right)^{\frac{1}{t}}$

(III) $a^* = a_2 \left(\dfrac{s_2}{s_1}\right)^{\frac{q}{t+q}} = a_2 \Delta^q, |t| < \Delta$

(IV) $a^* = a_2 |t|^q, p < p_c, |t| \ll \Delta$

where $\left(\sigma_2/\sigma_1\right)^{\frac{t}{t+q}} = \Delta$ – the area of spreading, $\tau = \left(p - p_c\right)/p_c$.

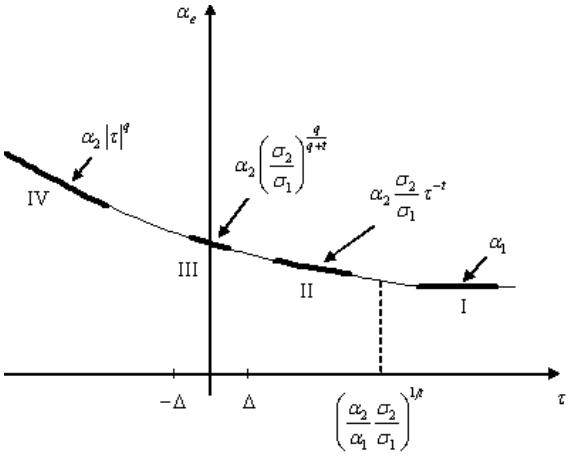


Fig 4. Concentration dependence of effective thermo-e.m.f. in the critical area if values of heat conductivity of phases are close $\kappa_1 \approx \kappa_2$.

Otherwise, when heat conductivities of phases considerably different ($\kappa_1 \ll \kappa_2$) changing of $\alpha^*$ from $\alpha_1$ up to $\alpha_2$ occurs in the critical area, Fig.5:

$$\begin{cases} \text{(I)}\ \alpha^* \approx \alpha_1, \tau \ll \left(\dfrac{\alpha_2}{\alpha_1}\right)^{\frac{1}{t+q}} \Delta,\ p > p_c \\ \text{(II)}\ \alpha^* \approx \alpha_2\left(\dfrac{\sigma_2}{\sigma_1}\right)\tau^{-(t+q)},\ \Delta \ll \tau \ll \left(\dfrac{\alpha_2}{\alpha_1}\right)^{\frac{1}{t+q}} \Delta,\ p > p_c \\ \text{(III)}\ \alpha^* = \dfrac{t}{t+q}\alpha_2,\ |\tau| < \Delta \\ \text{(IV)}\ \alpha_e = \alpha_2,\ |\tau| \gg \Delta, p < p_c \end{cases}$$

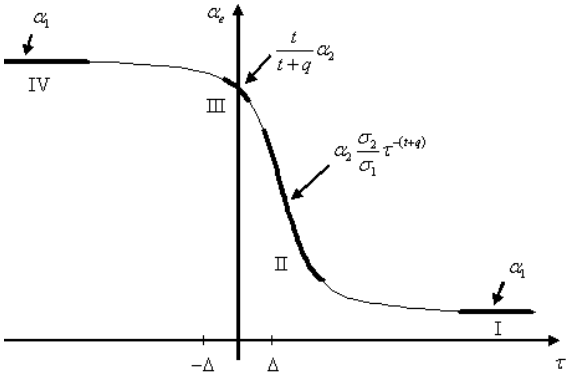


Fig.5. Concentration dependence of effective thermo-e.m.f. in the critical area if $\alpha_2 \ll \alpha_1$, $\alpha_2\sigma_2 \ll \alpha_1\sigma_1$ and $\sigma_2/\sigma_1 = \kappa_2/\kappa_1$.

Except of concentration dependences of usual EKC (electric and heat conductivities and thermo-e.m.f.) the significant interest represents the thermoelectric figure of merit of a composite. If the local figure of merit of phases $Z_1$ and $Z_2$ are small the effective one $Z^*(p)$ has usual properties. Really $Z^*(p)$ increase with increase of thermo-e.m.f. of phase/phases, it increase with decrease of heat conductivity of phase/phases, and $Z^*(p)$ increase with increase of $Z_1$ and $Z_2$. As it appeared such tendency is fair only for small values of local figure of merit [10]. It can be shown that for cases of large local figure of merit $Z^*(p)$ cannot be higher than some certain value, even at somehow large figure of merit of one of phases.

**Theoretical problems which should be solved**

A coordinate dependence of temperature $T = T(\mathbf{r})$ is neglected at standard calculation of thermoelectric EKC; this approximation gives an opportunity to solve the problem, and it is possible only if a temperature gradient is small enough. It is obvious that in various geometrical structures the criterion that $gradT$ is small can be completely various. Especially complicated is the question about smallness of $gradT$ near to the threshold of course. Here on the basic geometrical elements of percolation structures – single connected bonds and single disconnected bonds [7] considerable currents, voltage and temperatures differences are concentrated. Especially complicated is the question about a smallness of $gradT$ near the threshold of course. Accordingly, occurrence large $gradT$ here is possible [11]. Then the criterion of smallness of $gradT$ should include not only an average temperature gradient, but also local gradients.

On the other hand the necessity of account of temperature dependence of local kinetic coefficients always takes place in real semiconductors. If we can take into account such temperature dependence of

kinetic coefficients at fixed average *gradT* the value of local kinetic coefficients will be different in different points of a sample. Therefore it is impossible to use such essential concept as “homogeneity in a whole” to determination of EKC (in other words, the concept of correlation length can not be used). It means that we can not introduce correct definition of EKC in this case.

The other problem is the anisotropy of local kinetic coefficients. The method of isomorphism for a biphase thermoelectric medium cannot "consult" with the situation, when one (or both) phases have anisotropic transport properties.

The specific interest is represented with researches of EKC near the threshold of course for composites formed from particles with the different sizes. This problem is not investigated yet even for the simplest situation – "pure" conductivity. This problem is especially important because different sizes have nanoparticles in studies thermoelectric nanocomposites.

The close one is the problem about layers between crystallites in polycrystals when composites made from particles with an enclosure. In this case one of phases – the enclosure, occupies quite determined (instead of casual, as in usual models) position concerning another. For a biphase bidimentional case with determined, strictly periodic arrangement of particles with an enclosure such problem was studied in [12].

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