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Thermoelectric properties of composite materials based on lead telluride

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The study of composite materials based on mechanical mixtures of microdispersed PbTe and nanodispersed additional component ZnO, TiO_2, SiO_2 (50-70 nm) or microdispersed CdTe (32-50 μm) was performed. The purpose of this study is to reduce the thermal conductivity of the material. Measurements of specific electrical conductivity, Seebeck coefficient and thermal conductivity coefficient of the studied samples were measured. It is established that the achievement of low values of the thermal conductivity is complicated by the processes of agglomeration of the nanodispersed component at the temperatures of production and processing of composite samples, as well as the chemical interaction of the components of the additive and matrix.

Keywords: lead telluride, thermoelectric properties, composite materials.

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Introduction

Among the various alternative energy sources, thermoelectric generators are characterized by high reliability and longevity without the need for periodic maintenance [1-7]. This determines the prospects for their use, in particular, for military-technical needs and the needs of the space industry. The main disadvantage of thermoelectric converters is the relatively low efficiency compared to photovoltaic converters. One way to solve this problem is to modify the properties of already known materials used in thermoelectric converters.

One of the most well-known materials used to create medium-temperature (range 300-500° C) thermoelectric generators (TEG) is lead telluride. Improving the operational parameters of PbTe would significantly expand the scope of TEG based on it. The efficiency of the thermoelectric converter (η) functionally depends on the thermoelectric quality factor of the material Z:

$$\eta = \frac{T_h - T_c}{T_h} \cdot \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_c}{T_h}}$$

T_h and T_c are the temperatures of the hot and cold ends of the thermocouple. The value of Z is determined solely by the parameters of the material:

$$Z = \frac{\alpha^2 \sigma}{k}$$

Here σ is the specific electrical conductivity, α is the Seebeck coefficient, k is the thermal conductivity coefficient. The complexity of the problem of increasing the value of Z is that simultaneously with the increase in the specific conductivity of the material, for example by doping, due to increasing concentration of carriers, increases the thermal conductivity of the material and decreases the Seebeck coefficient. As a result, a significant improvement in thermoelectric quality factor is not observed. Given this, it may be promising to create materials in which the thermoelectric parameters can be controlled separately. One example is the use of composite materials obtained by pressing a mixture of powders of different materials [3]. The method of pressing the powder provides the formation of a significant number of intergranular boundaries in the sample, which should help reduce its thermal conductivity. Changing the pressure and size of the fractions makes it possible to effectively control the specific conductivity of the samples. A change in the Seebeck coefficient is possible if the grain size is commensurate with the electron free path length, but less than its broad wavelength [3]. Thus, it is possible to control the basic thermoelectric parameters when obtaining samples, and their numerical values may differ significantly from similar parameters for single crystals [8-9]. In addition, due to the use of powder for thermocouples, there is no need to grow single crystals, which is a complex technological procedure, and it is possible to carry out the synthesis of polycrystalline ingots.

According to [10], for thermoelements the optimal fractions are d = (1-100) μm. The use of nanodispersed powders for pressing leads to an increase in the specific electrical conductivity of the samples and a decrease in their thermal conductivity. When using nanodispersed materials, the dependence of properties on technological factors of production becomes even more significant [11-13] and achieving higher values of ZT in comparison with microdispersed powders is not always possible. In addition, in the case of hot pressing or annealing, the problem of agglomeration of nanoparticles is relevant [14]. Another factor that complicates the prediction of the properties of nanodispersed materials is the change in its fundamental properties with decreasing size [11]. Additional improvement of the properties of pressed samples, in particular reduction of its thermal conductivity, can be achieved by adding to the microdisperse powder base material nanodisperse powder of refractory oxides (ZnO, SiO_2, etc.) [15-18]. According to [3], the nature of the nanodisperse additive has virtually no effect on the effect of reducing thermal conductivity. Nanoparticles of metals can also be used, but in this case the expected effect is to increase the specific conductivity of the sample by creating a highly conductive metal contact between the grains [19]. According to [20], the creation of composites based on PbTe with dielectric filler can be one of the ways to solve the problem of high fragility of p-type materials, because when doped to hole concentrations $p \approx 10^{19}cm^{-3}$ impurity atoms significantly block the movement of dislocations.

In this work, in order to establish the possibility of reducing the thermal conductivity of pressed samples, the study of composite materials based on mechanical mixtures of microdispersed PbTe and nanodispersed additional component.

I. Methods of experimental research

The method of obtaining experimental samples and synthesis of PbTe is described in detail in [21, 22], and the method of measuring thermoelectric parameters in [21].

PbTe synthesis was performed in vacuum quartz ampoules [21]. The obtained ingots were ground, fractions (50-500) μm were selected, pressed under a pressure of 1.5 GPa and annealed at a temperature of 500°C. Exposure time under pressure was 15 minutes.

In the case of composite samples, the powder of the base material PbTe was mixed with nanodispersed powder of ZnO, TiO_2 or SiO_2. The particle size was 50-70 nm.

The materials of the additional component, according to [3], must have almost zero electrical conductivity (in the absence of shunting thermo-EMF generated by the grains of the base material), which is performed for the above materials. For most of the tested samples, the concentration of the additional nanocomponent was 1 wt.%.

The phase composition and structure of the synthesized ingots and samples were studied by X-diffraction methods. Surface morphology was studied using an optical and scanning electron microscope.

II. Research results and their analysis

The results of optical microscopy of the surface of the samples (Fig. 1) give reason to believe that the nanodisperse component prevents their compaction, at least to the level of compaction of the impurity-free material. The microhardness of composite materials is higher (HV = 365 MPa at 1 wt.% ZnO) compared to impurity-free PbTe (HV = 297 MPa), formed under the same technological conditions.

The surface morphology of PbTe-SiO_2 samples (Fig. 2) is similar to PbTe-ZnO. The hardness of the samples with 1.0 wt.% SiO2 after annealing is HV = 436 MPa.

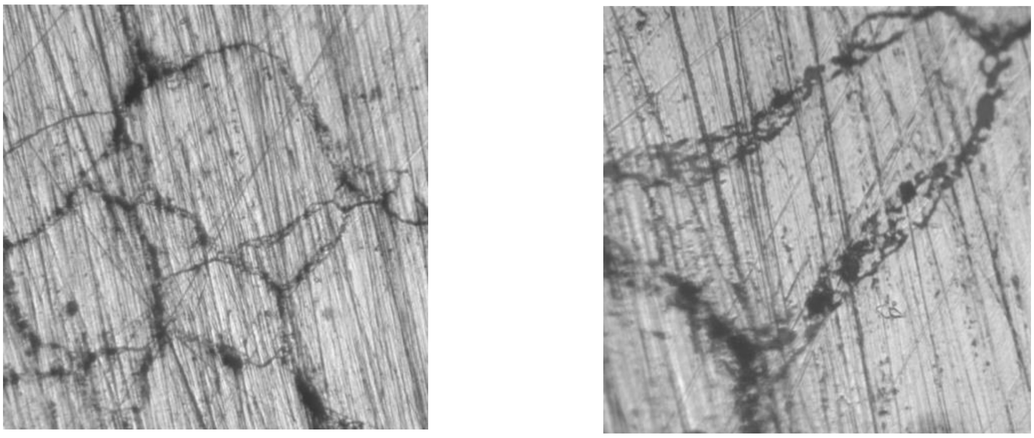
Based on X-ray diffraction studies (table) it was found that the addition of 1 wt.% ZnO increases the value of the unit cell parameter of the base material, and reflexes from the ZnO phase are not recorded, probably because the value of 1 wt. % is at the limit of sensitivity of the method. When the ZnO content is 3%, an additional phase of elemental lead is recorded in the samples. This result may indicate the chemical interaction of the base material and the nanosized additive. Diffusion of nanoadditive components, in particular, was noted in [23], in which Ti with TiO_2 penetrated into the matrix material.

Table 1

The results of X-diffraction analysis of extruded samples from mechanical mixtures of PbTe-ZnO powders.

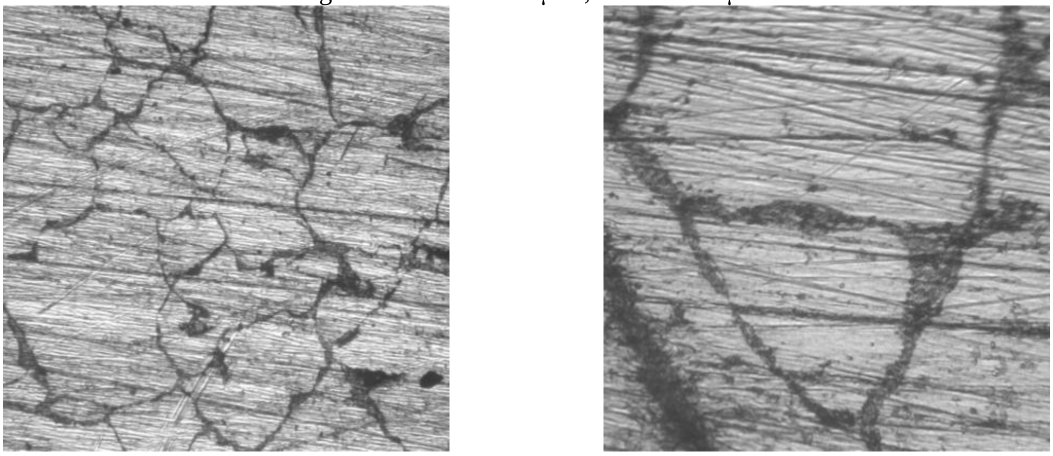
The composition of the sample	Phase composition	Lattice parameter a, Å
PbTe	PbTe	6.45892(19)
PbTe + 1 wt.% ZnO	PbTe	6.4599(2)
PbTe + 3 wt.% ZnO	PbTe, Pb (ST Cu) ~ 0.5 wt. %	6.4582(2)

Analysis of the thermoelectric properties of the studied samples shows that the addition of the nanodisperse component does not allow to achieve the desired result: a decrease in the thermal conductivity is not observed for any of the nanoadditives. And for some samples there is even some increase in the value of k. Moreover, it should be noted that the effect of different chemical composition of nanoadditives is almost the same. The main difference in the thermoelectric properties of PbTe-SiO_2, PbTe-ZnO and PbTe-TiO_2, which should be noted, is that the addition of silicon dioxide, unlike others, reduces the electrical conductivity of the samples (Fig. 3). However, the thermal conductivity of the samples, as for other materials with a nanodisperse



a) b)

Fig. 1. The surface structure of the composite sample PbTe + 1 wt. % ZnO. Image size: a - 450x450 μm^2, b- 110x110 μm^2.



a) b)

Fig. 2. The surface structure of the composite sample PbTe + 1 wt.% SiO_2. Image size: a - 450x450 μm^2, b - 110x110 μm^2.

component, within the error does not change compared to impurity-free PbTe. Measurement of the thermal conductivity coefficient was performed by the radial heat flux method (measurement error ± 20%). Of course, this is much higher than the error rate in the LFA method (± 5%). But it should be noted that the data obtained have always been reproducible for several samples (the graph shows data for only one). Thus, the relative changes in the thermal conductivity for different samples can be considered significant.

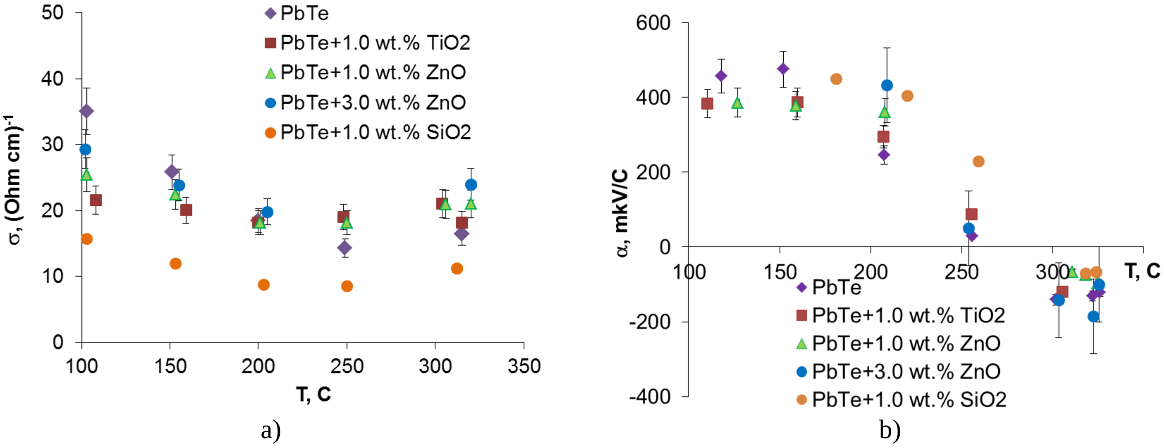
Analyzing the SEM image (Fig. 4) can explain the effect of increasing the thermal conductivity with the addition of nanodispersed oxides obtained. It has been found that the introduced nanosized zinc oxide particles combine to form agglomerates up to several micrometers in size, which may be one of the factors that prevents the recrystallization of the extruded samples.

In the studied samples, apparently, there are two ways of passing phonons between PbTe crystallites: partly through to some extent formed intergranular contacts between PbTe, and partly through ZnO (or TiO_2) grains.

It is likely that in the second case the thermal conductivity will be higher, because, firstly, nanodispersed powders agglomerated, thus increasing the area of the channel for the passage of phonons, and secondly, the thermal conductivity of ZnO is almost an order of magnitude higher than PbTe. Thus, summarizing the experimental data obtained for different materials, it can be argued that additional phases in medium or high temperature thermoelectric materials in addition to low specific conductivity should be characterized by low values of thermal conductivity and high melting point, which will partially compensate for their effects.

The observed regularities in the properties of the PbTe-SiO_2 system partially confirm the conclusions made. Due to the lower electroactivity of SiO_2 nanoparticles, it is possible to reduce the effect of the additional phase on the electrical properties of the matrix, which is manifested in a decrease in the specific conductivity with the addition of silicon oxide.

One of the possible options for achieving a reduction in the thermal conductivity of composite samples may be to increase the mass fraction of the nanodispersed additive. According to [15], for Sb_2Te_3, the optimal values of the mass fraction of nanoadditives are 50-60%. However, for our materials, the maximum values of the impurity content did not exceed 5%. At higher concentrations, the samples were characterized by high fragility. In the case of hot pressing, this problem is solved, however, significantly increases the agglomeration of nanoadditives.



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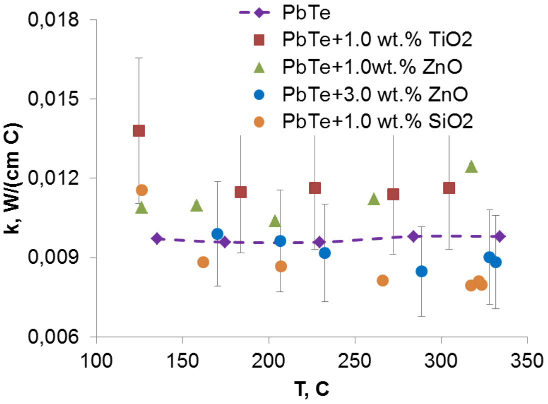
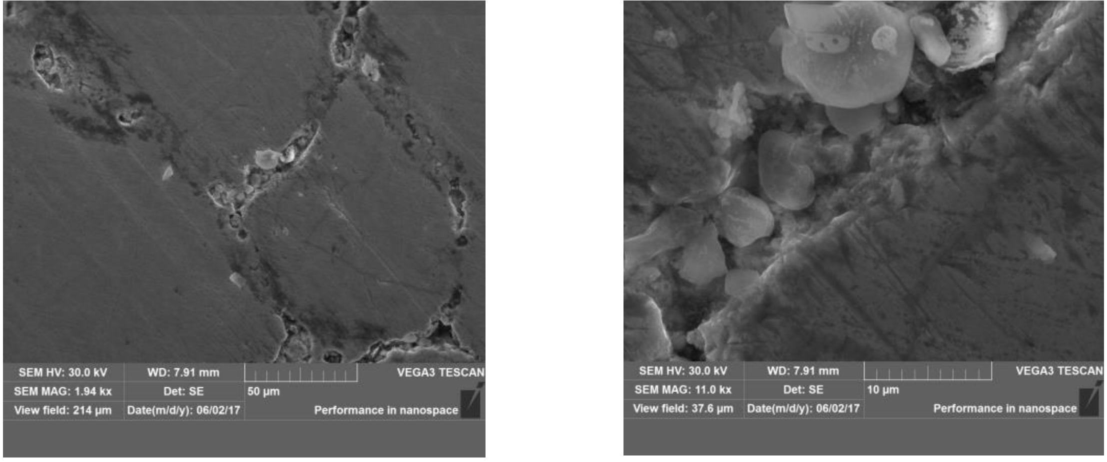


c)

Fig. 3. Temperature dependence of specific electrical conductivity σ (a), Seebeck coefficient α (b) and thermal conductivity coefficient k (c) of PbTe samples with impurities of nanodispersed powders.



a) b)

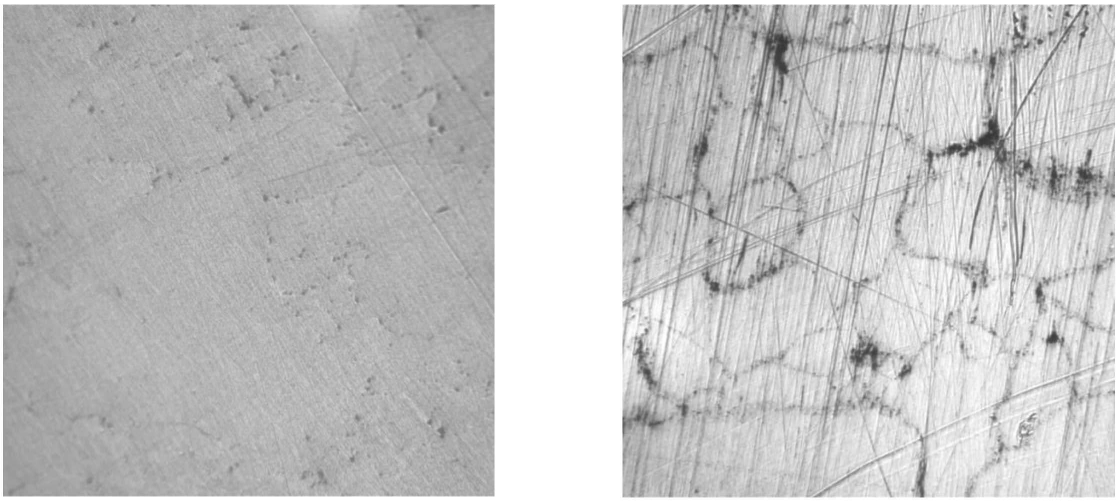
Fig. 4. SEM image of annealed composite samples of PbTe + 1 wt.% ZnO.

One way to ensure the absence of conditions for agglomeration of nanoparticles may be to use a finer powder of the base material, which will provide a better distribution of the nanomaterial over the volume of the sample. However, the effectiveness of the use of nanodisperse additives can be questioned. This is due to the fact that the increase in dispersion will already lead to an increase in the area of intergranular boundaries, which determines the efficiency of phonon scattering. And the type of materials that create these surfaces, as established in this paper and noted in [3], is not fundamentally important.

Another way is to create composite materials in which the additional component will be not nano- but microdisperse. PbTe / CdTe samples were studied as one of the possible options. PbTe / CdTe samples were studied as one of the possible options.

Cadmium telluride, like lead telluride, was obtained by fusion in vacuum quartz ampoules. In contrast to PbTe, ampoules for CdTe synthesis were graphitized. The obtained CdTe ingots were ground and fractions (32-50) μm were selected to create composite materials. The optimum pressing pressure for these compositions is 1.5 GPa, the holding time under pressure is 15 minutes, the size of the fractions of the base material is (0.05-0.5) mm. The obtained samples were annealed at a temperature of 500°C.

The surface structure of compressed PbTe-CdTe samples was less porous than in the case of composites with nanodispersed oxides (Fig. 5). The hardness is



a) b)

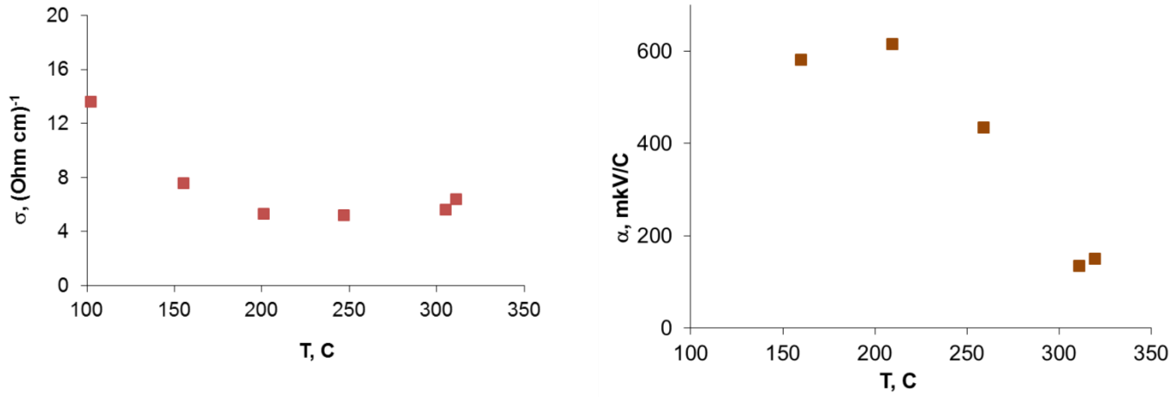
Fig. 5. Structure of the pressed and annealed surface at 500 C. (a) PbTe; (b) - composite sample PbTe-CdTe (1 wt.% CdTe) (photo size - 460x460 μm^2).

H_V = 312 MPa and does not differ significantly from impurity-free PbTe – H_V = 297 MPa (compression pressure 1.5 GPa, annealing temperature 500°C), which differs significantly from composites with nanodisperse additives.

The unit cell parameter of the base material PbTe in the composition of such composites decreased. Thus used to create composites impurity PbTe was characterized by a value of 6.4583 (2) Å, while for the compressed composite sample – a = 6.4566 (2) Å. This effect may be due to the influence of technological factors of the sample, and the chemical interaction of base and additional materials.

It is known [24] that the effect of Cd on the electrical properties of PbTe is weak. Therefore, we can assume that even with the diffusion of cadmium into lead telluride, the modification of its electrical properties (specific conductivity, electronic component of thermal conductivity and Seebeck coefficient) will be minimal.

As a result, the Seebeck coefficient practically does not change, and the specific conductivity of the samples, in contrast to ZnO or TiO_2, decreases with the addition of



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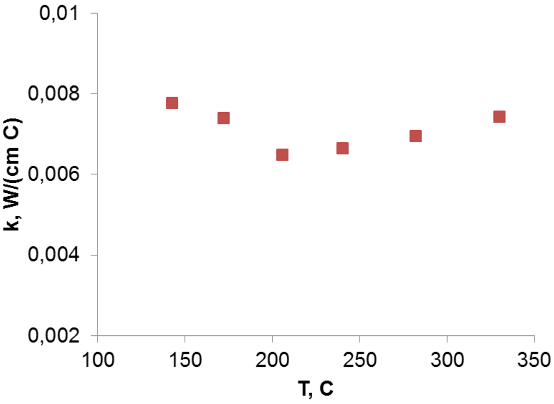

c)

Fig. 6. Temperature dependences of specific electrical conductivity (a), Seebeck coefficient (b) and thermal conductivity coefficient (c) for composite samples of PbTe-CdTe with the content of microdispersed component CdTe 1 wt.%.

CdTe.

In logarithmic coordinates, the dependence σ (T) is satisfactorily approximated by a line, according to the equation lg (σ) = A-2.5 lg (T). The coefficient of 2.5 indicates the dominance of the mechanism of carrier scattering on acoustic phonons. That is, the presence of an impurity does not change the dominant scattering mechanism (compared to impurity-free PbTe). In contrast to the studied PbTe-ZnO (TiO_2) nanocomposites, for PbTe-CdTe samples, a slight decrease in the thermal conductivity coefficient was recorded (Fig. 6). That is, on the one hand, the electrical conductivity of samples and their thermal conductivity decreases due to the addition of microdispersed CdTe, and on the other hand - scattering in composite materials is determined only by the interaction of current carriers with acoustic phonons. In view of the above, we can assume that the reduction of σ is not due to additional intergranular boundaries, but to the reduction of the "effective cross section of the sample" (total area of intergranular contacts in the plane perpendicular to the current direction), which is current transfer. In the case of phonons, it is likely that additional boundaries are the main factor in reducing the intensity of their scattering.

Conclusions

Creation of composite materials based on PbTe with nanodisperse additives, in particular, ZnO, TiO_2. SiO_2, in order to achieve low values of thermal conductivity, is associated with a complex of difficulties due to high temperatures of production and processing of such materials.

In particular, it was found that the addition of the above oxides, in particular zinc oxide, changes the value of the unit cell parameter of the base material, which may indicate the chemical interaction of components and, in particular, diffusion of nanoadditive components into the grains of base material.

It is also shown that the practical use of composite materials based on mixtures of PbTe base material and nanodisperse additives of refractory materials ZnO, TiO_2, SiO_2 is limited by agglomeration of nanodispersed component at operating temperatures, which leads to increased thermal conductivity and, accordingly, reduced thermoelectric quality.

A possible way to overcome these difficulties may be, firstly, the use of not nano- but microdispersed additional component, and secondly, additives must be selected so that the chemical elements that are part of it, do not significantly affect the electrophysical properties of the matrix, or this impact was minimized. One of the materials that meets these requirements may be microdispersed CdTe.

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Термоелектричні властивості композитних матеріалів на основі телуриду свинцю

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З метою зменшення теплопровідності термоелектричних матеріалів на основі пресованого PbTe, проведено дослідження композитних матеріалів на основі механічних сумішей мікродисперсного PbTe та нанодисперсного додаткового компоненту ZnO, TiO_2, SiO_2 (50-70 нм) чи мікродисперсного CdTe (32-50 мкм). Проведено вимірювання питомої електропровідності, коефіцієнта термо-ЕРС та коефіцієнта теплопровідності досліджуваних зразків. Встановлено, що досягнення низьких значень коефіцієнта теплопровідності ускладнюється процесами агломерації нанодисперсного компоненту при температурах отримання та обробки композитних зразків, а також хімічною взаємодією компонентів добавки і матриці.

Ключові слова: плюмбум телурид, термоелектричні властивості, композитні матеріали.