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Composite Thermoelectric Materials Based on Lead Telluride and Cadmium Telluride

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The results of the researching of thermoelectric properties of samples, which are obtained by compressing mechanical mixtures of microdisperse powders PdTe and CdTe, are presented. It was found that the using of cadmium for telluride as an additional component to the lead telluride contributes to a decrease in the coefficient of thermal conductivity of the materials of the studied system, which can be promising for the creation of thermoelectric converters based on them.

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Introduction

Lead Teluride is a semiconductor material, which is used to create on its basis thermocouples working in the temperature range 300 - 500 C [1]. The main disadvantage of using PbTe is the relatively low coefficient of efficiency of devices based on it (< 10 %). Therefore, finding ways to increase this value is an urgent task.

The efficiency of the material is determined by the parameter Z - thermionic quality factor:

$$Z = \frac{S^2 s}{k}$$

The complexity of the problem of increasing the value of Z lies in, because while increasing the specific electrical conductivity of the material, for example by doping, due to increased carrier concentration, the thermal conductivity of the material increases and the coefficient of thermo-EMF decreases. As a result, the significant improvement in thermoelectric quality isn’t observed.

Taking into account the above, it is relevant to study the thermoelectric samples, which are obtained by powder pressing method, which ensures the formation of a large area of intergranular boundaries. In addition to scattering of phonons, such limits can carry out the filtering of current carriers by passing electrons (holes) only with "high" energies, which should increase the coefficient of thermo-EMF of the material. It should be noted that an important factor is the size of the powder fraction for the pressed samples, which are used for compacting. The use of an additional nano-disperse component of another material can provide the creation of an additional scattering surface for phonons, and, in the case of the use of metallic nanoparticles, to create qualitative conductive contacts for the electrons between the grains [2-6].

In [7], the composite specimens, which are based on the mechanical mixtures of microdispersed PbTe were studied as a base material and nano-dispersed additives ZnO, TiO2. However, the predicted decrease in thermal conductivity was not observed. In view of this, the mechanical mixtures of microdisperses PbTe i CdTe were investigated in this paper. The main factor in choosing cadmium telluride is that its thermal conductivity is much smaller in comparison with zinc or titanium oxides.

I. Experiment methodology

Synthesis of PbTe was carried out in vacuumed quartz ampoules [8]. The resulting ingots were crushed, pressed under pressure (1.0 - 2.0) GPa and annealed at temperatures (200 - 500)$^\circ$C. In the case of mechanical mixtures, the base material powder was mixed with the microdisperse powder CdTe, the particle size was reached (32 - 50) mkm. The phase composition and structure of the synthesized ingots and samples were investigated by X-diffraction methods on the automatic diffractometer STOE STADI P. Surface morphology was studied using an optical microscope NEXUS 400A. Hall measurements were carried out in constant magnetic and electric fields using a four-zone method. The value of the coefficient of thermo-EMF was calculated by measuring the voltage at the ends of the sample when the temperature gradient was created ≈5°C. The specific electrical conductivity σ was determined by measuring the voltage drop on the sample at the passage of alternating current. The coefficient of thermal conductivity k was determined by the method of radial heat flux

Synthesis of cadmium telluride to produce the mechanical mixtures was carried out in the sealed quartz ampoules. Additionally, unlike the conditions for the synthesis of compounds IV-VI, the ampoules were grafitized by acetone pyrolysis. The temperature mode of synthesis consisted of several stages of heating and aging, and the direct synthesis was carried out at a temperature of 1120^0C. The resulting ingots were chopped in a ball mill.

II. Results of the research and their discussion

The chemical analysis of CdTe ingots showed a low content of uncontrolled impurities (Table 1.). The composition and technological parameters of preparation PbTe-CdTe sample are given in Table 2. The optimum pressure of compression for these compositions is 1.5 GPa, the shutter speed under pressure is 15 minutes, the size of the fraction of the base material - (0.05 - 0.5) mm. All samples were annealed at 500 C for 15 minutes. Unlike the mechanical mixtures powder, which was studied in [7], for these samples, an additional component was not used for pressure gauges, and a micrometer size in order to increase the volume of the additional phase, and not the number of additional limits, as in the previous cases.

Table 1

The chemical composition of the synthesized ingots of CdTe is determined by the method SIMS

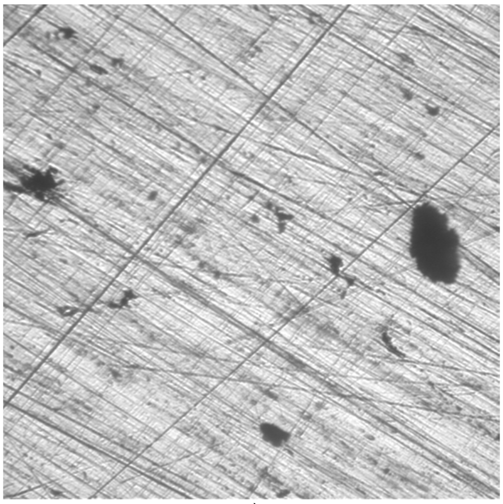
Impurity	Relative content, 10^4 mas. %
B	0.66
Na	0.62
Mg	0.03
Al	0.18
S	0.25
Cl	0.11
K	0.23
Ca	0.26
Fe	0.31
Co	0.13
Ni	2.27
Ag	1.31
Sb	0.15
I	2.68
Ba	0.15
Ta	0.01
W	0.23
Pb	9.23
Bi	0.44

Table 2

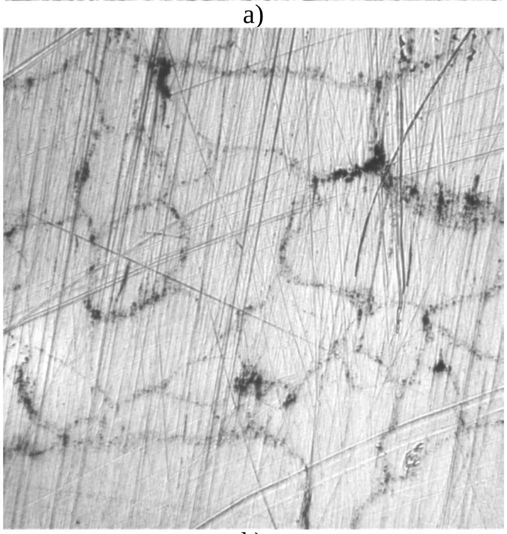
Composition materials of PbTe-CdTe

Number of sample	Composition
1a	PbTe
1b	PbTe
2a	PbTe+1mas.% CdTe (32-50) mkm
2b	PbTe +1mas.% CdTe (32-50) mkm
2c	PbTe +1mas.% CdTe (32-50) mkm

The parameter of elemental cell of a homogeneous PbTe is 6.4583(2) A, but for the pressed and annealed composite sample – 6.4566(2). Such an effect may be due to the influence of technological factors (pressing, annealing) [8], and the chemical interaction between the base and additional materials.



a)



b)

Fig. 1. Surface structure of the pressed at 1.5 GPa and annealed at a temperature of 500^0C for a sample PbTe (a) and composite sample PbTe-CdTe (1 mas. % CdTe) (b) (the size of the photo is 460x460 mkm^2).

Surface structure of pressed and annealed samples of PbTe-CdT at 500°C, it turned out to be more porous than in the case of homeless PbTe, but less porous than those investigated in [7] composites. The hardness is HV = 312 MPa, which, unlike those studied in [7] composites, which does not differ significantly from the homogeneous PbTe – HV = 297 MPa (pressure of pressing 1,5 GPa, annealing temperature 500^0C).

Based on the Hall effect study, it was found that when added CdTe (1 mas. % CdTe) the temperature dependence of the carrier concentration is decreasing (Fig. 2), however, the change in the value of nH in the measured temperature range is not significant and does not exceed the measurement error.

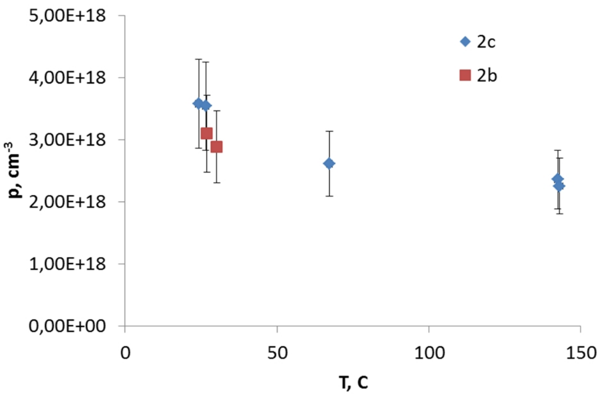


Fig. 2. Temperature dependences of carrier concentration in composite materials PbTe-CdTe.

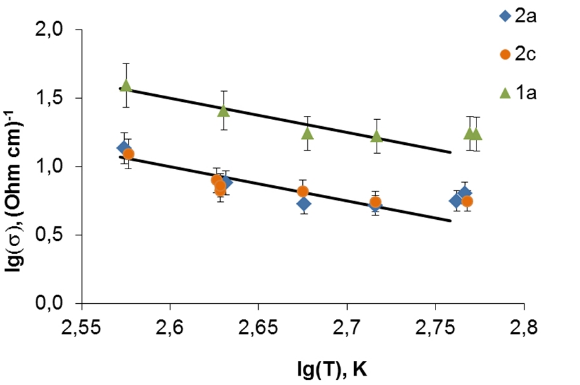
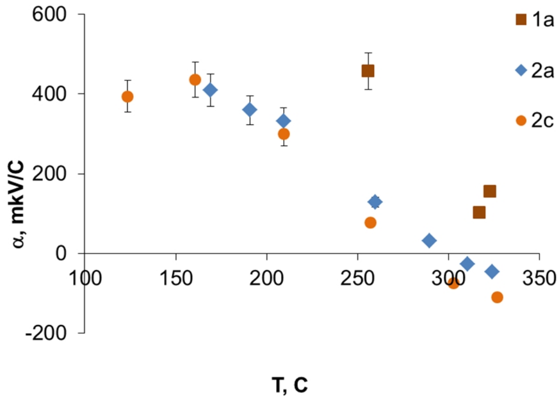
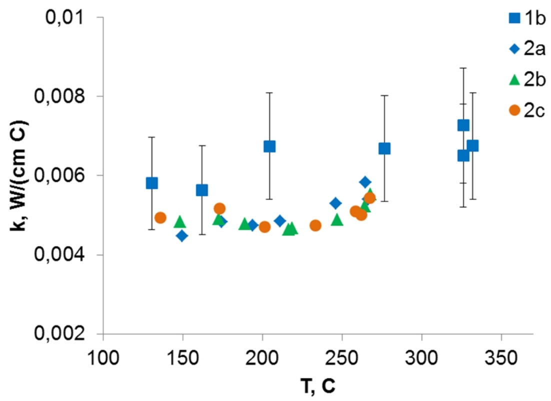


Fig. 3. Dependence of the logarithm of the specific conductivity from the logarithm of the temperature for the annealed samples of PbTe and the composite samples PbTe-CdTe (1 mas. % CdTe). Points - experiment, curves - calculation according to the equation lg(σ) = A-2.5 lg(T).

It seems logical to reduce the electrical conductivity of the samples and the invariability of the thermo-EMF coefficient coefficient when adding CdTe: the additional component reduces the total area of the conducting channels, it practically does not pass the current, and the kinetic parameters of the carriers passing between the cores of the base material have no effect on CdTe. In logarithmic coordinates, the dependence σ (T) is satisfactorily approximated by a straight line, according to the equation lg (σ) = A-2.5 lg (T). The coefficient 2.5 clearly indicates the dominance of the mechanism of scattering of carriers on acoustic phonons. The deviation from the linear of dependence for the points, which were obtained at the maximum temperature, most likely, indicates the beginning of the region of its own conductivity. It is important to note that the presence of an impurity does not change the dominant scattering mechanism. In particular, there is no appreciable effect of grain boundaries in the investigated materials.



a)



b)

Fig. 4. Temperature dependences of coefficients of thermo-EMF (a) and thermal conductivity (b) for composite specimens PbTe-CdTe with the contents of the microdisperse component CdTe 1 mas. %.

In contrast to the nanocomposites PbTe- ZnO (TiO_2), studied in [7], for samples PbTe-CdTe, a certain decrease of the coefficient of thermal conductivity is recorded (Fig. 4). That is, on the one hand, the electrical conductivity of the samples and their thermal conductivity decrease as a result of the addition of the microdisperse CdTe, and on the other - scattering in the composite materials is determined only by the interaction of current carriers with acoustic phonons. In view of the above, we can assume that responsibility for reducing of the quantities σ is not additional grain of boundaries, since the slope of the curves σ (T) in logarithmic coordinates for homogeneous and composite samples does not change, but a decrease in the effective cross section of the sample, which is carried out by the current transfer. In the case of phonons, it is most likely that the additional of boundaries are the main factor in reducing the intensity of their dissipation. Comparing the obtained data with the results, which are presented [7], it can also be argued that it is equally important that the thermal conductivity of the additional component is no less important. It is the fact that the thermal conductivity ZnO or TiO_2 is much higher than the thermal conductivity of the base material; in [7], it was not achieved to reduce the value of k.

Conclusions

Creation of composite materials, which are based on the mechanical blends of base thermoelectric material PbTe and micro or nano-dispersed additives of other materials is the promising direction of optimization of the thermoelectric properties. In this case, the thermal conductivity of the material is an additional component, which is no less important factor than the total area of interspecies grain of boundaries, which is created by the addition of a nanodisperse component.

Microdispersion component CdTe is the promising material for creating composites PbTe-CdTe with a lower coefficient of thermal conductivity.

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Композитні термоелектричні матеріали на основі телуридів свинцю та кадмію

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Представлено результати дослідження термоелектричних властивостей зразків отриманих шляхом пресування механічних сумішей мікродисперсних порошків PbTe та CdTe. Встановлено, що використання кадмій телуриду як додаткового компоненту до плюмбум телуриду сприяє зменшенню коефіцієнта теплопровідності матеріалів досліджуваної системи, які можуть бути перспективними для створення на їх основі термоелектричних перетворювачів.

Ключові слова: термоелектрика, телурид свинцю, композитні матеріали.