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COMPOSITE THERMOELECTRIC MATERIALS BASED ON LEAD AND CADMIUM TELLURIDES

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Lead Telluride is a semiconductor material, which is used to create on its basis thermocouples working in the temperature range 300-500 °C. 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.

Obtaining thermoelectric samples by powder pressing method, which ensures the formation of a large area of grain boundaries, is promising. In addition to scattering of phonons, such boundaries can filter current carriers that pass electrons (holes) with "high" energies only, which should increase the coefficient of thermo-EMF of the material. It should be noted that for the pressed samples an important factor is the size of the powder fractions, which are used for compaction. The use of an additional nanodispersed 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, create high quality conductive contacts for the electrons between the grains.

In present paper, mechanical mixtures of microdispersed PbTe and CdTe have been investigated. The main factor in the choice of cadmium telluride is its rather low thermal conductivity.

Synthesis of PbTe was carried out in vacuumed quartz ampoules [1]. The resulting ingots were crushed, pressed under pressure (1.0-2.0) GPa and annealed at temperatures (200-500) °C. In the case of mechanical mixtures, the base material powder was mixed with the microdispersed powder of CdTe, particle size of which was (32-50) μm. The phase composition and structure of the synthesized ingots and samples were investigated by X-ray 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 ≈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 [1].

Synthesis of cadmium telluride for obtaining the mechanical mixtures was carried out in the sealed quartz ampoules. Additionally, in contradistinction to the conditions of the synthesis of IV-VI compounds, the ampoules were graphitized by

acetone pyrolysis. The temperature mode of synthesis consisted of several stages of heating and exposing, and the direct synthesis was carried out at a temperature of 1120 °C. The resulting ingots were granulated in a ball mill.

The chemical analysis of CdTe ingots has shown a low content of uncontrolled impurities. Composition and technological parameters of preparation of PbTe-CdTe samples are given in Table. Optimum compression pressure for these compositions is 1.5 GPa, exposure time under pressure is 15 minutes, the size of the fraction of the base material is (0.05-0.5) mm. All samples were annealed at 500 °C for 15 minutes. Unlike the mechanical powder mixtures studied in [2], for these samples the used additional component was not nanometer but micrometer size in order to increase the volume of the additional phase, and not the number of additional boundaries, as in the previous cases.

Table. Composition of PbTe-CdTe composite materials (ingot XXXIX)

Number of sample	Composition
1a	PbTe
1b	PbTe
2a	PbTe + 1 mass % CdTe (32-50) μm
2b	PbTe +1 mass % CdTe (32-50) μm
2c	PbTe +1 mass % CdTe (32-50) μm

The lattice parameter of homogeneous PbTe is 6.4583(2) Å, but for the pressed and annealed composite sample – 6.4566(2) Å. Such an effect may be due to the influence of technological factors (pressing, annealing) [1] and the chemical interaction between the base and additional materials.
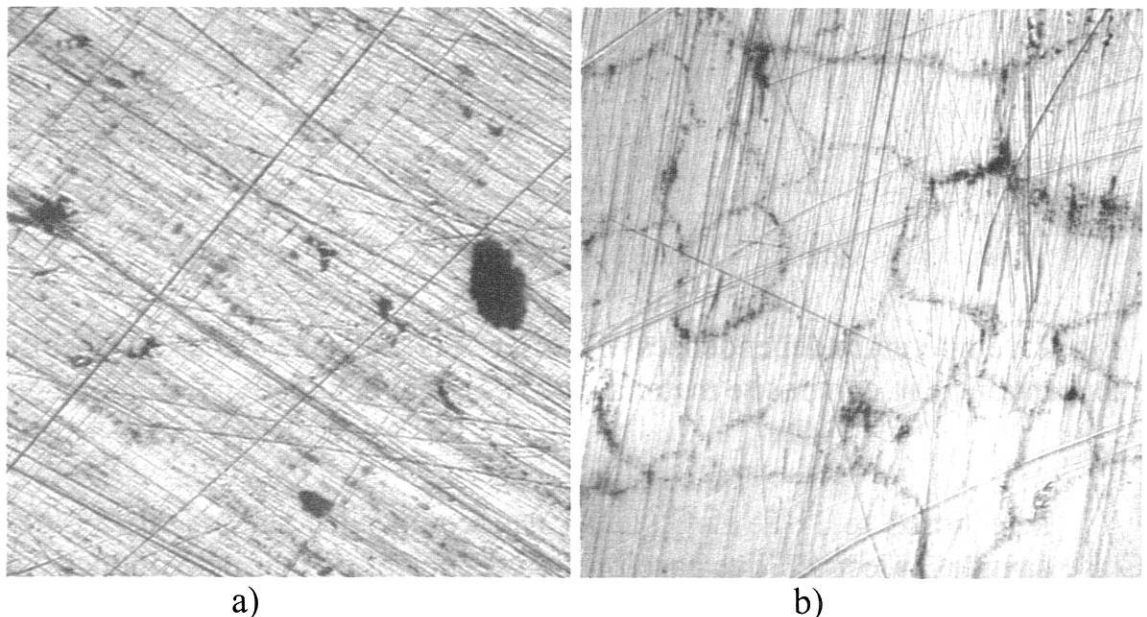

a)   b)

Fig. 1. Surface structure of pressed at 1.5 GPa and annealed at 500 °C sample of pure PbTe (a) and composite sample PbTe-CdTe (b) (1 mass % CdTe) (the size of the photo is 460x460 μm^2).

Surface structure of pressed and annealed at 500 °C PbTe-CdTe samples was more porous than in the case of pure PbTe, but less porous than in the case of composites investigated in [2]. The hardness is $H_V = 312$ MPa, which does not differ significantly from the pure PbTe – $H_V = 297$ MPa (pressing pressure was 1.5GPa, annealing temperature was 500 °C) unlike composites studied in [2].

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

Decrease in electrical conductivity of the samples and the invariability of the thermo-EMF coefficient when adding CdTe seems to be logical: the additional component reduces the total area of the conducting channels, in turn it practically does not conduct the current, and CdTe has no effect on the kinetic parameters of the carriers passing between the grains of the base material. In logarithmic scale, the dependence $\sigma(T)$ is satisfactorily approximated by a straight line according to the equation $\lg(\sigma) = A - 2.5 \lg(T)$. The coefficient 2.5 clearly indicates the dominance of the mechanism of scattering of carriers on acoustic phonons. The deviation from the linear dependence for the points 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 impurity does not change the dominant scattering mechanism. In particular, there is no appreciable effect of grain boundaries in the investigated materials.
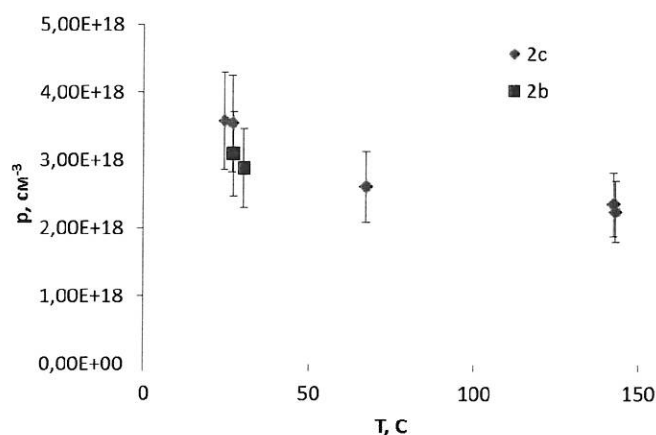

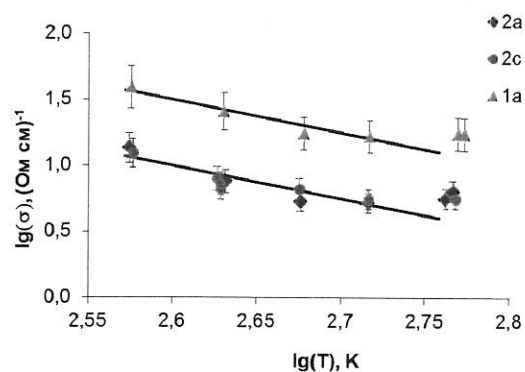**Fig. 2.** Temperature dependences of carrier concentration in composite materials PbTe-CdTe

Fig. 3. Dependence of specific electrical conductivity on temperature for PbTe and PbTe (1 mass % CdTe)

In contrast to PbTe-ZnO (TiO$_2$) nanocomposites studied in [2], for PbTe-CdTe samples, 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 microdispersed CdTe, and on the other hand, scattering in the composite materials is determined only by the interaction of current carriers with acoustic phonons. Given the above, we can assume that responsibility for reducing σ is not due to additional

grain boundaries, but decrease in the effective cross section of the sample, by which the current transfer is carried out, since the slope of the curve σ(T) in logarithmic scale for pure and composite samples is not changed. In the case of phonons, it is most likely that the additional boundaries are the main factor in reducing the intensity of their scattering. Comparing the obtained data with the results in [2], it can be said that no less important factor is thermal conductivity of the additional component. Precisely due to the fact that the thermal conductivity of ZnO or TiO_2 is much higher than the thermal conductivity of the base material, in [2], reducing the value of k was not achieved.
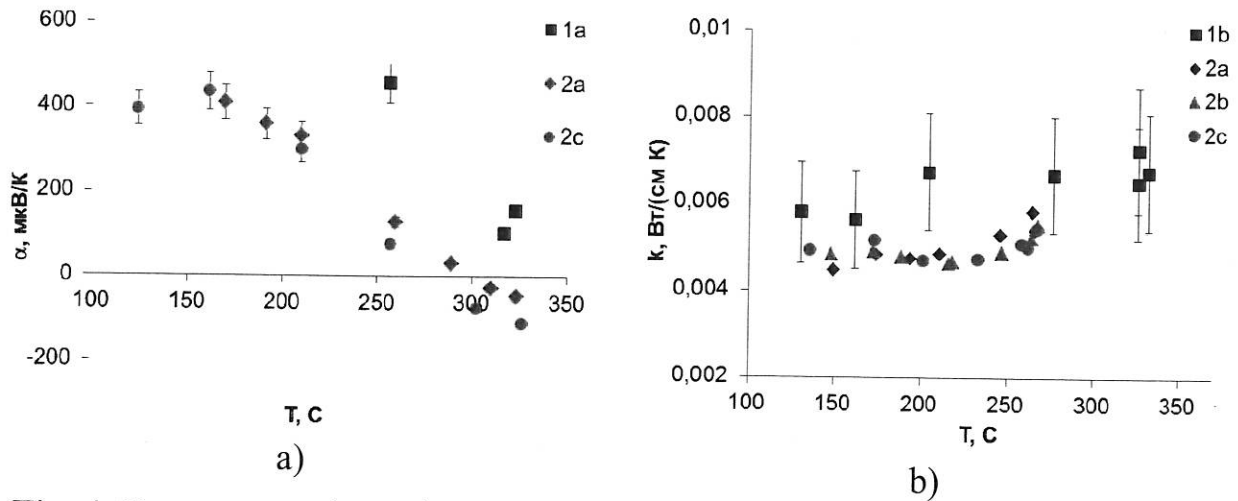
Fig. 4. Temperature dependences of coefficients of thermo-EMF (a) and thermal conductivity (b) for PbTe-CdTe composite samples with 1 mass % content of the microdispersed component of CdTe.

[1] І.В. Горічок, І.М. Ліщинський, С.І. Мудрий, О.С. Оберемок, Т.О. Семко, І.М. Хацевич, О.М. Матківський, Г.Д. Матеїк, Р.О. Дзумедзей. Технологічні аспекти отримання термоелектричного PbTe // SEMST. – 2017. – Т.14, № 3. – сс. 53-64.

[2] I.V. Horichok, M.O. Galushchak, O.M. Matkivskyj, I.P. Yaremij, R.Ya. Yavorskyj, V.S. Blahodyr, O.I. Varunkiv, T.O. Parashchuk. Thermoelectric Properties of Nanostructured Materials Based on Lead Telluride // JNEP. – 2017. – V.9, N.5. – pp. 05022-1 - 05022-7.