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Thermoelectric Composites on the Base of PbTe with Nanoiclusions of Colloidal Silver

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Formation of thermocouples by pressing powder of thermoelectric material with micro- and nano- size range creates large internal borders for additional phonon scattering. However, it need not only reduce the thermal conductivity, but also increase the Seebeck coefficient to improve the thermoelectric properties of material. For this case, around thermoelectric grain PbTe of the size of (0.5-1.0) micrometers prompted to create nano-channels for the stream of an electric current. In this paper was development technology of the conductive nano-channels on the base of colloidal Silver. It was finding that the introduction of Ag nanoparticles (size ~ 50 nm), not only reduces the thermal conductivity, but also increases the Seebeck coefficient after additional throttling of electrons on the barriers of Silver nanoparticles. Thermal conductivity of (0.06-0.2) W/(m·K) has been achieved in the case of the scattering of medium-wave phonons (MWP). The absolute value of Seebeck coefficient in these conditions increases up to 340 μV/K.

Keywords: Thermoelectric materials, Lattice thermal conductivity, Nanoparticles, PbTe, Silver.

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1. INTRODUCTION

The efficiency of thermoelectric materials is determined by thermoelectric figure of merit (Z):

$$Z = (S^2\sigma)/\chi, \tag{1}$$

where S is the Seebeck coefficient, σ is specific electrical conductivity, and χ is a coefficient of thermal conductivity.

Accordingly, such materials must be both good conductors of electricity as "electronic metal" (meaning high σ), and poor conductors of heat, as the "phonon glass" (meaning low χ) [1]. For such materials should be regarded as physical and technological limitations. A necessary condition for the figure of merit improvement of the thermoelectric materials is the modification of its properties that will change the phonon and electronic subsystems to lower the thermal conductivity (χ) and to increase the Seebeck coefficient (S) and the electrical conductivity (σ).

Recent studies propose two possible ways to further improve the efficiency of thermoelectric materials: usage of materials with low dimensionality (2D-, 1D- and 0D-structures) or creation of new composite materials through modification the size of grain in bulk materials [2].

The quantum-size effects are used to increase the Seebeck coefficient (S) and for the enhancement changes of specific electrical conductivity (σ) in the first case [3, 4]. In the second case, the creation the many limits leads to scattering of phonons more effectively than scattering of electrons. Moreover, the dominant scattering species are the phonons that have the greatest contribution to thermal conductivity (χ_L) [5]. Another important factor is the increase of Seebeck coefficient (S) to the field of strong degeneracy after selection of carriers through the creation of an energy barrier at the boundaries of crystallites or grains. It is particularly effective for the composite material [6].

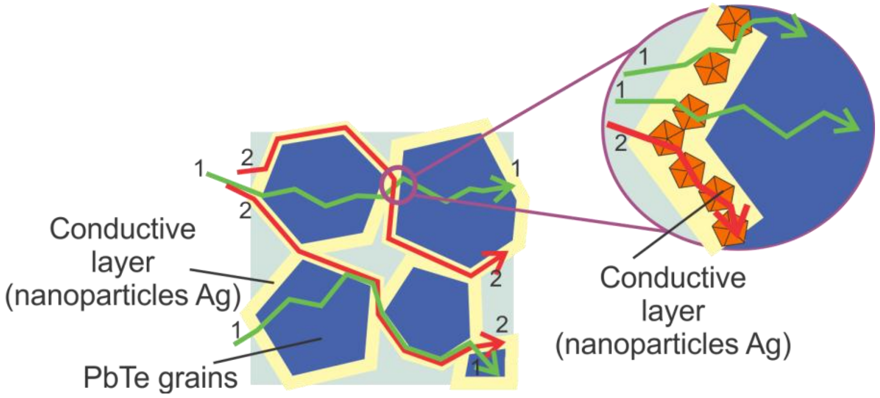


Fig. 1 – Formation scheme of the conductivity channels in composite materials. 1 – the way of the transfer of phonons (heat conductivity) by volume of the composite material; 2 – the way of the transfer of electrons (electrical conductivity) into conductive channels formed by silver nanoparticles

In this paper thermoelectric semiconductor composite materials based on PbTe with inclusion of Ag nanoparticles is explored. The relaxation time of phonons depends strongly on the grain size or length of the segments at the interfaces, as shown in [5]. According to [6], and on the base on the analysis of the phonon spectrum it has been shown that these phonons give the main contribution to thermal conductivity. In our case, the inclusion of the silver nanoparticles in the basic matrix of the composite provides an effective scattering of acoustic phonons of the medium frequency with mean free path less than 100 nm. The contribution of phonons with mean free path from 5 to 100 nm represents about 55 % of general scattering. Reduction of thermal conductivity is achieved in this case by reducing the mean free path of phonons with increase of temperature. These features cause significant reduction in the thermal conductivity (Fig. 1). The simultaneous increase of the value of S (Fig. 1) supports the additional filtration of carriers on energy barriers formed by silver nanoparticles.

2. MATERIAL AND METHODS

Synthesis of thermoelectric material was performed by melting Purified Pb and Te (Lead of the class of purity 99.9996 %, and Tellurium of the class of purity 99.9997 %) in quartz ampoules evacuated to pressure $2 \cdot 10^{-4}$ Pa [7]. Synthesis and grows of alloys were carried out in quartz ampoules with diameter of 13 mm, and length of 13-17 cm. The end of the ampoule was shaped capillary to increase the probability of growth only the single nucleus [8, 9]. Ampoules were washed in mixture HF : HNO_3 (1 : 2) for 30 min, and in distilled water for 1 hour at next stage. After these procedures ampoules were steamed in vapors of bi-distillate water during 15-20 min with their next dried without air at 420-470 K [10].

The starting components were loaded in the prepared ampoules (the weight of output components was 40-60 g within ~ 2/3 volume of ampoule). Weighing was performed on an analytical balance with correctness up to $5 \cdot 10^{-5}$ g. Ampoules were pumped to $2 \cdot 10^{-4}$ Pa, sealed, and placed in oven which temperature was slowly raised up to 40-60 degrees above the temperature of the solidus of PbTe (1220-1240 K) for prevent of the explosion of Tellurium [7].

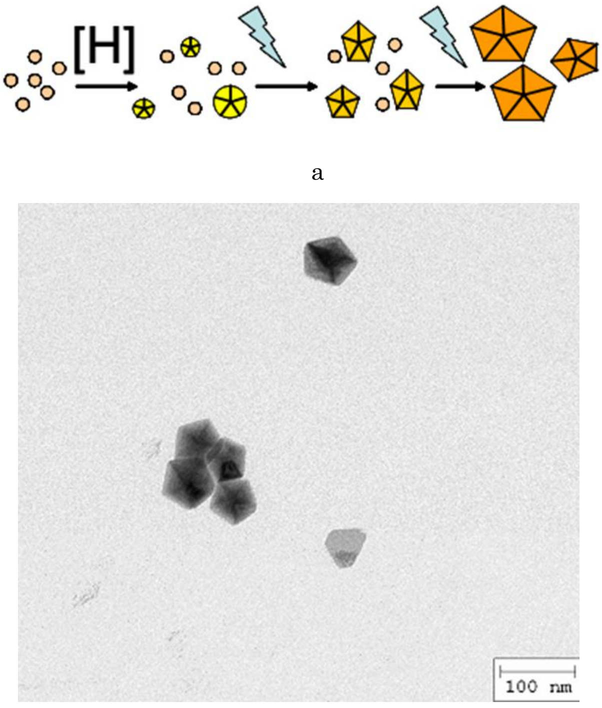
These bars are crushed and selected fraction of the size (0.05-0.5) mm was used for further processing by nanoparticles of Silver.

Photo stimulated synthesis was of Ag decahedra was carried out by the following procedure. 0.5 ml of the $AgNO_3$ (0.1 mmol/l) was mixed both with the 2.5 ml Na_3Ct (0.5 mmol/l) and the 3 ml of 1 % solution of polyacrylic acid (PAA), and next addition of 0.5 ml of $NaBH_4$ (10 mmol/l). These solutions have intense yellow color after few minutes, and thereafter they were irradiated with blue LED array [10].

The process of the growth of decahedral silver nanoparticles occurs in two stages. After the addition of reducing material the solution turns an intense yellow color - typical for spherical silver nanoparticles. In this case, the absorption spectrum appears at wavelength of 410 nm [10]. The peak position indicates that the size of nuclei was less than 30 nm. The process of decahedral formation corresponds to the growth model by Zheng et al. [11]. The spherical nuclei formed at the first stage which in the presence of free ions of Silver in solution gradually transformed into thermodynamically stable decahedra (Fig. 2). Photochemical influence performed by LED matrix with a wavelength of 470 nm. The resulting light intensity at distance of the location of test tubes with solutions was 4.000 Lux (Showtec Digital Luxmeter 91003).

Colloidal silver particles prepared via higher mentioned method were added to the equal mass of PbTe powder in quantities of 1 and 2 ml of colloidal solution. The content of silver nanodecahedra [Ag] of the solution was 0.4 mg/ml. The granulated PbTe added to suspension of colloidal silver and this mixture homogenized by ultrasound and dried (24 hours) at (350-370) K. There was periodical homogenization using ultrasound to constant weight. The TEM, and SEM results showed that obtained silver nanoparticles have planar decahedral structure with transverse diameter of about 50 nm and height of (30-40) nm. The presence of these sizes of particles provides the scattering of medium-wave phonons [6].

The resulting powder PbTe with Ag was compacted at the pressure 0.5 GPa by cold pressing. The receiving samples of cylindrical shape with diameter $d = 5$ mm and high $h \approx 8$ mm have been annealed in air at temperatures $T = 500$ K, 570 K, and 670 K.



a

b

Fig. 2 – The mechanism of formation and growth of decahedral silver nanoparticles under the influence of blue light (a) and TEM images of synthesized decahedra (b)

The magnitude of Seebeck coefficient (S) and specific conductivity (σ) was determined by the standard method [9], and thermal conductivity (χ) was determined by measurement of radial heat flow [9].

For X-ray studies the bulk samples were ground in an agate mortar. The resulting powder was applied evenly on amorphous film. The arrays of experimental intensities and angles of reflections for receiving samples obtained on an automatic diffractometer STOE STADI P (Company «STOE & Cie GmbH», Germany) with a linear position-precision detector PSD in scheme of modified geometry of Guignes in the transmission mode.

3. RESULTS AND DISCUSSION

Results of both phase and structural X-ray analysis of the studied composites are presented in table and illustrated in Fig. 3. Samples of lead telluride were almost of single phase. The main phase is PbTe with structure of NaCl type (space group Fm-3m), and addition in trace amounts was pure Pb, which recorded only on silver-free and unannealing samples N III-1B and N III-1Ba. The additional annealing of the samples, and their modification by silver leads to the single phase samples. It should also be noted a minor dominant orientation (texture) of the grains of main phase (texture axis 100).

The results of the measurement of Seebeck coefficient and coefficient of thermal conductivity for these composite materials are shown in Fig. 4. It can be seen, the inclusion of silver leads to some increase of the Seebeck coefficient (Fig. 4a) and to significant reduction of the coefficient of thermal conductivity (Fig. 4b). In particular, there was obtained the measured values of the coefficient of thermal conductivity 0.19 W/(m·K) at temperature 525 K for samples PbTe with Ag content of 0.4 mg, and 0.06 W/(m·K) for the samples PbTe with Ag content of 0.8 mg in the colloidal solution at temperature $T = 375$ K, respectively (Fig. 4b – curves 1, 2). The thermal conductivity of PbTe without inclusion of colloidal Silver for these cases was $\chi = 0.28$ W/(m·K), and 0.26 W/(m·K), respectively (Fig. 4b – curves 3). For comparison, the absolute value of Seebeck coefficient at temperature 525 K for samples PbTe with Ag content of 0.4 mg is 340 μV/K (Fig. 4a – curve 1), and 210 μV/K without inclusion of colloidal Silver (Fig. 4a – curve 3).

Composite structure formed by cold and hot pressing gives a multiple interfaces which consist with grain boundaries and separate phases due to compaction. These boundaries provide an additional mechanism for phonon scattering, which reduces the thermal conductivity of material. Considering the size of the PbTe grain boundaries (0.5-1.0 microns), most likely it is sold scattering of long-wave phonons [7].

That is, it may be noted that there is an additional throttling carriers. This causes passage high energy electrons through the barriers of Silver nanoparticles. This in turn leads to an additional increase in the Seebeck coefficient (Fig. 4,a b – curves 1, 2).

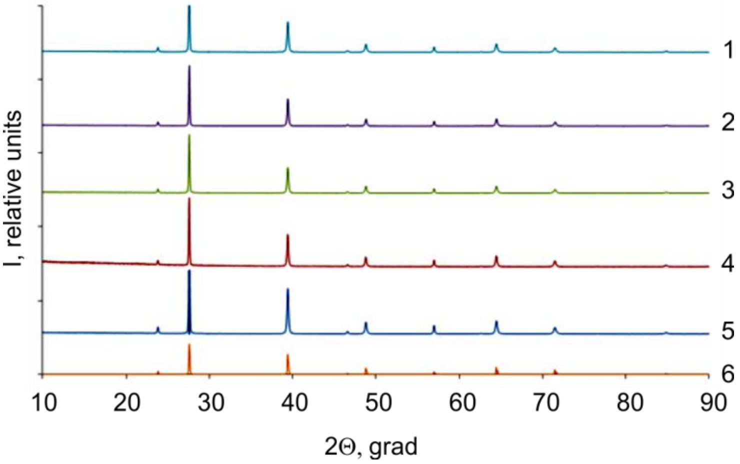
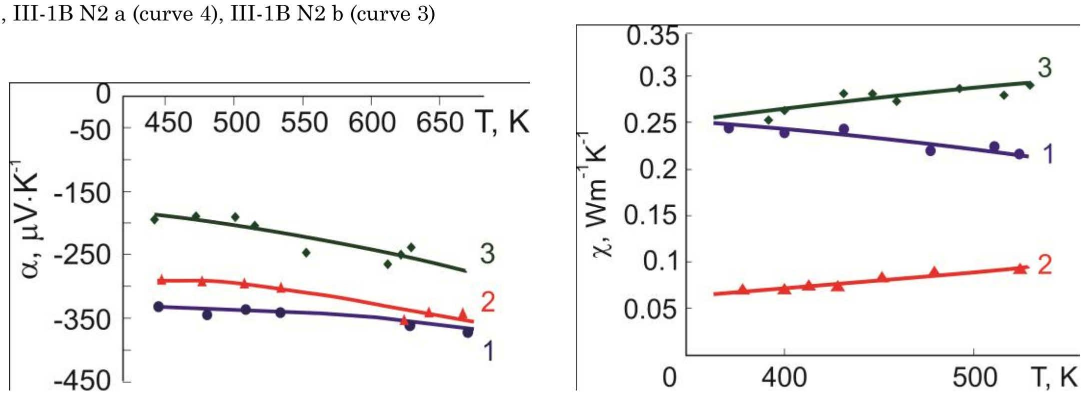


Fig. 3 – Diffraction pattern of PbTe with colloidal Silver nanoparticles and theoretical diffractogram PbTe (curve 6). Chemical composition of the samples and their processing conditions shown in the table above: III-1B (curve 1), III-1Ba (curve 2), III-1Bb (curve 5), III-1B N2 a (curve 4), III-1B N2 b (curve 3)



a b

Fig. 4 – Temperature dependences of Seebeck coefficient (a), and coefficient of thermal conductivity (b) for composite samples of PbTe (Ag) containing colloidal silver in amount 0.4 mg (curve 1) and 0.8 mg (curve 2). Curve 3 corresponds for pure PbTe

4. CONCLUSIONS

1. The compaction technology of thermoelectric composite materials based on PbTe with the inclusion of colloidal silver nanoparticles has been developed.

2. Reduction of the coefficient of thermal conductivity in the transition to composite PbTe with silver nanoparticles has been obtained. It was shown that double increase of the Ag concentration significantly reduces its thermal conductivity.

3. It was receive the increases of Seebeck coefficient after additional throttling of electrons on the barriers of Silver nanoparticles.

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Термоелектричні композити на основі PbTe з нановключеннями колоїдного срібла

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Формування термоелементів методом пресування порошкоподібного термоелектричного матеріалу із фракціями мікро- та нано- розмірів спричинює утворення значної кількості внутрішніх меж для додаткового розсіювання фононів. Однак, для поліпшення термоелектричних властивостей матеріалу потрібно не лише зменшити теплопровідність, але й підвищити коефіцієнт Зеебека. Для цього запропоновано навколо зерен термоелектричного PbTe розмірами (0,5-1,0 мкм) формувати струмопровідні наноканали. У цій роботі запропоновано технологію формування таких наноканалів шляхом введення частинок колоїдного срібла. Отримано, що введення наночастинок Ag (розмірами ~ 50 нм), не тільки зменшує теплопровідність, але й призводить підвищення коефіцієнта Зеебека через додаткове доселювання електронів на бар'ерах, сформованих наночастинками срібла. Також були отримані низькі значення коефіцієнта теплопровідності (0.06-0.2) Вт/(м·К), що спричинено внеском розсіювання середньохвильових фононів. Абсолютне значення коефіцієнта Зеебека при цьому зростає до 340 мкВ/К.

Ключові слова: Термоелектричні матеріали, Граткова теплопровідність, Наночастинки, PbTe, Ag.

Термоэлектрические композиты на основе PbTe с нановключениями коллоидного серебра

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Формирование термоэлементов методом прессования порошкового термоэлектрического материала с фракциями микро- и нано- размеров приводит к образованию значительного количества внутренних границ для дополнительного рассеяния фононов. Однако, для улучшения термоэлектрических свойств материала необходимо не только уменьшить теплопроводность, но и повысить коэффициент Зеебека. Для этого предложено вокруг зерен термоэлектрического PbTe размерами (0,5-1,0) мкм формировать проводящие электрический ток наноканалы. В этой работе предложена технология формирования таких наноканалов путем введения частиц коллоидного серебра. Получено, что введение наночастиц Ag (размерами ~ 50 нм), не только уменьшает теплопроводность, но и приводит к повышению коэффициента Зеебека из-за дополнительного дросселирования электронов на барьерах, сформированных наночастицами серебра. Также были получены низкие значения коэффициента теплопроводности (0.06-0.2) Вт/(м·К), что вызвано рассеиванием средневолновых фононов. Абсолютное значение коэффициента Зеебека при этом возрастает к 340 мкВ/К.

Ключевые слова: Термоэлектрические материалы, Решеточная теплопроводность, Наночастицы, PbTe, Ag.

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