Thermoelectric Properties of Nanostructured Materials Based on Lead Telluride

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The results of the thermoelectric properties study obtained by pressing the materials powder on the basis of two types of lead telluride are shown: mechanical mixtures of basic microdisperse PbTe and nano-dispersed additives ZnO or TiO$_2$; alloyed by antimony lead telluride and alloyed by silver lead-tin telluride in amount that exceeds the limit of impurity solubility, in order to provide additional phases. It has been established that the system heterophasicity, especially of the second type, provides the materials obtaining with low value of the thermal conductivity coefficient, which allows receiving effective thermoelectric materials with the thermoelectric figure of merit coefficient > 1.0.

Keywords: Thermoelectric materials, Lead telluride, Thermoelectric figure of merit.

1. INTRODUCTION

Thermoelectric converters are one of the most reliable in exploitation types of alternative sources of electric energy [1-7]. To their advantages also can be included a significant period of unattended exploitation, which may proceed decades of years. This determines the prospect of using thermoelectric generators for military technical needs and other systems in which the energetic autonomy is one of the main priorities.

Lead telluride is a semiconductor material that is already used to create thermoelements based on it, operating at temperature of 300-500 °C. The main drawback of the PbTe exploitation is the relatively low efficiency of devices based on it (≤ 10 %). Therefore, finding ways to increase this value is an urgent task.

The efficiency of a thermoelectric converter functionally dependents on the material thermoelectric figure of merit Z:

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

Here T_h, T_c are the temperature of the hot and cold ends of the thermocouple. The magnitude Z is proportional to the specific electrical conductivity of the material σ, to the square of the thermo-EMF coefficient α and it is inversely proportional to the coefficient of its thermal conductivity k:

$$Z = \frac{S^2 \sigma}{k}.$$

The tasks complexity of the increasing value Z lies in the fact that simultaneously with increasing the specific conductivity of the material, for example by doping, due to the increase in carrier concentration, the thermal conductivity of the material increases and the coefficient of thermo-EMF decreases. As a result, no significant rise in thermoelectric figure of merit is observed.

Therefore, a promising area of research is the creation of systems in which these parameters can be controlled separately. One example is the use of materials with defects of various dimensions: point defects and their complexes, nano- and micro-inclusion, grain boundaries [1]. In this case, control of the point defects concentration will ensure the receipt of the material with a given type and concentration of carriers and the presence of defects of various dimensions create conditions for the effective scattering of phonons with different wavelengths, which is necessary to achieve the low values of k.

Given the above, the study of thermoelectric samples obtained by the powder pressing method, which provides a large area of intergranular boundaries, is relevant. In addition to the scattering of phonons, such boundaries can filter current carriers, passing electrons (holes) only with "high" energies, which should increase the coefficient of material thermo-EMF. For pressed samples, an important factor is the size of the requested fractions used for compacting. In [3], it has been shown that the use of nanosized powder should carry to a significant reduction in the thermal material conductivity. 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, create qualitative conductive contacts for electrons between grains [8].

At the investigation of lead telluride from the above-described methods, only few of them have been realized before. The most studied ones are PbAgSbTe multicomponent compounds [9-12]. By selecting their chemical composition and synthesis conditions, the nanosized inclusions of additional phases are provided, which help significantly improved the properties of the base material. The properties of pressed samples using nanodispersed PbTe were investigated in [13]. However, with a significant reduction of the thermal conductivity (more than doubled), the thermo-EMF coefficient

of samples in the working temperature range also significantly decreased.

In this paper two types of materials are investigated. Firstly, the samples obtained from the mechanical mixture of the microscopic powder of the base material and the nanosized impurity powder (ZnO, TiO₂) were obtained by pressing method. Secondly, PbSbTe and PbAgSnTe systems, in which, by the choice of chemical composition and obtaining technological factors, are provided conditions of the nanoinclusion formation of additional phases.

2. EXPERIMENTAL PROCEDURE

Synthesis of materials carried out in vacuumed quartz ampoules [9]. The obtained ingots were crushed, pressed under pressure (1.0-2.0) GPa and annealed at the temperatures (200-500) °C. In the case of mechanical mixtures, the base material powder was mixed with a nanoparticle ZnO or TiO₂, the particle size of which was (50-70) nm. Phase structure and structure of synthesized ingots and samples were investigated by X-diffraction methods on the automatic diffractometer STOE STADI P. The surface morphology was studied using a scanning electron microscope. Hall measurements were carried out in con-

stant magnetic and electric fields using a four-zone method. The magnitude of the coefficient of thermo-MF was calculated by measuring the voltage at the ends of the specimen at the temperature gradient ≈5 °C. The specific electrical conductivity σ was determined by measuring the voltage drop on the sample the of alternating current passage. The coefficient of thermal conductivity k was determined by the method of radial heat flux [9].

3. RESULTS AND DISCUSSION

Temperature dependences of thermoelectric parameters of investigated materials PbTe, PbTe/ZnO, PbTe/TiO₂ are presented in Fig 1. The homogeneous PbTe is characterized by conductivity ≈ 5 (Ohm·cm)⁻¹, the temperature dependence σ (T) is nonmonotonic, with a minimum in the vicinity of 200 °C. At a temperature of 100 °C, the sample has hole type of the conductivity. At the temperature rises, near 250 °C, it is observed the transition of the material to the n-type. This effect is explained by the lowering zone maximum of light holes below zone maximum of heavy holes, which significantly increased their effective mass, and therefore, reduced the mobility. The coefficient of thermal conductivity of the non-admixture material is relatively low, it is slightly
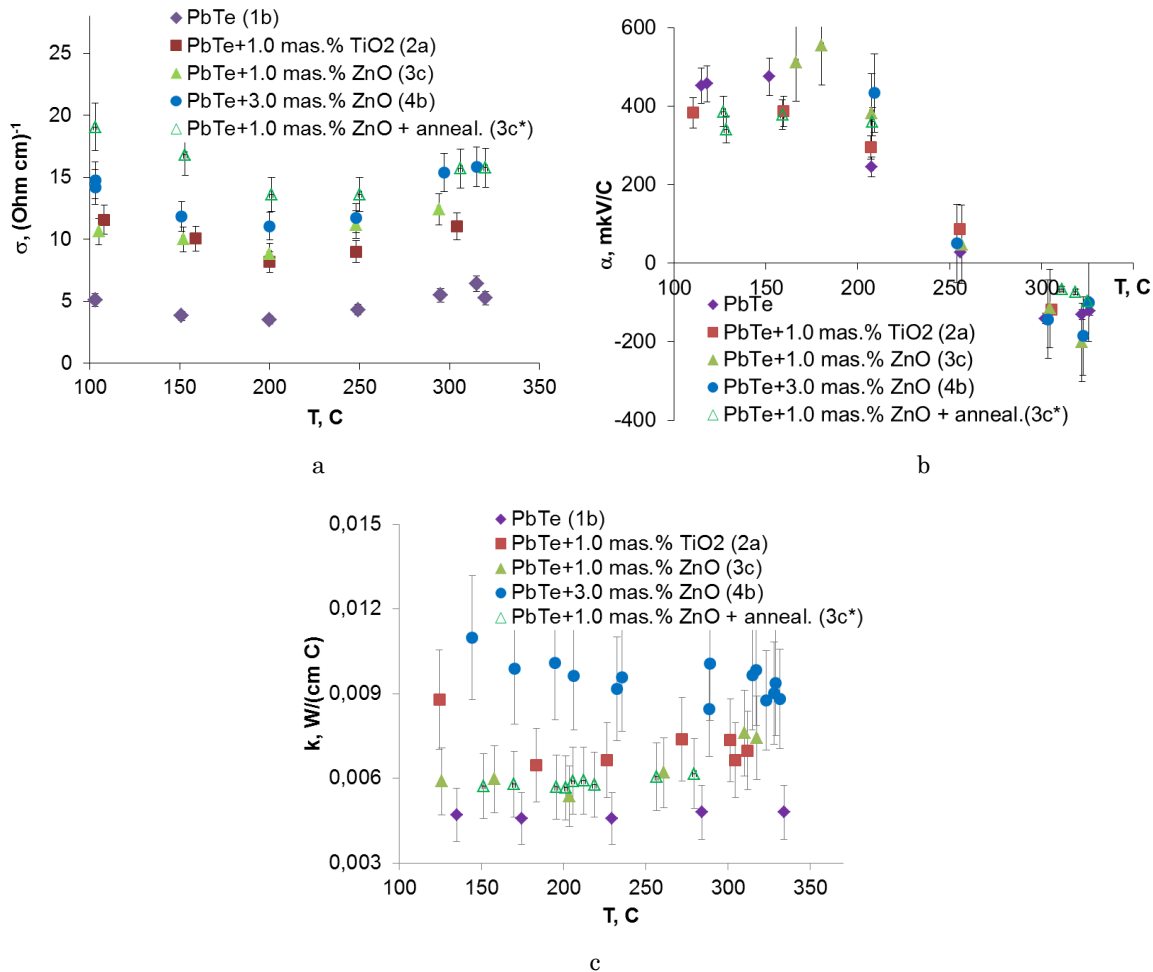

a

b

c

Fig. 1 – Temperature dependence of specific conductivity σ (a), thermoelectric coefficient α (b) and thermal conductivity k (c) at PbTe samples with the impurities of nanodispersed powders. For all samples: fractions PbTe is (0.05-0.5) mm, pressing pressure is 1,5 GPA. The sample 3c* was additionally burned for 15 minutes at 500 °C
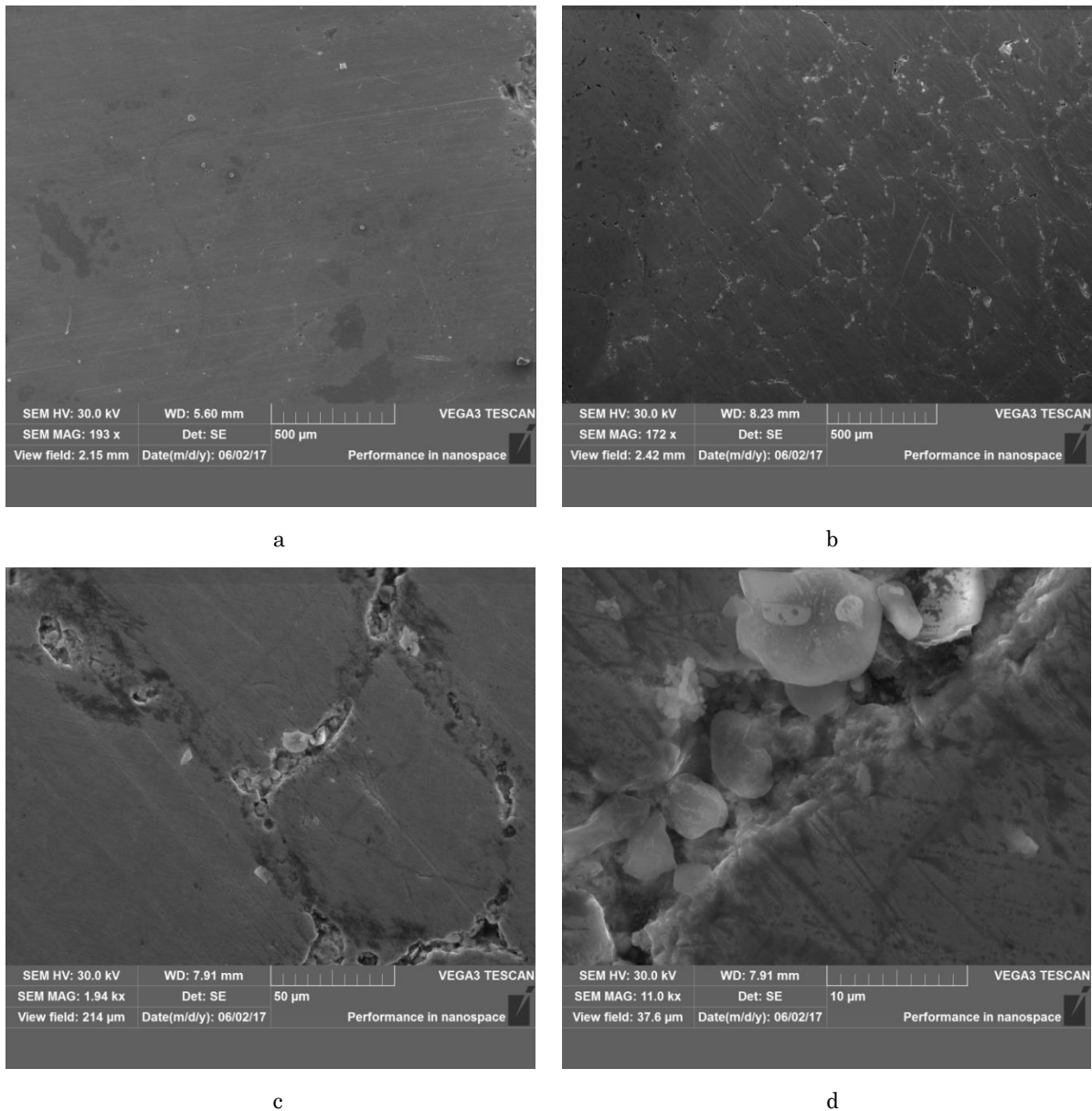
Fig. 2 – Morphology of the samples surface without (a) and with inclusions of nano-dispersed ZnO (b, c, d).

dependent on the temperature and is ≈ 0.005 W/(cm·C). Low values of the material specific conductivity and its thermal conductivity coefficient are caused by the features of cold pressing technology [9, 4].

The main effect of the adding a nanodispersed ZnO (TiO$_2$) powder, as we expected, should manifest itself on the temperature dependences of the heat conductivity coefficient. The adding metal oxides should lead to the increase of the number of dispersing surfaces, which would reduce the value of k. However, as a result of the measurements, it was found that with adding ZnO (TiO$_2$) the thermal conductivity coefficient of the material is increased. Also, the electrical conductivity of the material increases, and the coefficient of thermo-EMF practically does not change in comparison with pure PbTe. It should be noted that the properties of the investigated materials practically do not depend on the type of nanodispersed fraction (ZnO or TiO$_2$). A similar conclusion is made in [3].

From the surface morphology analysis (Fig. 2), it follows that the presence of a nanodispersed powder prevents the digestion of grains (Fig. 2b), as it is in the case of the non-homogeneous material (Fig. 2a), and the formation of conducting electrons (holes) channels. The zinc oxide nanoparticles, probably due to annealing, are combined with the formation of agglomerates up to several micrometers (Fig. 2 c, d). The lack of plastic inter-grain boundaries, obviously, is the reason also of the higher material microhardness. So, if for a homogeneous PbTe pressed at 1.5 GPa and annealed at 500 °C (15 min), it is 297 MPa, then for a sample of 1 mas. % ZnO it equals 365 MPa.

Based on Hall effect studies, it has been found that in nano-powder samples, the concentration of carriers is significantly increased, while the lattice constant decreases with increasing ZnO content (Fig. 3). This suggests that oxide nanoparticles are not electrically inactive. The increase of the holes concentration may

be due to the diffusion inside of PbTe both oxygen and zinc, which, under certain conditions, exhibits acceptor properties [15]. Probably, the growth of the thermal conductivity coefficient is also due to the growth of carrier concentration and, accordingly, the electronic component of the value *k*. It would seem that the absence of "good" intercrystal contacts should, at least in part, compensate this growth. But, as you can see from Fig. 1a and Fig. 1c, the growth of electrical conductivity is doubly accompanied by the increase of the thermal conductivity coefficient in the same number of times. In the studied samples, there are obviously two ways of phonons passing between the PbTe crystallites: partly due to some degree of intergranular contact between PbTe and partly through ZnO (or TiO₂) grains. And, in the second case, the heat conductivity will be better, because, firstly, the nanosized particles were agglomerated, increasing by this, the channel area for the pas-

sage of phonons, and, second, the ZnO thermal conductivity has almost an order higher magnitude than the thermal conductivity of PbTe.

Thus, in order to improve the effects associated with the introduction of nanoparticles, it is worthwhile to ensure that the conditions for agglomeration of nanoparticles had not been met. One embodiment of this may be the use of a more finely divided base material powder to provide a better distribution of nanomaterials by the sample volume. However, the effectiveness of using a nanodisperse additive can be questioned. This is due to the fact that an increase in dispersion already leads to an increase in the area of intergranular boundaries, which determines the efficiency of the phonons scattering. And the type of materials that create these surfaces, as has been established in this paper and noted in [3], is not fundamentally important.
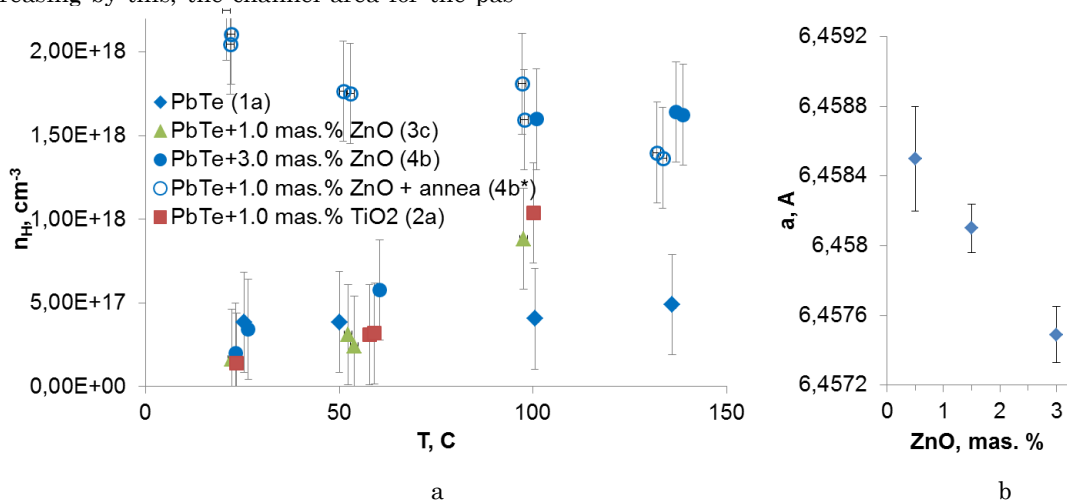

a   b

Fig. 3 – Hall concentration of carriers in PbTe/ZnO(TiO₂) composite samples (a) and the dependence on the lattice parameter of elementary cell of PbTe/ZnO samples and the content of ZnO (b)

From the point of view of improving the thermoelectric properties, the materials in which the additional phase is formed as a result of doping with an admixture in excess of the solubility limit (Fig. 4) proved to be

more effective. Two systems of PbSbTe and PbAgSnTe, the first of which are characterized by the n-type, and second – by p-type conductivity, were chosen for the study. The impurity of antimony manifests amphoteric
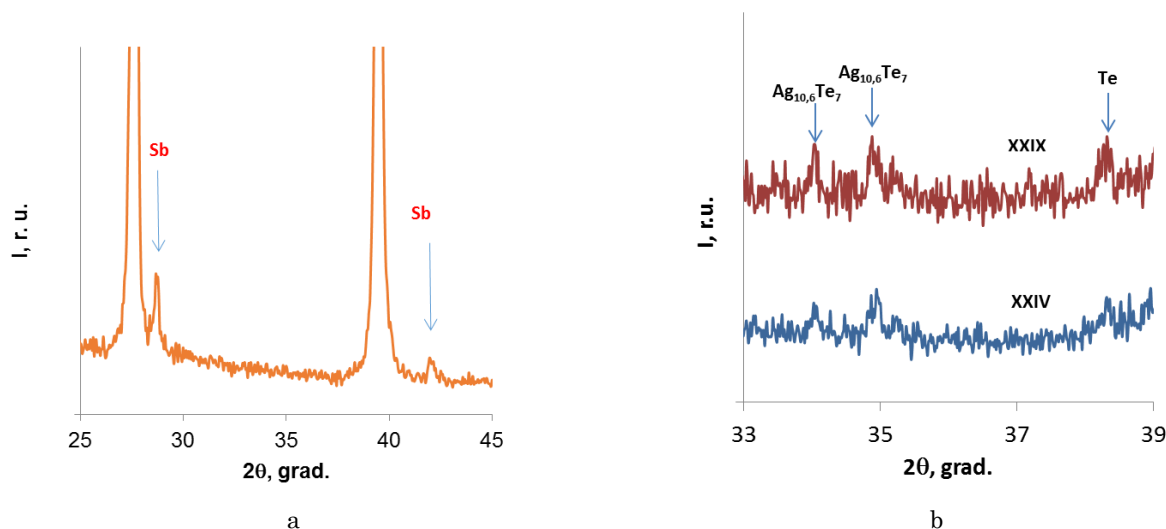

a   b

Fig. 4 – Fragments of diffractograms in the region of detected reflexes of the phase Sb in PbTe:Sb (8 at.% Sb) (a) and the phase Ag₁₀.₆Te₇ in Pb₁₆Sn₂Ag₂Te₂₀ (XXIV) and in Pb₁₄Sn₄Ag₂Te₂₀ (XXIX) (b)

properties, with the predominance of donor exposure. When replacing lead atoms, Sb contributes to the growth of the density of states at the edge of the conduction band [16], which increases the coefficient of thermo-EMF material and is valuable in terms of the use of PbTe:Sb in thermoelectric converters.

Based on the performed studies, it was found that in the case of a solid solution $Pb_{0.49}Sb_{0.01}Te$, the donor effect is significantly less pronounced than in the case of doping PbTe:Sb (1 at.% Sb). Most likely, this is associated with the possibility of formation during doping, in addition to substitution defects of the donor type

(Sb_{Pb}^{1+}) as well as interstitial donor defects Pb_i^{2+} [17]. At the expense of higher in comparison with solids the carrier concentration of PbTe:Sb (1 at %. Sb), the specific electrical conductivity and heat conductivity coefficient have high value for this material. An increase in the amount of impurity up to 8 at. % leads to the allocation of an additional phase of pure antimony, which contributes to a significant decrease in the value of k. This provides the obtaining material with a fairly high dimensional thermoelectric figure of merit: $ZT \approx 1.25$ at 200 °C. Size of the inclusion the Sb phase, determined using the Debye-Sherer formula, is 55 nm.
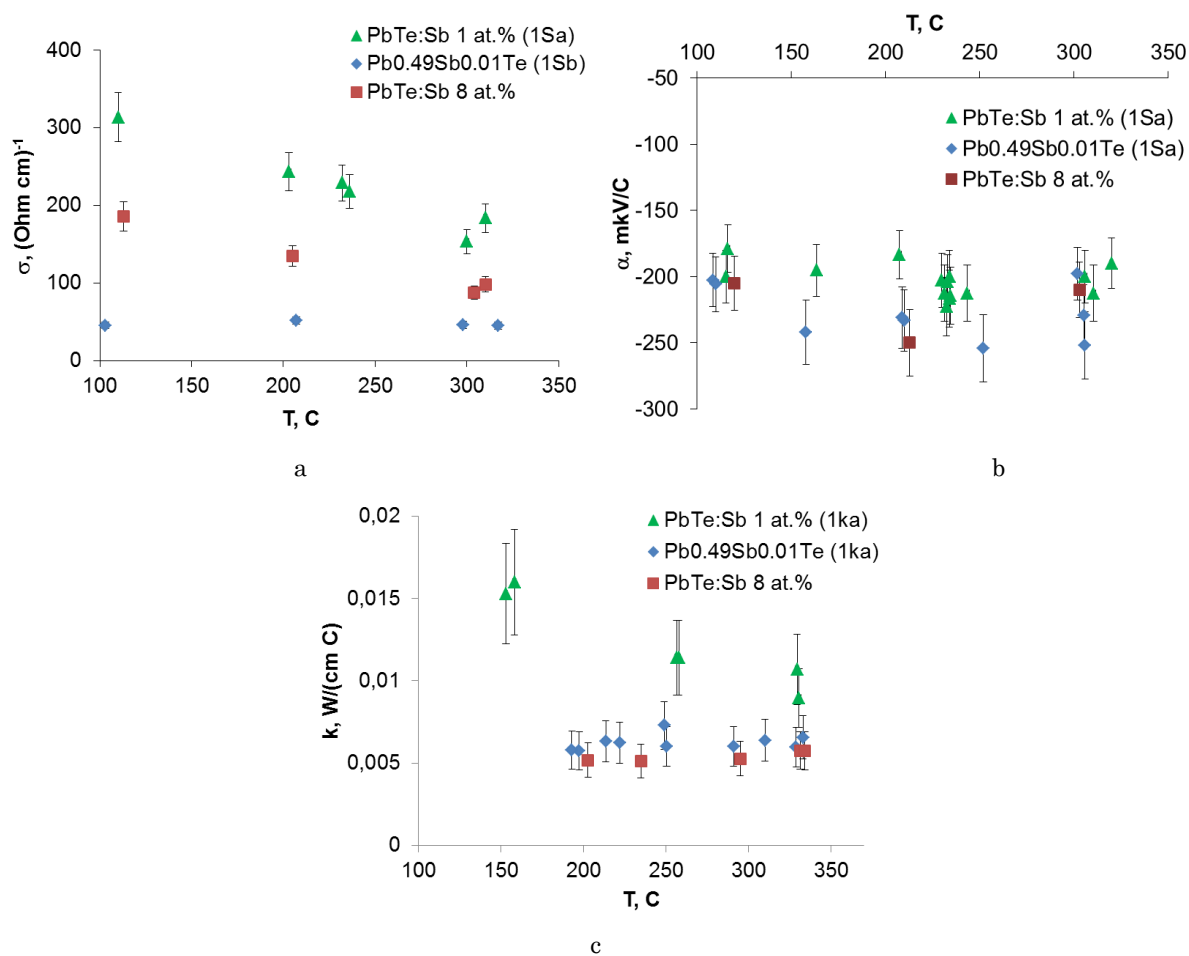

Fig. 5 – The temperature dependences of the specific conductivity σ (a), the of thermo-EMF coefficient α (b) and the thermal conductivity k (c) of the PbTe:Sb (1 at.%), PbTe:Sb (8 at.%) and $Pb_{0.49}Sb_{0.01}Te$ samples

Silver, like the antimony, is an amphoteric impurity, but with predominance of acceptor action. Unlike the PbSbTe system, in the case of the PbAgTe system, the acceptor effect of silver is more pronounced in solid solutions [18]. When the atoms have been replaced, the Ag impurity increased the density of states at the edge of the valence band [16]. PbAgSnTe solid solutions were studied for the purpose of creating a stable material of p-type conductivity for the needs of thermoelectricity. Partial substitution of lead atoms by tin atoms contributes to the growth of acceptor defects, which is positively reflected in the electrical conductivity of the investigated materials. The highest values of dimensionless thermoelectric figure of merit ($ZT \approx 0.55$ at 200 °C)

were achieved for the $Pb_{14}Sn_4Ag_2Te_{20}$ composition. Silver, which has not dissolved in crystal lattices, forms an additional phase of $Ag_{10.6}Te_7$ which promotes the receipt of a material with a low coefficient of thermal conductivity.

4. CONCLUSION

The thermoelectric properties of PbSbTe, PbSnAgTe and composite materials based on mechanical mixture of PbTe powders and additional nanodispersed fractions of ZnO or TiO_2 have been investigated. There are established the technological factors, which provide obtaining materials with given physical properties.
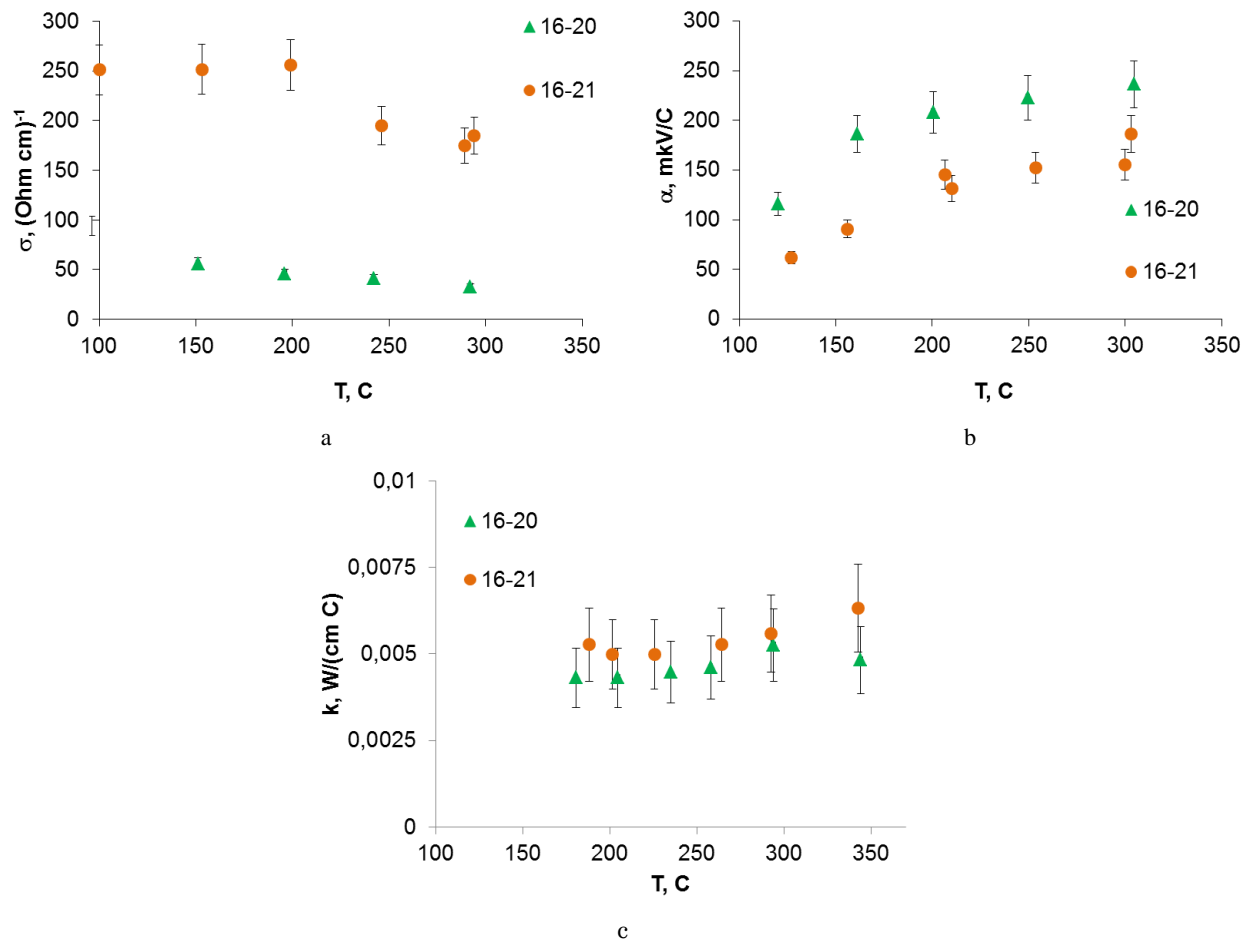
Fig. 6. The temperature dependences of the specific conductivity σ (a), the coefficient of thermo-EMF α (b) and the thermal conductivity k (c) of $Pb_{16}Sn_2Ag_2Te_{20}$ (sample 16-20) and $Pb_{14}Sn_4Ag_2Te_{20}$ (sample 16-21) materials were annealed at 500 °C.

It is shown that heterophasic materials obtained as a result of the saturation of the crystal of a matrix by an impurity are provided higher thermoelectric figure of merit compared with materials based on mechanical mixtures.

The technology of obtaining thermoelements by the method of cold pressing of powders under the choice of optimal technological factors allows to receive thermoelectric samples with a dimensionless figure of merit ZT > 1, which, with paying attention on the production cost, determines the prospect of its practical use.

Термоелектричні властивості наноструктурованих матеріалів на основі телуриду свинцю

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Представлено результати дослідження термоелектричних властивостей отриманих методом пресування порошку матеріалів на основі телуриду свинцю двох типів: механічні суміші базового мікродисперсного PbTe та нанодисперсних добавок ZnO чи TiO₂; легований сурмою телурид свинцю та легований сріблом телурид свинцю-олова в кількості, що перевищує межу розчинності домішки, з метою виділення додаткових фаз. Встановлено, що гетерофазність системи, особливо другого типу, забезпечує отримання матеріалів з низьким значенням коефіцієнта теплопровідності та дозволяє отримувати ефективні термоелектричні матеріали з коефіцієнтом термоелектричної добротності > 1.0.

Ключові слова: Термоелектричні матеріали, Телурид свинцю, Термоелектрична добротність.

Термоэлектрические свойства наноструктурированных материалов на основе теллурида свинца

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Представлены результаты исследования термоэлектрических свойств полученных методом прессования порошка материалов на основе теллурида свинца двух типов: механические смеси базового микродисперсного PbTe и нанодисперсных добавок ZnO или TiO_2; легированный сурьмой теллурида свинца и легированный серебром теллурида свинца-олова в количестве, превышающем предел растворимости примеси, с целью выделения дополнительных фаз. Установлено, что гетерофазность системы, особенно второго типа, обеспечивает получение материалов с низким значением коэффициента теплопроводности и позволяет получать эффективные термоэлектрические материалы с коэффициентом термоэлектрической добротности > 1.0.

Ключевые слова: Термоэлектрические материалы, Теллурид свинца, Термоэлектрическая добротность.

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