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THERMOELECTRICITY OF LEAD TELLURIDE DOPED WITH *Sb* AND *Bi*

X-ray investigations of antimony and bismuth doped lead telluride have been performed and its thermoelectric parameters (the Seebeck coefficient α *and electric conductivity* σ*) have been measured. It has been established that more optimal properties for use in thermoelectric generators are inherent in PbTe:Sb samples with impurity content 0.3 at.% whose electric conductivity is* $\sigma \approx 700\ (\Omega \cdot cm)^{-1}$*, and the Seebeck coefficient* $\alpha \approx 300\ \mu V/K$*, assuring thermoelectric power* $\alpha^2\sigma$ *higher than 50* $\mu W/cm\ K^2$*.*

Key words: lead telluride, thermoelectric properties, doping.

Introduction

As a result of many experimental and theoretical investigations [1-3] it has been shown that impurities of V group elements, especially *Sb* and *Bi*, make it possible to improve considerably the parameters of lead telluride which is widely used for creation of thermoelectric power converters working in the temperature range of (500 – 800 K).

Apart from other parameters, the effect of impurity on thermoelectric characteristics of crystals is essentially dependent on the manner of preparation of samples under study. The majority of known works, in particular, [2, 3], study single-crystal samples or samples cut of polycrystal ingots. However, thermoelectric converters mostly employ thermoelements made by meta-ceramic methods. Therefore, investigation of samples obtained by compaction of power *PbTe*:*Sb* (*Bi*) is of considerably greater practical interest.

This paper studies structural and thermoelectric properties of samples obtained by compaction of powder *PbTe*:*Sb* and *PbTe*:*Bi* with impurity concentration in the range of (0.0 – 1.0) at.% *Sb* (*Bi*).

Experimental procedure

Lead telluride, impurity-free and doped with bismuth and antimony in the amount of 0.1, 0.3 and 1.0 at.%, was synthesized by alloying in quartz ampoules evacuated to pressure of $2 \cdot 10^{-4}$ Pa. As the precursor components, purified *Pb*, *Te*, *Sb* and *Bi* were used. The obtained ingots were crushed in agate mortar and, after fractionation of size (0.05 – 0.5) mm, were compacted under pressure of 0.5 GPa. The obtained cylinder-shaped samples with $d = 5$ mm and $h \approx 8$ mm were annealed in the air at temperature $T = 500$ K for 5 hours.

The value of the Seebeck coefficient S and electric conductivity σ was determined by standard procedure detailed in [1]. The sample was located between two copper rods placed in the oven which heated it to given temperature. Temperature gradient on the sample ($\approx 10\ ^\circ$C) was created by additional oven on one of the copper rods. The temperature was measured by two chromel-alumel thermocouples placed in openings in the sample. Electrical conductivity was determined by measuring

voltage drop on the sample generated by DC voltage source. In so doing, one of the legs of each thermocouple was used as current lead.

For *X*-ray investigations the ground material was applied as a uniform layer on the amorphous film using amorphous glue for *X*-ray transmission experiments and fixed by another film in a special bath. Arrays of experimental intensities and reflection angles from the investigated samples were obtained on automatic diffractometer STOE STADI P (produced by "STOE & Cie Gmbh", Germany) with a linear precision position detector PSD according to the scheme of modified Guinier geometry by transmission method (CuK_{α_1} -radiation; concave Jogann-type *Ge*-monochromator (111); 2θ/ω-scanning, angle interval $10.000 \le 2\theta \le 125.185$ with a step 0.015°2θ; detector step 0.480 °2θ, scanning time in step 100 – 230 s, temperature of exposure $T = (297.6 \pm 0.3)$ K, $U = 40$ kV, $J = 35$ mA). Primary processing of experimental diffraction arrays, calculations of theoretical diffractograms of known compounds for the purpose of phase identification, specification of unit cell parameters was performed with the use of programs STOE Winxpow (version 3.03) and Powdercell (version 2.4).

Experimental Results

PbTe:*Sb*. The results of *X*-ray phase investigations are presented in Fig. 1. Diffraction lines from individual components (lead, tellurium) or their oxides were not discovered.

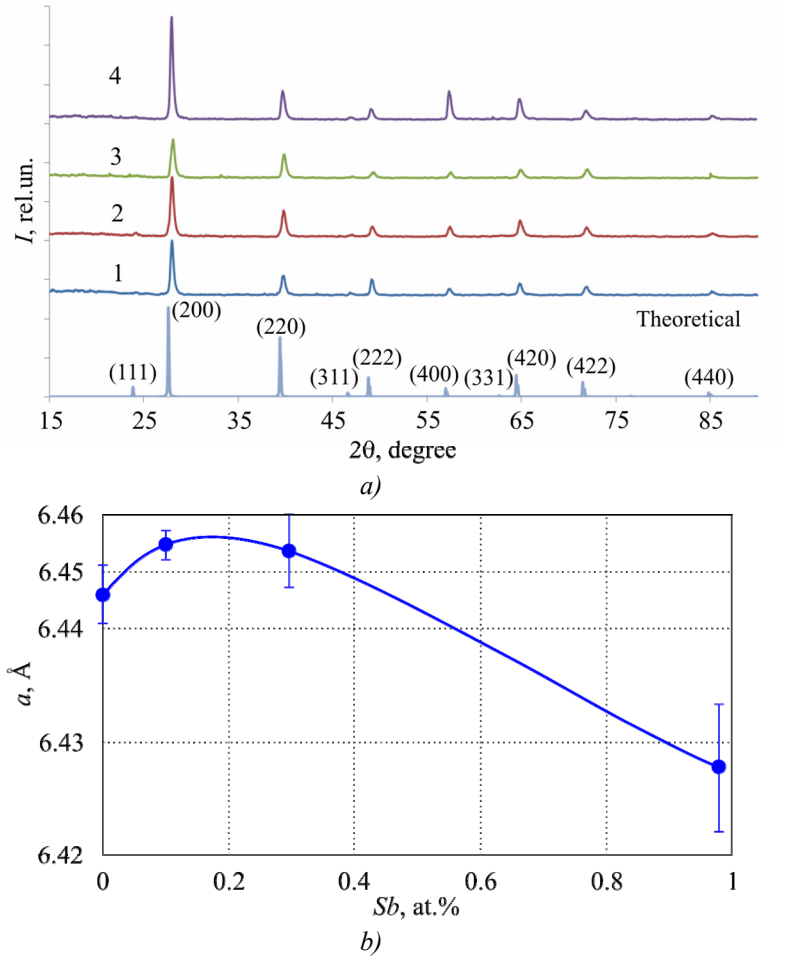

Fig. 1. (a) Comparative diffractograms of lead telluride with different content of antimony impurity (1 – sample 12-1 PbTe; 2 – sample 12-2 PbTe + 0.1 at.% Sb; 3 – sample 12-3 PbTe + 0.3 at.% Sb; 4 – sample 12-4 PbTe + 1 at.% Sb); (b) unit cell period a *of PbTe:Sb samples under study versus Sb impurity content.*

Comparison of the obtained diffractograms to the theoretical one shows a relative amplification of some and attenuation of other intensities of diffraction reflection line. Also, conspicuous is a non-monotonous change of lattice parameter (*a*) with increase in the number of introduced antimony atoms (Fig. 1, *b*). Up to impurity concentration 0.2 at.% *Sb* the (*a*) value of *PbTe* is increased, and at concentration > 0.3 at.% *Sb*-decreased.

Thermoelectric samples were of *n*-type conductivity (Fig. 2). Electric conductivity of lead telluride doped with 0.3 at. % *Sb* is $\sigma \approx (700 - 800)$ $(\Omega \cdot cm)^{-1}$.The Seebeck coefficient is reduced with increasing the amount of impurity introduced, but the absolute value remains rather high ($\alpha \approx (250 - 300)$ μV/K at $T \approx 500$ K). Impurity concentration increase to 1.0 at.% *Sb* brings about a considerable reduction of both the Seebeck coefficient and the electric conductivity of samples under study.

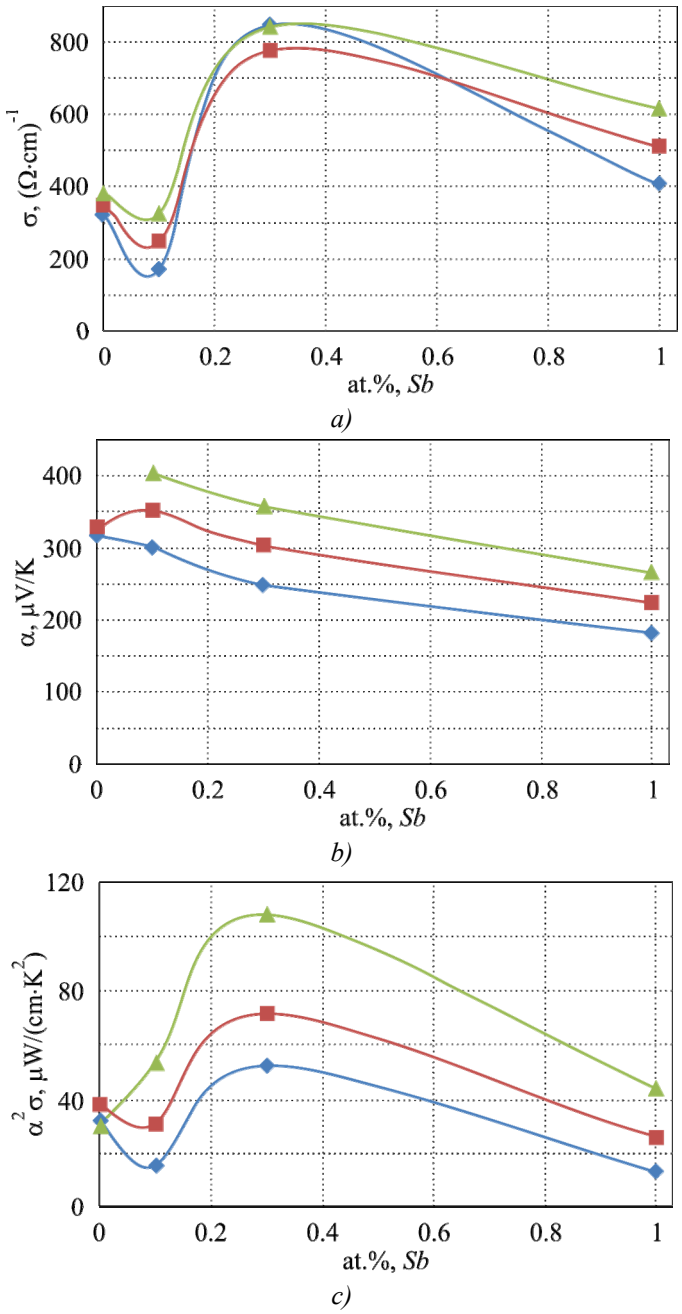

Fig. 2. Electric conductivity – a), the Seebeck coefficient – b), specific thermoelectric power – c), of doped PbTe versus Sb content at different temperatures T, K: 400 K – ♦, 500 K – ■, 600 K – ▲.

PbTe:Bi. The results of *X*-ray studies are presented in Figs. 3 – 4. Impurity-free lead telluride (sample 13-1) is characterized by the existence of one phase of structural type *NaCl* with parameter of face-centered cubic unit cell a = 6.4595(3) Å and space group *Fm*-3*m*. This unit cell parameter is in good agreement with precision structural studies performed by neutron diffraction on *PbTe* samples with the purity of precursor substances > 99.999 at.% [4].

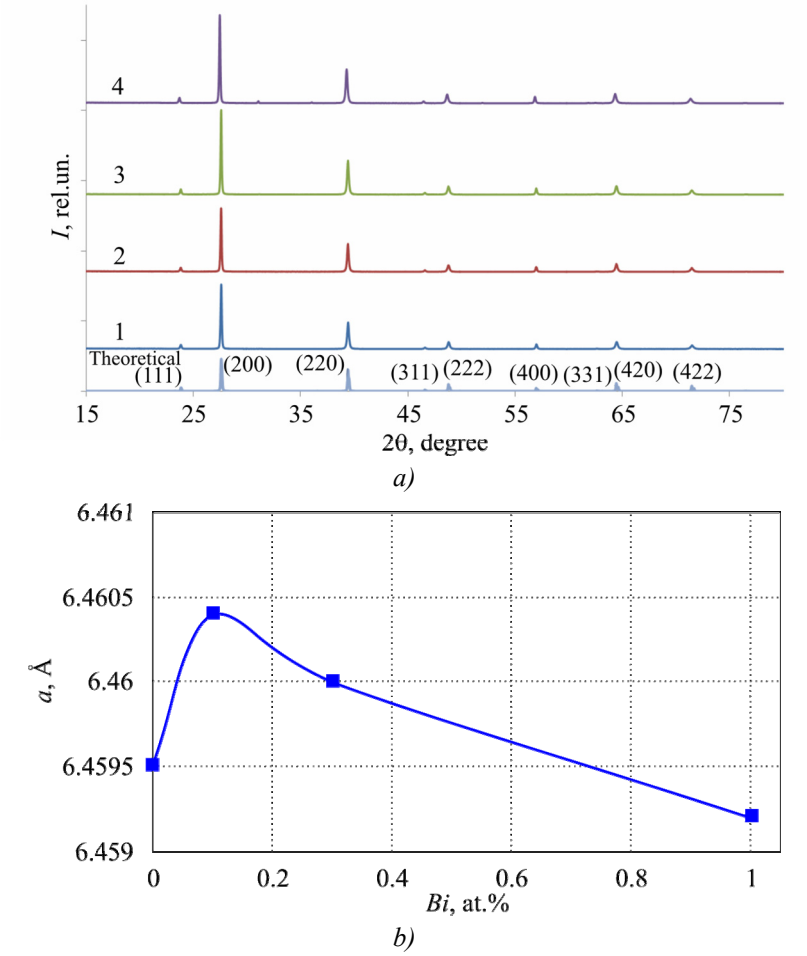

Fig. 3. (a) Comparative diffractograms of lead telluride with different content of bismuth impurity (1 – sample 13-1 PbTe; 2 – sample 13-2 PbTe + 0.1 at.% Bi; 3 – sample 13-3 PbTe + 0.3 at.% Bi; 4 – sample 13-4 PbTe + 1 at.% Bi); (b) unit cell period a of PbTe:Bi samples under study versus Bi impurity content.

Analysis of diffractograms of doped samples brings us to the conclusion about the existence in them of other phase inclusions, namely $Pb_{1-x}Bi_x$ (structural type *Cu*, space group *Fm*-3*m*) (Fig. 4). However, taking into account the precision of *X*-ray phase analysis which is generally ~ 3 – 5 %, and in the case for substances with high-symmetry lattice (cubic, tetragonal, hexagonal syngonies) with small unit cell parameters from 1 %, one can unambiguously state that an additional phase is present only in sample 13-4 for which the content of phase $Pb_{1-x}Bi_x$ is ≈ 1.4 mas. %. The unit cell parameter of this phase in sample 13-4 is 4.9626(5) Å. For pure *Pb* (purity 99.999 %) parameter a = 4.951 Å [4], and for the phase $Pb_{0.85}Bi_{0.15}$, according to [5], a = 4.9650 Å. That is, in our case for $Pb_{1-x}Bi_x$ phase parameter a has intermediate value, and phase composition is probably ≈ $Pb_{0.9}Bi_{0.1}$.

Like for other *PbTe* based materials in our study [6], synthesized according to a similar procedure, on the diffractograms there is a relative amplification of some and attenuation of other reflex intensities as compared to theoretical diffractogram of *PbTe*. It is most apparent in the variation of peak ratio of diffraction reflection I(200)/I(220).

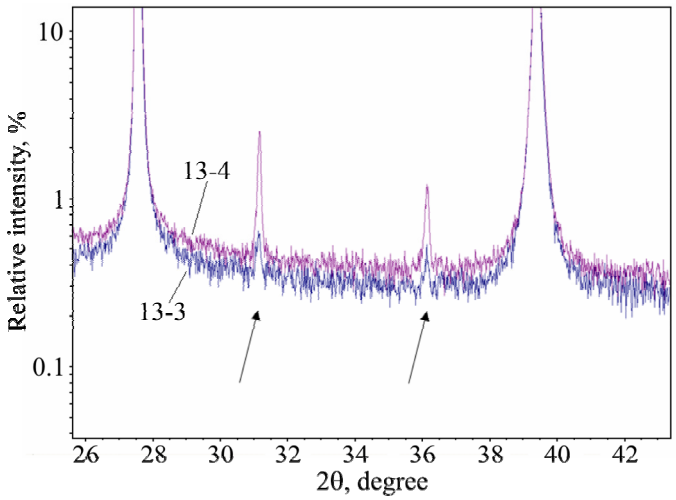

Fig. 4. Comparison of experimental diffractograms of samples 13-3 and 13-4. Reflexes from $Pb_{1-x}Bi_x$ phase (Cu structural type, Fm-3m space group) are arrowed. For better visualization the ordinate axis is represented on a logarithmic scale.

When comparing the unit cell parameters of the basic phase for samples with different *Bi* concentration, one can see certain growth of a value (Fig. 3, *b*) with bismuth content 0.1 at.% and its subsequent reduction with increasing impurity content.

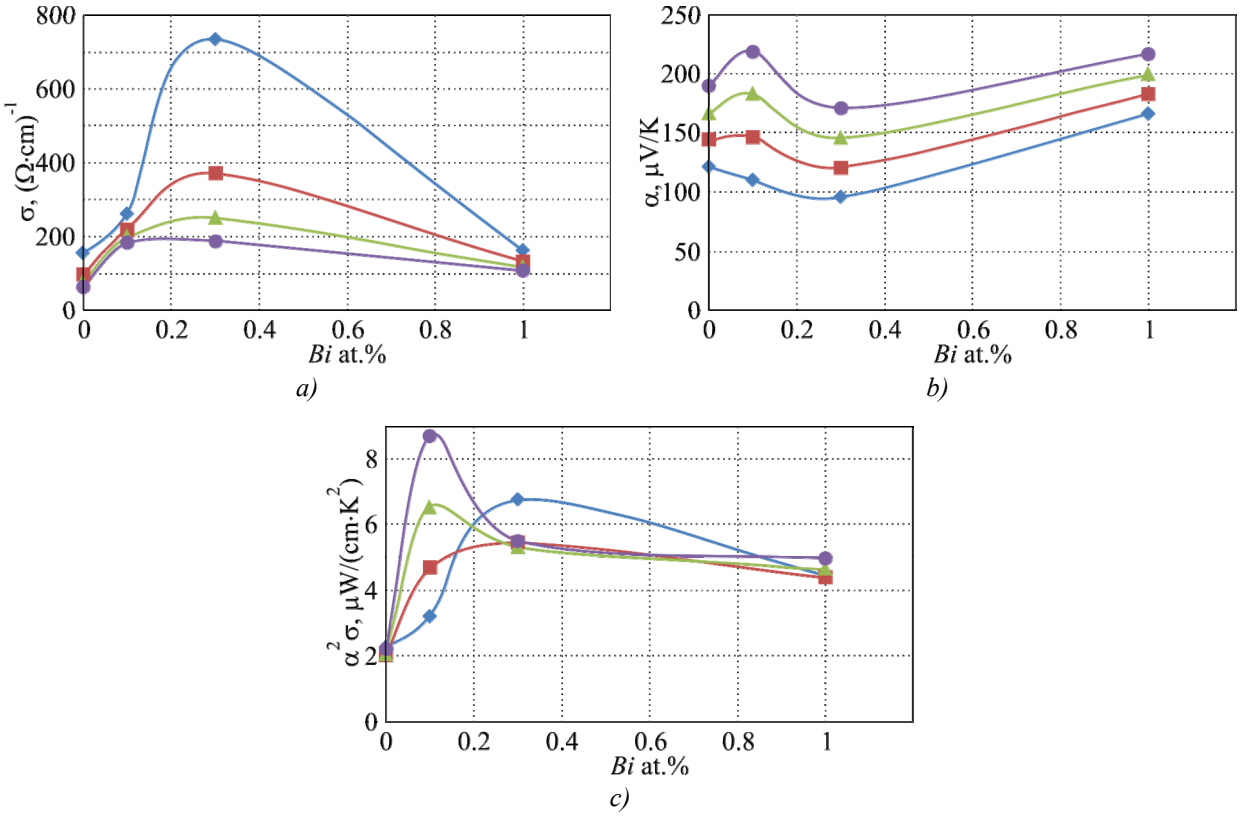

Fig. 5. Electric conductivity – a), the Seebeck coefficient – b), specific thermoelectric power – c), of doped PbTe versus Bi content at different temperatures T, K: 100 K – ♦, 200 K – ■, 300 K – ▲, 400 K – ●.

The results of measuring the Seebeck coefficient and electric conductivity are represented in Fig. 5, *a* and Fig. 5, *b*, and thermoelectric power calculated on their basis – in Fig. 5, *c*. All the samples had *n*-type conductivity. Electric conductivity grows from the values of $\sigma \approx 100 - 200\ (\Omega \cdot cm)^{-1}$ for

impurity-free to $\sigma \approx 600$ $(\Omega \cdot cm)^{-1}$ for lead telluride doped with 0.3 at.% *Bi*. The Seebeck coefficient for a sample with such impurity concentration has a minimum. Analyzing the thermoelectric power of samples under study it is seen that for sample 13-2 with impurity content 0.1 at.% *Bi* it is the highest.

Analysis of the investigation results

The relative change in the intensity ratios of diffraction reflection line in materials under study with different impurity content (Fig. 1, 3) is attributable to the presence of orientation direction of crystallites that was formed in the process of melt crystallization and was not completely destroyed in the process of powder preparation for analysis [6]. The non-monotonous concentration dependence of lattice constant of *PbTe*:*Bi* and *PbTe*:*Sb* is attributable to different mechanisms of impurity atoms (*Bi*, *Sb*) inclusion into lead telluride crystal lattice with different doping levels. Assuming that *n*-type of the obtained impurity-free *PbTe* is caused by tellurium vacancies, then introduction of up to 0.3 at.% *Sb* or 0.1 at.% *Bi* results in their filling with impurity atoms, which accounts for the growth of unit cell parameter. At concentration equal to 0.1 at.% in the case of *Bi* and 0.3 at.% in the case of *Sb* all tellurium vacancies are filled with impurity atoms, which predetermines maximum value of parameter a. At concentrations > 0.1 at.% *Bi* (> 0.3 at.% *Sb*) both the cation and anion sublattices are completed, where considerable concentrations of vacancies are absent, and certain reduction in the value of unit cell parameter is due to the fact that the sum of ionic radii Bi^{3+} (Sb^{3+}) and Bi^{3-} (Sb^{3-}) is somewhat smaller, though not much, than the sum of ionic radii Pb^{2+} и Te^{2-}. Thus, according to [7] r_{ion} (Sb^{3+}) + r_{ion} (Sb^{3-}) = 2.98 Å, r_{ion} (Bi^{3+}) + r_{ion} (Bi^{3-}) = 3.33 Å, whereas r_{ion} (Pb^{2+}) + r_{ion} (Te^{2-}) = 3.36 Å.

It should be noted that on condition of implementation of the represented mechanism of impurity inclusion into lead telluride crystal lattice, at concentrations of antimony atoms < 0.3 at.% and bismuth atoms < 0.1 at.% their arrangement in a vacant anion site will result in reduction of the Hall concentration of carriers per unit. However, because of high dielectric permittivity, the efficiency of carrier scattering by charged centres in *PbTe* is lower as compared to lattice deformations caused by point defects. That is, with identical concentrations of tellurium vacancies that cause relatively strong lattice deformation, carrier scattering is much more active compared to that of impurity ions, the lattice deformations in the neighbourhood of which should be smaller. This statement is partially confirmed by the results of [8] where it is shown that the Coulomb potential of tellurium vacancies has a considerably smaller effect on carrier mobility than its short-range component. Thus, it can be assumed that reduction of carrier concentration is compensated by their mobility increase, which results in electric conductivity growth in the sample with 0.3 at.% *Sb* or 0.1 at.% *Bi* as compared to undoped material.

With impurity content about 1 at.%, a large concentration of antimony (bismuth) ions in both sublattices results in reduction of carrier concentration and increased importance of ionized impurity scattering mechanism due to considerable growth of the number of scattering centres, which accounts for reduction of samples conductivity.

It should be also noted that in case of implementation of another possible mechanism of impurity inclusion into lead telluride crystal lattice, namely cation sublattice completion, a considerable number of tellurium vacancies should be formed, which will result in reduction of lattice parameter with increasing amount of bismuth introduced, hence, it will be difficult to explain the existence of maximum a value in Figs. 1 and 3.

Taking into account the presence in *PbTe*:*Bi* of additional phase, it is important to determine its influence on the thermoelectric properties of samples. Formation of $Pb_{1-x}Bi_x$ inclusions may be caused

by the presence in synthesized material of superstoichiometric lead which in the undoped *PbTe* results in the origination of a considerable number of tellurium vacancies. In one of our earlier works it was established [9] that additional phases that are formed in synthesized ingots may not be manifested any longer in pressed and annealed sample. Therefore, before attracting the fact of existence of $Pb_{1-x}Bi_x$ inclusions to the explanation of the resulting dependences, one should perform *X*-ray studies of those samples that have been measured, the more so that any abnormal numerical values of α or σ values that might have been caused by the existence of additional phase have not been discovered.

Conclusions

1. X-ray studies have been performed and thermoelectric parameters have been measured of antimony and bismuth doped lead telluride in the range of impurity concentration 0.0 – 1.0 at.% *Sb* (*Bi*).
2. It is shown that doping results in improvement of the basic thermoelectric characteristics of material. In particular, for *PbTe*:*Sb* with impurity content 0.3 at.% the electric conductivity is $\approx 700\ (\Omega\cdot cm)^{-1}$, and the Seebeck coefficient $\approx 300\ \mu V/K$. For *PbTe*:*Bi* an optimal impurity concentration is 0.1 at.% of *Bi* whereby $\sigma \approx 600\ (\Omega\cdot cm)^{-1}$ and $\alpha \approx 150\ \mu V/K$.
3. A non-monotonous variation of the unit parameter with increasing content of antimony (bismuth) atoms is established, which is attributable to different mechanisms of impurity inclusion into *PbTe* crystal lattice: up to concentration 0.3 at.% *Sb* (0.1 at.% *Bi*) there is filling with antimony (bismuth) atoms of tellurium vacancies, and at higher concentrations – a simultaneous completion of the anion and cation sublattices.

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Submitted 30.05.2014.