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**SYNTHESIS, PROPERTIES AND MECHANISMS
OF DOPING WITH *Sb*
OF THERMOELECTRIC LEAD TELLURIDE *PbTe:Sb***

The effect of Sb doped lead telluride n-PbTe:Sb fabrication factors on the electric conductivity and the Seebeck coefficient values was studied. It was established that optimal properties are inherent in the samples with impurity content 0.3 at% Sb the thermoelectric power of which reaches a maximum at a temperature of $T = 500$ K and makes $\alpha^2\sigma \approx 70 \mu W/(K^2cm)$. The crystal-chemical doping mechanisms and the dominant point defects of investigated crystals were determined.

Key words: lead telluride, doping mechanisms, thermoelectric properties.

Introduction

Lead telluride is a promising thermoelectric material for medium-temperature (500 – 700) K thermal energy converters [1-3]. The properties of *PbTe* can be improved by chemical composition modification, in particular, by doping and optimization of technological processes of compound synthesis and preparation of thermoelectric pellets.

Considerable interest has been shown recently in the investigation of properties of lead chalcogenides doped with V group elements of the periodic table [4]. According to [5], *Sb* and *Bi* impurities in *PbTe* are donors and the share of electrically active atoms is appreciably less than the number of introduced ones. It is explained either by formation of electrically inactive complexes in the lattice of *Sb₂Te₃* type compound, or the distribution of impurity between the cation (where it is a donor) and anion (where it is apparently an acceptor) sublattices [4, 6, 7]. In [4, 8] by means of the emission Mössbauer spectroscopy technique on ¹¹⁹*Sb* (^{119m}*Sn*) isotope it is shown that *Sb* impurity atoms in lead chalcogenide sublattices are distributed between the cation and anion sublattices, in which case in the electron samples the main share of *Sb* is localized in the anion sublattice, and in the hole samples – in the cation sublattice.

Thus, doping of lead telluride with *Sb* should result in the optimization of material thermoelectric parameters: increase in the electric conductivity of samples and reduction of their thermal conductivity. However, despite the already established general concepts of *PbTe:Sb* doping, the issue remains open as to the effect of samples preparation process on the mechanism of entering *Sb* impurity atoms into lead telluride crystal lattice and its influence on the thermoelectric figure of merit of material as a whole.

In this paper, the effect of *PbTe:Sb* samples fabrication and thermal treatment on their electrical characteristics is studied, and crystal-chemical models of crystal doping mechanisms are proposed.

Experimental procedure

Impurity-free and doped lead telluride was obtained by direct melting of prepurified components agitated during synthesis. To remove the impurities, metal lead was placed into cleaned and dried Pyrex or molybdenum ampoules which were evacuated to residual pressure 10^{-4} Pa, sealed and placed into a double-zone electric furnace. The temperature in heating zone was set 70 to 100°K higher than lead melting point. The temperature maintained in substance-free ampoule area was 340 to 350 K. In this state the ampoule was maintained for 5-6 hours. During this time, impurities with melting point lower than that of lead were evaporated and due to the effect of temperature gradient they were transferred to free ampoule end, being deposited on its walls. Following that, the free ampoule end was removed from the furnace and the ampoule was inclined in such a way that liquid lead slowly spread over the walls and immediately solidified. As long as lead oxide has melting temperature about 1160 K, it remained on the ampoule walls at loading place, together with high-melting impurities.

Sublimation technique was employed to purify tellurium from impurities. The evacuated ampoule with tellurium was placed into a double-zone furnace inclined in such a way that evaporation area (hot zone) was 7 to 10 cm lower than condensation area (cold zone). The hot zone temperature was set as 770 °K and in condensation area – 690 K. The process duration was up to 120 hours.

Purified components *Pb*, *Te* and *Sb* doping impurity in the appropriate mass ratios were loaded into prepared ampoules of C5-1 quartz glass. The ampoules were evacuated to a residual pressure of 10^{-4} Pa and sealed. Then they were placed in a double-zone resistance electric furnace, and chromel-alumel thermocouples were arranged on the ampoule edges for temperature control. The temperature 800 K was set in the furnace, whereby all the components passed into a liquid phase. To increase compound homogeneity [9], the electric furnace performed 6 full-wave oscillations with a deviation from the horizontal position by the angles $\pm 30^\circ$. After that, the electric furnace was held for 50 hours for the diffusion processes. Then, at a temperature of 1240 K, the furnace again made 6 full-wave oscillations. Afterwards, the electric furnace was installed horizontally, and in this state the process of synthesis lasted for another 70 hours.

The electric furnace with a synthesized compound was cooled down to 700 K at a rate of 5 K/hour, and, subsequently, at a double rate to room temperature.

The obtained material was ground in agate mortar and, on separating fractions of size 0.05 – 0.5 mm, it was compacted under pressure 0.5 – 1 GPa, which yielded cylinder-shaped samples with $d = 5$ mm and $l \approx 5 - 10$ mm. Following that, the samples were again annealed in the air for 5 hours at a temperature of 500 K.

The thermoEMF (α) and electric conductivity (σ) values were determined by standard procedure on the installation schematically shown in Fig. 1. The sample was placed in a furnace between two copper rods one of which was heated to create temperature gradient (≈ 10 K) on the sample. The temperature was measured by two

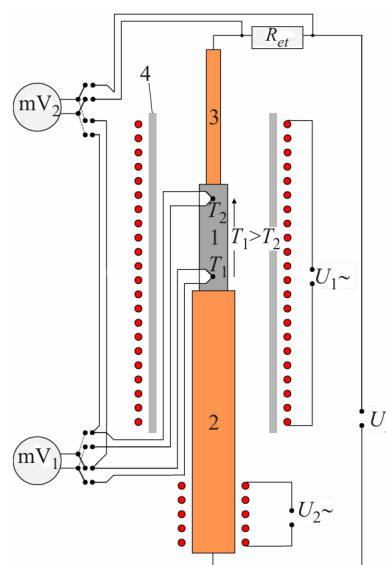


Fig. 1. Schematic of installation for measuring the Seebeck coefficient and electric conductivity: 1 – sample; 2, 3 – copper rods; 4 – quartz tube.

chromel-alumel thermocouples placed in the holes drilled in the sample. The electric conductivity was found by measuring a drop in the sample voltage generated by constant voltage source U_3 . In the process, one of the legs of each thermocouple was used as current conductor.

Experimental results

The resulting samples possessed stable n -type conductivity, and their thermoEMF and electric conductivity grew with a rise in temperature (Fig. 2). As is evident from the figures, doping of $PbTe$ with Sb leads to improvement of its basic thermoelectric characteristics. Thus, for instance, the electric conductivity grows from the values of $\sigma \approx (100 - 200) (\Omega \cdot \text{cm})^{-1}$ for impurity-free $PbTe$ to $\sigma \approx (700 - 800) (\Omega \cdot \text{cm})^{-1}$ for $PbTe$ doped with 0.3 at.% Sb . The Seebeck coefficient in this case is reduced on the average by 50 $\mu\text{V/K}$ over the entire temperature range, but the absolute value remains sufficiently high ($\approx 300 \mu\text{V/K}$). Increase in impurity concentration to 1.0 at. % Sb leads not only to essential reduction of the Seebeck coefficient, but also to decreased electric conductivity of doped samples.

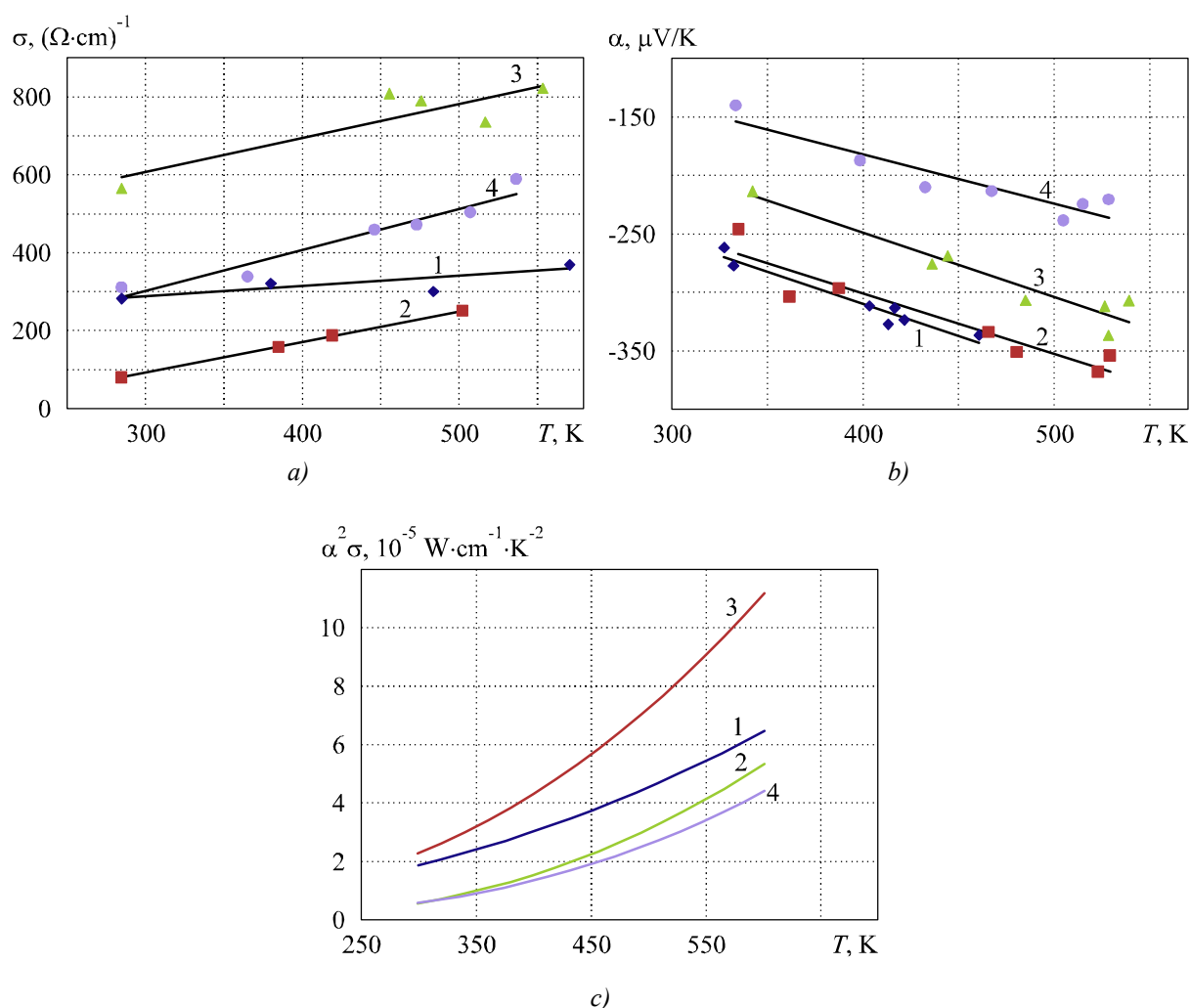


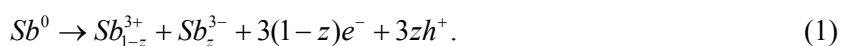
Fig. 2. The temperature dependence of electric conductivity σ (a), Seebeck coefficient α (b) and thermoelectric power $\alpha^2 \sigma$ (c) of $PbTe:Sb$. The content of Sb , at %: 1 (◆) – 0, 2 (■) – 0.1, 3 (▲) – 0.3, 4 (●) – 1.0.

Thus, based on the presented dependences, it can be stated that the optimal thermoelectric parameters are inherent in a material with impurity concentration 0.3 at.% Sb . The value of

thermoelectric power for samples made of such material at a temperature of ≈ 500 K is $\alpha^2\sigma \approx 70 \mu\text{W}/(\text{K}^2\text{cm})$, which is a fairly high figure.

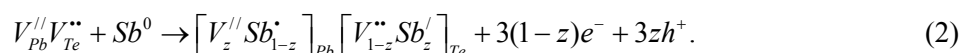
Crystal-chemical doping mechanisms

The behaviour of electron concentration depending on the content of *Sb* impurity can be related to the character of crystalline structure defect subsystem – the kind of point defects and their charge state [5]. The fact that *Sb* can occupy both lead and tellurium positions in *PbTe* crystalline structure can be described by its charge state disproportioning. *Sb*, when substituting lead in its sublattice, is a donor. In so doing, it is ionized from $Sb^0(5s^25p^3)$ state to $Sb^{3+}(5s^25p^0) + 3e^-$ state. Relative to Pb^{2+} sublattice, the impurity is in $Sb^{3+} \rightarrow Sb_{Pb}^{1+}$ state. In tellurium sublattice *Sb* is ionized as $Sb^0(5s^25p^3) \rightarrow Sb^{3-}(5s^25p^6) + 3h^+$ and is an acceptor, with that, relative to Te^{2-} sublattice the impurity is in $Sb^{3-} \rightarrow Sb_{Te}^{1-}$ state. Hence, impurity disproportioning will be written as follows:



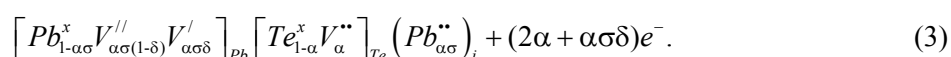
Here z is the value of *Sb* charge state disproportioning. It is the ratio between the concentrations of Sb^{3+} and Sb^{3-} that will determine the donor or acceptor effect of doping impurity.

In terms of crystal-quasi-chemical approach based on the concept of antistructure [10], doping cluster for *Sb* impurity under condition of *Sb* ions location both in the cation and anion sublattices will be represented as follows:

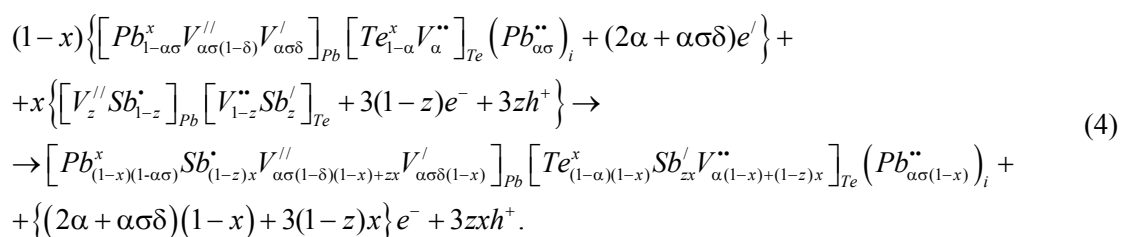


Here $V_{Pb}^{//}V_{Te}^{**}$ is *PbTe* antistructure, $V_{Pb}^{//}, V_{Te}^{**}$ are *Pb* and *Te* vacancies, respectively, e^- is electron, h^+ is hole, „ \bullet “, „ \prime “, „ \bullet “, „ \prime “, „ x “ are the negative, positive and neutral charges, respectively.

Crystal-quasi-chemical formula of *n-PbTe* with a complicated spectrum of point defects in the cation sublattice (single- and double-charge lead vacancies $V_{Pb}^{\prime}, V_{Pb}^{//}$), according to [11], is of the form:



Its superposition with the doping cluster will represent the crystal-quasi-chemical formula of *n-PbTe: Sb*:



Here, x is an atomic share of *Sb*, α is the value of initial deviation from stoichiometry on the side of *Pb*, δ is disproportioning coefficient of the charge state of lead vacancies, σ is the share of interstitial lead atoms.

The proposed doping mechanism and the obtained crystal-quasi-chemical formulae yield the analytical dependences of the concentration of individual point defects and current carriers on the deviation from stoichiometric composition in the basic compound α , the value of *Sb* atoms charge

state disproportioning z and its content x . Thus, according to crystal-quasi-chemical formula, full electroneutrality equation will be written as follows:

$$\begin{aligned} n + |q_{V_{Pb}''}|[V_{Pb}''] + |q_{V_{Pb}'}|[V_{Pb}'] + |q_{Sb_{Te}^{\prime}}|[Sb_{Te}^{\prime}] = \\ p + |q_{V_{Te}''}|[V_{Te}''] + |q_{Pb_i''}|[Pb_i''] + |q_{Sb_{Pb}^{\prime}}|[Sb_{Pb}^{\prime}], \end{aligned} \quad (5)$$

where $n = A((2\alpha + \alpha\gamma\delta)(1-x) + 3(1-z)x)$, $p = 3Azx$ $[Sb_{Te}^{\prime}] = Azx$, $[V_{Pb}''] = A(\alpha\sigma(1-\delta)(1-x) + zx)$, $[V_{Pb}'] = A\alpha\sigma\delta(1-x)$, $[Sb_{Pb}^{\prime}] = A(1-z)x$, $[V_{Te}''] = A(\alpha(1-x) + (1-z)x)$, $[Pb_i''] = A\alpha\sigma(1-x)$, $|q_{V_{Pb}''}| = |q_{Sb_{Pb}^{\prime}}| = |q_{Sb_{Te}^{\prime}}| = 1$, $|q_{V_{Pb}'}| = |q_{V_{Te}''}| = |q_{Pb_i''}| = 2$. Here, $A = \frac{2Z}{a^3}$, Z is the number of structural units in the unit cell, a is lattice parameter. The Hall concentration of current carriers n_H in this case will be determined as:

$$n_H = A|(2\alpha + \alpha\gamma\delta)(1-x) + 3(1-z)x - 3zx|. \quad (6)$$

Figs. 3 to 5 represent calculations of the Hall concentration of current carriers and the concentration of point defects in $PbTe:Sb$ crystals versus the impurity content and Sb atoms charge state disproportioning.

From the calculation of the Hall concentration (Fig. 3) it is seen that with the value of $z < 0.5$ the impurity has a donor effect ($[Sb_{Pb}^{1+}] > [Sb_{Te}^{1-}]$), and with the prevalence of antimony ions in tellurium positions ($z > 0.5$) – an acceptor effect. Thus, for the case of $z = 0.7$ with a growth in concentration of introduced impurity there is a decrease in the concentration of the major electrons, conversion of n - to p -type conductivity and further growth of hole concentration (Fig. 3 – curve 4). In the case of $z = 0.5$ (Fig. 3 – curve 3) there is full self-compensation of impurity (equal concentrations of Sb_{Pb}^{1+} and Sb_{Te}^{1-} ions) and the Hall concentration in both cases is reduced only marginally. The above behaviour peculiarities of the Hall concentration of current carriers versus the impurity content and its charge state are well illustrated in the space diagram (Fig. 4).

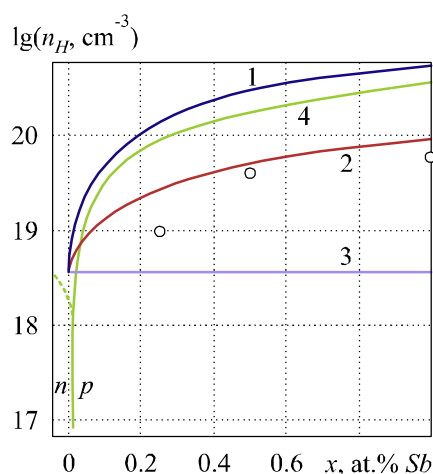


Fig. 3. The Hall concentration of current carriers in n-PbTe:Sb crystals versus Sb content for different values of Sb atoms charge state disproportioning z : 1 – 0.2; 2 – 0.45; 3 – 0.5; 4 – 0.7. The points correspond to experiment [7], the curves – to calculation.

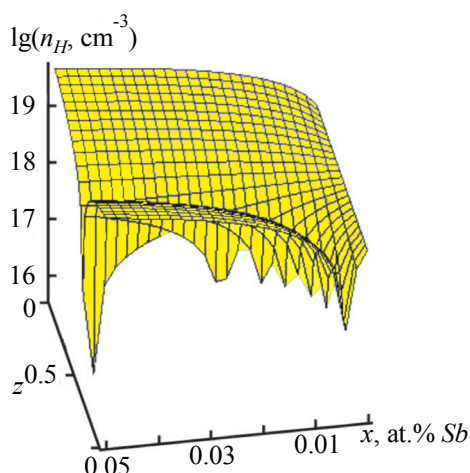


Fig. 4. Space diagram of the Hall concentration of current carriers for n-PbTe:Sb crystals versus the content of Sb x and the value of its charge state disproportionating z .

From the calculation of point defects concentration for the case of doping with Sb (Fig. 5) it is seen that the dominant defects are Sb ions introduced both into lead sublattice Sb_{pb}^+ and into tellurium sublattice Sb_{Te}^- of lead telluride, the concentration of which grows with increasing the content of Sb doping impurity. Considerable support to conductivity is also added by double ionized lead vacancies V_{pb}^{2-} and double charged tellurium vacancies V_{Te}^{2+} whose concentration grows with increasing the impurity content.

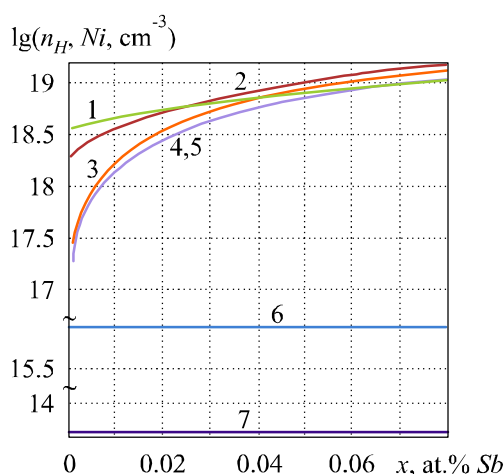


Fig. 5. The Hall concentration of current carriers ($1 - n_H$) and the concentration of dominant point defects N_i for n-PbTe:Sb crystals versus the content of Sb impurity (x) at $z = 0.45$.

$$N_i: 2 - [V_{Te}^{2+}]; 3 - [Sb_{pb}^+]; 4 - [Sb_{Te}^-]; 5 - [V_{pb}^{2-}]; 6 - [Pb_i^{2+}]; 7 - [V_{pb}^-]; 8 - [Te_i^0].$$

Analysis of investigation results

Based on the obtained experimental data, as well as the results of works [7, 12] on the donor impurity effect and taking into account possible models of crystal-chemical mechanisms of doping n-PbTe:Sb, it can be concluded that in our case the concentration of bismuth ions in Sb_{pb}^{1+} state is in excess over Sb_{Te}^{1-} concentration. In particular, by comparison of the experimental data of the Hall concentration in PbTe versus the content of Sb [7] with the calculations performed (Fig. 3), the value

of *Sb* impurity charge state disproportioning was determined as $z \approx 0.45$.

The character of obtained temperature dependences of the Seebeck coefficient corresponds to similar data in [12] and [7]. First, temperature growth causes an increase in the absolute value of α [7] and, second, on the concentration dependence of the Seebeck coefficient there is a maximum near the concentration of impurity 0.3 at.% *Sb* [12]. It is noteworthy that [7] dealt with investigation of crystalline samples cut of a synthesized ingot whose chemical formula is represented as $Pb_{1-x}Sb_xTe$. That is, the impurity was added with regard to substitution of lead atoms by *Sb* atoms. At the same time, in [12] the chemical formula of investigated samples obtained by the Bridgman method is represented as $PbTe+x$ at.% *Sb*. In so doing, at room temperature and equal impurity concentrations, the Seebeck coefficient value for samples investigated in [12] exceeds almost twice a similar value for samples investigated in [7].

This regularity is confirmed by the results of the present and one of our previous works [13]. That is, from the standpoint of α increase, doping with *Sb* by adding to stoichiometric charge of *PbTe*, is more efficient. In so doing, the fabrication technique of thermoelectric samples, namely cutting of synthesized ingot, cutting of ingot obtained by the Bridgman method or the use of metalloceramic method is not a governing factor for the Seebeck coefficient increase in the course of doping.

A change in the electric conductivity of samples with increasing amount of introduced impurity (Fig. 2.) is similar to that obtained in [7] and differs from a similar dependence obtained in [12]. Thus, according to [12], the increased number of *Sb* in *PbTe* causes a monotone reduction of σ value in the concentration range from 0 to 0.5 at.% *Sb*, whereas in [7] there was a growth in the electric conductivity of samples with increasing impurity concentration from 0.25 to 0.5 at.% *Sb* and its subsequent reduction at 1.0 at.% *Sb*. Note that the numerical value of the electric conductivity of undoped samples ($\approx 300 (\Omega \cdot \text{cm})^{-1}$) is close to the value represented in [12] ($\approx 400 (\Omega \cdot \text{cm})^{-1}$).

The temperature change in electric conductivity, unlike that represented in [7], is characterized by a positive slope. Representation of $\sigma(T)$ dependence in $\ln(\sigma) - 1/T$ coordinates allowed estimating the activation energies of conductivity which for samples doped with *Sb* in the amount of 0.1 and 0.3 at. % is $\approx (0.01 - 0.02)$ eV.

Assuming that at temperatures under study the dominant mechanism is electron scattering on optical phonons [14-15], based on the obtained $\alpha(T)$ dependences one can determine the position of the Fermi level which is one of the basic characteristics of semiconductor material and largely defines its kinetic properties. For this purpose, the Pisarenko formula valid for carrier concentrations less than 10^{19} cm^{-3} [7] was used in the form:

$$\alpha = \frac{k}{e} \left(\frac{5}{2} + r + \ln \left(\frac{N_C}{n} \right) \right) \tag{7}$$

$$= \frac{k}{e} \left(\frac{5}{2} + r + \ln \left(\frac{N_C}{N_C \cdot F_{1/2}(\mu, T)} \right) \right) = \frac{k}{e} \left(\frac{5}{2} + r - \ln(F_{1/2}(\mu, T)) \right).$$

Here, $N_C = (2\pi m_e^* kT / h^2)^{3/2}$ is the density of states in conduction band, $n = N_C \cdot F_{1/2}(\mu, T)$ is electron concentration in conduction band, $F_{1/2}(\mu, T)$ is the Fermi integral of order one-half.

From formula (7) we obtain $F_{1/2}(\mu, T) = \exp(5/2 + r - \alpha \cdot e / k)$. Then for impurity concentration 0.3 at.% *Sb* the chemical potential of electrons at a temperature of 300 K is 0.12 eV, and at 500 K – 0.05 eV. Accordingly, the electron concentrations are $\lg(n) = 18.6 \text{ cm}^{-3}$ and $\lg(n) = 18.1 \text{ cm}^{-3}$. In so doing, it is taken into account that the effective mass of electrons is a function of their concentration [16]:

$$m^* = m_0 \left(1 + \frac{2\mu}{E_g} \right). \quad (8)$$

Hence, crystals under study are weakly degenerate semiconductors where electron concentration decreases with a rise in temperature. The same $n(T)$ dependence was obtained in Ref. [7].

However, despite the position of the Fermi level, it is more reasonable to use instead of formula (7) the dependence

$$S = \frac{k}{e} \cdot \frac{\pi^2}{3} \frac{kT}{\mu} \left(r + \frac{3}{2} \right), \quad (9)$$

which is valid exactly for the degenerate semiconductors [1].

In this case, for the impurity concentration 0.3 at % Sb the chemical potential of electrons at temperatures 300 K and 500 K is 0.075 eV and 0.080 eV, and the respective electron concentrations found with the use of a numerical calculation of the Fermi integral are equal to $\lg(n) = 18.54 \text{ cm}^{-3}$ and $\lg(n) = 18.97 \text{ cm}^{-3}$. As with the use of (7), the effective mass dependence on their concentration was taken into account according to (8). Hence, with the use of (9) the electron concentration increases with a rise in temperature.

From the analysis of the calculated temperature dependence $n(T)$ represented in coordinates $\ln(n) - 1/T$ the activation energy 0.01 eV was obtained for PbTe crystals with Sb content 0.3 at. % Sb. Taking into account the proximity of determined activation energies from the temperature dependences of electric conductivity and electron concentration, it can be concluded that the main factor of σ growth is activation of electrons from defect levels, which is also confirmed by crystal-chemical analysis.

The obtained n values and represented in Fig. 2 $\sigma(T)$ dependences were used to determine the electron mobility. In particular, at impurity concentration 0.3 at.% Sb and temperatures 300 K and 500 K the values of μ are equal to $\approx 1180 \text{ (cm}^2/\text{V}\cdot\text{s)}$ and $\approx 540 \text{ (cm}^2/\text{V}\cdot\text{s)}$, respectively. Such high mobilities can testify to structural perfection of the obtained crystals.

It is noteworthy that the calculations performed are of approximate nature due to the fact that the semiconductor is weakly degenerate and the employed formulae are valid for material which is nondegenerate (7) and strongly degenerate (9). Besides, the Fermi integral used for the calculation of F and n , is represented in the approximation $E \sim k^2$, whereas in reality the conductivity band of PbTe is not parabolic.

Conclusions

1. Synthesis was conducted and the temperature dependences of the electric conductivity and the Seebeck coefficient of Sb doped lead telluride $n\text{-PbTe:Sb}$ were studied. It was established that doping promotes improvement of the basic thermoelectric characteristics of material.
2. Based on the proposed crystal-quasi-chemical formulae for nonstoichiometric crystals $n\text{-PbTe:Sb}$ taking into account a complicated spectrum of point defects in lead telluride (V_{Pb}^{2-} , V_{Pb}^{1-} , V_{Te}^{2+} , Pb_i^{2+} , Te_i^0) and different charge state of impurity atoms Sb^{3+} and Sb^{3-} , it was established that doping mechanism consists in the substitution by Sb atoms of both cation and anion vacancies, and its donor effect is determined by prevailing substitution by Sb atoms of cation vacancies ($[Sb_{Pb}^{1+}] > [Sb_{Te}^{1-}]$). The value of Sb impurity charge state disproportioning is $z = 0.45$.

3. Optimal parameters required of a material for n -legs of thermoelectric converters are inherent in lead telluride samples with the concentration of 0.3 at.% Sb, the thermoelectric power of which at a temperature of ≈ 500 K is $\alpha^2\sigma \approx 70 \mu\text{W}/(\text{K}^2\cdot\text{cm})$. The obtained samples possess a perfect structure, as evidenced by high values of current carrier mobility ($\approx 540 \text{ cm}^2/\text{V}\cdot\text{s}$).

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