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CHARGE CARRIER SCATTERING MECHANISMS IN THERMOELECTRIC PbTe:Sb

On the basis of the results of radiographic researches and measurements of thermoelectric parameters of antimony-doped lead telluride, such as the thermoelectric coefficient and the conductivity, the penetration mechanisms of impurity atoms into the crystal lattice of the matrix are established. The influence of impurity on the charge carrier mobility is revealed. The introduction of impurities up to 0.3 at.% is shown to favor the electron mobility owing to the filling of tellurium vacancies, which are active scattering centers, by antimony ions, the effect of which on the electron mobility is lower.

Keywords: lead telluride, doping, scattering mechanisms.

1. Introduction

Lead telluride (PbTe) is a promising thermoelectric material for medium-temperature (500–700 K) converters of thermal energy [1–3]. The basic operational characteristics of PbTe can be improved by modifying its chemical composition, in particular, by doping it with antimony [4–8].

According to the data of work [9], the elements of group V in the Periodic table are donors with respect to PbTe and stimulate a substantial growth of its conductivity. However, it was found that the fraction of electrically active atoms is substantially lower than the number of introduced ones. This can be explained by either the formation of electrically inactive complexes (of the Sb_2Te_3 type) in the compound lattice or the impurity distribution between the cation sublattice, where it is a donor, and the anion one, where it may probably be an acceptor [7, 10–12].

In work [5] on the basis of quasichemical crystal analysis of doped PbTe:Sb crystals, it was shown that the model of impurity atom redistribution between the metal and chalcogene sublattices can correctly explain the temperature dependence of the charge carrier concentration at the quantitative level, which makes it possible to draw a conclusion about its adequacy. However, the theoretical analysis of the defect subsystem, which was carried out in work [5], does not allow one to determine the influence of technological conditions on the ratio of atomic distributions between the sublattices and to explain why, at the simultaneous filling of cation and anion positions, the donor defects $[\mathrm{Sb}_{\mathrm{Pb}}^{1+}]$ prevail and the material is characterized by the electron type of conductivity. Moreover, since the growth of the conductivity, which is observed at the doping of lead telluride with antimony [5], can follow from the increase of both charge carrier concentration and mobility, it is expedient to analyze possible models describing the influence of Sb on the properties of PbTe with regard for both those quantities.

Besides other parameters, the influence of the impurity on the thermoelectric characteristics of crystals may substantially depend on the procedure of experimental specimen preparation. In the majority of known works (see, e.g., works [6, 7]), single-crystalline PbTe:Sb specimens or specimens cut off from polycrystalline PbTe:Sb ingots were studied. At the same time, in thermoelectric converters, thermoelements fabricated by metal-ceramic methods are mainly used. Therefore, the research of specimens prepared by pressing a PbTe:Sb powder is of much higher practical interest. The solution, at least partial, of the described problems would make it possible to improve the fabrication technology of thermoelectric materials on the basis of doped lead telluride with prescribed properties and to considerably improve its basic operational parameters.

2. Experimental Technique

Specimens of pure and doped lead telluride were prepared by directly alloying previously purified components in evacuated quartz ampoules [5, 8]. The obtained material was ground in an agate mortar and, after extracting the fractions with grain sizes of 0.05–0.5 mm, pressed under a pressure of 0.75 GPa. As a result, we obtained cylindrical specimens with the diameter $d = 5$ mm and the length $l = 5\div10$ mm. Afterward, the specimens were annealed in air for 5 h at a temperature of 500 K.

The phase composition of the obtained material was determined using radiography methods on a DRON-3 installation. Cu K_α radiation at ($\lambda = 1.5418$ Å) was applied. The specimen were studied within the powder method in the continuous scanning mode in the angular range $2\theta = 15\div90°$ at a rate of 1°/min. The time constant was $\tau = 1$ s, and the digitizing rate of output detector signals was 1 s^{-1}. As a monochromator, we used a single crystal of pyrolytic graphite placed on the path of a diffracted beam. The diffraction spectra were processed (smoothing, background extraction, determination of peak angular positions of peaks, indexing of diffraction patterns, and calculation of unit cell parameters) with the software package DHN_PDS.

The thermoelectric coefficient α and the specific conductance σ were determined following the standard techniques described in work [5] in detail. The specimen to study was placed into an oven between two copper rods, and one of them was heated to create a temperature gradient (of about 10 K/cm) across the specimen. The temperature was measured with two chromel-alumel thermocouples inserted into holes drilled in the specimen. The conductivity was determined by measuring the dc voltage drop across the specimen. In so doing, one of the wires of each thermocouple was used as a current guide. The maximum relative errors of measurements for α and σ amounted to 10 and 15%, respectively.

3. Experimental Results

The results of x-ray phase researches are depicted in Fig. 1. No diffraction lines from separate components (lead, tellurium, or their oxides) were revealed. While comparing the obtained diffraction patterns with the theoretical one, a relative enhancement of the intensity I of some diffraction reflections and a weakening of the others were observed. In particular, the ratio $I(200)/I(220)$ was characterized by a nonmonotonic dependence with a minimum at an impurity content of 0.3 at.%Sb. It is important to note that, for this content, the difference between the relative intensities of reflections in the experimental and theoretical diffraction patterns is typical not only of the 200 and 220 reflections, but also of all others.

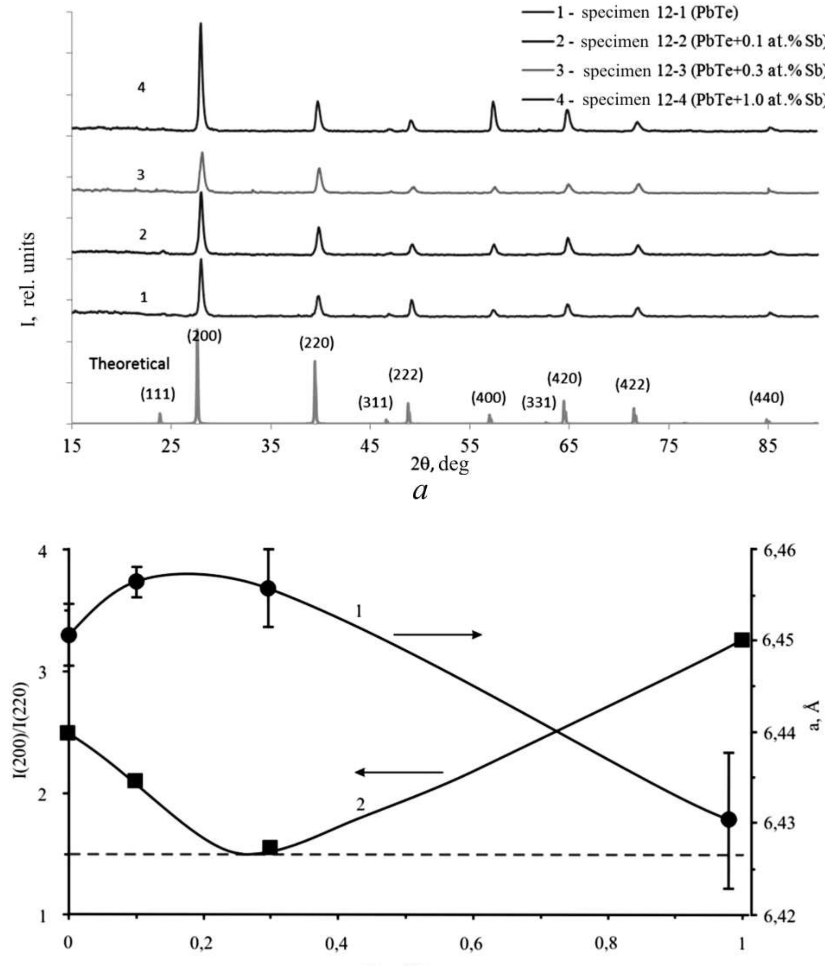
Attention is also attracted by the nonmonotonic dependence of lattice parameter a on the number of introduced antimony atoms (Fig. 1,*b*). Up to an impurity concentration of 0.2 at.%Sb, the parameter a of the PbTe lattice grows, whereas, at concentrations higher than 0.3 at.%Sb, it diminishes.

The fabricated thermoelectric specimens had conductivity of the n-type (Fig. 2). The specific conductance increased from the values $\sigma \approx 100\div200$ $\Omega^{-1}\cdot$cm^{-1} for pure to $\sigma \approx 700\div800$ $\Omega^{-1}\cdot$cm^{-1} for lead telluride doped to 0.3 at.%Sb. The thermoelectric coefficient α decreased as the amount of introduced impurity increased; however, the absolute value of α remained rather high (about $250\div300$ μV/K at $T \approx 500$ K). The impurity concentration growth to 1.0 at.%Sb resulted in a substantial reduction of both the thermoelectric coefficient and the specific conductance in the examined specimens.

The temperature dependences of the specific conductance, in contrast to those of the thermoelectric coefficient, are characterized by different slopes. The activation energies determined on their basis amount to 0.01, 0.06, 0.02, and 0.03 eV for specimens with impurity concentrations of 0, 0.1, 0.3, and 1.0 at.%Sb, respectively.

4. Analysis of the Results Obtained

The relative variation of the ratios between the diffraction reflection line intensities in the studied materials with different impurity contents (Fig. 1, *a*) can be explained by either the orientational alignment of crystallites formed at the melt crystallization, which has not been completely destroyed in the course of



a

b

Fig. 1. (*a*) Comparative diffraction patterns of lead telluride with various antimony impurity contents. (*b*) Dependences of the unit cell period a (circles) and the diffraction reflection intensity ratio $I(200)/I(220)$ (squares) in PbTe:Sb specimens on the Sb impurity content. The dashed line corresponds to the intensity ratio for the theoretical diffraction pattern

the powder preparation for the analysis [5], or the features in the impurity atom redistribution between the anion and cation sublattices. However, our theoretical calculations did not allow us to reveal a considerable influence of such a redistribution on the change of diffraction peak intensities at the studied impurity concentrations. Therefore, this effect is most likely associated with the orientational crystallization.

A probable explanation of the nonmonotonic concentration dependence of the lattice constant consists in different insertion mechanisms of antimony impurity atoms into the lead telluride crystal lattice at different doping levels. For instance, the stable n-type of obtained pure PbTe may probably result from a considerable number of tellurium vacancies of the donor type, with their formation giving rise to a little smaller value of lattice period in comparison with a value of 6.46 Å for the stoichiometric substance [13]. A certain growth of the lattice parameter as the impurity concentration increases to 0.3 at.%Sb is related to the filling of tellurium vacancies by Sb^{3+} ions. At a concentration of 0.3 at.%Sb, all tellurium

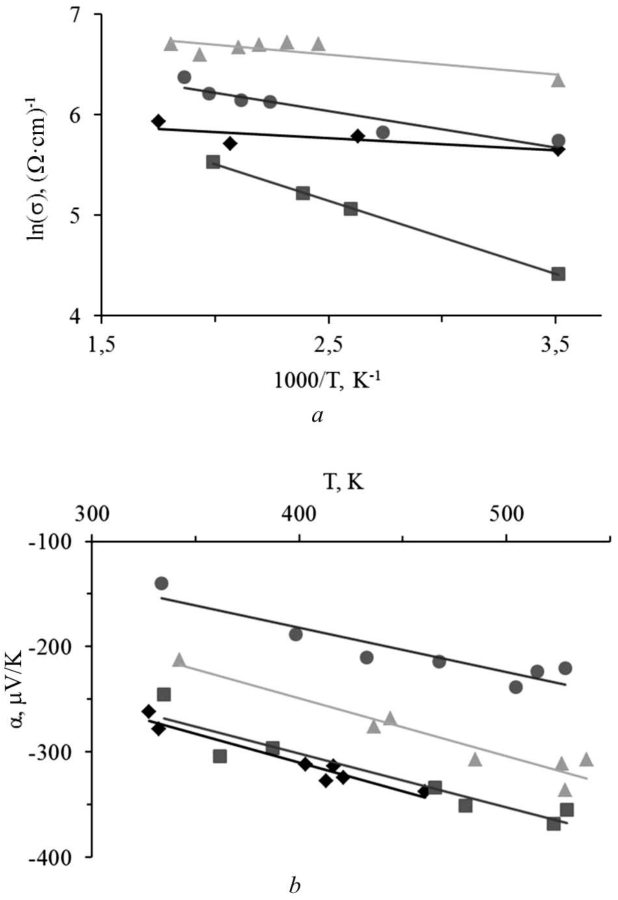


Fig. 2. Temperature dependences of (a) the specific conductance σ and (b) the thermoelectric coefficient α for PbTe:Sb specimens with various Sb contents: 0 (♦), 0.1 (■), 0.3 (▲), and 1.0 at.%Sb (●)

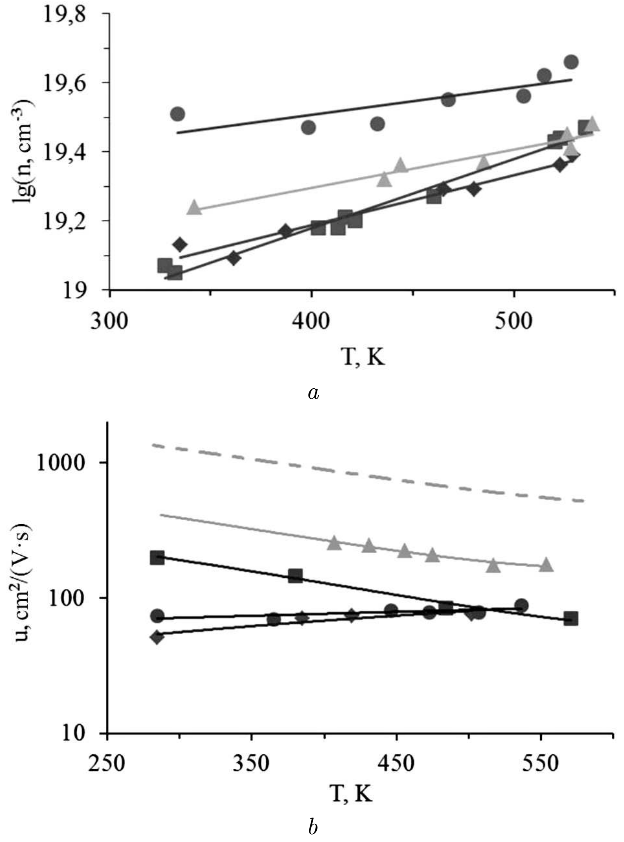


Fig. 3. Temperature dependences of (a) the electron concentration n and (b) the electron mobility u for PbTe:Sb specimens with various Sb contents: 0 (♦), 0.1 (■), 0.3 (▲), and 1.0 at.%Sb (●)

vacancies become filled with antimony atoms, which makes the value of parameter a maximal and provides the similarity between the experimental diffraction pattern obtained for the specimen with the indicated impurity content and the theoretical one (Fig. 1, b).

At impurity concentrations higher than 0.3 at. % Sb, the vacancies in both the cation and anion sublattices are filled. As a result, a reduction of the lattice parameter is observed, because the ionic radii of Sb^{3+} ($r_{\text{ion}} = 0.90$ Å) and Sb^{3-} ($r_{\text{ion}} = 2.08$ Å) are smaller than the ionic radii of Pb^{2+} ($r_{\text{ion}} = 1.26$ Å) and Te^{2-} ($r_{\text{ion}} = 2.10$ Å), respectively [14].

The results of structural researches are confirmed by the measurement data of thermoelectric properties. For instance, an optimal, from the viewpoint of material conductivity enhancement, doping level of 0.3 at.%Sb can be explained by either a higher concentration of charge carriers n in this specimen or their higher mobility u. The charge carrier concentration was determined with regard for a nonparabolic character of the conduction band by the formula [15]

$$n = \frac{(2m_{d,0}kT)^{\frac{3}{2}}}{3\pi^2\hbar^3} I^0_{3/2,0}\,(\eta,\beta). \qquad (1)$$

Here, $m_{d,0} = N^{\frac{2}{3}}\left(m^*_{\parallel}\right)^{1/3}\left(m^*_{\perp}\right)^{2/3}$ is the effective mass of the density of states at the conduction band bottom, N is the number of ellipsoids, $I^0_{3/2,\ 0}\,(\eta,\beta)$ is the Fermi integral, $\eta = \frac{\mu}{k_0T}$, $\beta = \frac{k_0T}{E_g}$, μ is the Fermi energy, and E_g is the energy gap width. Under the condition of polar electron scattering by optical phonons, which dominates in the studied crystals [16], the Fermi energy can be found on the basis of experimental thermoelectric data, $\alpha_{\exp}(T)$, and the dependence [15]

$$\alpha = -\frac{k}{e}\frac{\pi^2}{3}kT\left[(r+1)\frac{E_g+2\mu}{\mu\,(E_g+\mu)} - \frac{4}{E_g+2\mu}\right]. \tag{2}$$

At the same time„ the approximation of the calculated dependences $n(T)$ by linear functions allowed us, using the experimental dependences $\sigma_{\exp}(T)$, to determine the charge carrier mobility from the relation

$$u(T) = \frac{\sigma_{\exp}(T)}{e_0 n(T)}. \tag{3}$$

One can see from Fig. 3, *a* that the charge carrier concentration grows with the amount of the introduced impurity. . Electrons are characterized by the maximum mobility in the specimens with an impurity content of 0.3 at.%Sb (Fig. 3, *b*). Figure 3, *b* also exhibits the results of theoretical calculations for the mobility of charge carriers scattered by polar optical phonons (the dashed curve) carried out according to the formula [15, 17, 18]

$$u = \frac{e}{m_n\left(1+\frac{2\mu}{E_g}\right)}\frac{\hbar^2}{2e^2k_0T\left(\frac{1}{\chi_\infty}-\frac{1}{\chi_0}\right)}\sqrt{\frac{2\mu\left(1+\frac{\mu}{E_g}\right)}{m_n\left(1+\frac{2\mu}{E_g}\right)^2}}. \tag{4}$$

Here, m_n is the effective mass at the conduction band bottom in one ellipsoid, and χ_∞ and χ_0 are the high-frequency and static dielectric permittivities, respectively.

The theoretically calculated values of charge carrier mobility u turned out almost identical for specimens with different impurity contents. In addition, the specific values turned out higher than the corresponding values calculated on the basis of experimental data. This fact testifies to a substantial contribution of other scattering mechanisms. The influence of those mechanisms is the largest for the specimens with impurity concentrations of 0.1 and 1.0 at.%Sb, because the difference between the mobility values calculated by formulas (3) and (4) is the largest in those two cases. Different slopes of the temperature dependence $u(T)$ for the specimens with impurity concentrations of 0.1 and 1.0 at.%Sb, on the one hand, and 0 and 0.3 at.%Sb, on the other hand, point to a considerable contribution of the scattering by impurities. This conclusion is also confirmed by the fact that the scattering by lattice vibrations should not give rise to changes in the temperature behavior of the mobility, so that the dependence $u(T)$ should be qualitatively similar to the theoretical curves, which is observed, however, only for the specimens with impurity concentrations of 0 and 0.3 at.%Sb.

Hence, at impurity concentrations below 0.3 at. % Sb, electrons are actively scattered by polar optical phonons, as well as tellurium vacancies and antimony ions located at tellurium sites. Owing to a high dielectric permittivity of PbTe, the efficiency of the charge carrier scattering by charged centers is lower in comparison with lattice deformations induced by point defects. In other words, tellurium vacancies are more effective charge carrier scattering centers than impurity ions, provided their identical concentrations. This conclusion is partially confirmed by the results of work [16], where it was shown that the Coulomb potential of tellurium vacancies affects the mobility of charge carriers much weaker than its short-range component does. At a concentration of 0.3 at.%Sb, tellurium vacancies are filled with antimony atoms, which results in rather high mobility values. The growth of antimony ion concentrations in both sublattices enhances the role of the scattering mechanism by ionized impurities owing to the increase of their concentration and results in a reduction of the charge carrier mobility.

It is worth noting that, should the described mechanism of doping really take place, the optimum concentration of the impurity would change depending on the concentration of tellurium vacancies, which is determined by the stoichiometry of synthesized lead telluride.

5. Conclusions

1. The nonmonotonic behavior of the PbTe lattice parameter, which was observed as the concentration of antimony doping atoms increased, is found to result from different mechanisms of impurity introduction into the PbTe crystal lattice. At concentrations below 0.3 at.%Sb, antimony atoms fill tellurium vacancies, whereas, at higher concentrations, vacancies in the anion and cation sublattices are filled simultaneously.

2. The maximum value of the specific conductance in PbTe with an impurity concentration of 0.3 at.%Sb

is demonstrated to result from the increase of the electron mobility in the material owing to a reduction of their scattering at the short-range potential of tellurium vacancies, the concentration of which decreases, since they become filled with antimony ions.

3. Specimens of lead telluride with an impurity concentration of 0.3 at.%Sb turn out to have optimum parameters for their use as a material for n-branches in thermoelectric converters. They are characterized by the specific conductance $\sigma \approx 700 \div 800\ \Omega^{-1}\cdot \mathrm{cm}^{-1}$ and the thermoelectric coefficient $\alpha \approx \approx 200 \div 300\ \mu\mathrm{V/K}$ in the temperature interval $T \approx \approx 300 \div 500$ K.

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МЕХАНІЗМИ РОЗСІЮВАННЯ НОСІЇВ ЗАРЯДУ У ТЕРМОЕЛЕКТРИЧНОМУ PbTe:Sb

Резюме

На основі результатів рентгенографічних досліджень та вимірювання термоелектричних параметрів (коефіцієнта термо-ерс α та питомої електропровідності σ) легованого сурмою плюмбум телуриду, встановлено механізми входження домішкових атомів у кристалічну ґратку матриці та їх вплив на рухливість носіїв заряду. Показано, що введення домішки в кількості до 0,3 ат.% сприяє зростанню рухливості електронів внаслідок заповнення вакансій телуру, які є активними розсіюючими центрами, іонами стибію, вплив яких на рухливість є меншим.