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Scattering Mechanisms in pressed PbTe

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The results of studies of structural and thermoelectric properties obtained by the powder pressing method of PbTe samples are presented. In order to interpret the obtained results, a theoretical calculation of the specific conductivity and the Seebeck coefficient was performed on the basis of a model that takes into account two types of free charge carriers. Conclusions have been made about the mechanisms of carrier scattering.

Keywords: plumbum telluride, thermoelectric properties, scattering mechanisms.

Introduction

Lead semiconductor material A^4B^6 is used to create thermoelectric modules operating in the 200 - 500°C temperature range [1-4]. Analysis of published data shows that alternative materials that are less effective or much more expensive. Therefore, modification of the properties of PbTe to improve its thermoelectric parameters remains urgent task.

Preferably, PbTe obtained by pressing the powder is used to create thermocouples. Given the correct choice of technological parameters of obtaining such a material has several advantages over single crystalline, in particular, improved mechanical properties. However, the pressing process itself, the influence of its individual stages on the properties of the material are poorly understood. Such information can be used to optimize the technological factors of obtaining a material and to increase its thermoelectric figure of merit.

In articles [6-7], PbTe samples were obtained by cold pressing at 2 GPa. It is shown that the samples obtained at room temperatures are characterized by a p-type of conductivity, which changes with n-type with increasing temperature due to the manifestation of its own conductivity with the predominance of the electronic component. The p-type conductivity of the material at low temperatures is explained by the interaction of the material with oxygen, since some technological operations took place in the air [7]. It has been established that annealing of the samples at 500 °C

leads to recrystallization of the samples, which causes, in particular, an increase in their specific electrical conductivity. It should be noted that the parameter of the elementary cell of the material changes during the operations within the error, as well as the Hall concentration of carriers [6]. Thus, it can be assumed that the defective subsystem of samples does not change during technological operations, and the modification of thermoelectric parameters is caused only by recrystallization of grains.

The analysis of the obtained experimental dependences [6] was performed in [7]. In particular, it is shown that scattering on acoustic phonons is decisive in the formation of kinetic properties of current carriers (heavy holes) in the samples at temperatures up to 200 °C. Under certain technological conditions of sample preparation, the effect of thermoelectronic emission of carriers between grains on their kinetic properties is also possible. The conclusion drawn in [7] is partly consistent with the literature data. Thus, [8] found that light holes scatter on acoustic and polar optical phonons, while heavy holes only scatter on acoustic phonons. According to [8], in particular, the electrons in the temperature range 77 - 300 K are mainly scattered on the acoustic vibrations of the lattice [9]. The additional analysis thus requires the influence of thermoelectronic emission of carriers between grains, since the temperature range studied is relatively high, as for the manifestation of this mechanism.

The purpose of this work is a consistent theoretical analysis of the temperature dependences of the specific

electrical conductivity and the Seebeck coefficient for the samples described in [6, 7] and new ones obtained under other technological conditions.

I. Methods of experimental research

The complex of studies was performed for the samples obtained by cold pressing in air at pressure (1.5 GPa and 2.0 GPa) and hot pressing (T = 250 ºC) in argon at a pressure of 0,5 GPa, followed by annealing of the pressed samples at T = 500 ºC.

PbTe synthesis was carried out according to the following scheme: heating the charge to 500 °C for 0.5 h (holding 1 h), heating to 700 °C for 0.5 h (holding 3 h), heating to 1020 °C for 0.5 h (holding 1 h), cooling to 900 °C for 0.5 h, cooling outside the oven. AlfaAesar tellurium and lead (manufactured by Germany) were used for the synthesis. The content of the basic substance is the Te 99.999 wt. %, and Pb – 99.99 wt. %.

The resulting ingots were ground in a Pulverisette 6 automatic mill and fractions (0.05-0,5) mm were selected for sample production on the AS200 screening machine.

Techniques for studying structural thermoelectric properties are described in detail in [6].

II. Research results and their analysis

The synthesized ingots were characterized by a bright metallic luster, without visible macrodefects (Figs. 1a, 1b). Samples for measurements of electrophysical parameters were extruded from fractions (0.05 - 0.5) mm. From the analysis of micrographs of the surface of the ingots, it can be stated that grains of this size are most likely to be monoblocked with a small amount of crystallites.

On the basis of SEM studies, the effect of recrystallization of the pressed sample upon annealing at 500 °C was confirmed (Fig. 1c, 1d). The density of pressed 1.5 GPa samples is slightly lower than in the case of samples pressed at a pressure of 2 GPa [7], which, depending on other technological factors, is $\rho A = (8.05 - 8.15)$ g / cm3 and is ≈ 97 % of the x-ray density.

According to the results of radiographic studies, in the selected modes of synthesis, the obtained ingots were single-phase, the parameter of the unit cell a = 6.4591 (2) Å. The change of this value during powder pressing and annealing of the obtained samples at temperatures of 500 ˚C is within the error of the experiment ($a_{après+annealing} = 6.4589(2)$ Å), which may indicate the stability of the defective subsystem under such conditions. In addition, a comparative analysis of the structure of the reflex (220) of the ingot and the pressed PbTe sample (Fig. 2) makes it possible to conclude that there are no differences that could be caused by grinding, pressing or annealing stresses

Due to the polycrystallinity of the samples, the analysis of changes in the unit cell parameter at the level of 0.010 Å is complicated by a number of uncontrolled factors. However, on the other hand, obtaining series of
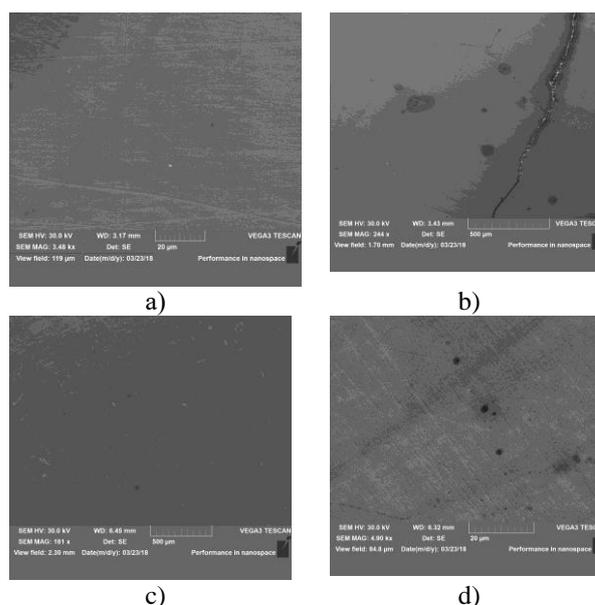

Fig. 1. SEM images of polished and etched surface of ingot PbTe (a, b) and pressed at a pressure of 1.5 GPa and annealed at 500 ° C samples of PbTe (c, d).
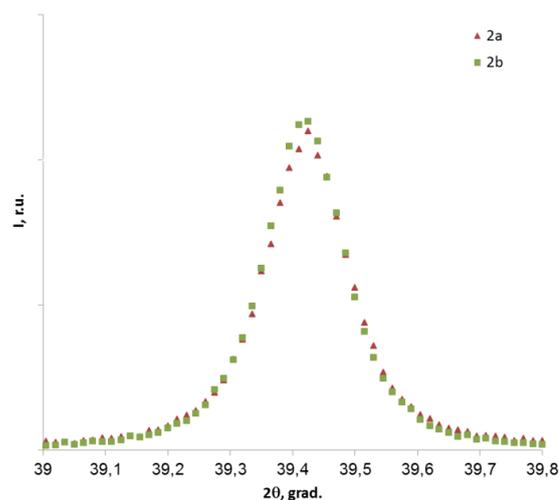

Fig. 2. Comparison of X-ray diffraction reflexes (220) of two samples obtained by the methods: cold pressing in argon and not annealed (2a) and hot pressing in argon at 250 °C and annealed at 500 °C (2b).

samples, both in this paper and previous ones [6], with the same parameters within the unit cell, within the errors, may indicate that we still control most of these factors.

The results of measurement of thermoelectric parameters are presented in Fig. 3. It can be seen that qualitative differences in the dependences α (T), σ (T) for the samples obtained by cold pressing in air and hot pressing in argon are not observed (Fig. 3). On the basis of such results, it can be concluded that the p-type conductivity of the samples to a measurement temperature of 250°C is caused, probably, by point defects of the crystal lattice, and not by an admixture of oxygen, which could enter the sample at separate stages of its preparation, as was supposed in [7].

Reducing the compression pressure from 2.0 GPa to

1.5 GPa leads to a decrease in the electrical conductivity throughout the studied temperature range without qualitatively changing the dependence of σ (T). As can be seen from Fig. 3, the annealed sample, which was compressed at a pressure of 1.5 GPa (2a *), has the same electrical conductivity as the sample obtained at a pressure of 2 GPa and is not annealed (XV 3, XVI 1Sa).

The Seebeck coefficient of annealed specimens slightly depends on the previous conditions of their receipt. For unannealed samples α (T) changes sign at a lower temperature. At the same time, qualitative changes in this dependence are not observed. The thermal conductivity of cold-pressed samples is relatively low. And when using the hot pressing method the coefficient of thermal conductivity is doubled.
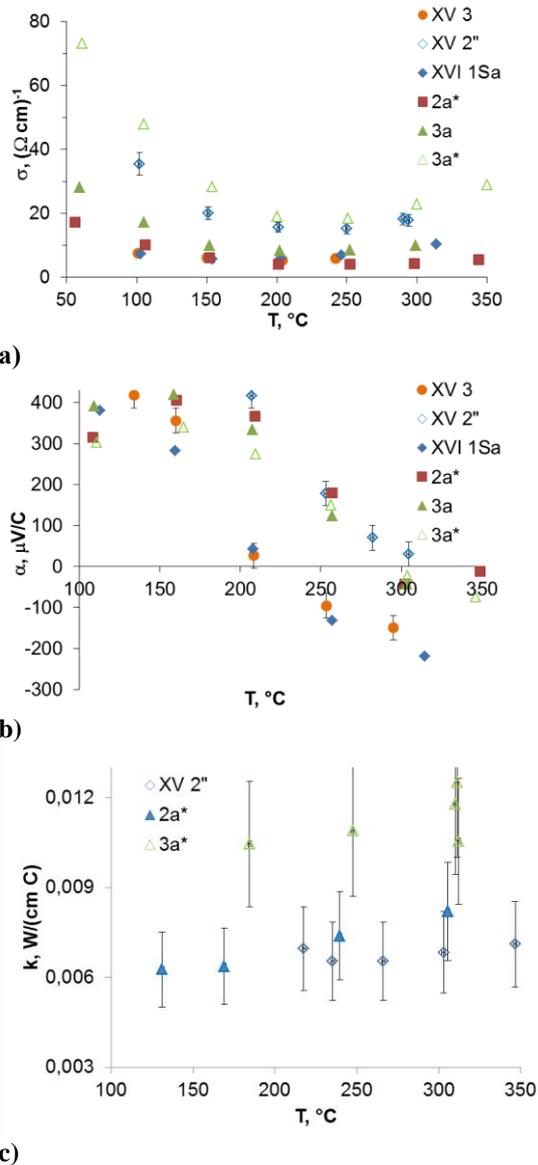

a)

b)

c)

Fig. 3. The temperature dependences of the electrical conductivity σ (a), the Seebeck coefficient α (b) and the thermal conductivity k (b) of the PbTe samples obtained under different technological conditions:XV 3, XVI 1Sa – cold pressing in air (2,0 GPa), unannealed; XV 2* – cold pressing in air, annealed at 500 ˚C; 2a* – cold pressing in argon (1.5 GPa), annealed at 500 ˚C, 3a – hot pressing in argon at 250˚C (0.5 GPa), 3a* – hot pressing in argon at 250 ˚C (0.5 GPa), annealed at 500 ˚C.
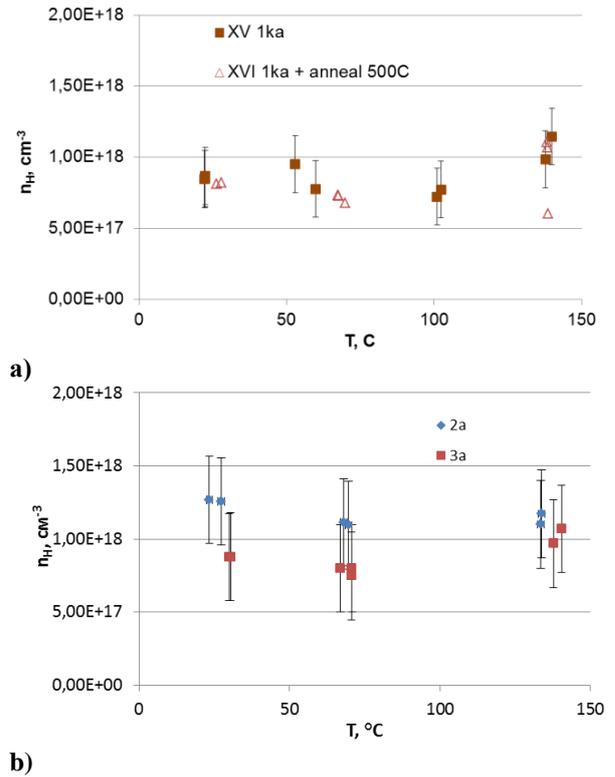

a)

b)

Fig. 4. a - temperature dependences of the Hall concentration of carriers in typical samples pressed at a pressure of 2 GPa (1ka – unannealed sample, 1ka+anneal 500 ˚C – annealed at 500 ˚C sample). b – The dependence of the Hall concentration of carriers on the temperature of cold-pressed and hot-pressed PbTe samples (2a* – cold. press. in the air + annealing 500 ˚C, 3a – hot press. in argon at 250 ºC).

Regarding the concentration of carriers, there are some differences in the properties of the samples obtained at compression pressures of 1.5 and 2.0 GPa. Thus, for samples of pressed at higher pressure, the Hall concentration of carriers is $\approx 1 \cdot 10^{18}$ cm^{-3} regardless of whether or not the sample was annealed (Fig. 4,a). In the case of samples obtained at a pressure of 1.5 GPa, annealed samples were always characterized by a concentration of $\approx 1 \cdot 10^{18}$ cm^{-3} (Fig. 4,b), whereas in unannealed samples the carrier concentration could vary within $(0.3 – 1.0) \cdot 10 \cdot 18$ cm^{-3}, although it was usually in the vicinity of the values characteristic of the annealed specimen.

Thus, regardless of the technological conditions of obtaining the sample (within the variations studied), the concentration of carriers remains constant within an error value of $\approx 1 \cdot 10^{18}$ см$^{-3}$. Together with the invariance of the parameter of the unit cell with the same variations of the technological factors of obtaining the sample, we can conclude that the defective subsystem, in particular the concentration of dominant point defects, which determine the numerical value of n_H, does not change. This conclusion requires additional experimental confirmation. But its importance is that the selected technological parameters allow to obtain mechanically stable samples without destroying the defective subsystem formed at higher temperatures during
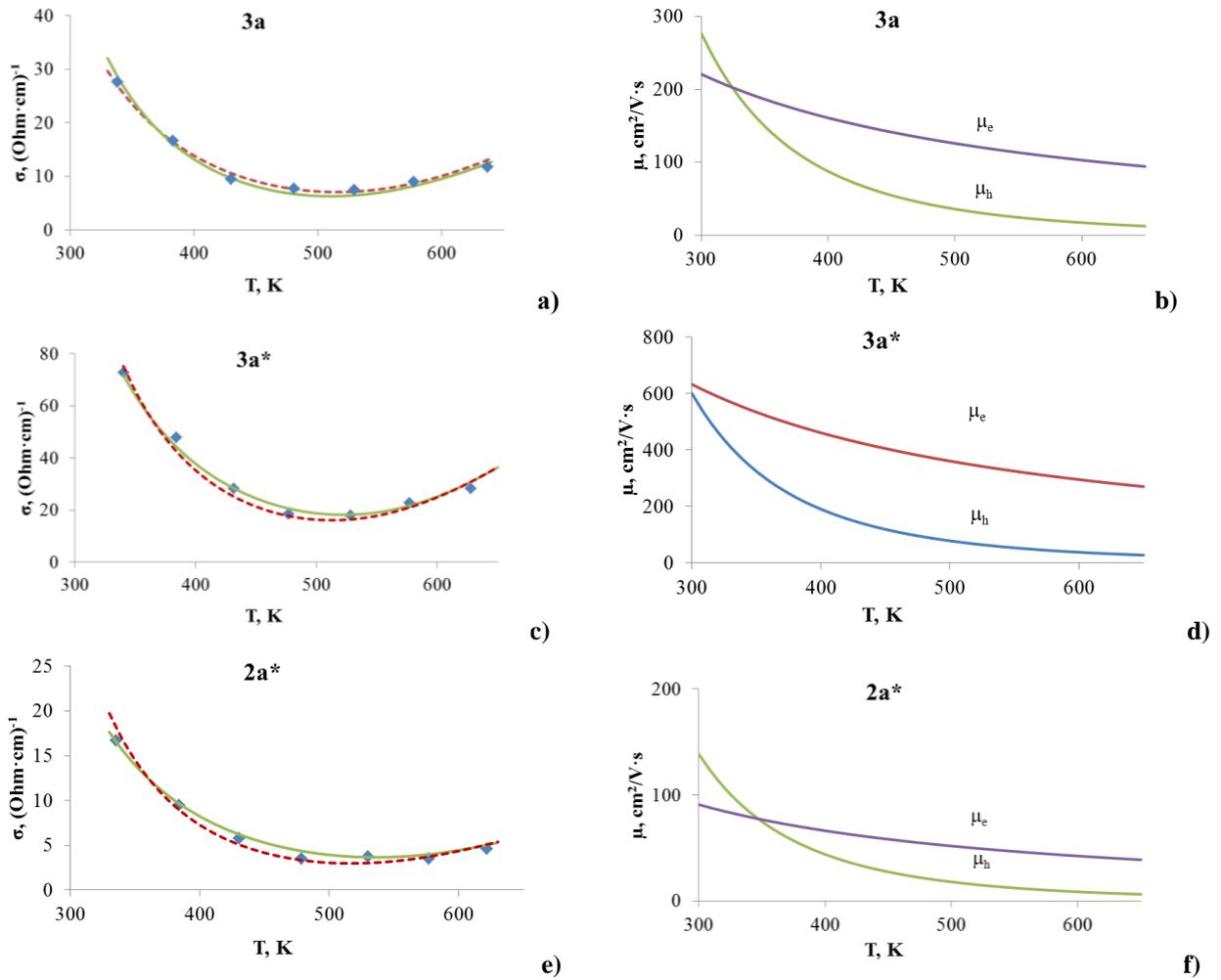
Fig. 5. a, c, e – are the experimental (♦) and calculated thermal dependences of the specific conductivity for the samples PbTe 3a, 3a *, 2 *: solid curve () is calculated using optimal (approximate) parameters; dashed curve (- -) - calculation for model case r_e = -1.1, r_h = -4.0. **b, d, f** – are calculated for the case of model r_e = -1.1, r_h = -4.0 electron and hole mobility for PbTe 3a, 3a*, 2* samples.
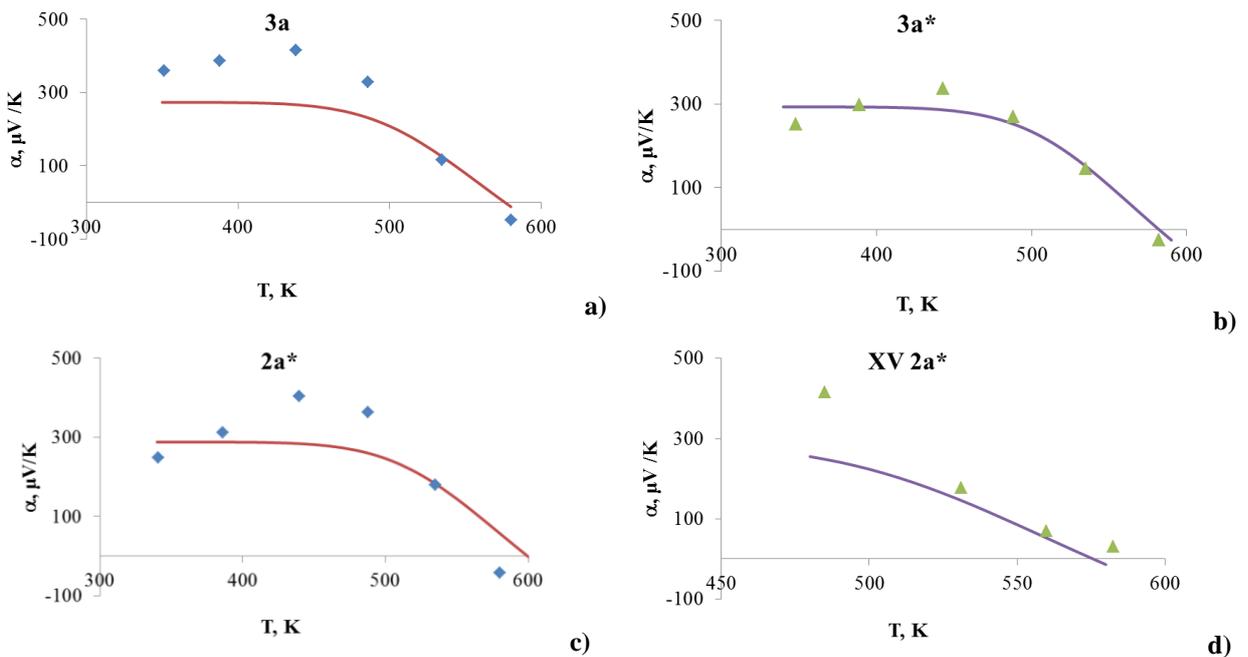

Fig. 6. The experimental temperature dependences of the Seebeck coefficient and calculated according to formula (12) for the case of model r_e = -1.1, r_h = -4.0 for the samples PbTe 3a, 3a *, 2a *, XV 2 *.

crystallization of the ingot.

The immutability of the carrier concentration makes it possible to qualitatively explain the temperature dependence of the Seebeck coefficient increase in the temperature range up to 150 ˚C. Thus, in the case of non-degeneration of holes up to 150 ˚C, the Seebeck coefficient will be determined according to the Pisarenko formula [10] ($\alpha = k/e[r+2 + \ln(N_v/p)]$). Given the constancy of magnitude p, as well as the fact that $N_v \sim T^{3/2}$, get $\alpha \sim a+b\cdot\ln(T)$. In the case of degeneracy, according to [11], $\alpha = 8\pi^2 k^2/(3eh^2m)\cdot T\cdot(\pi/3p)^{2/3}$. That is, in the first case, we obtain an increase in α with temperature by the logarithmic law, in the second case by a linear one. It is difficult to identify clearly which of the variants is true, since the semiconductor in this case is, in fact, weakly degenerate. Using dependency: $p = N_v \exp\left(-\left(\mu + E_g\right)/kT\right)$, we will get $-\left(\mu + E_g\right)/kT = \ln\left(p/N_v\right)$.

Here $N_v = 2\left(2\pi m * kT / h^2\right)^{3/2}$. At 150 ˚C the effective mass of light holes is $\approx 0.15\ m_0$ [12]. At a concentration of $1\cdot10^{18}$ cm⁻³, the Fermi energy calculated from the ceiling of the valence band is $\approx$-0.02 eV and its dimensionless value is $\approx$ -2. That is, the holes are slightly degenerate. In the case of heavy holes with effective mass $\approx 1,1m_0$ [13], this value will increase about three times, which, qualitatively, the picture will not change.

But the greatest difficulty of analyzing the temperature dependences of α (T) and σ (T) is the need to take into account the concentrations of both holes and electrons at temperatures above 150 - 200 ˚C. In this case, the observed temperature dependences of the specific conductivity and the Seebeck coefficient can be qualitatively and quantitatively correctly explained on the basis of a model that takes into account two types of carriers (electrons and holes). From a system of two equations:

$$n + N_a^- = p; \tag{1}$$
$$np = n_i^2, \tag{2}$$

we find separately the concentrations of electrons and holes (n and p), varying only the concentration of ionized N_a^- acceptors. Own the concentration n_i^2 hope gap width setting under three models: 1) $E_g = 0.38$ eB [14], 2) $E_g = 0.18 + 0.0004\ T$ [12], eB, 3) dependencies of the first and second models according to the temperature range.

$$n_i^2 = N_v N_c \exp(-E_g/kT), \tag{3}$$
$$N_c = 2(2\pi m_c^* kT/h^2)^{3/2},$$
$$N_v = 2(2\pi m_v^* kT/h^2)^{3/2},$$
$$m_c^* = 0,142\cdot m_e\cdot(T/120)^{0.4}\ [12],$$
$$m_{v,l}^* = 0,142\cdot m_e\cdot(T/120)^{0.4}\ [12],$$
$$m_{v,h}^* = 1,1m_e\ [13].$$

The mobility of electrons and holes is found by expressions:

$$\mu_e = \mu_{e300}(T/300)^{r_e}, \tag{4}$$
$$\mu_h = \mu_{h300}(T/300)^{r_h}, \tag{5}$$

varying μ_{e300} and μ_{h300} and r_e and r_h. Thus, the approximation dependence of the electrical conductivity:

$$\sigma = \sigma_e + \sigma_h, \tag{6}$$
$$\sigma_e = en\mu_e, \tag{7}$$
$$\sigma_h = ep\mu_h \tag{8}$$

has four variant parameters are presented in table. 1. The acceptor concentration varied within the error of the determined Hall concentrations of holes (Fig. 4). The approximation was performed in two steps. In the first one, all five parameters were arbitrarily varied to obtain the best correlation with the experimental data σ (T). For samples 3a and 3a * these results are shown in Table 1 (parameters in parentheses). It is worth noting that the most satisfactory correlation of the calculated curves σ (T) with the experimental ones was achieved in the case of acceptance for the studied temperature range:

$$E_g = const = 0.38\ eB.$$

The parameters μ_{e300} and μ_{h300} can vary arbitrarily, while r_e and r_h are determined by the scattering

Table 1

The most optimal (in parentheses) are 5 parameters of the approximation of the experimental dependence σ (T) and the optimal 3 parameters are fixed at 2, which characterize the scattering of electrons on polar optical phonons, and heavy holes on acoustic ones.

Sample	N_a^-, cm⁻³	μ_{h300} cm²/V s	μ_{e300} cm²/V s	r_h	r_e
3a*	1.23 (1.05)	601 (811)	633 (797)	-4(-4.74)	-1.1(-1.38)
3a	0.98 (0.67)	277 (467)	221 (129)	-4 (-4.7)	-1.1(-0.58)
XV3+XVI	1.21	88	547	-4	-1.1
XV 2*	1.2	471	548	-4	-1.1
2a*	1.16(1.11)	139(183)	91(235)	-4 (-5.3)	-1.1(-2.06)

Table 2

Mobility temperature dependence parameters and thermo-EMF coefficient for different scattering mechanisms [10]

Scattering on:	r	t	r_h	r_e	A=2+r
optical phonons (polar scattering)	1	3/2	-2	-1.1	3
optical phonons (deformation potential)	0	3/2	-4	-2.5	2
acoustic phonons	0	3/2	-4	-2.5	2
short-term potential	0	1/2	-3	-1.5	2
Coulomb potential	2	1/2	+1	1.3	4

mechanism. The temperature dependence of the conductivity will be determined by the temperature dependence of the mobility, which can be represented as [10]:

$$\mu \sim m^*(T)^{r-3/2-1}T^{r-t}. \qquad (9)$$

m^* – effective mass, r – carrier scattering parameter (r – a parameter that depends on the scattering mechanism: $r = 0$ when scattered on acoustic phonons, the strain potential of optical phonons, and the short-run potential of point defects; $r = 1$ when scattered on polar optical phonons; $r = 2$ when scattered on ionized impurities (Coulomb potential)), $t = 1/2$ for short-range potential and ionized impurities, $t = 3/2$ for acoustic phonons, polar and deforming optical phonons. Given that the effective mass of light holes, like electrons, is also a function of temperature ($m \sim T^{0,4}$ [12]), then dependence (9) can be represented as:

$$\mu_e = T^{(r-3/2-1)0.4+r-t} = T^{r_e} \qquad (10)$$

In the case of heavy holes, the effective mass is independent of temperature. Then

$$\mu_h = T^{(r-3/2-1)+r+t} = T^{2r-5/2-t} = T^{r_h} \qquad (11)$$

The calculated values of the degree index for different mechanisms are presented in Table. 2.

Comparing the data in the table 1 for samples 3a and 3a * with the data of table. 2, we can conclude that the most probable mechanisms of electron scattering are scattering on polar optical phonons (r_e (aprox) $\approx$ -0.58 (-1.38), r_e (theor) = -1.1). In the case of holes, the degree of the degree of the approximation determined by the approximation $\approx$-4.7 can be obtained only on condition that the influence of heavy holes is decisive in the formation of mobility. In this case, r_h (theor) = -4.0 and the scattering is carried out on acoustic phonons or deformation potential of optical phonons. Such a conclusion is completely consistent with the conclusion made in previous work [7] and [8]. An additional argument to support the decisive role of heavy holes is that the best correlations of the calculated data with the experiment are obtained provided that the bandwidth is 0.38 eV and does not change with temperature.

From the analysis of the numerical values of μ_{e300} and μ_{h300} we can conclude that the motions in the samples obtained by cold pressing at a pressure of 2 GPa and hot pressing at T = 250 ˚C are almost identical. Given the much lower values of the thermal conductivity of cold-pressed specimens, it can be considered that the high-pressure cold-pressing method is promising in terms of improving the thermoelectric figure of merit of PbTe-based materials.

With certain mechanisms of carrier scattering, it is possible to calculate the temperature dependence of the Seebeck coefficient:

$$\alpha = - k/e[A_e\sigma_e - A_h\sigma_h + \sigma_e\ln(N_c/n) - \sigma_h\ln(N_v/p)]/\sigma, \qquad (12)$$

where the constants A_e (A_h) are dependent on the charge

carrier scattering mechanism ($A = r+2$, tab. 2). The results of calculating α (T) are presented in Fig. 6. In the temperature range up to 450 K, there is a certain difference between the calculated curve α (T) and the experimental data. At the same time, for higher temperatures the correlation with the experiment is satisfactory. Obviously, the proposed model adequately characterizes the electronic subsystem (scattering mechanism, temperature dependence of the effective mass), and the influence of additional factors is possible for holes. Their manifestation may be due to the complex structure of the valence band in the temperature range of $\approx$ 450 K and, probably, additional scattering mechanisms, in particular, as noted in [7], scattering at grain boundaries. It should also be borne in mind that the formula used for the Seebeck coefficient is valid for the non-degenerate case, whereas the test specimens at the indicated temperatures are slightly degenerate.

Conclusions

1. The specific conductivity and Seebeck coefficient, in the samples obtained by hot pressing at a pressure of 0,5 GPa and T = 250 ˚C and cold pressing at a pressure of 2 GPa, are almost the same, which, with a lower coefficient of thermal conductivity of cold-pressed samples, determines the prospectivity of obtaining materials with high quality.

2. It is established that the dominant mechanism of electron scattering in powder PbTe samples obtained by powder compression is scattering on polar optical phonons and holes on acoustic phonons. Moreover, such a pattern is preserved for all the samples tested obtained by various technological factors.

3. Investigation of the unit cell parameter, the measurement of the Hall carrier concentration and the modeling of the electrophysical properties of the samples obtained under different technological conditions indicate slight changes in the defective subsystem (concentrations of dominant point defects) at the investigated pressing and annealing temperatures, which are important factors predefined properties of thermoelectric materials. That is, the defective material subsystem, and therefore the concentration of free charge carriers in it, can be formed at a separate stage of thermocouple creation, even before carrying out technological operations of briquetting.

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[1] L.-D. Zhao, V. P. Dravid, M. G. Kanatzidis, The panoscopic approach to high performance thermoelectrics, Energy Environ. Sci. 7, 251–268 (2014) (https://doi.org/10.1039/C3EE43099E).

[2] J.R. Sootsman, D. Y. Chung, M. G. Kanatzidis, New and Old Concepts in Thermoelectric Materials, Angew. Chem. Int. Ed. 48, 8616-8639 (2009) (https://doi.org/10.1002/anie.200900598).

[3] A.V. Dmitriev, I.P. Zvyagin, Sovremennyie tendentsii razvitiya fiziki termoelektricheskih materialov, UFN, 180(8), 821-838 (2010).

[4] H. Wang, J.-H. Bahk, Ch. Kang, J. Hwang, K. Kim, J. Kim, P. Burke, J. E. Bowers, A. C. Gossard, A. Shakouri, W. Kim, Right sizes of nano- and microstructures for high-performance and rigid bulk thermoelectrics, PNAS 111(30), 10949–10954 (2014) (https://doi.org/10.1073/pnas.1403601111).

[5] E. P. Sabo, Tehnologiya halkogenidnyih termoelementov. Fizicheskie osnovyi. Journal of Thermoelectricity 3, 30–46 (2000).

[6] I.V. Horichok, I.M. Lishchynskyi, S.I. Mudryi, O.S. Oberemok, T.O. Semko, I.M. Khatsevych, O.M. Matkivskyi, H.D. Mateik, R.O. Dzumedzei, Tekhnolohichni aspekty otrymannia termoelektrychnoho PbTe, Sensorna elektronika i mikrosystemni tekhnolohii 14(3), 53-64 (2017).

[7] I.V. Horichok, V.V. Prokopiv, R.I. Zapukhlyak, O.M. Matkivskyj, T.O. Semko, I.O. Savelikhina, T.O. Parashchuk, Effects of Oxygen Interaction with PbTe Surface and Their Influence on Thermoelectric Material Properties, Journal of Nano- and Electronic Physics 10(5), 05006(5pp) (2018) (https://doi.org/10.21272/jnep.10(5).05006).

[8] M.Y. Vynohradova, V.Y. Tamarchenko, L.V. Prokofeva, Parametryi slozhnoi valentnoi zonyi y osobennosty provodymosty v r-PbTe, FTP, 9(3) (1975).

[9] D.M. Zayachuk, The dominant mechanisms of charge-carrier scattering in lead telluride, FTP 31(2), 217-221 (1997) (https://doi.org/10.1134/1.1187322).

[10] B.M. Askerov, Elektronnyie yavleniya perenosa v poluprovodnikah, Nauka, 320 p. (1985).

[11] G. J. Snyder and E. S. Toberer, Complex thermoelectric materials, Nature materials 7, 105-114 (2008) (https://doi.org/10.1142/9789814317665_0016).

[12] B.M. Askerov, Elektronnyie yavleniya perenosa v poluprovodnikah, Nauka, 320 p. (1985).

[13] B.F. Gruzinov, I.A. Drabkin, G.F. Zaharyugina et el. Polozhenie urovnya Fermi v splavah PbTe, legirovannyih primesyu In, v oblasti vyisokih temperature, FTP, 13(2), 330-334 (1979).

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Механізми розсіювання носіїв у пресованому PbTe

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Представлено результати досліджень структурних та термоелектричних властивостей отриманих методом пресування порошку зразків PbTe. Для інтерпретації отриманих результатів проведено теоретичний розрахунок питомої електропровідності та коефіцієнту термо-ЕРС на основі моделі, що враховує два типи вільних носіїв заряду. Зроблено висновки про механізми розсіювання носіїв.

Ключові слова: плюмбум телурид, термоелектричні властивості, механізми розсіювання.