PHYSICS AND CHEMISTRY OF SOLID STATE
V. 19, № 3 (2018) P. 230-233
DOI: 10.15330/pcss.19.3.230-233

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 19, № 3 (2018) С. 230-233

PACS: 621.315.592.

ISSN 1729-4428

V.V. Prokopiv[1], I.V. Horichok[1], T.O. Semko[1], O.M. Matkivskiy[1], R.O. Dzumedzey[1], H.D. Mateik[2], O.P. Konevych[1]

Thermal Conductivity Mechanisms in Compressed Thermoelectric Materials Based on A_4B_6 Compounds

[1]Vasyl Stefanyk PreCarpathian National University, 57, Shevchenko Str., Ivano-Frankivsk, 76018, Ukraine, e-mail: fcss@pu.if.ua
[2]Ivano-Frankivsk National Technical University of Oil and Gas, 15, Karpatska Str., Ivano-Frankivsk, 76000, Ukraine

The factors influencing the value of the thermal conductivity coefficient of thermoelectric materials based on lead telluride obtained by powder pressing method have been analyzed. The model is presented and its parameters are defined, which explains qualitatively and quantitatively the temperature dependences of the thermal conductivity coefficient of PbTe and PbSnAgTe.

Keywords: Lead telluride, solid solutions, thermal conductivity, pressing.

Article acted received 11.08.2018; accepted for publication 15.09.2018.

Introduction

In the temperature range (200-300) K, for active elements of thermoelectric converters, the lead telluride is widely used, due to the uniqueness of its physical and chemical properties, as well as the relatively simple technology of obtaining qualitative crystals. One of the most significant problems of thermal generators, and not only on the basis of PbTe, is their relatively low efficiency - (6 - 9)%, the increase of which, in particular, by doping and creating solid solutions, is an actual task [1].

In our works [2-5], the thermoelectric properties (specific conductivity, Seebeck coefficient, thermal conductivity coefficient) of PbTe-based materials obtained by powder pressing method have been investigated. Methods for obtaining samples and measuring their properties are described in detail in the above-mentioned works. One of the characteristic features of the presented results is the relatively low values of the thermal conductivity of the samples under study (≤ 0,005 W / (cm K)), which is important from the point of view of practical use. Particularly low values of k (≈0,005 W / (cm K)) are observed for solid solutions of PbSnAgTe. Taking into account such results, the purpose of this work is a detailed analysis of the factors affecting the low values of k, including the accuracy of the measurement by the method of radial heat flux. Before all, let us note that similarly to our thermal conductivity values were also obtained for materials ($Ag_{1-x}Pb_{18}BiTe_{20}$ and PbTe-Ag_2Te) in works [6] (≈ 0.005 W / (cm K)) and [7] (≈ 0.003-0.005 W / (cm K)).

I. Errors in measuring the coefficient of thermal conductivity

The greatest disadvantage of the method used in [2-5] of measuring the thermal conductivity (radial heat flow method) is the need for samples to be obtained, with the preservation of the ratio of their length to the diameter L/d ≈ 4, as well as drilling the hole along the axis of the fragile sample. Failure to comply with these requirements, as well as inaccuracies in measuring geometric sizes, perturbation of the thermal front in the vicinity of the thermocouples, can cause an error of ≈ 25% [8].

To determine the real error, the thermal conductivity of fluoroplastic cylindrical samples with L/d ≈ 1 was measured, as in the investigated thermoelectric sample. The average value of the measured coefficient of thermal conductivity is 0.0027 W / (K cm) at a table value of 0.0025 W / (K cm). That is, the relative error is ≈ 10%. Given the proximity of the values of the thermal conductivity of fluoroplastics and our samples, one can hope that the error in both cases will be in the vicinity of this value.

Also, using the Wiedemann-Franz law ($k_e/\sigma = L_0T$, where $L_0 = \pi^2/2(k_B/e)^2$ for a degenerate semiconductor and $L_0 = 2(k_B/e)^2$ for a non-degenerate semiconductor)

Table 1

Dependence of sample density on chemical composition and technological factors of their obtaining*

Material	Pressure press. GPa	Time press. min	Annealing temper. T, K	Annealing time. h	Density. g/cm^3	X-ray density. g/cm^3
PbTe	2	15	500	5	8,19	8,268**
$Pb_{17}Ag_3Te_{20}$	2	15	500	5	7,90	8,2517**
$Pb_{16}Sn_2Ag_2Te_{20}$	2	15	500	5	7,88	8,3245**
$Pb_{14}Sn_4Ag_2Te_{20}$	2	15	500	5	7,75	8,3207**
$Pb_{14}Sn_4Ag_2Te_{20}$	1	30	770	0,25	7,05	

* – All samples are pressed from powder fractions – (0.05-0,5) mm.

** – Powder.

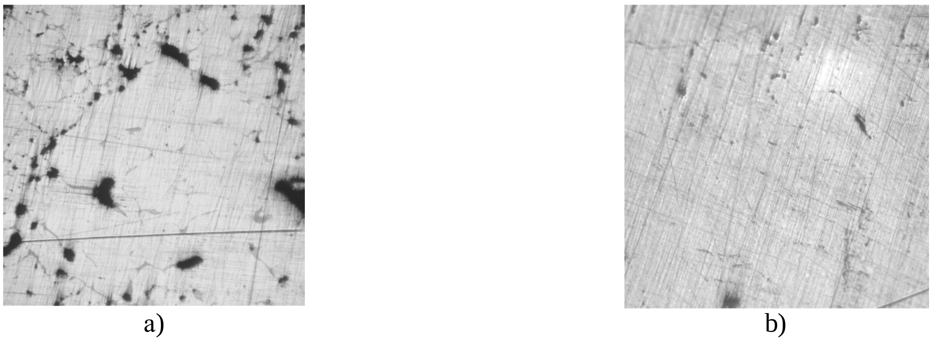
calculated electronic component of the thermal conductivity of individual samples. For a sample of the $Pb_{18}Ag_2Te_{20}$ composition, which according to our measurements has one of the lowest thermal conductivity coefficients, at a temperature T ≈ 500 K the calculated value of ke≈0.0012 W / (cm K) is calculated, while the measured value of the total thermal conductivity k ≈ 0.0016 W / (cm K). If our materials are non-degenerate, the calculated values of k_e will be almost two times smaller. Taking into account such results, we can assume that our values of thermal conductivity are obtained by the method of radial heat flux, are reliable.

One of the factors influencing the thermal conductivity of the pressed sample is its density (k ~ ρ). From Table 1, it can be seen that with increasing content of silver and, especially, tin, the density of samples, determined by the method of Archimedes, decreases. It should be noted that X-ray density, on the contrary, increases. And if in the first case, changes are observed in the first sign after the comma, then in the second one - in the second sign. Reduced density of pressed samples is due to the growth of microhardness of ingots with the addition of tin and silver, which reduces the possibility of their sealing at the application of pressure. So for a non-annealing sample ($Pb_{16}Sn_2Ag_2Te_{20}$) the microhardness is 103.3 HV, whereas for PbTe - ≈ 35 HV (Measurement was carried out at a load of 300gf, load time of 10 seconds. It is also worth noting the decrease in the microhardness of the sample after annealing on the air at 770 K, 15 min to 93.5 HV). Such a conclusion, in particular, is confirmed by the fact that, unlike the pure PbTe, the porosity of the pressed samples of solid solutions ($Pb_{16}Sn_2Ag_2Te_{20}$) is higher (Fig. 1).

II. Thermal conductivity mechanisms in pressed materials on the basis of lead telluride

It is known [9] that, in monocrystalline materials, the fundamental mechanism of phonon scattering is a phonon-phonon interaction that determines the dependence k ~ 1 / T. In the pressed samples, the effect of scattering on the grain boundaries will also be significant. Moreover, according to [10], the weak temperature dependence of heat conductivity, which is observed for most of the studied samples of different compositions, indicates that the main mechanism defining the character of k (T) is scattering on defects, and, regardless of the type of defects.

For temperatures above ≈ (450-500) K, in some samples the growth of the coefficient of thermal conductivity is observed. Similar dependencies, but more clearly expressed as a result of a wider temperature range of measurement, were obtained in [11] and [12], and in both works the increase of the thermal conductivity with increasing temperature above the extreme point was



a) b)

Fig. 1. Microfilms of the sample surface $Pb_{14}Sn_4Ag_2Te_{20}$ (a) and PbTe (b) after annealing at temperature 770 K 15 min) (image size – 460x460 μm^2)

explained by the effect of bipolar conductivity. According to [13] for bipolar thermal conductivity

$$k = \frac{\sigma_n \sigma_p}{\sigma_n + \sigma_p} T(\alpha_n + \alpha_p)^2$$

For temperatures below ≈ (700-750) K it is possible to carry out the theoretical calculation of the coefficient of thermal conductivity based on the dependence [14]

$$k = 3c_V v_s l \tag{1}$$

here C_V– specific heat capacity, v_s – speed of sound, l - length of free run of phonons. Since $l = v_s\tau$, then

$$k = 3c_V v_s^2 \tau \tag{2}$$

Given the dependence of these parameters on the frequency –

$$k = 3\int_0^{\omega_D} c_V(\omega) v_S(\omega)^2 \tau(\omega) d\omega \tag{3}$$

here ω_D – Debye frequency.

In the case of high temperatures (T> TD, TD - Debye temperature), as well as neglecting the difference between phase and group velocities –

$$c_V(\omega) = \frac{3k\omega^2}{2\pi^2 v_s^3} \tag{4}$$

The relaxation time is determined by the mechanism of scattering of phonons. The most important mechanism is the phonon-phonon scattering, namely U-processes for which τ is defined as:

$$\tau_U(\omega) = \frac{\left(6\pi^2\right)^{1/3}}{2} \frac{\overline{M} v_s^3}{k V^{1/3} \gamma \omega^2 T} \tag{5}$$

where, M – given mass of atoms of the matrix, V– atomic volume, γ – Gruneisen parameter.

However, under the conditions of the realization of this mechanism of scattering of phonons, it is impossible to explain the obtained experimental data (Fig. 2). In our opinion, a significant decrease in the coefficient of thermal conductivity is provided by active scattering of phonons at the boundaries of the grains. According to [14], the relaxation time for this mechanism is

$$\tau_B(\omega) = \frac{L}{v_s} P_B \tag{6}$$

here L– grain size, P_B – a coefficient that takes into account the nature of the material (for example, for InGaAs $P_B = 1{,}3 \cdot 10^{-3}$). For our samples, taking the average particle size equal to 200 µm, the satisfactory correlation of the theoretical curve k (T) with the experimental data is reached at the value $P_B = 0.2 \cdot 10^{-4}$ (fig.2).

An additional reduction in the thermal conductivity observed for solid solutions of the Pb (Sn) -Ag-Te system [5] can be explained as the realization of scattering mechanisms at point defects and on the boundaries of the inclusion of additional phases. In the case of the first of them, the relaxation time will be determined as

$$\tau_{PD}(\omega) = \frac{4\pi v_s^3}{V\omega^4} \left(\sum_i f_i \left(1 - \frac{m_i}{m}\right)^2 + \sum_i f_i \left(1 - \frac{r_i}{r}\right)^2 \right)^{-1} \tag{7}$$

For another

$$\tau_D(\omega) = \frac{k^3}{\omega^4 \hbar^3} \cdot \frac{4T_D^3}{3N_i R^2} \tag{8}$$

here f_i – atomic particle of impurity atoms, m_i/m – ratio of atomic masses of impurity and matrix atoms, r_i/r – the ratio of the atomic radiuses of the impurity and matrix atoms, N_i– concentration of inclusions of the additional phase, R – their radius.

Assuming that in the Pb14Sn4Ag2Te20 solid solution about 30% of the cationic atoms are occupied by an impurity whose atomic mass is two times smaller than the mass of the matrix atom, the calculated curve k (T) implies much lower thermal conductivity than is experimentally observed. Therefore, it can be assumed, and this assumption is confirmed by the data of X-ray diffractometry, that only tin atoms are soluble in cationic sublattice in full, and most of the introduced silver forms

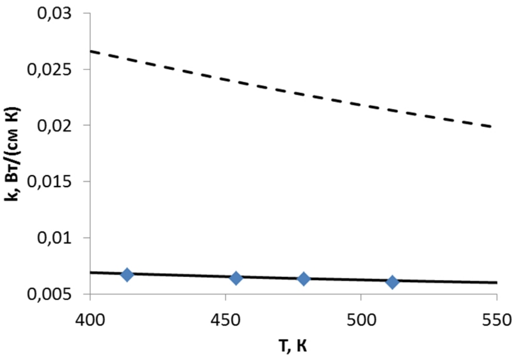


Fig. 2. Dependence of the coefficient of thermal conductivity on temperature: points - experimental data for pure PbTe pressed under pressure 1.5 GPa and annealing at 770 K; upper curve - calculation based on the assumption of domination of U-processes in the scattering of phonons, lower curve - taking into account U-processes and scattering on the boundaries of the grains.

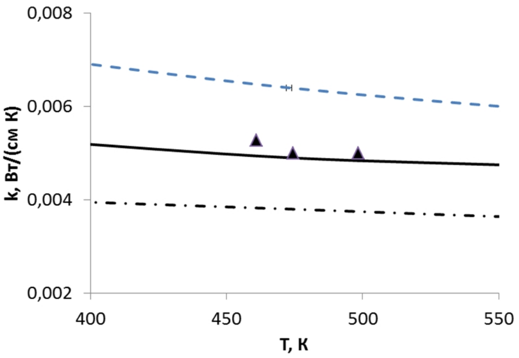


Fig. 3. Dependence of the coefficient of thermal conductivity on temperature: points - experimental data for the sample $Pb_{14}Sn_4Ag_2Te_{20}$; upper curve - calculation based on the assumption that the U processes are dominant in the scattering of phonons and scattering on the grain boundaries, the lower curve - taking into account U processes, scattering at grain boundaries and dispersion at impurities in the amount of 30 at.%, average curve - taking into account U-processes, scattering along the grain boundaries and scattering

the additional phases [5]. By adopting such a model, the calculated curve correlates with the experimental data much better (Fig. 3).

Conclusions

1. The temperature dependences of the thermal conductivity coefficient on the pure lead telluride are characterized by two sections: up to 500 K the experimental data are interpreted in the framework of the model of scattering of phonons on phonons (U-processes) and phonons at the boundaries of the grains; at higher temperatures, the bipolar component of the thermal conductivity is determining.
2. For solid solutions of PbSnAgTe, additional factors that reduce the thermal conductivity coefficient are scattering of phonons at point defects, the concentration of which in the samples is rather high, and the higher porosity of the compressed samples of solid solutions in comparison with samples of pure PbTe.

The work was carried out in the framework of implementation of projects under the state orders of the Ministry of Education and Science of Ukraine, state registration numbers 0117U006425 and 0117U002407.

Prokopiv V.V. candidate of physical and mathematical sciences, professor, head of the department of physics and chemistry of solid state;
***Horichok I.V.* -** Candidate of Chemical Sciences, Senior Researcher, Professor;
***Semko T.O.* -** Researcher;
***Matkivskiy O.M.* -** Researcher;
***Dzumedzey R.O.* -** Researcher;
***Mateik H.D.* -** candidate of physical and mathematical sciences, associate professor;
***Konevych O.P.* -** master's degree.

[1]. Li-Dong Zhao, Vinayak P. Dravid, Mercouri G. Kanatzidis, Energy Environ. Sci., 7 (2014) 251–268.
[2]. I. V. Horichok, I. M. Lishchynsky, S. I. Mudryy, O. S. Oberemok, T. O. Semko, I. M. Khatsevych, O. M. Matkivsky, G. D. Mateik, R. O. Dzumedzey, SEMST, 14(3) (2017) 53-64.
[3]. I.V. Horichok, M.O. Galushchak, O.M. Matkivskyj, I.P. Yaremij, R.Ya. Yavorskyj, V.S. Blahodyr, O.I. Varunkiv, T.O. Parashchuk, Journal of Nano- and Electronic Physics, 9(5) (2017), 05022-1 - 05022-7.
[4]. Ihor Horichok, Rasit Ahiska, Dmytro Freik, Lyubomyr Nykyruy, Stepan Mudry, Ostap Matkivskiy, Taras Semko, Journal of Electronic Materials, 45(3) (2016) 1576-1583; doi: DOI 10.1007/s11664-015-4122-9.
[5]. M. O. Halushchak, I. V. Horichok, T. O. Semko, S. I. Mudry, S. V. Optasyuk, R. O. Dzumedzey, Physics and Chemistry of Solid State, 18(2) (2017) 211-214; doi: 10.15330/pcss.18.2.211-214.
[6]. Yanzhong Pei, Aaron La Londe, Shiho Iwanagaand G. Jeffrey Snyder, Energy Environ. Sci., 4 (2011) 2085–2089.
[7]. Oliver Falkenbachr, Andreas Schmitzz, David Hartung, Torben Dankworf, Guenter Koch, Lorenz Kienlea, Peter J. Klar, Eckhard Muellerrand Sabine Schlechtr, The 2014 International Conference on Thermoelectrics, July 6-10, 2014, Nashville, Tennessee, USA (2014).
[8]. D. M. Freik, R. Y. Mykhaylyonka, V. M. Klanichka, Physics and Chemistry of Solid State, 5(1) (2004) 173-191.
[9]. Eric S. Toberer, Alex Zevalkink, G. Jeffrey Snyder, J. Mater. Chem., 21 (2011) 15843.
[10] Y. I. Ravych, I. A. Smirnov, V. V. Tyhonov. Semiconductors, 7(2) (1967) 206-210.
[11]. Y.-L. Pei, Y. Liu, Journal of Alloys and Compounds, 514 (2012) 40– 44.
[12]. O. I. Rogachova, I. M. Kryvulkin, Semiconductors, 43(6) (2001) 1000-1003.
[13]. O. I. Markov, 13 Seminar «Thermoelectrics and their application» (ноябрь 2012 г) 180-185 (2012).
[14]. K. K. Choudhary, D. Prasad, K. Jayakumar, D. Varshney, Internationale Journal of Nanoscience 8(6) (2009) 551-556.

В.В. Прокопів[1], І.В. Горічок[1], Т.О. Семко[1], О.М. Матківський[1], Р.О. Дзумедзей[1],
Г.Д. Матеїк[2], О.П. Коневич[1]

Механізми теплопровідності у пресованих термоелектричних матеріалах на основі сполук A_4B_6

[1]Фізико-хімічний інститут Прикарпатського національного університету імені Василя Стефаника,
вул. Шевченка, 57, м. Івано-Франківськ, 76018, Україна, e-mail: fcss@pu.if.ua
[2]Івано-Франківський національний технічний університет нафти і газу,
вул. Карпатська, 15, м. Івано-Франківськ, 76000, Україна

Проаналізовано фактори, що впливають на величину коефіцієнта теплопровідності термоелектричних матеріалів на основі телуриду свинцю отриманих методом пресування порошку. Представлено модель та визначено її параметри, що якісно і кількісно пояснює температурні залежності коефіцієнта теплопровідності PbTe та PbSnAgTe.

Ключові слова: плюмбум телурид, тверді розчини, теплопровідність, пресування.