G.O.Nikolaenko, O.S.Vodoriz, *cand. phys.-math. Sciences*
E.I. Rogacheva *doc. phys.-math. Sciences, Professor*
Tavrina T.V., *cand. phys.-math. Sciences, Associate Professor*
Lisachuk G.V. *doc. tehn. Sciences, Professor*

National Technical University "Kharkiv Polytechnic Institute"
2 Kyrpychova Str., Kharkiv, 61002, Ukraine

THERMAL CONDUCTIVITY OF $PbSe_{1-x}Te_x$ (x = 0 – 0.04) SOLID SOLUTIONS

The dependence of lattice thermal conductivity λ_L of pressed samples of $PbSe_{1-x}Te_x$ solid solutions on the composition (x = 0 – 0.04) at a temperature of 325 K is obtained. The $\lambda_L(x)$ curve shows a maximum near x = 0.0075. Measurement of the temperature dependence of λ_L in the range of 150-600 K showed that a concentration anomaly in the same range of compositions is also observed on the composition dependence of power factor β in the temperature dependence of λ_L . The non-monotonic character of the $\lambda L(x)$ and $\beta(x)$ dependences is associated with critical phenomena accompanying the transition of the percolation type from dilute to concentrated solid solutions. In the study and practical application of $PbSe_{1-x}Te_x$ solid solutions, it is necessary to take into account the non-monotonic nature of the change in thermal conductivity with composition. Bibl. 15, Fig. 3.

Key words: $PbSe_{1-x}Te_x$ solid solutions, thermal conductivity, composition, temperature, percolation.

Introduction

Semiconducting isovalent and isostructural substitutional $PbSe_{1-x}Te_x$ solid solutions are promising medium-temperature thermoelectric (TE) materials [1, 2]. Since the efficiency of using TE materials is determined by the figure of merit ZT ($ZT = S^2\sigma T / \lambda$, where S is the Seebeck coefficient, σ is the electrical conductivity, λ is the total thermal conductivity, and T is the absolute temperature), one of the ways to increase ZT is to decrease λ. The thermal conductivity of a semiconductor includes two main components - lattice (λ_L) and electronic (λe), which reflect the distribution of the heat flux in the substance by phonons and conduction electrons [1,2]. Enhancing phonon scattering and, therefore, decreasing λ_L without negatively affecting the electronic properties (S, σ) remains an urgent problem of TE materials science [1-3].

Experimentally, the thermal conductivity of polycrystalline $PbSe_{1-x}Te_x$ solid solutions was studied in many works [4-6], where the main attention was paid to the compositions from the side of $PbTe$. Thus, in [4, 5], the total λ decreased with an increase in the Se content to $x \sim 0.5$, and then increased again. It was shown in [6] that λ_L also decreases with an increase in the Se content

to $x = 0.25$, which, according to the authors, is due to phonon scattering because of local deformation caused by the difference in the masses of Te and Se atoms. The theoretical calculation of λ_L carried out by the authors of [7] showed that at room temperature at $x = 0.5$, a maximum decrease in λ_L by ~ 30 % is observed in comparison with λ_L of *PbTe* and *PbSe* compounds.

Earlier, in a number of works reviewed in [8], anomalies were found in the isotherms of properties, including thermal conductivity, in solid solutions based on IV-VI compounds at a low content of the second component (~ 0.5-1.5 at.%). According to the assumption of the authors of these works, the concentration anomalies are associated with the presence of phase transitions of the percolation type in going from dilute to concentrated solid solutions.

An anomalous area of thermal conductivity growth on the dependence of $\lambda(x)$ at room temperature was also observed by the authors [9] in the $PbSe_{1-x}Te_x$ solid solution from the side of *PbTe* in the range of $x = 0.9925 - 0.9875$. It was of interest to find out whether a similar effect will be manifested in the same $PbSe_{1-x}Te_x$ solid solutions only by *PbSe*. Therefore, in [10] a study of the concentration dependences of the microhardness *H, S,* σ of cast and extruded polycrystalline samples of $PbSe_{1-x}Te_x$ ($x = 0 - 0.045$) solid solutions at room temperature and near $x = 0.01$ revealed areas of abnormal decrease in *H* and *S* and growth of σ. However, the thermal properties of these samples were unstudied.

This work is devoted to the study of the effect of composition and temperature on the thermal conductivity of solid solutions based on lead selenide in the $PbSe_{1-x}Te_x$ system ($x = 0 - 0.04$).

Experimental

Polycrystalline $PbSe_{1-x}Te_x$ samples (x = 0, 0.0025, 0.005, 0.01, 0.0125, 0.015, 0.0175, 0.035, 0.04) were synthesized by alloying the initial elements in evacuated quartz ampoules at a temperature of 1380 K, followed by homogenizing annealing at a temperature of 870 K for 240 hours. All samples had *p*-type conductivity. To measure the thermal conductivity, hot-pressed cylindrical specimens with a diameter of 15 mm and a height of 5.5 mm (pressing temperature 650 K, pressure 0.4 GPa, holding time under load 10 s) were prepared from cast ingots, followed by annealing at 720 K for 250 h.

Thermal conductivity was measured in the temperature range of 150-600 K on a VT-λ-400 device using a dynamic calorimeter in a monotonic heating mode. Three measurements of λ were carried out for each sample. The relative measurement error did not exceed 5%. The lattice component of thermal conductivity λ_L was separated from the total thermal conductivity by subtracting the electronic component λ_e which was calculated according to the Wiedemann-Franz law $\lambda_e = L\sigma T$ (for a degenerate semiconductor the Lorentz number $L = \pi^2k^2/3e = 2.45 \cdot 10^{-8}$ $W \cdot Ohm \cdot K^{-2}$ [11]. The electric conductivity σ was measured by the four-probe method with an accuracy of 5 %.

Discussion of results

Fig. 1 shows a dependence of lattice thermal conductivity on the composition of $PbSe_{1-x}Te_x$ solid solution at a temperature of 325 K. It is seen that with a general tendency to decrease λ_L with increasing *Te* content on the dependence $\lambda_L(x)$ a maximum is observed near $x = 0.0075$, which indicates a decrease in phonon scattering and an increase in the propagation velocity of elementary excitations near $x = 0.0075$.

In this regard, it was of interest to find out what the nature of the concentration dependence of the power factor in the temperature dependence of λ_L will be. Therefore, the total thermal conductivity λ of the samples under study was measured in the temperature range 150-600 K. Fig. 2 shows the temperature dependences $\lambda(T)$ of some $PbSe_{1-x}Te_x$ ($x = 0$, 0.0025, 0.005, 0.0175) samples. The rest of the samples had a similar character of the dependences $\lambda(T)$. From Fig. 2 it can be seen that in the investigated temperature range the values of λ decrease, which is typical for phonon-phonon scattering and is consistent with the dependences $\lambda(T)$ given in [4 – 6].

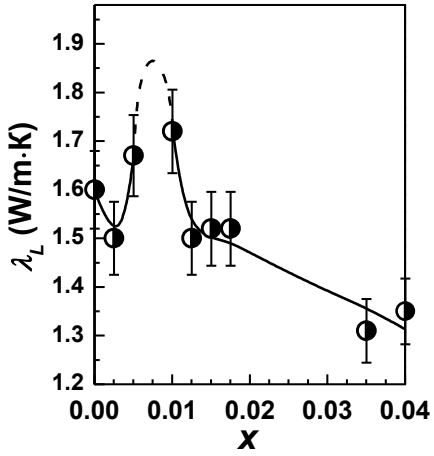

Fig. 1. Dependence of lattice thermal conductivity λ_L of $PbSe_{1-x}Te_x$ solid solution on the composition x at a temperature of 325 K

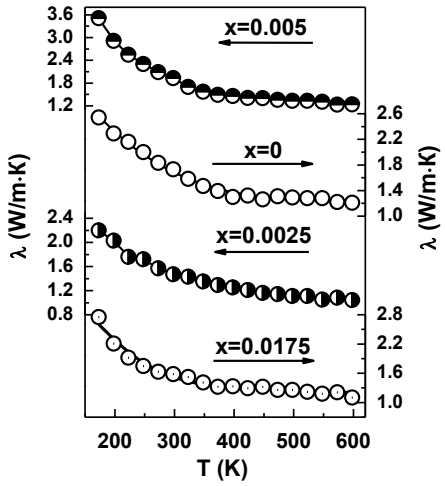

Fig. 2. Temperature dependences of total thermal conductivity λ of $PbSe_{1-x}Te_x$ solid solution

Our estimated calculation of the electronic component of thermal conductivity showed that for *PbSe* polycrystal at room temperature $\lambda_e = 1 \cdot 10^{-2}$ W/(m·K), λ_L/λ = 99.4%, and for $PbSe_{1-x}Te_x$ solid solution the value $\lambda_e = (0.5 – 1.4) \cdot 10^{-2}$ W/(m·K), λ_L/λ = (99.2 – 99.8)%. Thus, in PbSe and in the $PbSe_{1-x}Te_x$ solid solution on its basis, the main contribution to the thermal conductivity is made by λ_L. Based on this, it can be assumed that the experimental values of λ obtained in this work practically coincide with the values of the lattice thermal conductivity.

It is known that at temperatures above the Debye temperature Θ_D (for *PbSe* Θ_D = 138 K) λ_L of semiconductors with a rise in temperature decreases according to the law $\lambda_L \sim T^{-1}$ [11,12]. Assuming the power character of the temperature dependence λ_L ($\lambda_L \sim T^{-\beta}$), the power factor β was estimated for the studied samples (Fig. 3). As is evident from Fig. 3, after a decrease in β upon the introduction of the first portion of the impurity (x = 0.0025), one can observe a sharp increase in the power factor at x = 0.005, when β reaches an almost theoretical value (β = -1.05 ± 0.05). Besides, a subsequent sharp decrease to β = -0.5 ± 0.05 is observed, which indicates the presence of some transformations in the crystal, which significantly change the processes of heat transfer and phonon scattering. The subsequent increase in β and the constancy of λ_L in the range x = 0.0125 - 0.0175 indicate the complex nature of these transformations, which may be accompanied by ordering processes. It was interesting to compare the values of β obtained by other authors with the results of this work. A numerical estimate of the power factor β for a number of experimental dependences $\lambda_L(T)$ for *PbSe* polycrystals given in [5, 6, 13] showed that the values of β are β = -(0.7 - 0.9). The deviation of β values for pure *PbSe* from the theoretical value is obviously due to the presence of grain boundaries, nonstoichiometry defects and other imperfections in polycrystals.

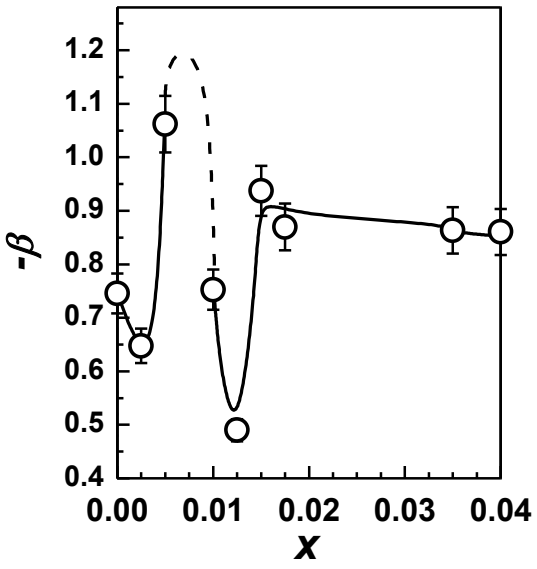

Fig. 3. Dependence of the power factor β in the temperature dependence of lattice thermal conductivity λ_L on the composition of the $PbSe_{1-x}Te_x$ solid solution

The anomalous growth of λ_L near x = 0.0075 can be described, as was done in [9], within the problem of the spheres of percolation theory [14, 15]. In this model, each introduced substitutional atom (in this case the Te atom), represented as a sphere, causes a field of static deformation with radius R_0 and excitation of the phonon spectrum in the crystal. When a certain critical concentration x_c of substitutional atoms (percolation threshold) is reached, a chain of interconnected atoms is formed that permeates the entire crystal (an infinite cluster). When the first portions of *Te* are introduced into the *PbSe* lattice, the crystal structure becomes disordered, which is manifested in a decrease in thermal conductivity at x = 0.0025. A further increase in the *Te* concentration leads to the fact that the deformation fields of neighboring substitutional atoms begin to overlap, which causes a decrease in local elastic lattice stresses, an increase in the rate of propagation of thermal oscillations of the crystal lattice and, consequently, an increase in thermal conductivity. Within the framework of the problem of the percolation theory spheres, using the assumption of the short-range nature of the deformation interaction, the critical concentration can be determined from the condition $4/3N_c(2R_0)^3 \approx 2.7$, where N_c is the average number of centers of spheres with radius R_0 per unit volume [15]. Assuming that the critical concentration with the maximum value λ_L corresponds to x_c = 0.0075, we obtained $R_0 = 1.39a_0$ (where a_0 is the unit cell parameter of *PbSe*). A further increase in the concentration of *Te* causes new crystal deformations in the solid solution, and hence a decrease in λ_L at $x > 0.015$. With a high probability, as noted above, such a percolation transition is accompanied by ordering processes.

Thus, we associate the anomalous growth of $\lambda_L(x)$ in the $PbSe_{1-x}Te_x$ solid solution near x = 0.0075 with the manifestation of critical phenomena accompanying the transition of the percolation type from dilute solid solutions to concentrated ones. The presence of such a growth region of $\lambda_L(x)$ should be taken into account when developing materials based on *PbSe*, therefore, an increase in thermal conductivity can lead to a decrease in the value of *ZT*. The results of the work once again confirm the assumption, grounded in [8], about the universal nature of such concentration anomalies.

Conclusions

The composition dependences of lattice thermal conductivity λ_L of pressed samples of $PbSe_{1-x}Te_x$ (x = 0 – 0.04) solid solutions at a temperature of 325 K and a power factor β in the temperature dependence of λ_L. On the dependences $\lambda_L(x)$ and $\beta(x)$ near x = 0.0075, clear maxima were observed, the presence of which indicated the existence of transformations in the lattice subsystem of the crystal, leading to an increase in the rate of phonon propagation and changes in their scattering processes. The non-monotonic nature of the dependences $\lambda_L(x)$ and $\beta(x)$ is associated with the manifestation of critical phenomena that accompany the phase transition of the percolation type, which occurs during the transition from dilute to concentrated solid solutions. The results of this work, as well as our previous data on the study of $PbSe_{1-x}Te_x$ solid solutions, show that when interpreting the results, optimizing the TE properties and practical application of

these materials, it is necessary to take into account the concentration anomalies of thermal conductivity in a certain range of compositions near the initial components *PbTe* and *PbSe*.

References

1. Rowe D.M. (1995). *CRC Handbook of Thermoelectrics*. Boca Raton, London, New York, Washington: CRC Press.
2. Anatychuk L.I. (1979). *Termoelementy i termoelektricheskiie ustroistva. Spravochnik [Thermoelements and thermoelectric devices. Reference book]*. Kyiv: Naukova dumka [in Russian].
3. Ren Z., Lan Y., Zhang Q. (2017). *Advanced thermoelectrics: Materials, contacts, devices, and systems*. Boca Raton: CRC Press Taylor & Francis Group.
4. Pei Y., Shi X., LaLonde A., Wang H., Chen L., Snyder G.J. (2011). Convergence of electronic bands for high performance bulk thermoelectrics. *Nature Letter*, 473, 66-69.
5. Basu R., Bhattacharya Sh., Bhatt R., Singh A., Aswal D. K., Gupta Sh. K. (2013). Improved thermoelectric properties of Se-doped n-type $PbTe_{1-x}Se_x$ ($0 \leq x \leq 1$). *Journal of Electronic Materials*, 42(7), 2292-2296.
6. Li J.Q., Li S.P., Wang Q.B., Wang L., Liu F.S., Ao W.Q. (2011). Synthesis and thermoelectric properties of the $PbSe_{1-x}Te_x$ alloys. *Journal of Alloys and Compounds*, 509, 4516-4519.
7. Tian Zh., Garg J., Esfarjani K., Shiga T., Shiomi J., Chen G. (2012). Phonon conduction in PbSe, PbTe, and $PbTe_{1-x}Se_x$ from first-principles calculations. *Phys. Rev. B*, 85, 184303.
8. Rogacheva E.I., Nashchekina O.N., Dresselhaus M.S. (2005). Thermal conductivity isotherm anomalies in semiconductor solid solutions based on IV-VI compounds. *J. Thermoelectricity*, 4, 82-90.
9. Rogacheva E.I., Vodorez O.S., Nashchekina O.N., Dresselhaus M.S. (2014). Concentration anomalies of the thermal conductivity in PbTe–PbSe semiconductor solid solutions. *Phys. St. Sol. B*, 251, 1231-1238.
10. Vodoriz O.S., Tavrina T.V., Nikolaenko G.O., Rogachova O.I. (2020). Mechanical and thermoelectric properties of $PbSe_{1-x}Te_x$ semiconductor solid solutions (x = 0 – 0.04). *Metallofiz. Noveishie Tekhnol*., 42(4), 487-495 (in Ukrainian).
11. Tritt T.M. (2004). *Thermal conductivity: theory, properties, and applications*. New York: Kluwer Academic, Plenum Publishers.
12. Berman R. (1976). *Thermal conduction in solids*. Oxford: Clarendon Press.
13. Pei Y.-L., Liu Y. (2012). Electrical and thermal transport properties of Pb-based chalcogenides: PbTe, PbSe and PbS. *J. Alloys and Compounds*, 514, 40-44.
14. Tarasevich Yu.Yu. (2002). *Percoliatsiia: teoriia, prilozheniia, algoritmy [Percolation: theory, applications, algoriythms]*. Moscow: Editorial URSS [in Russian].

15. Stauffer D., Aharony A. (1992). *Introduction to percolation theory. Wasington, DC: Taylor & Francis.*

Submitted 06.08.2020

Ніколаєнко Г.О., Водоріз О.С.,
Рогачова О.І., *докт. фіз.-мат. наук, професор*
Тавріна Т.В. *канд. фіз.-мат. наук, доцент*
Лісачук Г.В. *канд. фіз.-мат. наук, професор*

Національний технічний університет
«Харківський політехнічний інститут»,
вул. Кирпичова, 2, Харків, 61002, Україна

ТЕПЛОПРОВІДНІСТЬ ТВЕРДИХ РОЗЧИНІВ $PbSe_{1-x}Te_x$ (x = 0 – 0.04)

Одержано залежність граткової теплопровідності λ_L пресованих зразків твердих розчинів $PbSe_{1-x}Te_x$ від складу (x = 0 – 0.04) за температури 325 К. На кривій $\lambda_L(x)$ виявлено максимум поблизу x = 0.0075. Вимірювання температурної залежності λ_L в інтервалі 150 - 600 К показало, що концентраційна аномалія в цьому ж інтервалі складів спостерігається і на залежності степеневого коефіцієнта β у температурній залежності λ_L від складу. Немонотонний характер залежностей $\lambda_L(x)$ і β(x) пов'язується з критичними явищами, що супроводжують перехід перколяційного типу від розведених до концентрованих твердих розчинів. При дослідженні і практичному застосуванні твердих розчинів $PbSe_{1-x}Te_x$ необхідно враховувати немонотонний характер зміни теплопровідності зі складом. Бібл. 15, рис. 3.

Ключові слова: тверді розчини $PbSe_{1-x}Te_x$, теплопровідність, склад, температура, перколяція.

Николаенко Г.А., Водориз А.С.,
Рогачева Е.И., *докт. физ.-мат. наук, профессор*
Таврина Т.В., *канд. физ.-мат. наук, доцент*
Лисачук Г.В., докт. *техн. наук, професор*

Национальный технический университет
«Харьковский политехнический институт»,
ул. Кирпичева, 2, Харьков, 61002, Украина

ТЕПЛОПРОВОДНОСТЬ ТВЕРДЫХ РАСТВОРОВ $PbSe_{1-x}Te_x$ (x = 0 - 0.04)

Получена зависимость решеточной теплопроводности λ_L прессованных образцов твердых растворов $PbSe_{1-x}Te_x$ от состава (x = 0 - 0.04) при температуре 325 К. На кривой $\lambda_L(X)$ выявлен максимум вблизи x = 0.0075. Измерение температурной зависимости λ_L в интервале 150 - 600 К показало, что концентрационная аномалия в этом же интервале составов наблюдается и на зависимости степенного коэффициента β в температурной зависимости λ_L от состава. Немонотонный характер зависимостей $\lambda_L(x)$ и β(x)связывается с критическими явлениями, сопровождающими переход перколяционного типа от разбавленных к концентрированным твердым растворам. При исследовании и практическом применении твердых растворов $PbSe_{1-x}Te_x$ необходимо учитывать немонотонный характер изменения теплопроводности с составом. Библ. 15, рис. 3.

Ключевые слова: твердые растворы $PbSe_{1-x}Te_x$, теплопроводность, состав, температура, перколяции.

References

1. Rowe D.M. (1995). *CRC Handbook of Thermoelectrics*. Boca Raton, London, New York, Washington: CRC Press.
2. Anatychuk L.I. (1979). *Termoelementy i termoelektricheskiie ustroistva. Spravochnik [Thermoelements and thermoelectric devices. Reference book]*. Kyiv: Naukova dumka [in Russian].
3. Ren Z., Lan Y., Zhang Q. (2017). *Advanced thermoelectrics: Materials, contacts, devices, and systems*. Boca Raton: CRC Press Taylor & Francis Group.
4. Pei Y., Shi X., LaLonde A., Wang H., Chen L., Snyder G.J. (2011). Convergence of electronic bands for high performance bulk thermoelectrics. *Nature Letter*, 473, 66-69.
5. Basu R., Bhattacharya Sh., Bhatt R., Singh A., Aswal D. K., Gupta Sh. K. (2013). Improved thermoelectric properties of Se-doped n-type $PbTe_{1-x}Se_x$ ($0 \leq x \leq 1$). *Journal of Electronic Materials*, 42(7), 2292-2296.
6. Li J.Q., Li S.P., Wang Q.B., Wang L., Liu F.S., Ao W.Q. (2011). Synthesis and thermoelectric properties of the $PbSe_{1-x}Te_x$ alloys. *Journal of Alloys and Compounds*, 509, 4516-4519.
7. Tian Zh., Garg J., Esfarjani K., Shiga T., Shiomi J., Chen G. (2012). Phonon conduction in PbSe, PbTe, and $PbTe_{1-x}Se_x$ from first-principles calculations. *Phys. Rev. B*, 85, 184303.

8. Rogacheva E.I., Nashchekina O.N., Dresselhaus M.S. (2005). Thermal conductivity isotherm anomalies in semiconductor solid solutions based on IV-VI compounds. *J. Thermoelectricity*, 4, 82-90.
9. Rogacheva E.I., Vodorez O.S., Nashchekina O.N., Dresselhaus M.S. (2014). Concentration anomalies of the thermal conductivity in PbTe–PbSe semiconductor solid solutions. *Phys. St. Sol. B*, 251, 1231-1238.
10. Vodoriz O.S., Tavrina T.V., Nikolaenko G.O., Rogachova O.I. (2020). Mechanical and thermoelectric properties of $PbSe_{1-x}Te_x$ semiconductor solid solutions (x = 0 – 0.04). *Metallofiz. Noveishie Tekhnol*., 42(4), 487-495 (in Ukrainian).
11. Tritt T.M. (2004). *Thermal conductivity: theory, properties, and applications*. New York: Kluwer Academic, Plenum Publishers.
12. Berman R. (1976). *Thermal conduction in solids*. Oxford: Clarendon Press.
13. Pei Y.-L., Liu Y. (2012). Electrical and thermal transport properties of Pb-based chalcogenides: PbTe, PbSe and PbS. *J. Alloys and Compounds*, 514, 40-44.
14. Tarasevich Yu.Yu. (2002). *Percoliatsiia: teoriia, prilozheniia, algoritmy [Percolation: theory, applications, algoriythms]*. Moscow: Editorial URSS [in Russian].
15. Stauffer D., Aharony A. (1992). *Introduction to percolation theory. Wasington, DC: Taylor & Francis.*

Submitted 06.08.2020