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Changes in heat transfer in $PbSe_{1-x}Te_x$ semiconductor solid solutions under transition to the impurity continuum

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Lead chalcogenides PbX (X = S, Se, Te) and their solid solutions are well-known as promising materials for thermoelectric generators, infrared detectors, photoresistors, and related applications, and interest in their study continues to grow. An important physical characteristic that determines the possibility of practical use of these materials is thermal conductivity and particularly its dependence on composition, temperature, and other external parameters. The purpose of this work was to investigate the composition dependence of the power-law coefficient β in the temperature dependence of the lattice thermal conductivity $\lambda_p(T)$ on the composition for the $PbSe_{1-x}Te_x$ solid solutions within the range x = 0-0.045. The dependence $\beta(x)$ in the temperature interval 150-350 K was plotted. It was found that the $\beta(x)$ dependence exhibits a complex oscillatory behavior: a pronounced sharp maximum appears near x = 0.005, and additional rather intense maxima are observed near x = 0.015 and x = 0.025. The obtained $\beta(x)$ dependence agrees very well with the previously established $\lambda_p(x)$ behavior. The observed effects are interpreted in terms of a percolation-type phase transition associated with the emergence of an impurity continuum, as well as subsequent self-organization processes (short-range ordering) within the solid solution.

Зміни у теплопереносі в напівпровідникових твердих розчинах $PbSe_{1-x}Te_x$ при переході до домішкового континууму. *О.І. Рогачова, О.С. Водоріз, Т.В. Тавріна, К.В. Мартинова,*

Напівпровідникові халькогеніди свинцю PbX (X = S, Se, Te) та тверді розчини на їх основі добре відомі як перспективні та широко використовувані матеріали для термоелектричних генераторів, інфрачервоних детекторів, фоторезисторів тощо, і інтерес до їх вивчення продовжує зростати. Важливою фізичною властивістю, що визначає можливість практичного використання цих матеріалів, є теплопровідність та її залежність від складу, температури та інших зовнішніх параметрів. Метою цієї роботи було дослідження залежності степеневого коефіцієнта β у температурній залежності решіткової теплопровідності $\lambda_p(T)$ від складу твердих розчинів $PbSe_{1-x}Te_x$ в діапазоні x = 0-0,045. Було побудовано графік залежності $\beta(x)$ в температурному інтервалі 150-350 К. Було виявлено, що залежність $\beta(x)$ демонструє складну коливальну поведінку: яскраво виражений гострий максимум з'являється поблизу x = 0,005, а додаткові досить інтенсивні максимуми спостерігаються поблизу x = 0,015 та x = 0,025. Отримана залежність $\beta(x)$ дуже добре узгоджується з раніше встановленою поведінкою $\lambda_p(x)$. Спостережувані ефекти інтерпретуються з точки зору фазового переходу перколяційного типу, пов'язаного з виникненням домішкового континууму, а також подальших процесів самоорганізації (ближнього впорядкування) у твердому розчині.

1. Introduction

Ccurrently, IV-VI semiconductor compounds (IV-Pb, Sn, Ge; VI - S, Se, Te) and their solid solutions are widely used in thermoelectric (TE) generators, infrared detectors, photoresistors, and other devices, and interest in their study and applications continues to grow [1-3]. Due to the high sensitivity of their band structure to various external factors, such as temperature and composition, IV-VI semiconductors also serve as convenient model objects for investigating phase transitions of various types.

For materials used in TE energy generation through direct conversion of thermal energy into electrical one, thermal conductivity is one of the key parameters determining the dimensionless TE figure of merit $ZT = (S^2\sigma T)/\lambda$, where S is the Seebeck coefficient, σ is the electrical conductivity, λ is the thermal conductivity, and T is the absolute temperature. This parameter characterizes the efficiency of a TE material and, consequently, of a TE converter. It follows that increasing ZT requires reducing λ as much as possible.

The formation of a solid solution based on a semiconductor compound introduces additional phonon scattering on impurity atoms, which reduces the lattice thermal conductivity λ_L. For this reason, the conventional method for increasing ZT is the so-called "solid solution method", which involves forming a sold solution over a sufficiently wide composition range to lower λ_L and subsequent doping to optimize the charge carrier concentration, which determines to a significant extent the value of (S^2 o). In addition, since TE devices operate within certain temperature ranges, it is important to know how λ and λ_L change with temperature. Note also that because improving ZT requires minimizing λ, polycrystalline ceramic (pressed) TE materials are considered more promising than single crystals ones due to their higher density and variety of defects and, consequently, increased phonon scattering.

Within the approximation of ideal solid solutions, λ_L and other properties are expected to change monotonically with impurity concentration. However, by now numerous studies [4-6] have reported a pronounced maxima in the composition dependences of λ_L at low impurity concentrations (~1 at.%). To explain the observed effects, the authors of [4-6] used a percolation model [7,8] for describing processes in disordered systems, and applied it to solid solutions. The anomalies in the concentration dependences of λ_L and other properties were attributed to critical phenomena accompanying the percolation transition to the impurity continuum. Experimental confirmation of the proposed universality of this phenomenon requires investigations of different solid solutions and different properties determined by the electronic and lattice subsystems of the crystal.

The objects of this study were the $PbSe_{1-x}Te_x$ solid solutions formed by anionic substitution, which belong to the promising TE materials [1-3]. In earlier investigations of their structural, kinetic, and TE properties near the PbTe-rich side [9,10], extrema were observed in the concentration dependences of electronic and lattice properties near the composition corresponding to ~0.75 mol.% PbSe. These anomalies were attributed to a percolation-type phase transition. Subsequently, when studying the room temperature concentration dependences of S, σ, microhardness H [11] and λ_L [12] in the same $PbSe_{1-x}Te_x$ system, but in the PbSe-rich region (x = 0-0.045), we also detected peaks near x = 0.005-0.01 and also attributed them to a percolation-type phase transition. However, in [12], for the study of λ and λ_L we used a limited number of compositions, which did not allow for a detailed analysis of the underlying mechanisms. In the work [13], the number of compositions investigated in $PbSe_{1-x}Te_x$ near PbSe was increased. As a result, in addition to the percolation-type peak, two further peaks in the $\lambda_L(x)$ dependences were observed near x = 0.015 and x = 0.025. The appearance of these additional peaks was attributed to self-organization processes in the $PbSe_{1-x}Te_x$, which become possible after reaching the percolation threshold.

The goal of the present study was to determine for $PbSe_{1-x}Te_x$ solid solutions in the range x = 0–0.045 the compositional dependence of the exponent β in the power law temperature dependence of the lattice thermal conductivity λ_L=A $T^{-\beta}$, where A is a coefficient depending on the degree of anharmonicity of the crystal lattice vibrations.

The obtained results showed that the $\beta(x)$ dependence, similar to the previously reported behavior of $\lambda_L(x)$ dependences [13], exhibits not only the peak associated with the percolation transition but also two additional peaks. These two peaks indicate the occurrence of further phase transformations in the solid solution after reaching the percolation threshold.

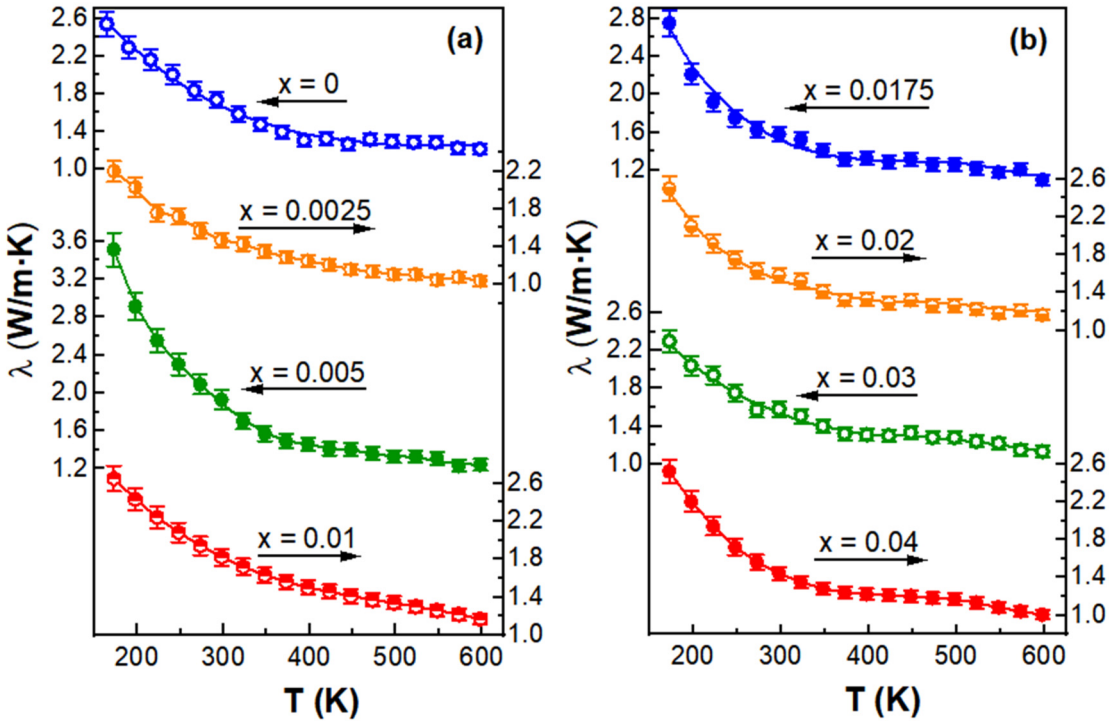

Fig. 1. Temperature dependences of the lattice thermal conductivity λ_L for $PbSe_{1-x}Te_x$ solid solutions of various compositions (x = 0-0.045). The compositions of the samples are indicated next to the corresponding curves.

2. Experimental

Polycrystalline $PbSe_{1-x}Te_x$ samples with various compositions in the range x = 0-0.045 were synthesized by melting Pb, Te and Se in vacuum-sealed quartz ampoules at (1380 ±10) K followed by homogenizing annealing at (870±10) K for 240 h. Fourteen samples were obtained, all exhibiting p-type conductivity. For total thermal conductivity λ measurements, hot-pressed cylindrical samples were prepared and then additionally annealed at (720±10) K during 250 h. λ was measured in the temperature range 150-600 K using the dynamic calorimeter method in the monotonous heating mode with an error not exceeding 5%. The lattice thermal conductivity λ_L was isolated from λ by subtracting the electronic component λ_e, which was calculated according to the Wiedemann-Franz law. The methods for preparing and characterizing bulk and pressed samples, as well as for measuring λ, were described in detail in [13]. The electrical conductivity σ was measured using the van der Pauw method with an accuracy of 5%. The contribution of λ_e to the total λ was found to be negligible within the accuracy of λ and β determination, and therefore disregarded in estimating β. The β values for different x were determined from the temperature dependences of λ_L in the interval 150–350 K, where the contribution of the bipolar component to λ can be ignored.

3. Results and discussion

Fig. 1 presents the temperature dependences $\lambda_L(T)$ for different $PbSe_{1-x}Te_x$ compositions (x= 0-0.045). It can be seen that for all samples studied, λ_L decreases with increasing temperature.

In Fig. 2, the $\beta(x)$ dependence in the temperature interval 150–350 K is shown. The dependence exhibits a pronounced non-monotonic behavior with three distinct peaks near x = 0.005, 0.015, and 0.025.

Let us analyze the experimental data obtained.

According to the Debye-Peierls theory [14,15], at temperatures above the Debye temperature θ (for PbSe, θ = 138 K [16]), the phonon mean free path in a defect-free crystal is limited by three-phonon anharmonic interactions (normal N-processes and Umklapp U-processes), and λ_L decreases inversely with temperature: $\lambda_L \sim 1/T$, which corresponds to $\beta = -1$. However, in crystals containing defects, an additional temperature-independent thermal resistance appears, leading to a change in the crystal phonon spectrum and, accordingly,

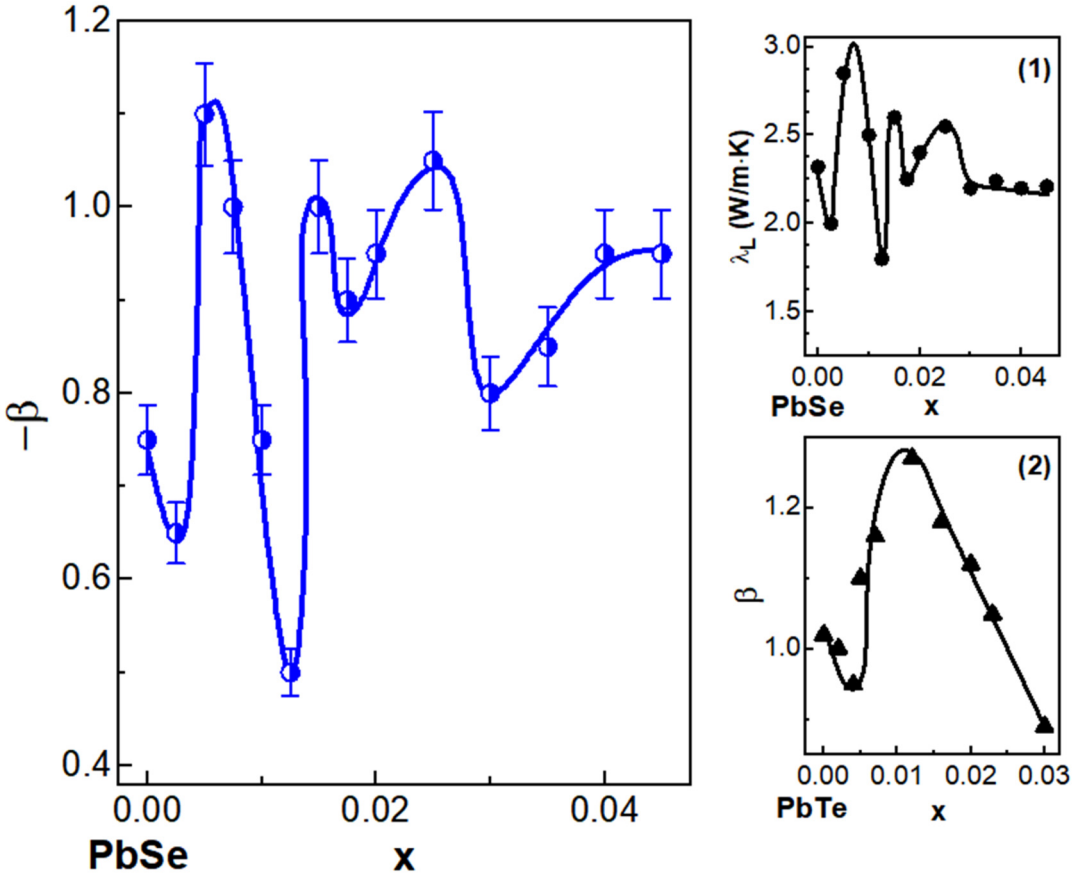

Fig. 2. The dependence of the exponent β in the power-law temperature dependence of lattice thermal conductivity λ_L on composition for the $PbSe_{1-x}Te_x$ solid solutions (x = 0-0.045). Inset (1): the dependences of λL on composition for $PbSe_{1-x}Te_x$ solid solutions (x = 0-0.045) [13]. Inset (2): the dependence of the exponent β on composition for $PbTe_{1-x}Se_x$ solid solutions (x = 0-0.03).

in the β values. As shown in Fig. 2, for stoichiometric PbSe, β differs from β = -1 (β = -0.75 ± 0.05). This deviation is apparently due to the presence of various types of defects, including nonstoichiometric defects, grain boundaries in polycrystals, etc. Our analysis of the temperature dependences of λ_L for polycrystalline PbSe reported by other authors (for example, [17-21]) and our subsequent calculation of the β values based on those dependences confirmed that the β value which we determined for PbSe in our work is in good agreement with those obtained for PbSe by other authors.

Inset (1): the dependences of λ_L on composition for $PbSe_{1-x}Te_x$ solid solutions (x = 0-0.045) [13]. Inset (2): the dependence of the exponent β on composition for $PbTe_{1-x}Se_x$ solid solutions (x = 0-0.03).

As shown in Fig. 2, the introduction of small amounts of Te atoms (up to x = 0.0025), which substitute Se atoms in $PbSe_{1-x}Te_x$ solid solution, leads to a decrease in the absolute value of β, which can naturally be attributed to the introduction of additional phonon scattering centers. With further increase in x, β grows sharply, approaching the values characteristic of a defect-free crystal (β ~ –1) and reaching its maximum near x = 0.007. As noted earlier, the sharp increase in λ_L near x = 0.007 observed for the $PbSe_{1-x}Te_x$ in [13] was associated with a percolation-type phase transition, in which the formation of percolation channels enhances phonon mobility and thus increases λ_L. The emergence of an infinite cluster is accompanied by critical phenomena, which manifest themselves through anomalies in the concentration dependences of different properties. Upon reaching the percolation threshold, the sensitivity of the system to such external factors as temperature increases sharply, and this can account for the growth of β. Therefore, the observed non-monotonic character of the β(x) dependence, with the sharp rise in β near x = 0.007, can also be reasonably attributed to a percolation-type phase transition.

This is convincingly confirmed by the comparison of the concentration dependences $\beta(x)$ and $\lambda_L(x)$. The inset in Fig. 2 shows the $\lambda_L(x)$ isotherm at 200 K for the $PbSe_{1-x}Te_x$ in the range x = 0-0.045, as constructed in [13]. It is seen that the behavior of the $\beta(x)$ dependence obtained in the present work is very similar to the behavior of $\lambda_L(x)$ dependence reported in [13] for the same system in the same composition range. This indicates that the deviation from the additive dependence, characteristic of ideal solid solutions, observed in both $\lambda_L(x)$ and $\beta(x)$ dependences in the same compositional range is caused by similar phase transformations that modify the crystal phonon spectrum.

Note that in the present case, percolation processes do not occur in an ideal defect-free single crystal into which impurities are introduced, but in crystal that already possess a certain defect structure and a certain conductivity. However, despite this, the transition to the impurity continuum is manifested quite clearly.

Thus, reaching the percolation threshold, when perturbations of the crystal lattice induced by impurity atoms become delocalized, leads to qualitative changes in the properties of the solid solution. Further introduction of Te atoms occurs in a crystal, where impurity atoms interact through their force fields and corresponding wave functions, forming an impurity continuum. As a result, increasing x beyond the percolation threshold enables self-organization processes in the solid solution, such as long- or short-range ordering. Long-range order is defined as a state in a solid solution where dissimilar atoms are arranged in a regular pattern, However, the difference in the interaction energy between atoms of the same and different types may be sufficient to ensure that each atom is predominantly surrounded by neighbors of a particular type, even in the absence of long-range order in the solid solution. This phenomenon is referred to as short-range ordering, or a correlation in the mutual arrangement of atoms. In simple cases, short-range order extends over one or two coordination spheres; more often, correlations is spread over greater distances. It has been established that short-range ordering significantly influences various physical properties, giving rise to features in the functional dependencies of various characteristics of alloys. The degree and nature of short-range order depend strongly on composition, temperature, aging of alloys, heat and mechanical treatments, and other factors.

The appearance of additional peaks in the $\beta(x)$ dependence near x = 0.015 and 0.025 indicates that self-organization processes occur in the solid solution, and that the nature of short-range ordering depends on the solid solution composition. Establishing the specific structure of the short-range order would require detailed structural studies, which were beyond the scope and objectives of the present work.

It is of interest to compare the composition dependences of the coefficient β after reaching the percolation threshold in different concentration ranges of $PbSe_{1-x}Te$ solid solutions: near the PbSe compound (this work, Fig. 2) and near the PbTe compound [10,11]. The results obtained in [10,11] are shown in inset 2 of Fig. 2. It can be seen that while three peaks are observed near PbSe in the range x = 0-0.045, corresponding to the percolation transition and short-range ordering processes, only a single peak appears near PbTe. With further increase in Se concentration, the $\beta(x)$ dependence exhibits a monotonic behavior, which is characteristic of an ideal solid solution. The fact that in both PbTe- and PbSe-based solid solutions, a sharp maximum is observed upon introduction of the first portions of impurity further confirms the universal character of critical phenomena associated with the percolation-type transition to an impurity continuum.

The absence of additional features in the $\beta(x)$ dependence near PbTe can be explained by the fact that the occurrence and the rate of short-range ordering processes depend on multiple factors, including the characteristics of the defect structure, which largely determine the stresses arising in the crystal lattice. It can be assumed that when a larger anion (Te) is replaced by a smaller one (Se), the resulting stresses are significantly smaller than when Se is replaced by larger anions (Te). In the latter case, the driving force for ordering increases, as reflected by the presence of two clearly defined additional peaks in the $\beta(x)$ dependence. It can be expected that expanding the composition range, applying thermal or mechanical treatments, aging, or other factors could reveal self-organization phenomena and additional peaks in the $\beta(x)$ dependence of PbTe-based solid solutions.

4. Conclusions

In $PbSe_{1-x}Te_x$ semiconductor solid solutions (x = 0–0.045), the composition dependence of the exponent β in the power-law temperature dependence of lattice thermal conductiv-

ity was determined in the temperature range 150-350 K and discussed within the framework of previously proposed ideas. The main conclusions are as follows.

The $\beta(x)$ dependence exhibits a non-monotonic behavior with three distinct peaks near x = 0.007, 0.015, and 0.025. The first peak is attributed to a percolation-type phase transition to an impurity continuum, while the other two peaks to the manifestation of the self- organization processes in $PbSe_{1-x}Te_x$. The complex behavior of the $\beta(x)$ dependence indicates changes in heat transfer and phonon scattering with composition.

These results provide further confirmation of the assumption about the universal character of critical phenomena accompanying the percolation-type phase transition to an impurity continuum.

The presence of self-organization processes in solid solutions represents an important factor for controlling and optimizing the properties of semiconductor materials.

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References

1. D.M. Rowe (Ed.) CRC Handbook of Thermoelectrics, London, New York, Washington: CRC Press, Boca Raton, 1995.
2. L. Chen, R. Liu, X. Shi, Thermoelectric Materials and Devices, China, Science Publishing & Media Ltd. Published by Elsevier Inc; 2020.
3. A. Rogalski, *Prog. Quantum Electron*, **27 (2-3),** 59 (2003). https://doi.org/10.1016/S0079-6727(02)00024
4. E.I. Rogacheva, O.N. Nashchekina, M.S. Dresselhaus, *J. Thermoelectricity*, **4,** 82 (2005).
5. E.I. Rogacheva, J. Thermoelectricity, **2,** *61* (2007).
6. E.I. Rogacheva, O.N. Nashchekina, Percolation effects in semiconductor IV-VI based solid solutions and thermoelectric materials science, in: Chong Rae Park, Advanced Thermoelectric Materials (ed), John Wiley & Sons Inc, New York, 2020, pp. 383 – 436.
7. D. Stauffer, A. Aharony, Introduction to Percolation Theory, DC: Taylor & Francis, London, Washington, 1992.
8. B.I. Shklovskii, A.L. Efros, Electronic Properties of Doped Semiconductors, Springer-Verlag, New York, 1984.
9. E.I. Rogacheva, O.S. Vodorez, *J. Thermoelectricity*, **2**, 61 (2013).
10. E.I. Rogacheva, O.S. Vodorez, O.N. Nashchekina, M.S. Dresselhaus, *Phys. St. Sol. B*, **251**, 1231 (2014). https://doi.org/10.1002/pssb.201350293
11. O.S. Vodoriz, T.V. Tavrina, G.O. Nikolaenko, O.I. Rogachova, *Metallofiz. Noveishie Tekhnol*, **42**, 487 (2020) (in Ukrainian). https://doi.org/10.15407/mfint.42.04.0487
12. G.O. Nikolaenko, O.S. Vodoriz, O.I. Rogacheva, T.V. Tavrina, G.V. Lisachuk, *J. Thermoelectricity*, **4**, 5 (2020). https://doi.org/10.63527/1607-8829-2020-4
13. E.I. Rogacheva, G.O. Nikolaenko, A.V. Meriuts, O.N. Nashchekina, *Phase Transitions*, **97**, 508 (2024). https://doi.org/10.1080/01411594.2024.2352436
14. R. Berman, Thermal conduction in solids, Clarendon Press, Oxford, 1976.
15. V.M. Mogilevskii, A.F. Chudnovskii, Thermal conductivity of semiconductors, Nauka, Moscow, 1972.
16. Yu.I. Ravich, B.A. Efimova, I.A. Smirnov, Semiconducting Lead Chalcogenides, Plenum Press, New York, 1970.
17. R. Basu, Sh. Bhattacharya, R. Bhatt, A. Singh, D.K. Aswal, Sh.K. Gupta, *J. Electr. Mater.*, **42,** 2292 (2013).
18. J.Q. Li, S.P. Li, Q.B. Wang, L. Wang, F.S. Liu, W.Q. Ao, *J. Alloys and Compounds*, **509**, 4516 (2011). https://doi.org/10.1016/j.jallcom.2011.01.033
19. .L. Pei, Y. Liu, *J. Alloys and Compounds*, **514**, 40 (2012). https://doi.org/10.1016/j.jallcom.2011.10.036
20. Y. Pei, X. Shi, A. LaLonde, H. Wang, L. Chen, G.J. Snyder, *Nature. Letter*, **473,** 66 (2011). https://doi.org/10.1038/nature09996
21. T.M. Tritt, Thermal conductivity: theory, properties, and applications, Kluwer Academic, Plenum Publishers, New York, 2004.