E.I. Rogacheva[1], O.S. Vodorez[1], O.N. Nashchekina[1], M.S. Dresselhaus[2]

[1]National Technical University "Kharkov Polytechnic Institute", 21 Frunze St.,
Kharkov 61002, Ukraine
[2]Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, USA

PECULIARITIES OF CONCENTRATION DEPENDENCES OF THERMAL CONDUCTIVITY IN $(PbTe)_{1-x}$ $(Bi_2Te_3)_x$ SEMICONDUCTOR SOLID SOLUTIONS

For the semiconductor $(PbTe)_{1-x}$ $(Bi_2Te_3)_x$ solid solutions, the temperature (T = 250 – 670 K) and concentration (x = 0 – 0.07) dependences of the total λ and lattice λ_p thermal conductivities were obtained. It was established that the dependences $\lambda(x)$, $\lambda_p(x)$ and $\beta(x)$ (where β is the exponent in the $\lambda_p \sim T^{-\beta}$ dependence) have a non-monotonic dependence on x in this range of x. While showing a general tendency to decrease with increasing x, the three variables λ, λ_p, and β exhibit maxima at x = 0.005, 0.015 and x = 0.03. The oscillatory character of these dependences is attributable to the changes in thermal transfer processes and the mechanisms of phonon scattering under transitions from the dilute to the concentrated and associated solid solutions, with the transitions due to spatial ordering processes. The effective cross-section σ_s for phonon scattering by impurity atoms was estimated on the basis of the experimental data and theoretical calculations in accordance with the Klemens theory. The mean σ_s value in the homogeneity region of PbTe (x = 0 – 0.05) found experimentally coincides with the theoretically calculated σ_s value. However, in the region of the dilute solid solutions (x < 0.005), the σ_s value considerably exceeds the mean σ_s value. Also long-term aging reduces λ by ~ 15%.

Key words: $(PbTe)_{1-x}(Bi_2Te_3)_x$ solid solutions, thermal conductivity, isotherms, concentration anomalies, percolation, self-organization, critical phenomena.

Introduction

A conventional method for enhancing the dimensionless thermoelectric (TE) figure of merit ZT ($ZT = S^2\sigma T/\lambda$, where S is the Seebeck coefficient, σ is the electrical conductivity, λ is the thermal conductivity, and T is the absolute temperature) of semiconductor compounds is the formation of the solid solutions. The purpose of using solid solutions is for decreasing the lattice thermal conductivity λ_p, and for their subsequent doping to obtain the optimal carrier concentration [1, 2]. It is usually assumed that in the range of solid solutions, the physical properties of materials change monotonically and that under doping, the lattice properties and λ_p practically do not change. However, in a number of solid solutions based on the semiconductor IV-VI compounds, in the region of small impurity content (less than ~1 at.%), we revealed concentration dependent anomalies of the mechanical, galvanomagnetic, and TE properties (see, for example, [3-7]) and attributed their existence to critical phenomena accompanying the transition to an impurity continuum [7,8]. Besides, in some concentrated solid solutions [9], we observed an oscillatory character of the property–composition dependences, which we attributed to ordering processes that occurred when the interaction between impurity atoms starts to make a significant contribution to the free energy of the crystal. These concentration anomalies must be taken into account when

developing more efficient TE materials and these anomalies call for further detailed studies in this direction, as are presented here.

IV-VI compounds and solid solutions based on these compounds are among the best medium-temperature TE materials, which at present are used extensively for energy generation [1, 2]. The PbTe-based solid solutions in the Pb – Bi – Te system have attracted special attention for a long time because, firstly, Bi is counted among the major donor impurities in PbTe for controlling the electron concentration and for obtaining the maximal ZT value, and, secondly, there is available information about a substantial λ reduction under the introduction of Bi in PbTe [1, 2, 10].

Bi can be introduced in PbTe in a variety of ways: one can for example introduce elementary Bi [11, 12], or BiTe [13, 14] and Bi$_2$Te$_3$ compounds [14-22], etc. In all cases, under the introduction of Bi into stoichiometric p-PbTe, an inversion of the sign of the conductivity takes place at a Bi concentration of less than 0.1 at.%. In most works the PbTe-based solid solutions along the quasi-binary (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ section of the Pb – Bi – Te ternary system [14-22] are studied (brief overviews of those works are given in [21,22]).

Recently, we have reported [21,22] the results of our detailed studies on the room temperature dependences of the X-ray diffraction line width, the microhardness H, σ, S, Hall coefficient R_H, and charge carrier mobility μ in the (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ solid solutions on composition in the concentration range $x = 0 – 0.06$, corresponding to the interval of PbTe-based solid solutions. According to [21,22], the concentration dependences of the properties exhibit a non-monotonic behavior that is unusual for solid solutions, indicating that qualitative changes in the defect subsystem take place under increasing the Bi$_2$Te$_3$ concentration. The observed peculiarities were attributed to the transition from the dilute to the concentrated solid solutions, and then to associated solid solutions, as well as to the pertinent ordering processes [21, 22].

The influence of small concentrations of Bi$_2$Te$_3$ on the PbTe thermal conductivity was studied in [16-18]. The authors of [16,17], who investigated the concentration range of $x = 0.002 – 0.0085$ in the (PbTe)$_{1-x}$Bi$_2$Te$_3$)$_x$ system, showed that at room temperature, with increasing x, the electronic component λ_e of the total thermal conductivity monotonically increases, λ_p decreases, and λ practically does not change. Almost similar results in terms of both the behavior of the concentration dependences of λ, λ_e and λ_p and the values of the thermal conductivity were obtained in [18], where a still narrower concentration range in the vicinity of PbTe (x = 0 – 0.13) was studied. Like in [17], no concentration anomalies were observed, and all alloys, including the initial compound PbTe, exhibited n-type conductivity.

The goal of the present work is to study the thermal conductivity of (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ solid solutions in the concentration range of $x = 0 – 0.07$ with the purpose of establishing whether or not the λ isotherms exhibit a non-monotonic behavior like the isotherms for the properties described above.

One of the important factors, which determine the operating efficiency of TE devices, is the device lifetime. That is why studying the influence of the material aging on its thermal conductivity is also of interest, and is reported in the present work.

Experimental details

(PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ cylindrical samples with a height of 5 mm and a diameter of 15 mm for the thermal conductivity measurements were prepared by hot pressing at the temperature $T_p = 650$ K and loading $P = 0.4$ GPa from polycrystalline alloys, synthesized using a method described in [21,22].

After pressing, all samples were annealed at 720 K for 200 hours. The chemical composition and homogeneity of the samples were controlled by electron-probe microanalysis and by energy dispersive X-ray spectroscopy using a scanning electron microscope. It was shown that the chemical compositions of the samples corresponded to what was intended with an accuracy of not less than 5 % and the degree of the sample homogeneity was satisfactory. Besides, we investigated the pressed samples, prepared earlier by a similar method and these samples had been subjected to aging at room temperature for 25 years.

The thermal conductivity was measured by the dynamic calorimeter method [23] in the mode of monotonic heating in the temperature range 170 – 670 K. There were at least three measurements of λ for each sample. The shift of the $\lambda(T)$ curves for different measurements on the same samples (which resulted from a possible non-identical setting of a sample in the measuring cell) did not exceed ~ 3 %. The accuracy of the λ measurement was ± 5 %. The electrical conductivity σ was measured using the van der Pauw method with the accuracy not worse than ~ 5%. The lattice component λ_p of the total thermal conductivity λ was isolated by the subtraction of the electronic component λ_e determined using the Wiedemann - Franz law $\lambda_e = L\sigma T$, where L is the Lorentz number ($L = (\pi^2/3)(k/e)^2 \approx 2.47 \cdot 10^{-8}$ WΩK^{-2}).

Results and discussion

In Fig. 1, a, the temperature dependences of the total thermal conductivity of as-prepared (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ samples with different compositions are presented. All curves have a similar character: as the temperature increases up to ~ 450 - 500 K, λ decreases, but under further increase in temperature, λ starts to increase.
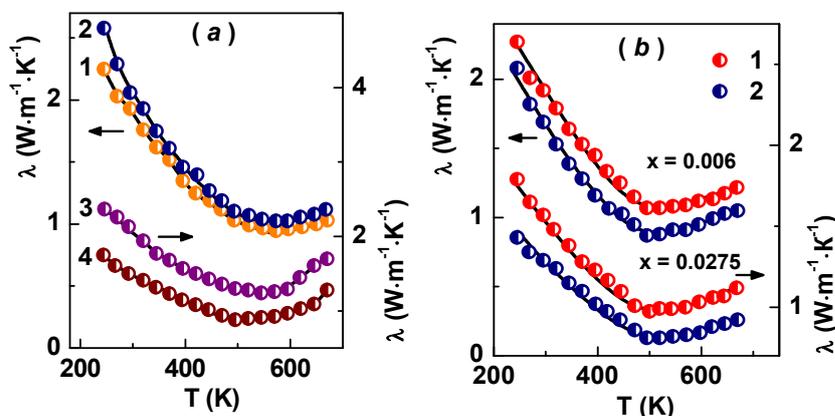
Fig.1. The temperature dependences of the total thermal conductivity λ for (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ solid solutions. a – as-prepared samples, 1 – PbTe (x = 0); 2 – x = 0.0035; 3 – x = 0.01; 4 – x = 0.025; b – as-prepared samples (1), and samples after aging (2).

It is known that heat in semiconductors can be transferred by crystal lattice vibrations, the electron gas, electromagnetic radiation, as well as by the bipolar diffusion of charge carriers; thus the equation for calculating the total thermal conductivity λ must include the lattice λ_p, electronic λ_e, photon λ_{ph}, and bipolar λ_b components [24-26]:

$$\lambda = \lambda_p + \lambda_e + \lambda_{ph} + \lambda_b \tag{1}$$

Taking into account that the PbTe optical absorption coefficient α is rather high ($\alpha \sim 200$ cm^{-1} [26]), the heat transfer by electromagnetic radiation can be neglected. Indeed, the estimation of λ_{ph} using the formula: $\lambda_{ph} = 16\, n^2\, \sigma_0\, T^3/3\, \alpha$, where n is the refractive index, σ_0 is the Stefan–Boltzmann constant, α is the absorption coefficient, and T is the absolute temperature, shows that over the entire temperature range, the contribution of λ_{ph} from photons to λ does not exceed ~0.5 %. The increase in λ observed at temperatures above ~ 450 K can be explained, like in PbTe, by the appearance of a bipolar diffusion of charge carriers caused by the occurrence of the intrinsic conductivity [26]. Below ~ 450 K, the bipolar component practically does not make any contribution, and one can assume that λ is determined mainly by λ_p and λ_e.

In Fig. 1 (*b*), for comparison, the $\lambda(T)$ dependences for as-prepared samples and for the samples aged for 25 years at room temperature ($x = 0.006$ and $x = 0.0275$) are presented. It is seen that both curves have a similar character (running virtually in parallel), but after aging, the λ values decrease on average by ~ 15 %.

On the basis of the $\lambda(T)$ dependences for as-prepared samples, the λ isotherms in the temperature range 250 – 470 K were plotted (Fig. 2). It is seen that while exhibiting a general tendency to decrease in λ with increasing x, these dependences have a complex oscillatory character. At $x > 0.05$, λ does not depend on concentration x, which is explained by reaching the boundary of the solubility region for Bi$_2$Te$_3$ in PbTe and entering the two-phase region [21, 22].
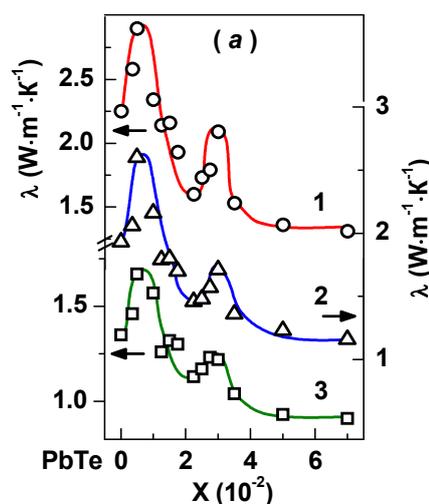
Fig.2. The isotherms of the total thermal conductivity λ for (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ solid solutions at various temperatures 1 – 250 K; 2 – 300 K; 3 – 450 K.

In Fig. 3 (a), the dependence of the room-temperature lattice thermal conductivity λ_p on composition is presented. Similar to the total thermal conductivity, λ_p shows a general trend to decrease under increasing Bi$_2$Te$_3$ concentration (in Fig. 3a the monotonic component of the $\lambda_p(x)$ dependence is shown with a dashed line), but at the same time, three distinct maxima near $x = 0.005$, 0.015 and 0.03 are observed in the $\lambda_p(x)$ curve.

Thus, the experimental results obtained in the present work demonstrate that the $\lambda_p(x)$ dependence exhibits a complex behavior, which can be treated as an overlapping of the monotonic and oscillatory λ_p components. The presence of three maxima in this dependence shows that at certain concentrations of the solid solution, phonon scattering decreases and the velocity of the propagation of elementary excitations increases.
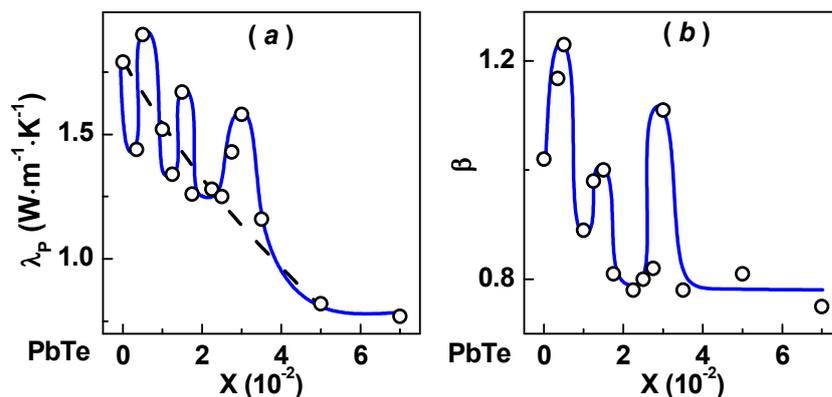
Fig.3. The dependences of the lattice thermal conductivity λ_p (a), and the exponent β in the temperature dependence of λ_p (b), on (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ solid solutions composition x.

It is known [24-26] that at temperatures above the Debye temperature Θ (for PbTe Θ = 130 K [27]), the phonon mean free path is limited mainly by three-phonon interactions and by the interaction of phonons with crystal lattice defects. In this case, in accordance with the Debye-Peierls theory of the thermal conductivity, at temperatures near and above Θ, the lattice thermal conductivity decreases inversely with temperature: $\lambda_p \sim 1/T$.

It was of interest to find out whether such a dependence of $\lambda_p(T)$ is also observed in the (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ solid solutions. Assuming a power law for the temperature dependence of the λ_p ($\lambda_p \sim T^{-\beta}$), we estimated the exponent β values for the alloys of different compositions in the temperature range 250 – 450 К, when the contribution of the bipolar diffusion is insignificant and can be neglected. In Fig. 3(b), the β (x) dependence is shown. It is seen that $\beta = 1 \pm 0.02$ only for PbTe (which is in good agreement with the Debye - Peierls theory and experimental results obtained by other authors for PbTe [26, 27]). However the introduction of Bi$_2$Te$_3$ in PbTe leads to a complex oscillatory dependence β (x) with maxima near x = 0.005, 0.015 and 0.03. The most pronounced maxima correspond to x = 0.005 and x = 0.03. The change in the exponent β in the (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ solid solutions under changing x and the extreme character of the β (x) dependences indicate a change in the heat transfer and phonon scattering processes at certain compositions x.

According to generally accepted concepts of the classical physicochemical analysis, the "property vs. composition" dependences of solid solutions should represent monotonic curves. It is assumed in the quasi-chemical approximation that the interaction energy between atoms does not depend on the solid solution concentration. Within the framework of these views, it is logical to suppose that with increasing impurity concentration in the range of the solid solution regime, λ_p will decrease due to an increase in phonon scattering by impurity atoms [24-26]. That is why the observed complex behavior of the λ, λ_p, and β isotherms requires explanations.

According to our views [7, 8], in any solid solution, independent of the nature of particles interactions, reaching the percolation threshold x_c corresponds to the formation of an impurity continuum and must be accompanied by critical phenomena, – anomalies in the concentration dependences of the physical properties. It is the concentration corresponding to the percolation threshold x_c that can be considered to be a boundary separating dilute and concentrated solid solutions.

In accordance with these views, the anomalous growth in λ_p in the concentration range x = 0.0035 - 0.005 can be attributed to critical phenomena accompanying a transition of a percolation type

taking place in the impurity subsystem of the crystal when the impurity concentration reaches the percolation threshold [28,29]. At small impurity concentrations, when the distance between impurity atoms is large and the deformational fields of nearest neighbor impurity atoms do not overlap, impurity atoms make an additive contribution to the lattice thermal resistivity ($1/\lambda_p$), either increasing $1/\lambda_p$ or decreasing λ_p. As the impurity concentration increases, the overlapping of the elastic fields of neighboring atoms starts to become important and produces a partial compensation of the impurity-imposed elastic stresses, thereby causing the oscillatory behavior observed at very low values of x. On reaching the percolation threshold, an «infinite cluster» (chain of interacting impurity atoms) is formed, thereby penetrating the entire crystal. Under further increase in x, the density of the «infinite cluster» increases over a sufficiently narrow concentration interval, and after that one can assume the formation of an impurity continuum. A percolation transition is similar to a type II (second order) phase transition, which is accompanied by critical phenomena [28, 29]. The increase in λ_p is associated with the compensation of stresses which take on a collective character, thereby facilitating the propagation of phonons, and reducing phonon scattering. After the process of elastic stress compensation spreads over the entire crystal volume, this entire crystal volume becomes filled with "impurity liquid". Further introduction of impurity atoms leads to new lattice distortions, and, consequently, to a decrease in the λ_p value. Taking into account the abrupt increase in λ_p near $x = 0.0035$, the possibility of impurity atom ordering on reaching the percolation threshold should not be excluded.

After the transition from the dilute to concentrated solid solution occurs (near $x = 0.0035$), when all the impurity atoms become connected, self-organization processes become possible. The observed increase in λ_p in the concentration ranges $x = 0.0125 - 0.015$ and $x = 0.025 - 0.03$ suggests that such self-organization processes take place, and with the highest probability they are caused by a possible short-range ordering, i.e. by the formation of groups of atoms (clusters) in a macroscopically homogeneous solution as a result of the interactions of atoms not only with their nearest neighbors but also with those in the next neighbor coordination range. Apart from the short-range order of a general type, which is present in any solid solution and is associated with the difference in the interaction energies of different atoms, there can exist a short-range ordering connected with the manifestation of a chemical interaction in the solid solution. The introduction of a dopant in the form of a stable chemical compound (in our case the Bi$_2$Te$_3$ compound) with the crystal structure differing from the matrix structure (in our case PbTe) stimulates the formation of regions with short-range ordering (complexes) and chemical bonds corresponding to the composition of that compound. In [30] on the basis of the analysis of experimental data on the concentration dependences of the various physical properties and the results of theoretical calculations using appropriate phenomenological methods for modeling cluster components, it was shown that in solid solutions formed by stable compounds, the chemical interaction between impurity and matrix atoms leads to the formation of neutral chemical complexes and microheterogeneous structures within the solid solution. Physico-chemical properties of a solution also depend on the type of neutral associates that are formed in the solid solution.

The oscillatory character of the λ, λ_p and β dependences that is observed in this work may indicate a change in the type of clusters formed under changing solid solution composition, i.e. a change in atomic configurations corresponding to minima of the potential energy.

If the concentration of complexes is so high that percolation channels linking complexes and penetrating the entire crystal are formed and if the crystal structure of complexes differs from the matrix structure, then in the percolation theory approximation one can suggest the existence of another percolation threshold x_k.

The anomalous increase in λ_p in the vicinity of $x = 0.03$, as well as earlier observed peculiarities in the isotherms of other properties near the indicated composition [21,22] (an increase in the electrical conductivity and charge carrier mobility, the constancy of the X-ray line width B for as-made samples and a sharp decrease in B after long-term aging, etc.), all allow us to suggest that the observed effects are connected with the formation of percolation channels linking not separate impurity atoms, but rather associates of the impurity atoms (i.e. molecules or clusters of molecules) are in this case reaching the percolation threshold x_k. With the highest probability, the composition of such associates corresponds to the composition of the precipitated phase that reaches the solubility limit (Bi$_2$Te$_3$ or the ternary PbBi$_2$Te$_4$ compound). The decrease in B at $x = 0.03$ almost down to the B value for the initial PbTe after long-term aging, indicates a high degree of local ordering and suggests that after the formation of the infinite cluster, short-range ordering (the formation of molecular complexes) is accompanied by long-range ordering of the molecular complexes within the solid solution [21,22].

From the concentration dependence of λ_p in the range $x = 0 - 0.0035$, i.e. in the region of PbTe-based dilute solid solutions, the effective phonon cross-section σ_s of scattering by Bi impurity atoms was estimated using the Ioffe formula [31]:

$$\frac{\lambda_{p_o}}{\lambda_p} = 1 + \Phi \cdot \frac{N}{N_o} \cdot \frac{l_o}{d} \qquad (2)$$

where λ_{p0} and λ_p are, respectively, the lattice thermal conductivity of the crystal without impurities and with impurities, N_0 and N are, respectively, the total number of all atoms and the number of impurity atoms per unit volume, d is the distance between impurity atoms, l_0 is the phonon mean free path, which enters into the equation for the lattice thermal conductivity λ_{p0} of the undoped crystal:

$$\lambda_{p_o} = (1/3) \cdot l_o \cdot C_v \cdot V_g \qquad (3)$$

where C_v is the heat capacity per unit volume, and V_g is the mean phonon group velocity, and Φ is a dimensionless coefficient which enters into the equation $\sigma_s = \Phi d^2$. From equation (2) one can easily determine Φ and σ_s.

However, there arises a problem, insofar as it is the phonon group velocity V_g that appears in equation (3), and not the sound phase velocity V_p. The latter can be experimentally measured relatively easily, but the difference between the two velocities V_g and V_p can be rather significant. For example, the calculation [33] performed for PbTe shows that $V_g = V_p/3$. Theoretical calculations of phonon group velocity V_g with frequency – and branch-dependent analysis have been performed in some other works too, for example in [34, 35], where the authors used first-principles-based anharmonic lattice dynamics simulations. The group velocity was averaged for transverse and longitudinal acoustic branches to be a function of frequency. There obtained very low values of the group velocity for the long-wave transverse acoustic phonons along the [100] direction. That is why, if when calculating Φ one uses the mean sound phase velocity, an error will be introduced, and to correct the result one should multiply the value of Φ thus obtained by $\alpha = V_g/V_p$ [36].

Since at present an accurate experimental value of the group velocity for PbTe is unknown, when calculating Φ we used a value of the mean sound phase velocity instead of V_g, which, in turn, was calculated as $V_p = (V_l + 2 V_t)/3 = (3000+2 \cdot 2430)/3 = 2620$ m/s, where V_l and V_t are the longitudinal and transverse components of the sound velocity of PbTe, respectively [26].

It should be also noted that numerical values of σ_s and Φ that are obtained in this way depend significantly on the particular range of Bi concentrations for which these values have been determined,

because in general the λ_p - composition dependences are not linear. It follows from the above discussion that any comparison of the calculated values of Φ with the literature data is possible only when the same concentration ranges are considered and the same values of the phonon group velocities are used for the pertinent calculations.

Substituting values of λ_{p0}, λ_p, N, N_0, as well as C_v [25]·and V_g into equation (2), we obtain that for the concentration range $x = 0 – 0.05$, $\Phi = 4.9$ and $\sigma_s = 4.9\ d^2$ at 300 K (Table 1). These values correspond to a drop in λ_p over the entire homogeneity range ($x = 0 – 0.05$). If we consider the interval $x = 0 – 0.0035$, i.e. the region of the initial drop in λ_p, we will obtain a considerably higher value $\Phi = 13$ and $\sigma_s = 13\ d^2$, which indicates a drastic increase in phonon scattering when the early introduction of the first portions of impurity atoms occurs. Such an increase can be explained by the fact that the introduction of the first portions of the impurity atoms leads to a sharp growth in the configuration entropy, denoting the probability of the impurity atoms being delocalized increases relative to their basic structural positions, specifically, allowing the impurity atoms to enter the interstices of the crystal lattice. The first portions of the impurity are introduced into the PbTe host material not as a neutral Bi$_2$Te$_3$ compound, but rather as separate Bi and Te atoms, which, with a high probability, occupy interstices in the PbTe crystal lattice.

According to the Klemens theory [37, 38], point defect scattering may be considered to be the combined effect of scattering due to the mass difference $\Delta M/M$, the change in the force constants at the defect site $\Delta G/G$, and the strain field caused by the dilation or contraction of the lattice around a defect resulting from the difference in the effective size of the host atom (ion) and the substituting defect $\Delta R/R$. According to Klemens [37, 38], the total scattering cross-section can be expressed as follows:

$$\sigma_s = \frac{V_o^2 \cdot \omega^4}{4\pi \cdot V_g^4}\left\{\left(\frac{\Delta M}{M}\right)^2 + 2\left(\frac{\Delta G}{G} - \frac{b}{\sqrt{5}} \cdot \gamma \cdot \frac{\Delta R}{R}\right)^2\right\} \qquad (4)$$

where ω is the frequency (we assume that ω is the Debye frequency: $\omega = \omega_D = k\Theta_D/\hbar$), V_g is the phonon group velocity, M is the molar mass, G is the elastic modulus, γ is the Grüneisen constant, R is the ionic radius, and V_o is the volume per atom. Assuming $\Theta_D = 130$ K [27], $\gamma = 2$ [35], $b = 14.2$ [35], $V_g = (V_1 + 2\ V_t)/3 = 2620$ m/s [28], we obtain $\sigma_S = 5.9\ d^2$, i.e. $\Phi = 5.9$ (Table 1).

Table 1

Phonon scattering cross-sections σ_s and the multiplying dimensionless factors Φ
for (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ alloys

Concentration range, x	σ_s (10^{-20} m^2)		Φ	
	Experiment	Theory	Experiment	Theory
0 – 0.0035	135	61.4	13	5.9
0 – 0.05	51	61.4	4.9	5.9

It is seen from Table 1 that the maximum scattering of phonons occurs in the range of the smallest impurity concentrations, i.e. in the region of the most dilute solid solutions, when the crystal has the broadest variety of defects, which is stimulated by a sharp growth in configurational entropy under the introduction of the first range of impurity concentration in the crystal. It is also seen from Table 1 that the results of the theoretical calculations are in good agreement with the experimental data if we consider the concentration range ($x = 0 – 0.05$) corresponding to the entire homogeneity

region and ignore the regions of x where the anomalous behavior occurs (the dashed line in Fig. 3a). This fact can be explained rather easily if we take into consideration that the calculation according to the formula (4) assumes an ordinary cation or anion substitution [37, 38] and does not take into account the existence of defects other than substitutional defects, as, for example, interstitial species.

Conclusions

1. In the isotherms of the lattice thermal conductivity λ_p for (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ solid solutions ($x = 0 – 0.07$), with λ_p exhibiting a general tendency to decrease with increasing x (monotonic component in the $\lambda_p(x)$ dependence), three maxima are revealed near $x = 0.005$, 0.015 and 0.03. The existence of the first maximum at $x = 0.005$ is attributed to the critical phenomena accompanying a percolation type transition to an impurity continuum when the crystal lattice perturbation becomes delocalized. This transition is accompanied by both a partial compensation of stresses in the crystal lattice and an increase in the velocity of phonon propagation. The second maximum at $x = 0.015$ is attributed to the formation of an intermediate structure with short-range ordering, and the third maximum is identified with the formation of percolation channels through the neutral chemical complexes, which are formed in the solid solution at the stage preceding the precipitation of the second phase inclusions where the precipitation starts after reaching the solubility limit. In the latter case, the reaching of the percolation threshold is accompanied by ordering processes, whose presence is supported by our earlier observations [21], specifically a sharp decrease in the X-ray line width almost down to the X-ray line width value in PbTe observed near $x = 0.03$ after long-term aging. It is also shown in the present study that long-term aging of the (PbTe)$_{1-x}$ (Bi$_2$Te$_3$)$_x$ solid solutions leads to an insignificant decrease in λ.

The study of the temperature dependences of the thermal conductivity showed that there are three maxima in the dependence of the exponent $\beta(x)$ in the $\lambda(T)$ dependences, corresponding to the same values of the composition x of the solid solution. The changes of β with x also indicates that there are qualitative changes in the processes of the heat transfer taking place in the phonon scattering mechanisms when changing the solid solution compositions.

2. The phonon effective scattering cross-section σ_s for Bi impurity atoms was estimated on the basis of the experimental data using the Ioffe formula and on the basis of the theoretical calculations using the Klemens theory. It is found that the mean σ_s value over the large range of compositions for the PbTe homogeneity region ($x = 0 – 0.05$) determined experimentally using the monotonic component of the $\lambda_p(x)$ dependence ($\sigma_s = 4.9 \, d^2$) yields good agreement with the results of the theoretical calculations. However, in the region of the very dilute solid solutions ($x = 0 – 0.0035$), the abrupt increase in the σ_s value ($\sigma_s = 13 \, d^2$) is here connected with the increasing assortment of possible structural defects and the rapidly increasing configuration entropy.

3. The observation of the concentration anomalies provides additional support for the idea of the existence of a percolation type transition in any solid solution in the range of very small impurity concentrations and indicates the non-monotonic behavior of the isotherms of specific properties within the more concentrated solid solutions region. The results obtained here suggest that when interpreting and predicting the expected properties (e.g. thermal conductivity) of solid solutions and doped semiconductors, it is necessary to take into account the existence of concentration anomalies connected with the interaction of impurity atoms among themselves within the matrix as well as with the matrix atoms.

References

1. L.I. Anatychuk, *Thermoelements and Thermoelectric Devices: Reference Book* (Kyiv: Naukova Dumka Publishers, 1979) (in Russian].

2. *CRC Handbook of Thermoelectrics*, ed. D.M. Rowe (CRC Press: Boca Raton, London, New York, Washington, 1995).

3. E.I. Rogacheva, Concentration-Dependent Microhardness in Semiconductor Solid Solutions, *Izv. AN SSSR. Neorgan. Mater.,* **25**, 643-646 (1989).

4. E.I. Rogacheva, I.M. Krivulkin, V.P. Popov, and T.A. Lobkovskaya, Concentration Dependences of Properties in Pb$_{1-x}$Mn$_x$Te Solid Solutions, *Phys. status solidi* A **148**, K65-K67 (1995).

5. E.I. Rogacheva, I.M. Krivulkin, Isotherms of Thermal Conductivity in PbTe-MnTe Solid Solutions, *Physics of the Solid State* **43**, 1000-1003 (2001).

6. E.I. Rogacheva, I.M. Krivulkin: The Temperature and Concentration Dependences of the Charge Carrier Mobility in PbTe-MnTe Solid Solutions, *Semiconductors*, 36, p. 966 – 972 (2002).

7. E.I. Rogacheva, Percolation Effects and Thermoelectric Materials Science, *J. Thermoelectricity* **2**, 61-72 (2007).

8. E.I. Rogacheva, Critical Phenomena in Heavily-Doped Semiconducting Compounds, *Jpn. J. Appl. Phys*, **32 S**, 775-777 (1993).

9. E.I. Rogacheva, O.S. Vodorez, Peculiarities of the Concentration Dependences of Structural and Thermoelectric Properties in Solid Solutions PbTe-PbSe, *J. Thermoelectricity*. **2**, 61-73 (2013).

10. L.E. Shelimova, O.G. Karpinskii, P.P. Konstantinov, E.S. Avilov, M.A. Kretova, I. Yu. Nikhezina, and V.S. Zemskov, *Perspektivnye Materialy* **5**, 5-13 (2009).

11. E.I. Rogacheva, S.G. Lyubchenko, Thermoelectric and Mechanical Properties of Lead Telluride Doped with Bismuth, *J. Thermoelectricity* **3**, 24-31 (2005)

12. L.D. Borisova, Thermoelectric Properties of Impurity Doped PbTe, *Phys. Stat. Sol.* **53 A**, K19-K22 (1979).

13. T.V. Tavrina, E.I. Rogacheva, V.I. Pinegin, Structural, Thermoelectric and Galvanomagnetic Properties of PbTe-BiTe Semiconductor Solid sSlutions, *Mold. J. Phys. Sci.* **4**, 430-434 (2005).

14. B.A.Efimova, G.F.Zakharyugina, and L.A.Kolomoyets, Thermoelectric Properties of Solid Solutions PbTe-Bi$_2$Te$_3$ and PbSe-Bi$_2$Se$_3$ *Izv. Akad. Nauk, SSSR. Neorgan. Mater.* **4**, 32-36 (1968).

15. E.I. Rogacheva, S.A. Laptev, V.S. Ploskaya, and B.A. Efimova, PbTe-based Solid Solutions in the Pb-Bi-Te System, *Izv. Akad. Nauk, SSSR. Neorgan. Mater.* **20**, 1350-1353 (1984).

16. P.W. Zhu, Yo. Imai, Yu. Isoda, Yo. Shinohara, X-P. Jia, and G-T. Zou, High Thermoelectric Properties of PbTe Doped with Bi$_2$Te$_3$ and Sb$_2$Te$_3$, *Chin. Phys. Lett.* **22**, 2103-2105 (2005).

17. P.W. Zhu, Yo. Imai, Yu. Isoda, and Yo.Shinohara, Composition-Dependent Thermoelectric Properties of PbTe Doped with Bi$_2$Te$_3$, *J. Alloys and Compounds* **420**, 233-236 (2006).

18. T. Su, P.W. Zhu, H. Ma, G. Ren, L. Chen, W. Guo, Y. Iami, and X. Jia, Electrical Transport and High Thermoelectric Properties of PbTe Doped with Bi$_2$Te$_3$ Prepared by HPHT, *Solid State Communs* **138**, 580-584 (2006).

19. T. Ikeda, M. Toussaint, K. Bergum, S. Iwanaga, and G.J. Snyder, Solubility and Formation of Ternary Widmanstatten Precipitates in PbTe in the Pseudo-Binary PbTe-Bi$_2$Te$_3$ System, *J. Mater. Sci* **46**, 3846-3854 (2011).

20. J.-H. Yim, K. Jung, H.-J. Kim, H.-H. Park, C. Park, J.-S. Kim, Ju-Hyuk Yim, Effect of Composition on Thermoelectric Properties in PbTe-Bi$_2$Te$_3$ Composites, *J. Electr. Mater.* **40**, 1010-1014 (2010).

21. E.I. Rogacheva, O.S. Vodorez, V.I. Pinegin, and O.N. Nashchekina, Evidence for Self-Organization Processes in PbTe-Bi$_2$Te$_3$ Semiconductor Solid Solutions, *J. Materials Research* **26**, 1627-1633 (2011).

22. E.I. Rogacheva, O.S. Vodorez, and O.N. Nashchekina, Oscillations of Transport Properties in PbTe - Bi$_2$Te$_3$ Solid Solutions, *J. Phys. Chem. Solids* **74**, 35-39 (2013).

23. E.S. Platunov, *Thermophysical Measurements in Monotonic Regime* (Moscow: Energiya, 1972) (in Russian).

24. R. Berman, *Thermal Conduction in Solids* (Oxford: Clarendon Press, 1976).

25. V.M. Mogilevskii, A.F. Chudnovskii, *Thermal Conductivity of Semiconductors* (Moscow: Nauka, 1972), 536 p. (in Russian).

26. Yu.I. Ravich, B.A. Efimova, and I.A. Smirnov, *Semiconducting Lead Chalcogenides* (New York: Plenum Press, 1970).

27. N.H. Abrikosov and L.E. Shelimova, *Semiconducting Materials Based on A^4B^6 compounds* (Moscow: Nauka, 1975) (in Russian).

28. B.I. Shklovskii, A.L. Efros, *Electronic Properties of Doped Semiconductors* (New York: Springer-Verlag, 1984).

29. D. Stauffer, *Introduction to Percolation Theory* (London/Philadelphia: Taylor and Francis, 1985).

30. E.I. Rogacheva, The Specificity of Structure and Electrical Behavior of Multinary Solid Solutions Formed by Chemical Compounds, *Phys. Status Solidi C* **6**, 1307-1311 (2009).

31. A.F. Ioffe, Heat Transfer in Semiconductors, *Canadian J. Phys.* **34**, 1342-1355 (1956).

32. A.V. Ioffe, A.F. Ioffe, Thermal Conductivity of Semiconductor Solid Solutions, *Solid State Physics* **2**, 781-792 (1960).

33. A.L. Efros, *Solid State Physics* **3**, 2065 (1961)

34. T. Shiga, J. Shiomi, J. Ma, O. Delaire, T. Radzynski, A. Lusakowski, K. Esfarjani, and G. Chen, Microscopic Mechanism of Low Thermal Conductivity in Lead Telluride, *Phys. Rev. B* **85**, 155203 (2012).

35. T. Hori, G. Chen, and J. Shiomi, Thermal Conductivity of Bulk Nanostructured Lead Telluride, *Appl. Phys. Lett.* **104**, 021915(1-5) (2014).

36. A.F. Ioffe, *Semiconducting Thermoelements,* (Moscow-Leningrad: Akad. Nauk SSSR, 1960)(in Russian).

37. P.G. Klemens, The Scattering of Low-Frequency Lattice Waves by Static Imperfections, *Proc. Phys. Soc.* **A68**, 1113-1128 (1955).

38. P.G. Klemens, Thermal Resistance due to Point Defects at High Temperatures, *Phys. Rev.* **119**, 507-509 (1960).