

Marharyta Krainova, Ostap Matkivskyi, Ihor Horichok

Optimization of charge carrier concentration in PbTe to achieve maximum thermoelectric figure of merit

Vasyl Stefanyk Carpathian National University, Ivano-Frankivsk, Ukraine, ihor.horichok@cnu.edu.ua

The main method for obtaining effective thermoelectric materials is the creation of micro- and macrodefects to reduce the lattice thermal conductivity coefficient, as well as doping with electroactive impurities to achieve the optimal value of the chemical potential of charge carriers η and, accordingly, the optimal concentration of charge carriers n (or p). Since the dimensionless thermoelectric figure of merit ZT is a non-monotonic function of the chemical potential of carriers, determining the optimal doping level is a relatively complex problem, which in the case of its experimental solution requires significant resources. In this work, using a model of electrical conductivity that takes into account one dominant mechanism of charge carrier scattering and a model of thermal conductivity that takes into account phonon scattering on phonons, grain boundaries and nanodefects, the optimal values of the chemical potential of carriers and their concentrations at which the $ZT(\eta)$ function reaches a maximum at a given temperature are determined. The calculation was performed for lead telluride of electron and hole conductivity types, taking into account two types of carriers (major and minor) and taking into account the bipolar component of the thermal conductivity coefficient. The average values of the thermoelectric figure of merit for functionally gradient materials of n and p conductivity types in the temperature range (400-800) K were calculated.

Keywords: lead telluride, thermoelectric figure of merit, doping.

Received 24 April 2026; Accepted 03 September 2026; Published 19 September 2026.

Introduction

Thermoelectric converters are devices capable of converting thermal energy into electrical energy (and vice versa) and are characterized by a number of significant advantages over other sources of electrical energy. Foremost among these are their reliability and operational longevity [1-3], which make them particularly promising for use in autonomous systems and devices requiring no maintenance over extended periods. Lead telluride – a narrow-gap A^4B^6 semiconductor – is one of the best materials for producing thermoelectric generators operating in the 500–800 K temperature range. Despite extensive research into this material [4, 5], researchers regularly propose new methods for modifying its properties to enhance operational performance [6, 7, 8].

The operating efficiency of a thermoelectric converter is functionally determined by the numerical value of the material's dimensionless thermoelectric figure of merit [1–4]:

$$ZT = \frac{S^2 \sigma}{k} T$$

where S - Seebeck coefficient, σ - electrical conductivity, and k - thermal conductivity, which can be decomposed into lattice (k_{lat}) and electronic (k_{el}) components. For the semiconductor material in question, all these parameters (S , σ , k) are functions of the carrier chemical potential μ (or, more conveniently, the reduced chemical potential $\eta = \mu/k_0T$); varying this parameter allows one to influence the numerical values of the thermoelectric figure of merit. For this class of materials, controlling the chemical potential is relatively easily achieved through doping with electroactive impurities – donors or acceptors.

It is known [9] that $ZT(\eta)$ is a non-monotonic function of η , characterized by a maximum (ZT_{max}) in the vicinity of $\eta \approx 0$. Determining the position of this maximum (that is, the optimal value of the chemical potential, η_{opt}) makes it possible to establish the optimal carrier concentration n_{opt} (p_{opt}) and dopant concentration required to achieve the

maximum thermoelectric figure of merit. Thus, this problem is of significant practical importance for the development of efficient thermoelectric materials. Addressing it is relevant for materials with diverse structures, including single crystals and polycrystals [4, 10], multiphase materials [11], superlattices [12], and low-dimensional crystalline materials [13]. In doing so, researchers employ various approximations – such as degenerate versus non-degenerate statistics, parabolic versus non-parabolic bands, and others – which can sometimes substantially influence calculation results and the applicability of the findings to other materials. A detailed analytical review of studies investigating the extremum behavior of the $ZT(\eta)$ dependence is provided in [14].

A convenient approach often employed in the analysis of $ZT(\eta)$ involves expressing the thermoelectric figure of merit as $ZT = f_1(\eta)/[1/B + f_2(\eta)]$, where $f_1(\eta)$ and $f_2(\eta)$ are functions depending solely on the carrier chemical potential, and B is a thermoelectric quality factor independent of the chemical potential; its numerical value is determined by the carrier density-of-states effective mass (m_{d0}^*), mobility (u), and the lattice thermal conductivity component (k_{lat}): $B \sim (m_{d0}^*)^{3/2} \cdot u/k_{lat}$. Subsequently, determining ZT_{max} often relies on empirically derived values for u/k_{lat} [15], which does not always allow for establishing a clear link between the extremum coordinates (η_{opt}) and the scattering mechanisms of charge carriers or phonons. This complicates the analysis of potential strategies for engineering thermoelectric materials with specific properties. In contrast, work [14], for instance, calculated carrier mobility – along with S , σ , and k_{el} – analytically as a function of η when determining ZT_{max} . This enabled an analysis of how various potential carrier scattering mechanisms influence the ZT_{max} value for both n -type and p -type materials. A limitation of that study is that the calculations did not account for the contribution of minority carriers. Furthermore, the study assumed the lattice thermal conductivity component to be equal to that of single-crystal PbTe, whereas thermoelectric materials – including PbTe – are typically produced via powder pressing. Accordingly, it is necessary to take into account the influence of grain boundaries on heat transfer processes.

The objectives of this work are: 1) to calculate – using the approach described in [14] and additionally accounting for minority charge carriers – the optimal chemical potential values for PbTe and the corresponding free charge carrier concentrations that yield the maxima of the $ZT(\eta)$ dependence within the 400–800 K temperature range; 2) to estimate, based on an analytical calculation of the lattice thermal conductivity component (accounting for various phonon scattering mechanisms), the effectiveness of reducing the material's thermal conductivity through the creation of defects of various sizes and dimensions in PbTe; and 3) to evaluate the effectiveness of using PbTe-based functionally graded materials.

I. Calculation methodology

By separating the thermal conductivity into lattice (k_{lat}) and electronic (k_{el}) components, and using the Wiedemann-Franz law to determine k_{el} ($k_{el} = L_0 T \sigma$), the thermoelectric figure of merit ZT can be expressed as:

$$ZT = \frac{S^2 \sigma}{k_{lat} + L_0 T \sigma} T = \frac{S^2}{k_{lat}/\sigma + L_0 T} T \quad (1)$$

Here, L_0 is the Lorenz constant. It is worth noting in advance that the Seebeck coefficient and the Lorenz constant depend functionally only on Fermi integrals, whereas the calculation of k_{lat} and k_{el} is more complex and requires knowledge of numerous material parameters.

Within the two-band Kane model [16]:

$$S = -\frac{k_0}{e_0} \left[\frac{I_{r+1,2}^1(\eta, \beta)}{I_{r+1,2}^0(\eta, \beta)} - \eta \right] \quad (2)$$

Here, r is a parameter characterizing the charge carrier scattering mechanism ($r = 0$ – scattering by the deformation potential of acoustic (DA) and optical (DO) phonons, as well as the short-range potential of defects (SP); $r = 1$ – scattering by the polarization potential of optical phonons (PO); $r = 2$ – scattering by the Coulomb potential of ionized defects (ID)), and $I_{n,k}^m(\eta, \beta)$ are Fermi integrals, which, according to [16], are defined as

$$I_{n,k}^m(\eta, \beta) = \int_0^\infty \left(-\frac{\partial f_0}{\partial x} \right) \frac{x^m (x + \beta x^2)^n dx}{(1 + 2\beta x)^k}$$

In the presented expression, $x = E/k_0 T$ is the reduced energy, $\eta = \mu/k_0 T$ is the reduced chemical potential of the carriers (μ is the chemical potential of the carriers), $\beta = k_0 T/E_g$ is the band non-parabolicity parameter, E_g is the band gap, and $f_0 = (1 + e^{x-\eta})^{-1}$ is the Fermi-Dirac distribution function.

The Lorenz number L_0 for the two-band Kane model is expressed in terms of two-parameter Fermi integrals as follows [16]:

$$L_0(\eta, \beta) = \left(\frac{k_0}{e_0} \right)^2 \left[\frac{I_{r+1,2}^2(\eta, \beta)}{I_{r+1,2}^0(\eta, \beta)} - \left(\frac{I_{r+1,2}^1(\eta, \beta)}{I_{r+1,2}^0(\eta, \beta)} \right)^2 \right] \quad (3)$$

Specific electrical conductivity is defined as the product of carrier mobility, carrier concentration, and the elementary charge:

$$\sigma = n u e \quad (4)$$

For a non-parabolic band [16], the carrier concentration within it is determined by:

$$n = \frac{(2m_{d0}^* k T)^{3/2}}{3\pi^2 \hbar^3} I_{3/2,0}^0(\eta, \beta) \quad (5)$$

Here m_{d0}^* is the effective density-of-states mass at the band edge. Carrier mobility [16]:

$$u = e \frac{\tau_0(T)}{m_{n,0}^*} \cdot \frac{I_{r+1,2}^0(\eta, \beta)}{I_{3/2,0}^0(\eta, \beta)} \quad (6)$$

Here $m_{n,0}^*$ is the effective mass at the bottom of the band. Thus, the electrical conductivity is:

$$\sigma = e^2 \cdot \frac{(2m_{d,0}^* kT)^{3/2}}{3\pi^2 \hbar^3} \cdot \frac{\tau_0(T)}{m_{n,0}} \cdot I_{r+1,2}^0(\eta, \beta) \quad (7)$$

Expressions for $\tau_0(T)$ for various possible scattering mechanisms are given in Appendix 1. In the case where several scattering mechanisms act simultaneously, mobility can be determined using Matthiessen's rule:

$$\frac{1}{u} = \sum \frac{1}{u_i}$$

The effective density-of-states masses of light holes and electrons were considered to be functions of temperature and were defined as:

$$m_{d,0}^* = m_0^* \left(\frac{T}{T_0} \right)^\alpha \quad (8)$$

where $T_0 = 120$ K, $\alpha = 0.4$, $m_0^* = 0.142m_0$ [17]. For heavy holes, since the band is parabolic, the density-of-states effective mass is constant and equals $1 \cdot m_0$ [17]. The effective mass at the band edges was determined from the equation $m_{d,0}^* = N^{2/3} m_{n,0}^*$, where N is the number of band extrema in the Brillouin zone (for PbTe, $N = 4$ for electrons and light holes, and $N = 12$ for heavy holes [18]).

The lattice component of the thermal conductivity coefficient was calculated using expression [19]:

$$k_{lat} = \frac{1}{3} \int_0^{\omega_D} c_v(\omega) v_s(\omega)^2 \tau(\omega) d\omega \quad (9)$$

Here, C_V is the heat capacity per unit volume, v_s is the speed of sound, $\tau(\omega)$ is the relaxation time for phonon scattering processes, and ω_D is the Debye frequency, calculated using the expression $\omega_D = k\theta / (\hbar/2\pi)$, where θ is the Debye temperature (for PbTe, $\theta = 125$ K [20]). In the case of high temperatures ($T > \theta$), and also neglecting the difference between phase and group velocities [19]:

$$c_v(\omega) = \frac{3k\omega^2}{2\pi^2 v_s^3} \quad (10)$$

The speed of sound in (9) and (10) is usually treated as a constant equal to an empirical value, while expressions for phonon relaxation times $\tau(\omega)$ for various scattering mechanisms are given in Appendix 2. When multiple mechanisms act simultaneously – as is the case with charge carrier scattering – the total relaxation time is determined using Matthiessen's rule.

The expressions given above allow for the calculation of the thermoelectric figure of merit in the case of unipolar conduction. In the presence of two types of carriers (electrons and holes) with comparable concentrations, the electrical conductivity of the material is determined as [15]:

$$\sigma = \sigma_n + \sigma_p = |e|(u_n n + u_p p) \quad (11)$$

Seebeck coefficient:

$$S = \frac{S_n \sigma_n + S_p \sigma_p}{\sigma_n + \sigma_p} \quad (12)$$

Electronic component of the thermal conductivity coefficient:

$$k_{el} = k_{el,n} + k_{el,p} \quad (13)$$

At the same time, the chemical potentials of electrons and holes are related by the following relationship:

$$\eta_p = -E_g - \eta_n \quad (14)$$

In the case of two types of charge carriers, in addition to the lattice and electronic components of the thermal conductivity coefficient, it is also necessary to account for the contribution of bipolar thermal conductivity [15]:

$$k_{bip} = \frac{\sigma_n \sigma_p}{\sigma_n + \sigma_p} (|S_n| - |S_p|)^2 T \quad (15)$$

II. Results and their analysis

Mobility. A key component of the algorithm used to calculate $ZT(\eta)$ is a model describing free charge carrier scattering processes in PbTe. For this semiconductor, the model is considered relatively well-developed [21] and is implemented within the relaxation-time approximation. The main limitations of this approximation stem from the difficulty of accounting for inelastic interactions and determining the energy characteristics of the interaction between carriers and scattering centers. Regarding the first limitation, the primary carrier scattering mechanisms are elastic within the temperature range where PbTe is practically applied in thermoelectric generators. As for the second, years of research have yielded a mutually consistent set of model parameters for most scattering mechanisms, enabling an adequate description of experimental data. However, in most cases, these values were obtained at temperatures $T \leq 300$ K; thus, their application at high temperatures requires refinement. On the other hand, in many instances, this set of parameters successfully describes experimental data even at high temperatures [22].

Figures 1 and 2 present the calculated carrier mobilities as functions of carrier concentration and temperature. Based on these results, conclusions can be drawn regarding the dominance of various carrier scattering mechanisms under different conditions. In the calculations, the concentration of impurity ions was assumed to be $N_{ID} = n/2$. The concentration of centers with a short-range potential (N_{SP}) was assumed to be the same. Furthermore, the energy parameters E_I and U_0 (Appendix 1) – characterizing the interaction of carriers with the deformation potential of acoustic phonons and the short-range potential, respectively – were assumed to be identical for electrons and holes (although, in the general case, they may differ [16]).

Several important conclusions can be drawn from an analysis of the presented graphs. First, doping PbTe with donor or acceptor impurities to a concentration of a few atomic percent has practically no effect on the total mobility (100 at.% corresponds to $1.48 \cdot 10^{22} \text{ cm}^{-3}$; this is

the concentration of anionic or cationic sublattice sites in PbTe, given a unit cell parameter of 6.461 Å [23] and 4 anions (or cations) per cell). Second, for *p*-PbTe, the primary scattering mechanism in the investigated temperature range (400–800 K) is carrier scattering by the deformation potential of acoustic phonons. It should be noted that only heavy holes were considered for *p*-PbTe; at temperatures above 450 K, the heavy-hole band extremum lies above the light-hole band extremum, implying that heavy holes would dominate kinetic processes – specifically, their concentration would be higher and their mobility lower, making them the determining factor. According to [24], heavy holes can play a decisive role even at temperatures slightly below 450 K. Given that the lower operating temperature limit for PbTe typically exceeds 400 K, we did not employ a two-hole-type model, although at ≈ 400 K, such a model would likely have resulted in only minor changes to the

obtained $u(n, T)$ dependencies. For *n*-PbTe, carrier scattering by the deformation potential of acoustic phonons is the dominant mechanism at temperatures above 400 K, whereas scattering by the polarization potential of optical phonons dominates at lower temperatures.

Subsequently, the calculations of $ZT(\eta)$ and the determination of ZT_{max} and η_{opt} relied on a model involving only a single dominant scattering mechanism: scattering by the deformation potential of acoustic phonons. However, judging by the results presented in Figs. 1 and 2, a more precise calculation for both *n*-PbTe and *p*-PbTe could also account for carrier scattering by the deformation potential of optical phonons. Although the contribution of this mechanism is smaller than that of acoustic phonon scattering (DA), it is of the same order of magnitude.

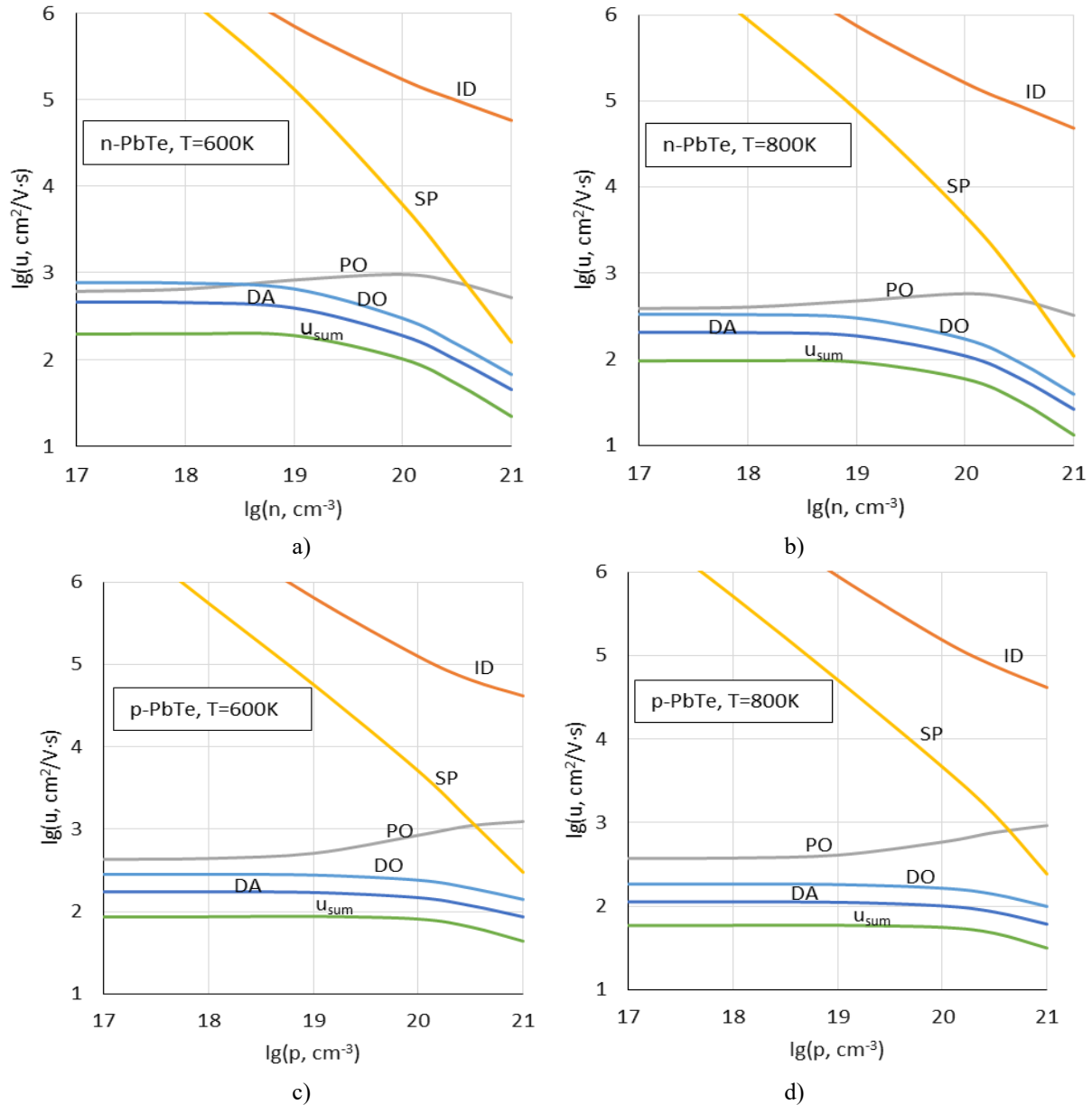


Fig. 1. Dependence of the total carrier mobility u_{sum} and its partial contributions due to various mechanisms (DA, DO – deformation potential of acoustic and optical phonons, respectively; PO – polarization potential of optical phonons; SP – short-range potential of point defects; ID – Coulomb potential of ionized point defects) in *n*-PbTe (a, b) and *p*-PbTe (c, d) at temperatures of 600 K and 800 K.

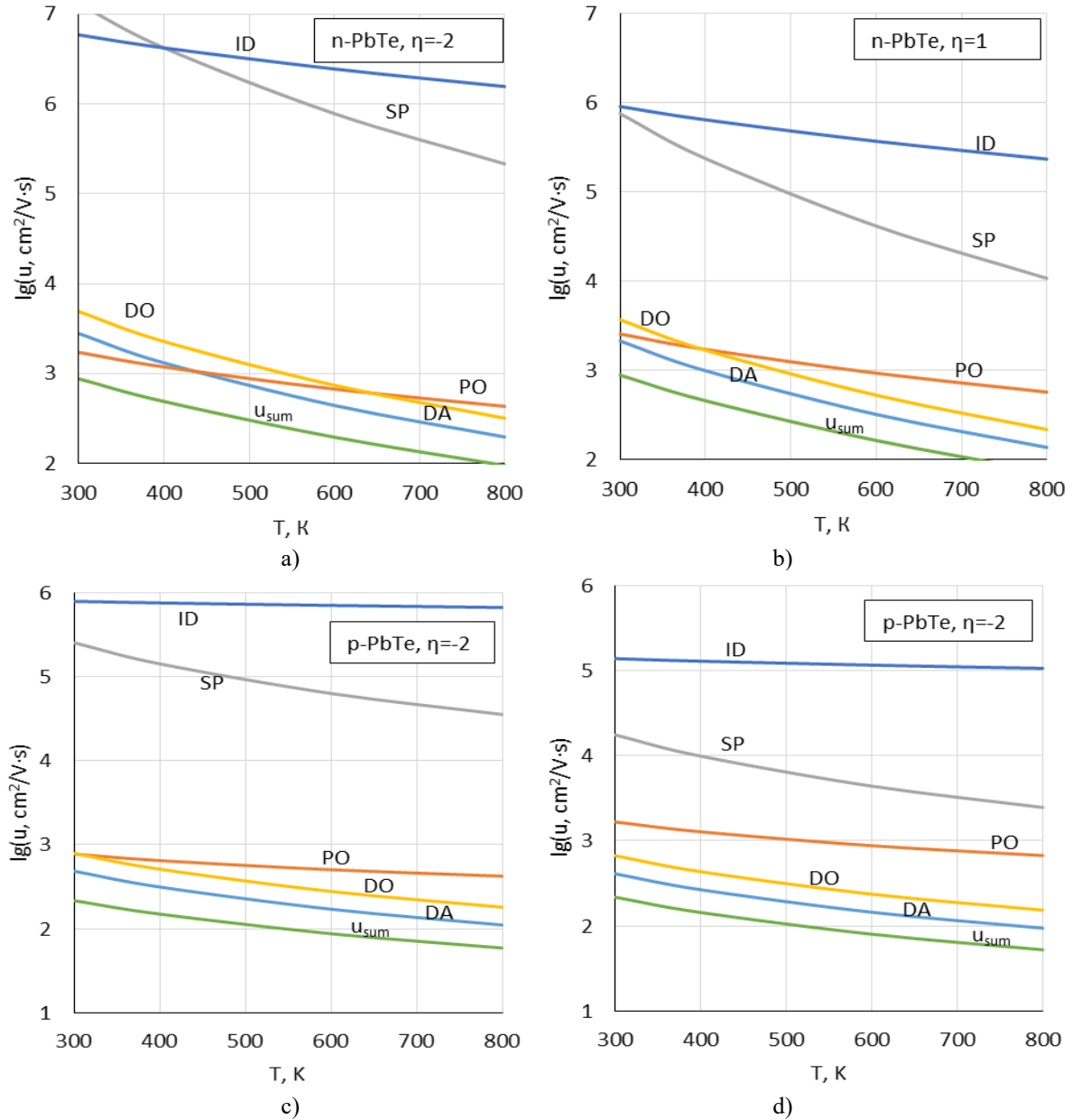


Fig. 2. Dependence of the total carrier mobility u_{sum} and its partial contributions due to various mechanisms (DA, DO – deformation potential of acoustic and optical phonons, respectively; PO – polarization potential of optical phonons; SP – short-range potential of point defects; ID – Coulomb potential of ionized point defects) in n -PbTe (a, b) and p -PbTe (c, d) for two different values of the reduced chemical potential: $\eta = -2$ та $\eta = 1$.

Thermal conductivity. In study [14], the algorithm of which is utilized here, the calculation of ZT_{max} assumed that the numerical value of the lattice component of thermal conductivity is determined solely by phonon-phonon scattering. This study analyzes possible values of this parameter – specifically, k_{lat} – while accounting for other mechanisms present in materials with various types of structural disorder: phonon scattering by point defects, grain boundaries, and nanoscale defects. In Fig. 3, the solid curve represents $k_{lat}(T)$ calculated considering only phonon-phonon scattering. The $k_{lat}(T)$ calculation algorithm used here – which differs from that in [14] – yields lattice thermal conductivity values that are approximately 30% higher. For instance, at 300 K, a value of $k_{lat} = 2.1$ W/(m·K) was obtained, whereas study [14] reported 1.6 W/(m·K). The influence of various parameters on the calculated k_{lat} value is analyzed in study

[25].

The use of materials with a high density of grain boundaries – that is, polycrystalline materials such as pressed ones – results in a reduction of lattice thermal conductivity. As shown in Fig. 3, for a grain size of 200 μm , k_{lat} decreases by approximately 10%, whereas for 25 μm , it decreases by approximately 30%.

Introducing 10 at.% of impurity atoms into the crystal lattice – that is, forming a solid solution (for instance, the calculations for the data in Fig. 3 considered Sn-for-Pb substitutional atoms) – results in the same reduction in k_{lat} as using pressed materials with a grain size of $d = 200$ μm . Increasing the impurity content to 40 at.% leads to a reduction in k_{lat} comparable to that achieved by pressing impurity-free PbTe grains with a size of 25 μm . Forming solid solutions is a well-known, effective method for reducing lattice thermal conductivity. However, a

drawback is that significant changes to the base material's chemical composition also substantially alter other material properties – such as carrier effective mass and bandgap width – in addition to k_{lat} . Moreover, changes in these parameters do not always favor an increase in ZT . For example, in the formation of a PbSnTe solid solution, increasing the Sn content reduces the material's thermal conductivity [25, 23]; however, the bandgap width simultaneously decreases, leading to a significant impact of intrinsic carriers on thermoelectric parameters. Consequently, the gain in ZT is not as substantial as one might expect based solely on the reduction in k_{lat} .

An effective method for reducing lattice thermal conductivity k_{lat} without significantly affecting other fundamental material properties is the introduction of nanoscale inclusions of additional phases (nanodefects). Well-known examples of such materials include PbTe-SrTe [6] and PbTe-CdTe [8]. With a surface concentration of nanodefects of 10^{15} cm^{-2} and a radius of 30 nm, the thermal conductivity at room temperature can be reduced by one-third (Fig. 3). Controlling the stability of the defect subsystem in such materials is a complex yet solvable challenge [26].

Simultaneous crystal lattice disordering at both micro and macro levels makes it possible to reduce k_{lat} by more than half (Fig. 3). For instance, when using a pressed material with 25 μm grains and nanodefects of the aforementioned sizes and concentrations, the k_{lat} value is 0.90 W/(m K) at 300 K and 0.50 W/(m K) at 800 K. These specific values were subsequently used to calculate $ZT(\eta)$.

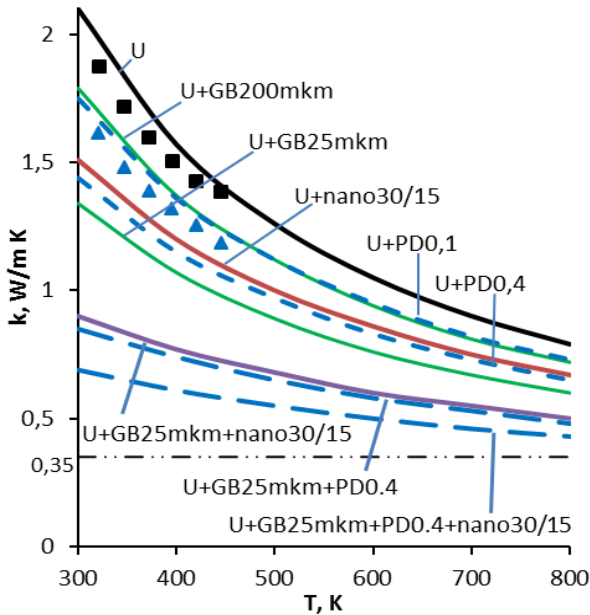


Fig. 3. Temperature dependence of the thermal conductivity of PbTe calculated considering various combinations of possible phonon scattering mechanisms: U – phonon-phonon scattering; GB200 μm , GB25 μm – phonon scattering at grain boundaries with diameters of 200 μm and 25 μm , respectively; PD0.1, U+PD0.4 – phonon scattering by SnPb substitutional atoms with atomic fractions of 0.1 and 0.4, respectively; nano 30/15 – phonon scattering by nanodefects with a radius of 30 nm and a surface concentration of 10^{15} cm^{-2} .

Figure 3 also presents an estimate of the thermal conductivity coefficient of PbTe, assuming its hypothetical existence in an amorphous structure. This value, k_{glass} , was calculated using the relationship from [27]:

$$k_{glass} = \frac{0.76}{3} k_0 V^{-2/3} (2v_T + v_L) \quad (16)$$

where v_L and v_T are the longitudinal and transverse components of the speed of sound. This value of $k_{glass} = 0.35 \text{ W/(m K)}$ can be considered an asymptote; actually achieving it while preserving the crystal structure and other fundamental parameters that determine the advantages of PbTe over other materials is highly unlikely.

$ZT(\eta)$. Using the previously described model to calculate the parameters S , σ , and k , we computed $ZT(\eta)$ for temperatures ranging from 400 K to 800 K in 100 K increments. Figure 4 shows the dependencies obtained for temperatures of 600 K and 800 K. The two curves (solid and dashed) in each plot correspond to models that either account for (solid) or neglect (dashed) the presence of minority carriers. Additionally, the solid curve incorporates the contribution of bipolar thermal conductivity to the material's total thermal conductivity. The results indicate that at 800 K, the influence of minority carriers – manifesting as a reduction in the $ZT(\eta)$ maximum – is quite significant, particularly in n -type material. This effect arises from a decrease in the total Seebeck coefficient and an increase in the total thermal conductivity. For instance, at 800 K, the thermal conductivity of n -PbTe at the $ZT(\eta)$ maximum is 1.08 W/(m K) (with $k_{lat} = 0.48 \text{ W/(m K)}$), whereas for p -PbTe, it is 1.23 W/(m K) (with the same k_{lat} value). Notably, the bipolar contribution (k_{bip}) is 0.15 W/(m K) for n -PbTe, compared to only 0.05 W/(m K) for p -PbTe. As the temperature decreases, the influence of minority carriers on $ZT(\eta)$ diminishes. At 600 K, the reduction in the numerical value of ZT_{max} resulting from their inclusion is $\approx 10\%$, whereas at 400 K, it is less than 5%.

The significant influence of minority carriers in n -type material results in a non-monotonic $ZT_{max}(T)$ dependence (Fig. 5), with a maximum of ≈ 1.3 near 600 K. For p -type material, $ZT_{max}(T)$ is a monotonically increasing function within the studied temperature range, reaching a maximum of ≈ 2.4 at 800 K. The average ZT_{ave} values calculated from the obtained data points for the 400–800 K temperature range are shown in Fig. 5; they are 1.20 for n -PbTe and 2.07 for p -PbTe. Interestingly, despite the significant differences noted between n - and p -type materials and across the temperature ranges, the optimal values of the reduced chemical potential are very similar under all conditions: $\eta \approx -1$ (Fig. 4).

$ZT(n)$. Figure 6 shows the dependence of ZT on n at various temperatures. For p -type material, n_{opt} varies from $\approx 1.5 \cdot 10^{19} \text{ cm}^{-3}$ at 400 K to $\approx 3.8 \cdot 10^{19} \text{ cm}^{-3}$ at 800 K – that is, by more than a factor of two. For n -type material, the numerical values of n_{opt} range from $\approx 0.5 \cdot 10^{19} \text{ cm}^{-3}$ at 400 K to $\approx 1.8 \cdot 10^{19} \text{ cm}^{-3}$ at 800 K. Thus, the optimal concentration is lower than that of the p -type material, and its variation with temperature is somewhat greater.

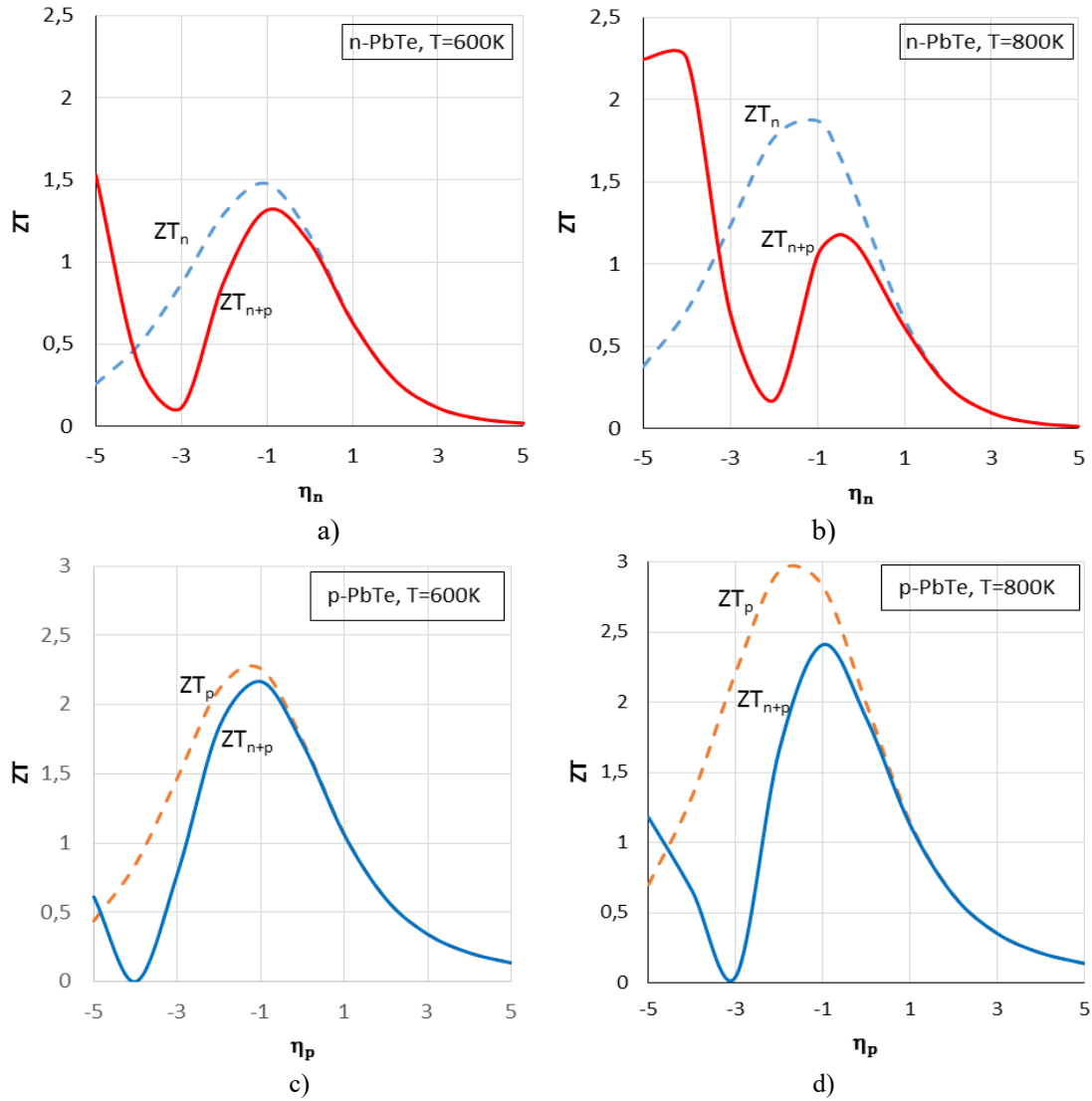


Fig. 4. Dependence of the dimensionless thermoelectric figure of merit on the reduced chemical potential of carriers for *n*-PbTe (a, b) and *p*-PbTe (c, d) at temperatures of 600 K and 800 K. The solid curve represents the model accounting for minority carriers and the bipolar component of thermal conductivity; the dashed curve represents the model without accounting for them.

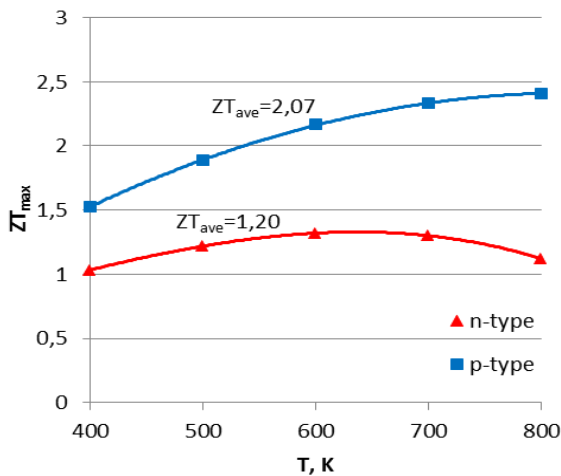


Fig. 5. Dependence of the maximum thermoelectric figure of merit ZT_{max} on temperature for *n*-PbTe and *p*-PbTe.

The existence of the $n_{opt}(T)$ relationship highlights the potential of using functionally graded thermoelements –

specifically, *n*- and *p*-type thermoelement legs where the carrier concentration varies along the sample, or more precisely, along the temperature gradient. However, calculation results indicate that if a *p*-type material with a constant carrier concentration of $\approx 2.4 \cdot 10^{19} \text{ cm}^{-3}$ is used across the temperature range, its ZT_{ave} would be ≈ 1.99 , this is only 0.07 units (or $\approx 3\%$) lower than the corresponding value for a thermoelement with a concentration gradient matching n_{opt} .

For *n*-type material, this difference is more significant. For example, at $n \approx 0.75 \cdot 10^{19} \text{ cm}^{-3}$, $ZT_{ave} \approx 1.0$, which is 0.2 units (or 20%) lower than the corresponding value for a thermoelectric element with a concentration gradient corresponding to n_{opt} .

This effect can be attributed to the distinct slopes of the $ZT(n)$ dependencies for materials with different types of conductivity; this, in turn, stems from differences in parameters characterizing the majority carriers—specifically, density-of-states effective masses and the parabolic or non-parabolic nature of the majority-carrier band.

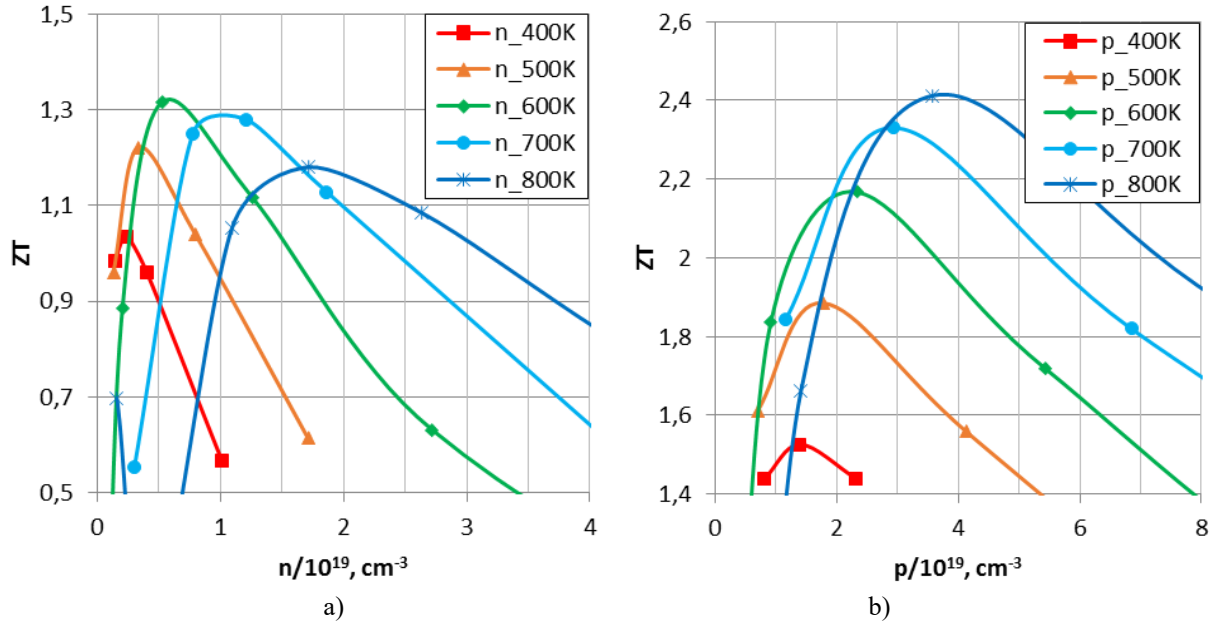


Fig. 4. Dependence of the dimensionless thermoelectric figure of merit on the reduced chemical potential of carriers for n -PbTe (a, b) and p -PbTe (c, d) at temperatures of 600 K and 800 K. The solid curve represents the model accounting for minority carriers and the bipolar component of thermal conductivity; the dashed curve represents the model without accounting for them.

The values of $n_{opt}(T)$ and $p_{opt}(T)$ shown in Fig. 7 allow for the estimation of the optimal dopant concentration, N_{opt} . Given that the dopant contributes one additional carrier and that the total concentration – for instance, the electron concentration n_{opt} – is determined by the sum of the intrinsic and extrinsic carrier concentrations, it follows that $N_{opt} = n_{opt} - n_i$. The calculation of the optimal dopant concentration for p -type conductivity is performed in a similar manner. The intrinsic carrier concentration n_i for PbTe is also presented in Fig. 7.

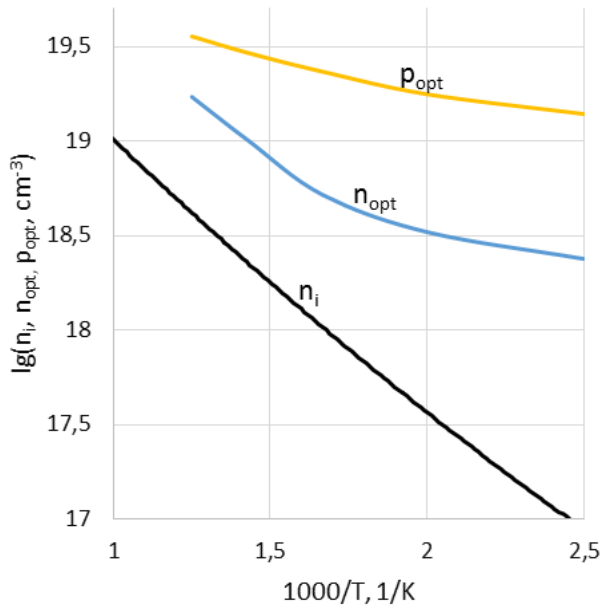


Fig. 7. Dependence of the concentration of intrinsic carriers n_i in PbTe, as well as the optimal concentration of electrons n_{opt} and holes p_{opt} for n -PbTe and p -PbTe, respectively, on the inverse temperature.

Such a calculation algorithm is valid if the impurity is ionized at all temperatures under consideration. One of the conditions for this state is $\varepsilon_i < kT$, where ε_i is the impurity ionization energy. This condition holds for most common impurities in PbTe, such as Na or I. Otherwise, to determine N_{opt} , it is necessary to solve the electroneutrality equation in the form (for donor and acceptor impurities, respectively):

$$n_{opt} - n_i = N_{opt} \left(1 - \frac{1}{1 + e^{\varepsilon_i^* - \eta_{n,opt}}} \right) \quad \text{or} \\ p_{opt} - n_i = N_{opt} \left(\frac{1}{1 + e^{\varepsilon_i^* - \eta_{p,opt}}} \right) \quad (17)$$

Here, $\varepsilon_i^* = \varepsilon_i/k_0T$ the function in parentheses, which depends on ε_i , η , and T , determines the probability of an electron being present (for p_{opt}) or its absence (for n_{opt}) at a localized energy level created by an impurity atom [16].

Equation (17) becomes more complicated if the impurity can donate more than one carrier to the zone, or the concentration of N_{opt} will be proportional to the concentration of intrinsic defects. Lead telluride is often obtained with a concentration of intrinsic defects in the vicinity of $\approx 10^{18} \text{ cm}^{-3}$ [5], which is of the same order of magnitude as the obtained n_{opt} values for n -PbTe. Also, certain complications may arise when using amphoteric impurities or double doping. However, with known values of the ionization energy of impurities and a given η_{opt} , this problem can be technically solved.

Conclusions

The optimal value of the carrier chemical potential in PbTe, at which the maximum dimensionless thermoelectric figure of merit is achieved in the 400–

800 K temperature range, lies in the vicinity of $\eta_{opt} \approx -1$ for both n -type and p -type PbTe. The optimal carrier concentration n_{opt} corresponding to η_{opt} increases with temperature for materials of both conductivity types: for p -PbTe, from $\approx 1.5 \cdot 10^{19} \text{ cm}^{-3}$ at 400 K to $\approx 3.8 \cdot 10^{19} \text{ cm}^{-3}$ at 800 K, and for n -PbTe, from $\approx 0.5 \cdot 10^{19} \text{ cm}^{-3}$ at 400 K to $\approx 1.8 \cdot 10^{19} \text{ cm}^{-3}$ at 800 K.

The calculated ZT_{ave} for a functionally gradient material with the parameters $n_{opt}(T)$ determined in the work is 2.07 for p -PbTe and 1.20 for n -PbTe. In the case of a fixed carrier concentration of $\approx 2.4 \cdot 10^{19} \text{ cm}^{-3}$ in the p -type material, the conductivity ZT_{ave} will be 1.99, which is only 3% less than the corresponding value for a material with a concentration gradient. In the case of an n -type conductivity material, the use of functionally gradient thermocouples increases the average value of their thermoelectric figure of merit by 20%. Thus, for p -PbTe, the creation of functionally gradient thermoelements does not lead to a significant increase in the thermoelectric figure of merit of the materials.

Appendix 1. Expressions for τ_0 for various charge carrier scattering mechanisms.

For the scattering of charge carriers by the deformation potential of acoustic phonons [16]:

$$\tau_0(T) = \frac{2\pi\hbar^4 \rho v_s^2}{(2m_{n,0} k_0 T)^{\frac{3}{2}} E_1^2} \quad (1a)$$

where $\rho = 8.24 \text{ g/cm}^3$ [21], $E_1 = 15 \text{ eV}$ [21], $v_s = 1.92 \text{ km/s}$ [23].

When scattering on the deformation potential of optical phonons (for $k_0 T \gg \hbar\omega_0$) [16]:

$$\tau_0(T) = \frac{2}{\pi} \left(\frac{\hbar\omega_0}{E_0} \right)^2 \frac{\hbar^2 a^2 \rho}{(2m_{n,0} k_0 T)^{\frac{3}{2}}} \quad (2a)$$

where $\hbar\omega_0 = 0.0136 \text{ eV}$ [21], $a = 6.461 \text{ \AA}$ [23], $E_0 = 26 \text{ eV}$ [21].

When scattering on the polarization potential of optical phonons (for $k_0 T \gg \hbar\omega_0$) [16]:

$$\tau_0(T) = \frac{\hbar^2}{e_0^2 \sqrt{2m_{n,0} k_0 T} \left(\frac{1}{\chi_\infty} - \frac{1}{\chi_0} \right)} \quad (3a)$$

where $\chi_\infty = 32.6$ [21], $\chi_0 = 400$ [21].

For scattering by the short-range potential of defects [16]:

$$\tau_0(T) = \frac{\pi\hbar^4}{m_{n,0} (2m_{n,0} k_0 T)^{\frac{1}{2}} U_0^2 N_{SP}} \quad (4a)$$

N_{SP} – defect concentration, $U_0 = 3 \cdot 10^{-34} \text{ erg/cm}^3$ [21].

Upon scattering by the Coulomb potential of ionized impurity atoms [16]:

$$\tau_0(T) = \frac{\chi_0^2 (2m_{n,0})^{\frac{1}{2}} (k_0 T)^{\frac{3}{2}}}{\pi e^4 N_{ID}} \quad (5a)$$

N_{ID} – concentration of ionized defects.

When calculating ZT for all scattering mechanisms, corrections for the Bloch form of the wave functions (for

carriers in a non-parabolic band) were taken into account in accordance with [16]; additionally, for polar optical phonons and ionized impurities, a correction for the screening of scattering centers by free charge carriers (regardless of band type) was applied.

This correction for scattering by acoustic phonons is defined as:

$$F_{ak}(k) = 1 - \frac{10}{3} L + \left[\frac{191}{60} + \frac{11}{60} \left(\frac{v_L}{v_T} \right)^2 \right] L^2 \quad (6a)$$

where v_L and v_T are the longitudinal and transverse components of the speed of sound, defined as

$$v_L = [(C_{11} + 2C_{12} + 4C_{44})/3\rho]^{\frac{1}{2}},$$

$$v_T = [(C_{11} - C_{12} + C_{44})/3\rho]^{\frac{1}{2}},$$

where C_{ij} are the stiffness coefficients [28].

For scattering by a short-range potential and the deformation potential of optical phonons:

$$F_{KP} = 1 - \frac{8}{3} L + \frac{13}{6} L^2 \quad (7a)$$

For scattering by the polarization potential of optical phonons:

$$F_{PO} = 1 - \frac{2}{\xi} \ln(1 + \xi) + \frac{1}{1+\xi} - \frac{1}{2} (4L - L^2) B + L^2 C \quad (8a)$$

where $\xi = (2kr_0)^2$, k is the wave number and r_0 is the screening radius.

For scattering by an ionized impurity:

$$F'_{ID} = \ln(1 + \xi) - \frac{\xi}{1+\xi} - (4L - L^2) A + \frac{3}{2} L^2 B \quad (9a)$$

In the formulas provided:

$$L = \frac{E}{E_g + 2E}, \quad A = 1 + \frac{1}{1+\xi} - \frac{2}{\xi} \ln(1 + \xi),$$

$$B = 1 - \frac{4}{\xi} - \frac{2}{\xi(1+\xi)} + \frac{6}{\xi^2} \ln(1 + \xi),$$

$C = 1 - \frac{3}{\xi} + \frac{9}{\xi^2} + \frac{3}{\xi^2(1+\xi)} - \frac{12}{\xi^3} \ln(1 + \xi)$. The shielding radius when calculating ξ was determined as

$$r_0^2 = \frac{\chi_0 k_0 T}{6\pi e_0^2 n} \cdot \frac{I_{3/2,0}^0(\eta, \beta)}{I_{3/2,-1}^0(\eta, \beta)} \quad \text{and the wave number}$$

$$k = \sqrt{\frac{2m_{n,0}}{\hbar^2} \bar{E} \left(1 + \frac{\bar{E}}{E_g} \right)}.$$

The average value of the energy included in this expression was determined as $\bar{E} = \frac{1}{n} \int_0^\infty E \cdot g(E) \cdot f_0(E, \mu) dE$ and

$$\bar{n} = \int_0^\infty g(E) \cdot f_0(E, \mu) dE. \quad \text{Density of states}$$

$$g(E) = \frac{(2m_{n,0})^{\frac{3}{2}}}{2\pi^2 \hbar^3} E^{\frac{1}{2}} \left(1 + \frac{E}{E_g} \right)^{\frac{1}{2}} \left(1 + \frac{E}{E_g} \right).$$

The correction was applied by dividing the corresponding values of τ_0 by the correction factor. The adequacy of the calculation model was verified by comparing the calculated $u(n)$ results with the results from [21] (Fig. 1a).

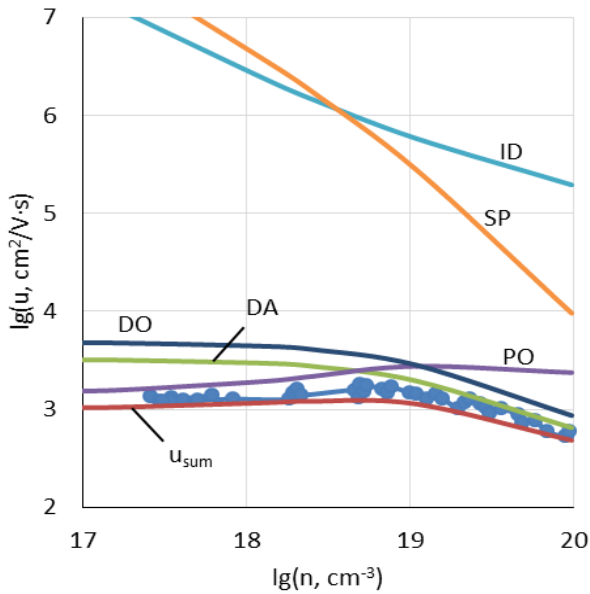


Fig. 1a. Dependence of the total carrier mobility u_{sum} and its partial contributions due to different mechanisms (DA, DO – deformation potential of acoustic and optical phonons, respectively; PO – polarization potential of optical phonons; SP – short-range potential of point defects, ID – Coulomb potential of ionized point defects) in n-PbTe at a temperature of 300 K. Experimental data – [21].

Appendix 2. Expressions $\tau(\omega)$ for various phonon scattering mechanisms.

The main mechanism of phonon scattering, which determines the order of magnitude of the lattice component of the thermal conductivity coefficient of single-crystal materials, is phonon-phonon scattering [29]. In the interaction of phonons, a distinction is made between U - (Umklapp) and N - (Normal) processes. The thermal conductivity coefficient is determined primarily by U -processes, as N -processes do not generate thermal resistance [29, 30]. Although N -processes can play a significant role in generating thermal resistance in certain materials, in the case of PbTe, a thermal conductivity model accounting only for U -processes accurately describes the known empirical data for single crystals; thus, the assertion that the contribution of U -processes outweighs that of N -processes is well-founded. The relaxation time for U -processes is [19]:

$$\tau_U(\omega) = \frac{(6\pi^2)^{1/3}}{2} \frac{M v_s^3}{k_B V^{1/3} \gamma^2 \omega^2 T} \quad (1b)$$

where M is the average atomic mass, v_s is the speed of sound, V is the atomic volume (determined as a^3/N , where N is the number of atoms in the unit cell and a is the unit cell parameter; for PbTe, $N = 8$ and $a = 6.461 \text{ \AA}$ [23]), and γ is the Grüneisen parameter (for PbTe, $\gamma = 1.96$ [31]).

For heavily doped materials and solid solutions, phonon scattering by substitutional atoms can also be significant. For this mechanism [19]:

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

where f_i is the atomic fraction of impurity atoms, m_i/m is the ratio of the atomic masses of the impurity and matrix atoms, and r_i/r is the ratio of the atomic radii of the impurity and matrix atoms. The calculation was performed for the case of Pb atoms being replaced by Sn atoms. In this instance, $m_i/m = 118.7/207.2$ and $r_i/r = 1.02/1.26$ (ionic radii from [32] were used here).

For phonon scattering at grain boundaries [33]:

$$\tau_B(\omega) = \frac{L}{v_s} P_B \quad (3b)$$

Here, L is the grain size, and P_B is a coefficient accounting for the specific nature of the material's grain boundaries. For example, for InGaAs, $P_B = 1.3 \cdot 10^{-3}$ [33]. In [34], this value was used to calculate k_{lat} for cold-pressed PbTe samples, and the calculation showed good agreement with experimental data. Therefore, this numerical value - $P_B = 1.3 \cdot 10^{-3}$ - is also used in the present work.

During phonon scattering by nanoinclusions [33]:

$$\tau_D(\omega) = \frac{k^3}{\omega^4 \hbar^3} \cdot \frac{4\theta^3}{3N_i R^2} \quad (4b)$$

Here, N_i is the surface concentration of nanoscale inclusions of an additional phase, R is their radius, and θ is the Debye temperature ($\theta = 125 \text{ K}$ [20]).

Krainova Marharyta – MS student;

Matkivskiy Ostap – Candidate of Physical and Mathematical Sciences, Senior Researcher

Horichok Ihor – Doctor of Physical and Mathematical Sciences, Professor of the Department of Physics and Astronomy.

- [1] M.A. Zoui, S. Bentouba, J.G. Stocholm, M. Bourouis, *A review on thermoelectric generators: Progress and applications*. Energies, 13, 3606 (2020); <https://doi.org/10.3390/EN13143606>.
- [2] L. Chen, R. Liu, X. Shi, *Thermoelectric Materials and Devices*. Amsterdam. Elsevier, (2021); <https://doi.org/10.1016/c2018-0-02472-x>.
- [3] I. Petsagkourakis, K. Tybrandt, X. Crispin, I. Ohkubo, N. Satoh, T. Mori, *Thermoelectric materials and applications for energy harvesting power generation*. Science and Technology of Advanced Materials, 19, 836 (2018); <https://doi.org/10.1080/14686996.2018.1530938>.
- [4] A. F. Joffe, L. S. Stil'bans, *Physical Problems of Thermoelectricity*. Reports Prog. Phys., 22(1), 167 (1959); <https://doi.org/10.1088/0034-4885/22/1/306>.
- [5] Y.I. Ravich, B.A. Efimova, I.A. Smirnov, *Semiconducting Lead Chalcogenides*. (Plenum Press, New York, 1970); <https://doi.org/10.1007/978-1-4684-8607-0>.

- [6] K. Biswas, J. He, I. D. Blum, C. I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid, M. G. Kanatzidis, *High-Performance Bulk Thermoelectrics with All-Scale Hierarchical Architectures*. Nat., 489(7416), 414 (2012); <https://doi.org/10.1038/nature11439>.
- [7] M. Dutta, R. K. Biswas, S. K. Pati, K. Biswas, *Discordant Gd and Electronic Band Flattening Synergistically Induce High Thermoelectric Performance in n-type PbTe*. ACS Energy Lett, 6(4) 1625 (2021); <https://doi.org/10.1021/acsenergylett.1c00450>.
- [8] M. Szot, P. Pfeffer, K. Dybko, A. Szczerbakow, L. Kowalczyk, P. Dziawa, R. Minikayev, T. Zajarniuk, K. Piotrowski, M. U. Gutowska, A. Szewczyk, T. Story, W. Zawadzki, *Two-Valence Band Electron and Heat Transport in Monocrystalline PbTe-CdTe Solid Solutions with Cd Content up to 10 Atomic Percent*. Phys. Rev. Mater., 4(4), 044605 (2020); <https://doi.org/10.1103/PhysRevMaterials.4.044605>.
- [9] Y.S. Budzhak, *Do Pytannia pro Lehuvannia Napivprovidnykovykh Krystaliv z Maksymalnoiu Termoelektrychnoiu Efektyvnistiu*. J. Thermoelectr., 4, 41 (2007).
- [10] Z. H. Dughaish, *Lead Telluride as a Thermoelectric Material for Thermoelectric Power Generation*. Phys. B Condens. Matter., 322(1–2), 205 (2002); [https://doi.org/10.1016/S0921-4526\(02\)01187-0](https://doi.org/10.1016/S0921-4526(02)01187-0).
- [11] A.A. Snarskii, M.I. Zhenirovskii, I.V. Bezsudnov, *Limiting Values of the Quality Factor of Thermoelectric Composites*. Semiconductors, 42(1) 80–85 (2008); <https://doi.org/10.1134/s1063782608010119>.
- [12] J. O. Sofo, G. D. Mahan, *Thermoelectric Figure of Merit of Superlattices*. Appl. Phys. Lett., 65(21) 2690–2692 (1994); <https://doi.org/10.1063/1.112607>.
- [13] V.S. Zakordonets, G. N. Logvinov, *Thermoelectric Figure of Merit of Monopolar Semiconductors with Finite Dimensions*. Semiconductors, 31(3) 265–267 (1997); <https://doi.org/10.1134/1.1187123>.
- [14] O. Khshanovska, T. Parashchuk, I. Horichok, *Estimating the upper limit of the thermoelectric figure of merit in n- and p-type PbTe*. Materials Science in Semiconductor Processing, 160, 107428 (2023); <https://doi.org/10.1016/j.mssp.2023.107428>.
- [15] L. P. Bulat, V. S. Zakordonets, *A limited thermoelectric figure-of-merit of crystalline semiconductor materials*, PTS 29(10), 1743(1995).
- [16] B.M. Askerov, *Electron Transport Phenomena in Semiconductors* (World Scientific Publishing, Singapore, 394, (1994).
- [17] D.B. Chesnokova, M.I. Kamchatka, *Modeling of Defect Formation in Lead Chalcogenides and Their Properties*. Inorg. Mater., 37(2), 111 (2001); <https://doi.org/10.1023/A:1004189006526>.
- [18] Y. Matsushita, *Superconductivity and mixed valency in thallium-doped lead telluride*. Dissertation submitted to the department of materials science and engineering and the committee on graduate studies of Stanford university in partial fulfillment of the requirements for the degree of doctor of philosophy, 164 (2007).
- [19] E. S. Toberer, A. Zevalkink, G. J. Snyder, *Phonon Engineering through Crystal Chemistry*, J. Mater. Chem., 21(40), 15843 (2011); <https://doi.org/10.1039/c1jm11754h>.
- [20] D.M. Freik, V.V. Prokopiv, M.O. Halushchak, M.V. Pyts, H.D. Mateik, *Crystal Chemistry and Thermodynamics of Atomic Defects in A4B6 Compounds* (Plai, Ivano-Frankivsk, 1999).
- [21] D. M. Zayachuk, *The Dominant Mechanisms of Charge-Carrier Scattering in Lead Telluride*. Semiconductors, 31(2), 173 (1997); <https://doi.org/10.1134/1.1187322>.
- [22] Y. Pei, A. D. LaLonde, H. Wang, G. J. Snyder, *Low effective mass leading to high thermoelectric performance*. Energy & Environmental Science, 5, 7, 7963 (2012); <http://dx.doi.org/10.1039/c2ee21536e>.
- [23] R. Knura, T. Parashchuk, A. Yoshiasa, K. T. Wojciechowski, *Origins of Low Lattice Thermal Conductivity of Pb_{1-x}Sn_xTe Alloys for Thermoelectric Applications*. Dalt. Trans., 50 (12), 4323 (2021); <https://doi.org/10.1039/d0dt04206d>.
- [24] I.V. Horichok, V.V. Prokopiv, R.I. Zapukhlyak, O.M. Matkivskyj, T.O. Semko, I.O. Savelikhina, T.O. Parashchuk, *Effects of Oxygen Interaction with PbTe Surface and Their Influence on Thermoelectric Material Properties*. Journal of Nano- and Electronic Physics, 10(5), 05006(5pp) (2018); [https://doi.org/10.21272/jnep.10\(5\).05006](https://doi.org/10.21272/jnep.10(5).05006).
- [25] O.Z. Khshanovska, M.O. Halushchak, O.M. Matkivskyi, I.V. Horichok, *Analysis of heat conductivity mechanisms in PbSnTe solid solutions*. Physics and chemistry of solid state, 24(3), 564 (2023); <https://doi.org/10.15330/pcss.24.3.564-577>.
- [26] I.V. Horichok, T.O. Parashchuk, *Point defects in PbCdTe solid solutions*. Journal of Applied Physics, 127(5), 055704 (2020); <https://doi.org/10.1063/1.5130747>.
- [27] D. G. Cahill, S. K. Watson, R. O. Pohl, *Lower Limit to the Thermal Conductivity of Disordered Crystals*. Phys. Rev. B., 46(10), 6131 (1992); <https://doi.org/10.1103/PhysRevB.46.6131>.
- [28] Harrison Walter A., *Electronic structure and the properties of solids* (Dover Public. Inc., New York, 384) 1989.
- [29] A.M. Kosevich, *Fundamentals of Crystal Lattice Mechanics* (Nauka, Moscow, 1972).
- [30] P.G. Klemens, *Thermal Resistance due to Point defects at high temperatures*, Phys.Rev., 119(2), 507 (1960).
- [31] Y. Zhang, X. Ke, C. Chen, J. Yang, P. R. C. Kent, *Thermodynamic properties of PbTe, PbSe, and PbS: First-principles study*, Phys. Rev., B 80, 024304 (2009); <https://doi.org/10.1103/PhysRevB.80.024304>.
- [32] B.I. Boltaks, *Diffusion and point defects in semiconductors* (Nauka, L., 1972).
- [33] K. K. Choudhary, D. Prasad, K. Jayakumar, D. Varshney, *Effect of embedding nanoparticles on thermal conductivity of crystalline semiconductors: phonon scattering mechanism*. Internationale Journal of Nanoscience, 8(6), 551 (2009); <https://doi.org/10.1142/S0219581X09006389>.

- [34] I. Horichok, M. Maksymuk, O. Cherniushok, O. Matkivskyi, V. Balan, T. Parashchuk, K. T. Wojciechowski, *Revisiting Cold Pressing: A Viable Alternative to Conventional Thermoelectric Sintering Methods*. *Ceramics International*, 51(25), part C, 46958-46969 (2025); <https://doi.org/10.1016/j.ceramint.2025.07.400>.

Маргарита Крайнова, Остап Матківський, Ігор Горічок

Оптимізація концентрації носіїв заряду у РbТе для досягнення максимальної термоелектричної добротності

Карпатський національний університет імені Василя Стефаника, м. Івано-Франківськ, Україна,
ihor.horichok@cnu.edu.ua

Основним методом отримання ефективних термоелектричних матеріалів є створення мікро та макродефектів для зменшення коефіцієнта ґраткової теплопровідності, а також легування електроактивними домішками для досягнення оптимального значення хімічного потенціалу носіїв заряду η та, відповідно, оптимальної концентрації носіїв заряду n (чи p). Оскільки безрозмірна термоелектрична добротність ZT є немонотонною функцією від хімічного потенціалу носіїв то визначення оптимального рівня легування є відносно складною задачею, що у випадку її експериментального способу вирішення, потребує значних ресурсів. У даній роботі, використовуючи модель електропровідності, що враховує один домінуючий механізм розсіювання носіїв заряду та модель теплопровідності, що враховує розсіювання фононів на фононах, границях зерен та нанодфектах визначено оптимальні значення хімічного потенціалу носіїв та їх концентрації при яких функція ZT (η) за заданої температури досягає максимуму. Розрахунок проведено для телуриду свинцю електронного та діркового типу провідності з врахуванням двох типів носіїв (основних та неосновних) та з врахуванням біполярної складової коефіцієнту теплопровідності. Розраховано середні значення термоелектричної добротності для функціонально градієнтних матеріалів n та p типів провідності в діапазоні температур (400-800) К.

Ключові слова: телурид свинцю, термоелектрична добротність, легування.