

OPTIMAL CARRIER CONCENTRATION FOR HIGH THERMOELECTRIC PERFORMANCE OF LEAD SUBSTITUTED BISMUTH TELLURIDE IN P-TYPE DOPING

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Abstract. *Bi₂Te₃ and its alloys are the well-known state-of-the-art thermoelectric materials operating at around room temperature. With lead substituted, the newly formed quasi-binary compound PbBi₄Te₇, shows relatively high electrical conductivity and Seebeck coefficient. In this report, we employed the solution of the Boltzmann Transport Equation in a constant relaxation-time approximation within a first-principles density-functional-theory calculation to explore the role of the electronic thermal conductivity, κ_e , on the thermoelectric performance of the compound with p-type doping. Results show that κ_e increases drastically with the increases of both temperature and carrier concentration. Even the power factor has been found to be markedly improved with the increase of the carrier concentration, a rapid increase of κ_e emerges as a big hindrance to improve the dimensionless figure of merit, ZT, of the compound. This is responsible for the limit of ZT. The larger ZT is found in low temperatures and carrier concentrations. The highest ZT of about 0.48 occurs at 223 K and at the carrier concentration of $6 \times 10^{17} \text{ cm}^{-3}$. At room temperature the maximum ZT is slightly smaller. We demonstrated that at a particular temperature to maximize the thermoelectric performance of the compound, the carrier concentration must be optimized. Results show that the compound with p-type doping is a promising thermoelectric materials operating at around room temperature.*

Keywords: first-principles calculation, thermoelectric materials, p-type doping PbBi₄Te₇, electronic thermal conductivity.

Classification numbers: 31.15.A-; 71.15.Mb; 72.20.Pa; 84.60.Rb; 71.20.-b.

I. INTRODUCTION

The future now is dealing with the energy crisis and environmental impacts of fossil fuels. The renewable energy resources are therefore demanded. One of the methods is to convert unused waste heat directly into electricity by utilizing the thermoelectric (TE) effect [1]. Thermoelectric modules have been known to operate friendly with environment and to easily hybrid with electronic devices. In spite of that, the practical applications have still been inefficient due to the poor performance. The thermoelectric performance of a material or a device is determined by the dimensionless figure of merit, which is [2, 3]

$$ZT = \frac{\sigma S^2 T}{\kappa}, \quad (1)$$

where S is the Seebeck coefficient, T the temperature, σ the electrical conductivity and $\kappa = \kappa_e + \kappa_L$ is the total thermal conductivity which includes the electronic thermal conductivity κ_e and the lattice thermal conductivity κ_L . To improve ZT , S and σ are demanded to be large whereas κ must be low. Nonetheless, these coefficients have interrelationship. The increase of σ usually reduces S and increases κ and vice versa. Thus, the highest ZT values of typical thermoelectric materials operating at room temperature found so far are only around unity or even lower [4]. Many methods have been introduced to solve the problem including making superlattices [5], defects, element substitutions [6], alloy compositions, strains, tuning band structures, etc. [4, 6–8]. The best TE materials operating at around room temperature have been found in chalcogenide compounds. The element substitutions in these compounds have been found to manifest many potential effects which arise from the change of band near Fermi level and the increase of phonon scattering [9–12].

Recently, the class of compounds $A^{IV}\text{Te}-\text{Bi}_2\text{Te}_3$ ($A^{IV} = \text{Pb, Ge, Sn}$) was reported to have a complex crystalline structure which significantly enhances phonon scattering at long-period leading to the low lattice thermal conductivities. In addition, the high density of states near the Fermi energy gives rise to a rather large Seebeck coefficient [13, 14]. PbBi_4Te_7 in the class reveals an impressive high power factor. Therewith, its lattice thermal conductivity is relative small [12, 13, 15–17]. Recently, it has been demonstrated that the power factor of the compound can be significantly improved by increasing the carrier concentration and temperature [13]. Nonetheless, the discussion on the effect of the thermal conductivity was neglected [13]. In that scene, the suggestion was raised by the general optimized carrier concentration to maximize the TE performance, technically relying on the power factor $S^2\sigma$, not on the figure of merit, ZT . Since the thermal conductivity was unknown. The effect of thermal conductivity on the TE performance of the compound therefore is still under investigation. The important fact stems from its electronic component, κ_e . As reported, the increasing power factor originates also from the electrical conductivity [13]. According to the Wiedemann-Franz law, this leads to a rapid increase of κ_e which is detrimental for ZT . The question emerged is what level of this effect on the TE performance of PbBi_4Te_7 . In this work, we present our calculation of κ_e as a function of temperature T and carrier concentration n by utilizing the semi-classical Boltzmann Transport Equation. We demonstrate that the electronic thermal conductivity plays an important role to determine the TE performance of the compound. Accordingly, a big ZT is found in low carrier concentrations due to the small κ_e . We show the optimal carrier concentrations for various temperatures and figure out the best operating temperature for the TE performance of the compound.

II. CRYSTAL STRUCTURE AND COMPUTATIONAL METHOD

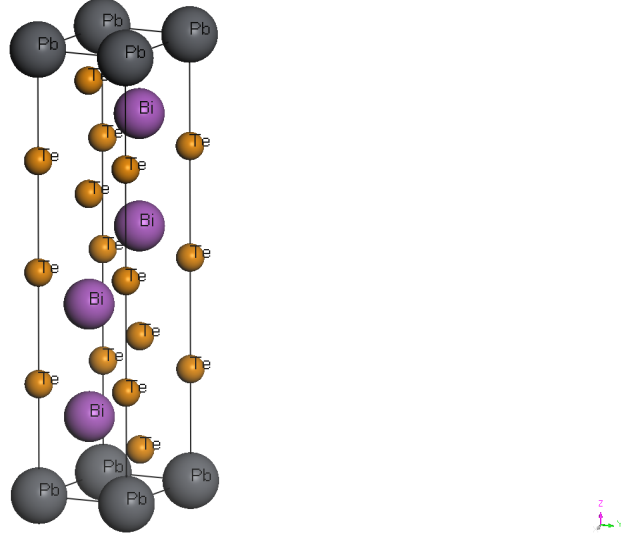


Fig. 1. Primitive cell of PbBi_4Te_7 crystal structure.

PbBi_4Te_7 compound belonging to the class of quasi-binary $A^{IV}\text{Te}-\text{Bi}_2\text{Te}_3$ ($A^{IV} = \text{Pb, Ge, Sn}$) series might be regarded as the intergrowths of PbTe – type and Bi_2Te_3 –type structures [16, 18–23]. The crystal structure of PbBi_4Te_7 is hexagonal with the primitive cell shown in Fig. 1. We used the experimental crystal lattice constants [24, 25], i.e. $a = 4.46\text{\AA}$ and $c = 23.65\text{\AA}$ for our calculations. To describe transport properties, we utilized the solution of the semi classical Boltzmann Transport Equation to estimate the transport coefficients [26] in which the electronic thermal conductivity was derived from the heat current. In that scene, it can be expressed in term of the integral of transport distribution function as following

$$\kappa_e = \frac{1}{e^2 T} \left(ITD_{ij}^{(2)} - \sum_{l,k=x,y,z} ITD_{il}^{(1)} ITD_{lk}^{(0)-1} ITD_{kj}^{(1)} \right), \quad (2)$$

where

$$ITD_{ij}^{(\alpha)} = \int d\varepsilon \frac{\partial f}{\partial \varepsilon} (\varepsilon - \mu)^\alpha TD_{ij}(\varepsilon)$$

is the integral of transport distribution function (ITD); TD is the transport distribution function defined by [26]

$$TD_{ij}(\varepsilon) = e^2 \sum_{\vec{k}} \tau_{ik}(\vec{k}) \delta(\varepsilon - \varepsilon(\vec{k})) \vec{v}_k(\vec{k}) \vec{v}_j(\vec{k}), \quad (3)$$

in which ε is band energy, e the elementary charge, τ the relaxation time constant, μ chemical potential, f the Fermi-Dirac distribution function, δ Dirac delta function, v group velocity. Such band dependent quantities, i.e. ε and v , are derived from the ground state which were carried out from first-principle calculation within density functional theory. The dimensionless thermoelectric figure of merit can be therefore estimated by using Eq. (1).

III. RESULTS AND DISCUSSIONS

PbBi_4Te_7 is a narrow band gap semiconductor. In our most precise calculation, as reported in Ref. [13], the band gap of the compound is of about 0.11 eV obtained in the screened-exchange (sX) local-density approximation (LDA) with spin-orbital coupling (SOC) calculation (so called sX-LDA+SOC calculation). For the transport properties, we invoke the solution of the Boltzmann Transport Equation in which the eigenvalues are used to estimate the group velocity in Eq. (3). Accordingly, the eigenvalues which were conducted from a dense k-grid mesh in LDA+SOC calculation together with the use of the rigid band approximation [27] are used for further calculations. Thus, the bands above the Fermi energy are shifted to achieve the target band gap acquired in the sX-LDA+SOC calculation. To show, we illustrate in Fig. 2 such the band structure of PbBi_4Te_7 calculated by using LDA+SOC with the shifted sX-LDA+SOC band gap [13, 28–30]. The p-type doped semiconductor is considered as the dominant effect of valence band on the desired property, e.g. the thermoelectric property. The dominant effect of conduction bands, i.e. n-type doping, will be considered in another work.

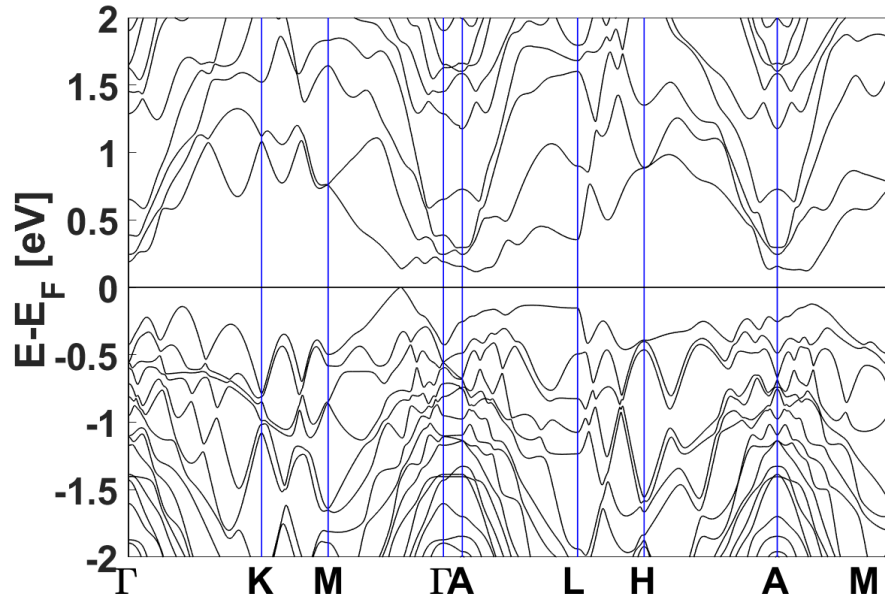


Fig. 2. Band structure of PbBi_4Te_7 calculated by using LDA-SOC with shifted band gap obtained from the self-consistent sX-LDA+SOC calculation.

The utmost important task appeared is to estimate the transport distribution function (see Eq. (3)). This task, as described, is carried out by calling the eigenvalues collected in the LDA+SOC calculation with the shifted sX-LDA+SOC band gap. The calculation of the transport coefficients, i.e. κ_e , σ , S , etc. are therefore straight forward. In this report, we focus on κ_e to analyze ZT of PbBi_4Te_7 . The electronic thermal conductivity (as well as the electrical conductivity) is proportional to the relaxation time constant, τ , as shown in Eq. (2) and Eq. (3) within the relaxation

time approximation. τ is an empirical parameter which is found by comparing some calculated quantities such as S , σ , or ZT with available experimental quantities [10, 30]. The typical τ for bismuth telluride and its alloys is about 10^{-14} s [10, 14, 28, 30, 31]. It is noted that in the approximation concerned, κ_e/τ is relaxation time independence (see Eq. (2)). Accordingly, we present our results in terms of κ_e/τ as a reduced electronic thermal conductivity. The results are presented in Fig. 3 which shows temperature (unit in K) and carrier concentration (unit in \log_{10} , cm^{-3}) dependences. The contour lines present κ_e with the equal values. As clearly shown, κ_e is drastically increased with the increase of the carrier concentration at a certain temperature. For a fixed carrier concentration, κ_e is also gradually increased with temperature. It is noted that the power factor, $S^2\sigma$, has been reported to increase monotonically with the carrier concentration [13]. The increase of the power factor is likely to be linearly, the increase of κ_e with a power-law become prominent to reduce ZT . This is a main reason for the constraint of ZT .

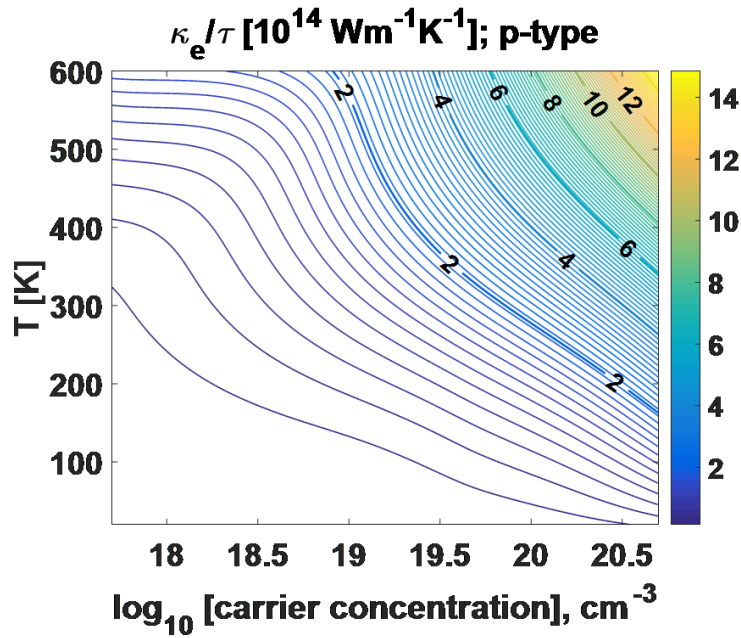


Fig. 3. (Color online) The calculated electronic thermal conductivity, κ_e/τ , as a function of temperature (unit in K) and carrier concentrations n (unit in \log_{10} , cm^{-3}).

Owing to the Wiedemann - Franz law [1, 22], the increase of κ leads to increase of σ . Thus, their opposite tendencies shape the thermoelectric efficiency, ZT . To substantiate this point, we compute ZT as a two-variable function of temperature and carrier concentration. For this task, we assume that the compound is an ideal phonon-glass thermoelectric material of which the lattice thermal conductivity is much smaller than the electronic thermal conductivity, i.e. the ratio κ_L/κ_e is negligible. Hence, the figure of merit approaches to the following value

$$ZT = \frac{\sigma S^2 T}{\kappa_e}. \quad (4)$$

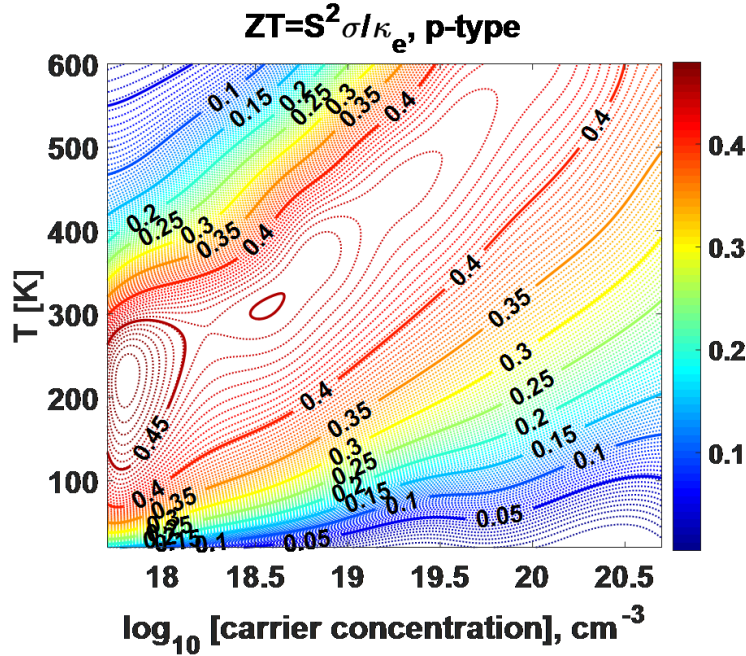


Fig. 4. (Color online) Temperature, T (in K) and carrier concentration n (in 10^{19}cm^{-3}) dependences of ZT .

It is noted that σ/κ_e is relaxation time independence so is ZT . Fig. 4 presents our calculated results. As can be shown, there are two obvious peaks of ZT . One occurs at low carrier concentration and temperature, i.e. $6 \times 10^{17}\text{cm}^{-3}$ and 223 K. This peak arises from the Seebeck coefficients [13]. At low temperatures and low carrier concentrations, the bipolar conduction is weak. Thus the band gap plays a great barrier to keep the intrinsic carriers from thermal excitation. This feature remains the Seebeck coefficient to be high enough [13]. In addition, κ_e as shown above is very low in this area. The second peak occurs at higher carrier concentration and temperature, i.e. $3.6 \times 10^{18}\text{cm}^{-3}$ and 307 K. This stems from the compromise between the gradual rise of σ and κ and the reduction of S . It also explains the reason why ZT at this peak is slightly smaller than that at the former peak.

To elucidate the dependences, we explicitly calculate ZT as a function of temperature at various carrier concentrations and as a function of carrier concentration at various temperatures. We present such these results in Fig. 5. As can be seen, at a fixed carrier concentration, ZT almost increases monotonically with the temperature. In addition, Fig. 5a shows the monotonic decrease of ZT with the increase of the carrier concentration. In contrast, Fig. 5b shows that ZT can be greatly improved with an optimized carrier concentration at a particular temperature. It is noted that at low temperatures, e.g. below 200 K, the peak of ZT in Fig. 5b is sharp. It implies that ZT is not stable with the change of the carrier concentration. In this fashion, the most stable ZT is at around room temperature. At temperatures above room temperature, the peak of ZT is gradually sharp. The peaks occurred at different temperatures show that the maximum value of ZT may achieved with a relevant optimal carrier concentration. In Table 1, we list the optimal carrier

concentration with various temperatures and the corresponding maximum ZT values. As shown, the highest maximum ZT of 0.48 is reached at a low temperature, i.e. 220 K and at the optimal carrier concentration of $6.0 \times 10^{17} \text{ cm}^{-3}$. At room temperature, the optimized ZT slightly reduces to be 0.47. And at temperatures around 400 K, ZT is of about 0.44. This result is in accordance with experimental observation in which ZT was reported to be ~ 0.4 at 500 K [15]. We also note that our maximum ZT achieved by optimizing carrier concentration is significantly improved in comparison with experimental ZT of 0.01 at 300 K [17]. This indicates that at a particular temperature, to improve ZT the carrier concentration must be carefully optimized, especially at low carrier concentrations, e.g. around $6.0 \times 10^{17} \text{ cm}^{-3}$. By taking into account the effect of electronic thermal conductivity, we suggest that PbBi_4Te_7 with p-type doping is a promising TE candidate for thermoelectric application operating at around room temperature. Careful analyses and calculations finding out the effect of impurities, defects, etc. which yield p-type doping on ZT were not considered and appeared to be an interesting issue for future studies.

Table 1. The maximum ZT at various temperatures T (unit in K) at appropriate optimized carrier concentration n_{opt} (unit in 10^{19} cm^{-3}).

T (K)	100	200	223	300	400	500
$n_{opt}(10^{19} \text{ cm}^{-3})$	0.05	0.06	0.06	0.20	0.87	3.36
ZT	0.43	0.47	0.48	0.47	0.44	0.44

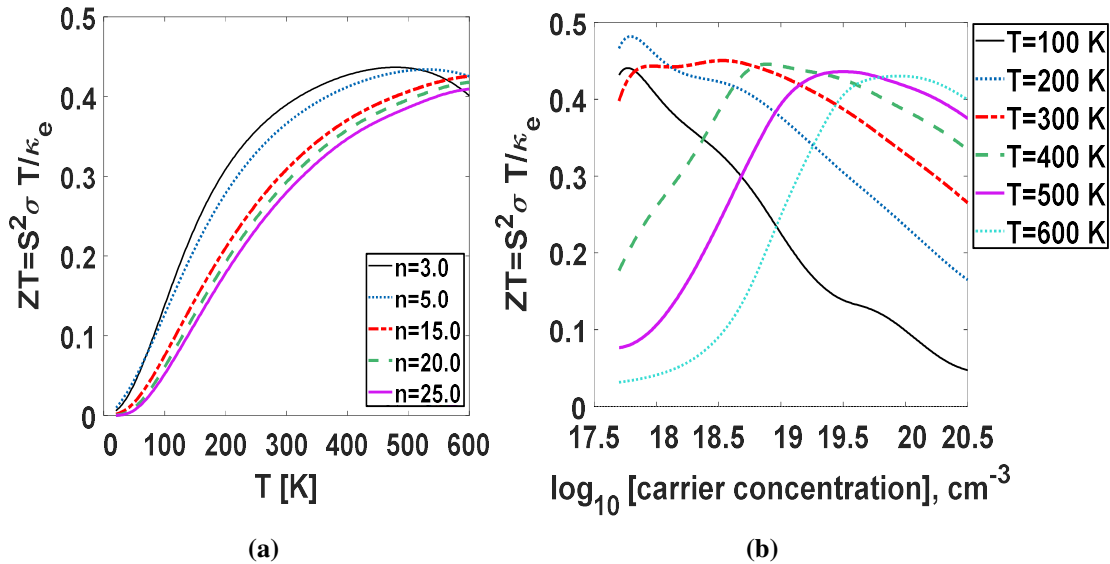


Fig. 5. (Color online) Calculation of $ZT = S^2 \sigma T / \kappa_e$ as a function of (a) temperature at various carrier concentrations n (unit in 10^{19} cm^{-3}) and (b) carrier concentration (unit in $\log_{10}, \text{ cm}^{-3}$) at various temperatures.

IV. CONCLUSIONS

We reported the effect of the electronic thermal conductivity on thermoelectric properties of the quasi-binary compound, PbBi_4Te_7 , with p-type doping by employing the solution of the Boltzmann Transport Equation in a constant relaxation-time approximation. We found that the increase of carrier concentration leads to a drastic increase of the electronic thermal conductivity. Therefore, it lowers the thermoelectric performance. Nevertheless, at a fixed temperature, ZT can be improved significantly by optimizing carrier concentration. Assuming the ideal phonon-glass, we computed ZT and obtained that the maximum ZT can reach 0.48 at a low temperature, i.e. 220 K and at carrier concentration of $6.0 \times 10^{17} \text{ cm}^{-3}$. At room temperature, the optimized ZT slightly reduces with the value of around 0.47. Our findings suggest that PbBi_4Te_7 with p-type doping is a promising TE materials operating at around room temperature.

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