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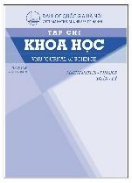

Original Article

Electronic Thermal Conductivity and Thermoelectric Performance of n-type $PbBi_4Te_7$

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Abstract: Bismuth telluride and its related compounds are the state-of-the-art thermoelectric materials operating at room temperature. Bismuth telluride with Pb substituted, $PbBi_4Te_7$, has been found to be a new quasi-binary compound with an impressive high power factor. In this work, in the framework of density functional theory, we study the electronic thermal conductivity of the compound by employing the solution of Boltzmann Transport Equation in a constant relaxation-time approximation. The results show that the electronic thermal conductivity drastically increases with the increase of temperature and carrier concentration which have a detrimental effect on the thermoelectric performance. At a particular temperature, the competition between the thermal conductivity, the Seebeck coefficient and the electrical conductivity limits the thermoelectric figure of merit, ZT. The maximum ZT value of about 0.47 occurs at 520 K and at the carrier concentration of 5.0×10^{19}cm^{-3} for n-type doping. This suggests that to maximize the thermoelectric performance of the compound, the carrier concentration must be carefully controlled and optimized whereas the best operating temperature is around 500 K.

Keywords: Electronic thermal conductivity, thermoelectric material, $PbBi_4Te_7$, first-principles calculation.

1. Introduction

Nowadays, the demand for new energy resources due to environmental impacts and exhausted fossil fuels is increasing. One of the potential methods is the scavenging of waste heat with thermoelectric modules which are able to convert unused waste heat directly into electricity silently, reliably and

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scalably without moving parts. Nevertheless, thermoelectricity has still been inefficient due to the low efficiency in practical applications and cost demanding in fabrications. The thermoelectric efficiency is qualified by the figure of merit, which is defined by [1].

$$ZT = \frac{\sigma S^2 T}{\kappa}, \tag{1}$$

where σ is the electrical conductivity, S the Seebeck coefficient, T the temperature and κ the thermal conductivity. Accordingly, a high ZT is desired. Therefore, S and σ are required to be large accompanied by a low κ. However, these coefficients are not independent. A rise in σ leads to a reduction in S and an increase in κ and vice versa. This mutual dependence limits ZT around unity or even lower [2]. The scope of today's research has introduced many variables such as making superlattices [3], element substitutions, alloy compositions, defects, strains, band engineering, etc. [2,4–6] to solve the problem. So far, the highest ZT for the best materials operating at around room temperature (RT) has been found in Bi_2Te_3 and its related compounds. Elements substitutions into this compound were found to be promising techniques which lead to many peculiar properties due to the change of band topology around Fermi energy and the increase of phonon scattering which lowers the thermal conductivity [7–10].

Recently, the quasi-binary compound $A^{IV}Te–Bi_2Te_3$ ($A^{IV} = Pb,Ge,Sn$) were reported to have a complex crystalline structure, low lattice thermal conductivity due to effective phonon scattering at long-period lattices experimentally and high density of states near the Fermi energy theoretically, which gives rise to a rather large Seebeck coefficient [11,12]. In these series, $PbBi_4Te_7$ emerged as a potential candidate with relatively high power factor and low κ [10,11,13–15]. The thermal conductivity κ is contributed by the lattice thermal conductivity, κ_L and the electronic thermal conductivity, κ_e. κ_e contributes drastically to κ in regular thermoelectric materials. The systematic study of κ_e and ZT of $PbBi_4T_7$ is therefore important. Though $PbBi_4T_7$ has been reported to give a high power factor in p-type doping, the value of ZT has been found to be still small [11,16]. In this work, by utilizing the semi-classical Boltzmann Transport Equation, we present our calculation of κ_e as a function of temperature T and carrier concentration n in n-type doping. We demonstrated that the electronic thermal conductivity in this doping type is drastically increased with the increases of the temperature and the carrier concentration. The competition between the opposite tendencies of κ and the power factor is responsible for the limit of ZT. We show optimal carrier concentrations and the best operating temperature to maximize the thermoelectric performance of the compound in n-type doping.

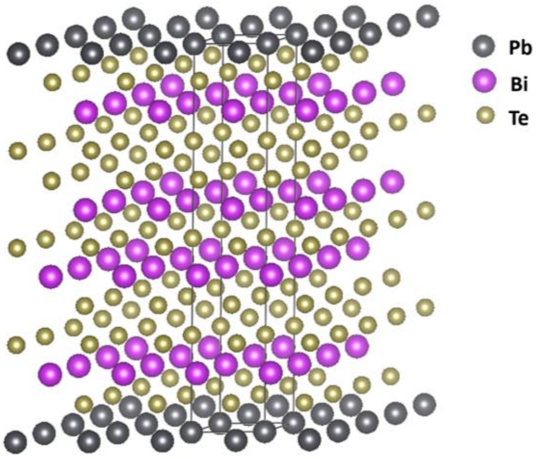

Figure 1. Crystal structure of $PbBi_4Te_7$.

2. Crystal Structure and Computational Method

The quasi-binary $A^{IV}Te$–Bi_2Te_3 (A^{IV} = Pb, Ge, Sn) series with emphasis on $PbBi_4Te_7$ might be regarded as the intergrowths of $PbTe$ – type and Bi_2Te_3 –type structures [14,17–22]. The crystal structure of such material is depicted in FIG. 1. The experimental crystal lattice constants [23,24], i.e. a = 4.46 Å and c = 23.65 Å have been used in the calculation.

From the ground state of the compound carried out from first-principle calculation within density functional theory [25], we utilized the solution of the semi classical Boltzmann Transport Equation to estimate the transport coefficients [26]. Accordingly, these coefficients are presented via the integral of transport distribution function [26]

$$\Lambda_{ij}^{(\alpha)} = \int d\varepsilon \sum_{\vec{k}} \frac{\partial f}{\partial \varepsilon} (\varepsilon - \mu)^{\alpha} e^2 \tau_{ik}\left(\vec{k}\right) \delta\left(\varepsilon - \varepsilon\left(\vec{k}\right)\right) \vec{v}_k\left(\vec{k}\right) \vec{v}_j\left(\vec{k}\right), \tag{2}$$

in which ε is band energy, μ chemical potential, f the Fermi-Dirac distribution function, e the elementary charge, τ the relaxation time constant, δ Dirac delta function, v group velocity. The electronic thermal conductivity is derived from the heat current. In that scene, it can be expressed in term of the integral of transport distribution function as following

$$\kappa_e = \frac{1}{e^2 T}\left(\Lambda_{ij}^{(2)} - \sum_{l,k=x,y,z} \Lambda_{il}^{(1)} \Lambda_{lk}^{(0)-1} \Lambda_{kj}^{(1)}\right). \tag{3}$$

The calculation of the power factor, i.e. $S^2\sigma$, has been presented in ref. [11]. The dimensionless thermoelectric figure of merit can be therefore estimated by using Eq. (1).

3. Results and Discussion

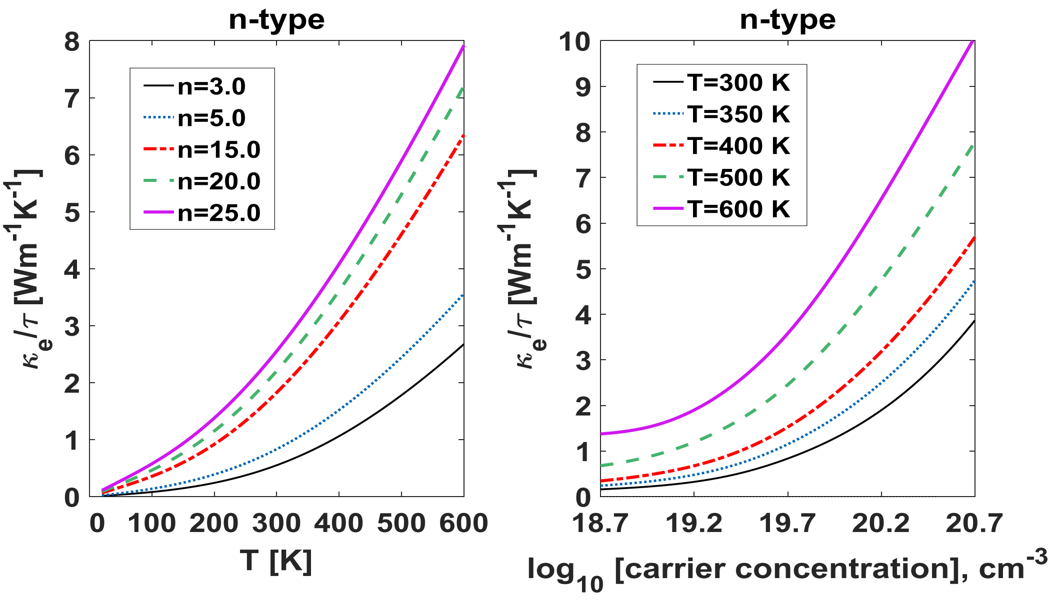

Figure 2. (Color online) The reduced electronic thermal conductivity, κ_e/τ, as a function of (a) temperature at various carrier concentrations n (in 10^{19}cm^{-3}) and (b) carrier concentration (in log$_{10}$, cm^{-3}) at various temperatures T.

The electronic thermal conductivity (as well as the electrical conductivity), in the relaxation time approximation, is proportional to the relaxation time constant, τ as shown in Eq. (4). The parameter τ can be found by comparing one of the calculated quantities such as either S, σ, or ZT with the relevant experimental quantities [8,27]. The typical value of τ for bismuth telluride based compounds is about $10^{-14}s$ [8,12,27–29]. Due to the relaxation time independence, we present here the calculation of κ_e/τ as a reduced electronic thermal conductivity. The results are presented in FIG. 2 which shows the temperature dependence at various carrier concentrations, i.e. n = 3.0, 5.0, 15.0, 20.0 and 25.0 (unit in 10^{19}cm^{-3}) (see FIG. 2(a)) and the carrier concentration (unit in log$_{10}$, cm^{-3}) dependence at various temperatures, i.e. T = 300, 350, 400, 500, and 600 (unit in K). As clearly shown, κ_e is drastically increased with the increase of the carrier concentration. In contrast, the power factor, $S^2\sigma$, has been reported to increase monotonically with the carrier concentration [11]. While the power factor is likely to increase linearly which facilitates an increase in ZT, the increase of κ_e with a power-law is a big hindrance and is responsible for the constraint of ZT.

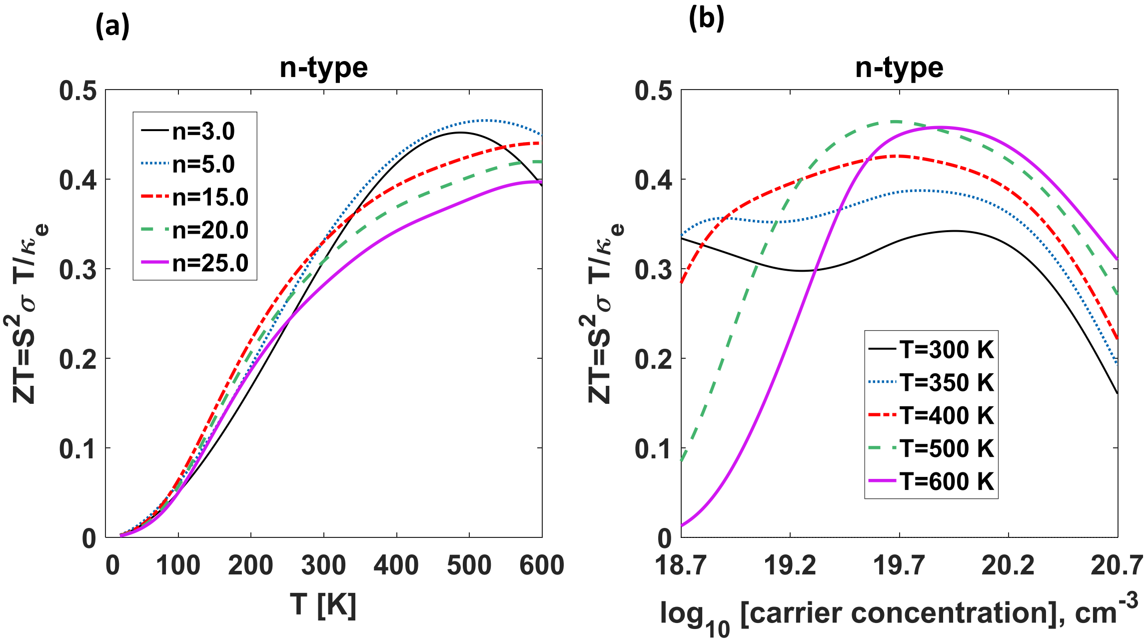

Figure 3. (Color online) Figure of merit, ZT, as a function of (a) temperature at various carrier concentrations n (in 10^{19}cm^{-3}) and (b) carrier concentration (in log$_{10}$, cm^{-3}) at various temperatures T.

According to the Wiedemann - Franz law [1, 22], the increase of κ is accompanied by the increase of σ. These competitions therefore limit the thermoelectric performance. To elaborate this point, we estimate ZT by assuming that the compound is an ideal phonon-glass thermoelectric material in which the lattice thermal conductivity is much smaller than the electronic thermal conductivity, i.e. $\kappa_L/\kappa_e \rightarrow 0$. Hence, the figure of merit approaches to the following value

$$ZT = \frac{\sigma S^2 T}{\kappa_e}. \tag{4}$$

Interestingly, this is relaxation-time independent. We present our calculated results in FIG. 3. As can be shown, there emerged two clear points. The first one relates to the temperature dependence. In FIG. 3a, with temperatures below 400 K and around the room temperature, ZT rapidly increases with temperature. And it slowly increases beyond that temperature for various fixed carrier concentrations. This suggests that the optimal temperature for maximized *ZT* is above 400 K. Nonetheless, the increase of temperature above 400 K does not significantly increase *ZT*. The second one relates to the carrier concentration dependence which supports the first points. As clearly shown in FIG. 3b, *ZT* can be maximized by optimizing the carrier concentration. With temperatures below 400 K, the shape of *ZT* is flatter, i.e. *ZT* is more stable with the change of *n* whereas with the temperatures above 400 K the maximum *ZT* is slightly raised. The maximum peak occurs at the carrier concentrations varied from 4.0 to $8.0\times10^{19}\,cm^{-3}$ with a sharper peak at high temperatures. The peak of *ZT* at 500 K is higher than that at 600 K which indicates that *ZT* can reach higher maximum values at an optimal temperature rather than keeping in increasing the temperature. Our results are in good agreement with the experiment in which *ZT* is about 0.4 at 500 K [13]. And the values are significantly improved in comparison with experimental *ZT* of 0.01 at 300 K [15].

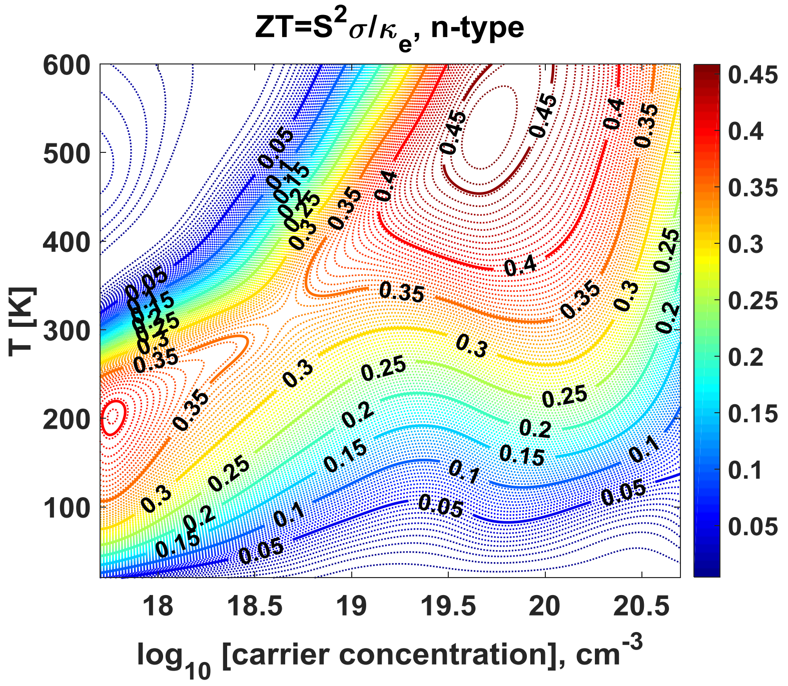

Figure 4. (Color online) Temperature, *T* (in *K*) and carrier concentration, *n* (in $\log_{10}n$, cm^{-3}) dependences of *ZT*.

To search for the highest *ZT* value, we calculated its value as a function of two variables, i.e. *n* and *T*. We illustrate the calculated results in FIG. 4. These are two peaks of *ZT*; one occurs at low temperature and the other occurs at higher one. The first peak is determined by *S* and κ whereas the latter is determined by σ and it is significantly higher than the first one. This indicates that at a particular temperature, to improve *ZT* the carrier concentration must be optimized. In Table 1, we tabulate the optimized carrier concentrations with various temperatures and the corresponding maximum *ZT* values. Especially, the highest maximum *ZT* of 0.47 is obtained at temperature of 520 K and carrier concentration of $5.0\times10^{19}\,cm^{-3}$ (corresponding to the first peak above). Thus, to maximize the thermoelectric performance of this compound, we suggest that one should control the carrier concentration around $5.0\times10^{19}\,cm^{-3}$ and the operating temperature of around 500 K.

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)	300	350	400	500	520	600
n_{opt} (10^{19}cm^{-3})	7.0	6.0	5.2	4.6	5.0	8.0
ZT max	0.34	0.39	0.43	0.46	0.47	0.45

4. Conclusion

We examined the electronic thermal conductivity of the quasi-binary compound $PbBi_4Te_7$ with n-type doping by employing first-principles density functional theory and the solution of Boltzmann Transport Equation in a constant relaxation-time approximation. We demonstrated that the increase of carrier concentration drastically increases the electronic thermal conductivity. This increase is responsible for the limit of *ZT*. At a particular temperature, *ZT* can be maximized by optimizing carrier concentration. Assuming the ideal phonon-glass, we estimated *ZT* and obtained that the highest *ZT* can reach 0.47 at 520 K at the carrier concentration of $5.0\times10^{19}\,cm^{-3}$. We expect that our findings spur further experimental investigations to determine the facts that improve *ZT* of $PbBi_4Te_7$.

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