I. Introduction

Thermoelectric (TE) materials, which can directly convert heat into electricity or vice versa, have been receiving substantial attention because of their already available and potential applications not only in the energy conversion industry but also in providing power for electronics.\textsuperscript{1-16} The TE conversion efficiency and performance-price ratios of TE devices developed so far and those under development are insufficient to compete with fossil fuel based energy resources. Some intrinsic issues need to be solved for TE materials design and synthesis, and some of them have been lasting for decades. The bipolar effect as often found in a lot of semiconductors with a relatively narrow band gap represents one of them.\textsuperscript{17-24} This work intends to touch this issue.

It is known that the TE performance of a material is usually measured by the so-called figure of merit (FOM) \( ZT = S^2\sigma T/\kappa_{\text{tot}} \) where \( S^2\sigma \) is the power factor PF, \( S \) is the Seebeck coefficient, \( \sigma \) is the electrical conductivity, \( T \) is the absolute temperature, and \( \kappa_{\text{tot}} \) is the thermal conductivity including both the electronic thermal conductivity \( \kappa_e \) and the lattice thermal conductivity \( \kappa_L \), i.e., \( \kappa_{\text{tot}} = \kappa_e + \kappa_L \). In order to enhance both the \( ZT \) and PF, large \( \sigma \) and \( S \) but low \( \kappa_{\text{tot}} \) are required. However, in many cases these requirements cannot be satisfied simultaneously for stoichiometric semiconducting compounds due to the counteracting relationships among parameters \( \sigma, \kappa_{\text{tot}}, \) and \( S \). The favorable and also well-demonstrated strategy is to search for those compounds with sufficiently high \( S \) and low \( \kappa_{\text{tot}} \) and then to perform carrier-doping of these compounds which usually have small \( \sigma \), without seriously damaging the Seebeck effect.

For TE applications \( (T < 1000 \, \text{°C}) \), the bipolar effect is usually significant in those semiconductors with a narrow band gap \( \Delta \) (e.g., \( \Delta < 0.5 \, \text{eV} \)) and it originates from the excitation of electrons from valence bands to conduction bands at a finite \( T \) and leaves holes in the valence band.\textsuperscript{25} This effect can be schematically illustrated in Fig. 1(a) as a guide to the eye.

For a given band gap \( \Delta \), both electrons and holes can be excited, filling, respectively, the conduction bands and valence bands near the Fermi-level. If a temperature gradient is imposed on the TE material sample under test, with the hot-end \( (T_h) \) and the cool-end \( (T_c) \), this effect would be expected to produce several consequences. First, the Seebeck effects from the two types of carriers have opposite signs, making the total Seebeck effect cancel each other, unfavorable for applications. Second, a strong bipolar effect will enable via two processes the thermal conductivity larger than the cases where only one type of carrier is dominant. The first process is that both types of carriers diffuse along the negative thermal gradient direction, carrying more heat from the hot-end to the cold-end and thus making the thermal conductivity larger than the single type of carrier does. The second process is related to the fact that more electrons/holes will be excited near the hot-end than the cold-end, and more electrons/holes will be annihilated near the cold-end.
than the hot-end. This implies that more heat is absorbed near the hot-end due to the electron/hole excitation and more heat is released near the cold-end due to the electron/hole recombination, which also makes the thermal conductivity larger. Therefore, the electronic thermal conductivity \( \kappa_{\text{e}} \) would be large for bipolar semiconductors although it may be still far smaller than \( \kappa_{\text{l}} \) for most cases. Third and in contrast, the excitation of both types of carriers may be beneficial to the electro-transport. As a general tendency, the bipolar effect imposes a negative impact much stronger than the positive impact on the \( ZT \) and the PF factor. In particular, its serious damage to the Seebeck effect is vital.

In principle, the bipolar effect would be more or less inevitable in semiconductors, but details of this effect depend on the electronic structure. On one hand, the geometric difference between the conduction bands and the valence bands may give rise to different effective masses and mobility values of the excited electrons and holes as well as the induced Seebeck coefficients. On the other hand, lattice, impurity, and defects may scatter electrons and holes in different ways, enabling different electro- and thermal-transport behaviors. Unfortunately, so far neither theoretical approach nor experimental characterization of the bipolar effect in TE materials has been sufficient. For instance, determination of the concentration and mobility of electrons and holes simultaneously using the Hall measurement is somehow challenging even if possible. A separate measurement of the Seebeck coefficients of electrons and holes is also a nearly impossible task. Surely, the bipolar effect, if strong enough, is believed to exhibit some signatures in the measured TE properties, such as the decaying Seebeck coefficient \( S \) as a function of \( T \) in the high-\( T \) range, but unveiling some details of the bipolar effect from these signatures seems far from established.

Theoretically, the comprehensive framework for calculating the TE properties is to utilize the first-principles calculations to obtain the electronic structure and the phonon spectrum and then the semi-classical Boltzmann transport theory is employed to evaluate the TE parameters. Along these lines, extensive investigations have been reported. It is claimed that all the TE properties can be quantitatively calculated for the given lattice composition/structure and carrier concentration \( n \). This framework takes into account the thermally induced carrier excitation and in this sense the bipolar effect is at least partially considered. Nevertheless, in this framework, the electronic and phononic structures are calculated using the ideal stoichiometric compound instead of the real doped compound, which does not consider the influence of any carrier doping, lattice imperfection, and impurity on the electronic and phononic structures. However, a realistic TE system must have a nonzero carrier concentration \( n \). To account for this fact, the semi-classical Boltzmann transport theory sets in the Fermi level \( (E_F) \) inside the band gap so that the carrier concentration integrated from the electronic band structure is equal to the given value \( n \). In a strict sense, this somehow artificial shifting of \( E_F \) is expected to impose several side-effects associated with the bipolar effect among others. First, shifting the Fermi level will distort the profile of density of states. A set of parameters such as carrier relaxation time, effective mass, and mobility of electrons and holes will be affected, leading to a difference between calculated and real electro-transport behaviors. Consequently, the electronic thermal conductivity will be affected too. Second, the Fermi level shifting does not change the band structure geometry which should be distorted by carrier doping if any, leading to a discrepancy of the Seebeck coefficient from the measured values. Third, such Fermi level setting may impose more significant influence on the TE parameters in TE materials with a narrow band gap than those with a wide band gap, since the former shows stronger carrier excitation than the latter. Fourth, the bipolar effect will be more seriously manifested in a TE material with lower \( n \) since the excited carriers in such a system will have a high proportion.

In this work we intend to deal with the bipolar effect, choosing a specific compound. The main motivation is to check whether the bipolar effect can be properly considered in the current framework. First, the compound to be chosen should have a proper band gap, and the conduction bands and valence bands should have similar geometry so that the bipolar effect can be as strong as possible. Third, experimental data on this system are available for evaluating the bipolar effect. Recently, a \( p \)-type Zintl compound \( \text{CaMg}_2\text{Bi}_2 \) was reported to exhibit relatively high \( ZT \) and \( \text{PF} \). A preliminary first-principles calculation predicted a direct band gap of \( \sim 0.4 \text{ eV} \) and roughly
symmetric band profiles near the conduction band minimum (CBM) and the valence band maximum (VBM). These are proper indications of a strong bipolar effect. It is known that CaMg\(_2\)Bi\(_2\) possesses a trigonal structure (No. 164, space group \(P3m1\)). The earlier reported \(ZT\) values on CaMg\(_2\)Bi\(_2\) are below \(\sim 0.15\).\(^{31}\) Optimized experiments on a hot-pressed polycrystalline system, reported recently,\(^{34}\) revealed a \(ZT\) value of \(\sim 0.24\) at \(T = 580\) K and \(\sim 0.82\) at \(T = 871\) K. As expected, the measured Seebeck coefficient \(S\) and electrical resistivity \(\rho(1/\sigma)\) begin to fall at \(T > 470\) K,\(^{34}\) a claimed feature of the bipolar effect. Therefore, the compound CaMg\(_2\)Bi\(_2\) is a suitable system for studying the bipolar effect.

The remaining part of this article is organized as follows. In Section II we outline briefly the framework of computations based on the first-principles and Boltzmann transport theory. The calculated results are summarized in Section III, where a discussion of the bipolar effect signature will be given. A modified approach to the bipolar effect using a \(T\)-dependent effective carrier concentration \(\langle n_{\text{eff}}\rangle\) will be proposed in Section IV so that the calculated results are in good agreement with measured values. Section V is devoted to a brief conclusion.

II. Computational methods and details

As mentioned above, so far theoretical approaches to TE materials have been based on the first-principles calculations on the electronic structure and the phononic structure, followed by the semi-classical Boltzmann transport computations of the TE parameters. The details of this computational framework were reported earlier\(^{36}\) and only a brief description is presented here for illustrating how the bipolar effect if remarkable is considered or improperly neglected. The trigonal structure of CaMg\(_2\)Bi\(_2\) is shown in Fig. 1(b). There are five atoms in the primitive cell and the experimentally determined lattice constants are \(a = b = 4.73\) Å, and \(c = 7.68\) Å. The computations were performed on this pre-assigned lattice.

2.1. Electronic and phononic structures

The electronic band structures are calculated using density functional theory (DFT) and the Vienna \textit{ab initio} simulation package (VASP)\(^{35}\) by adopting the projected augmented wave (PAW)\(^{16}\) method. Here, the exchange correlation functional was described by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional form.\(^{37}\) To describe the ionic cores, the PAW pseudopotentials with \(3p^5\)\(3s^2\), \(3s^2\), and \(6s^6p^6\) valence electron configurations were used for Ca, Mg, and Bi atoms, respectively. The cutoff energy for the plane wave basis was set to 500 eV in all calculations. A Monkhorst–Pack special \(k\)-point sampling method was used for the charge integration in the first irreducible Brillouin zone, and an \(8 \times 8 \times 4\) \(k\)-mesh was employed for the structural optimization and self-consistent calculation. The convergence threshold was set to \(1.0 \times 10^{-6}\) eV in energy and \(0.001\) eV Å\(^{-1}\) in force. All these parameters have been fully tested to ensure a better convergence of energy and force.

The phonon spectrum calculation is performed using the Phonopy code\(^{39}\) combined with the data from density functional perturbation theory (DFPT)\(^{39}\) embedded in the VASP code. In the DFPT computations, we employed a \(2 \times 2 \times 2\) super-cell from the primitive cell and a \(4 \times 4 \times 2\) Monkhorst–Pack special \(k\)-mesh was adopted to evaluate the force constants needed for evaluating the phononic and thermodynamic properties.

In order to find the ground state for CaMg\(_2\)Bi\(_2\), the lattice structure and the atomic positions are fully optimized by position relaxation until the changes in energy and force satisfy the assigned criterions. The optimized structural parameters are \(a = b = 4.7941\) Å and \(c = 7.7353\) Å. These results are in good agreement with experimental values and earlier theoretical data,\(^{31–33}\) showing that the input parameters are reasonable and the obtained structure is correct. Owing to that, the optimized structure is adopted to carry out the subsequent calculations.

2.2. Boltzmann transport computations

With the electronic and phononic band spectra, all the TE parameters are calculated within the framework of Boltzmann transport theory, as reported earlier.\(^{40}\) In brief, first, the carrier concentration \(n\) near \(E_F\) is calculated from the band structure. We adjust the value of \(E_F\) to obtain the assigned \(n\) for the TE property optimization. Then the lattice elastic constants are evaluated from the band structure too via the stress–strain scenario. Second, by employing the deformation potential (DP)\(^{41}\) approach to a series of dilated lattices, the effective relaxation time is evaluated by assuming the carrier excitations for both electrons and holes at the conduction (valence) band edges. Then the effective carrier mass and mobility for the two types of carriers are calculated. With this corrected relaxation time, one can compute the three parameters \(\sigma, S,\) and \(\kappa_L\).

Third, one can evaluate the isometric specific heat \(C_v\) and thus the Debye frequency from the phonon band structure. An integration of the phonon spectrum over the reciprocal lattice space gives rise to the Grüneisen parameter. Consequently, the intrinsic lattice thermal conductivity \((\kappa_L)_{\text{in}}\) is obtained using the approach proposed by Klemens.\(^{42}\) Finally, parameters PF and \(ZT\) can be evaluated from the above calculated parameters. Here, it should be mentioned that we are dealing with the TE calculations for a series of carrier concentrations up to \(n \sim 10^{21}\) cm\(^{-3}\) in this work. This variation may be realized by chemical doping but the bipolar effect should be remarkable in the cases of low \(n\) and high \(T\). It is estimated that atomic doping at a level of \(\sim 2\%\) is enough to obtain a carrier concentration of \(\sim 10^{21}\) cm\(^{-3}\) and of \(0.2\%\) to obtain \(\sim 10^{20}\) cm\(^{-3}\). Therefore, it is safe to neglect the effect of such doping on lattice thermal conductivity \(\kappa_L\), allowing \(\kappa_L \sim (\kappa_L)_{\text{in}}\).

As highlighted above, given the ground state electronic and phononic structures, the current framework always starts from an assigned \(n\), and then shifts \(E_F\) so that the integrated density of states near the CBM and the VBM is equal to this assigned \(n\). The calculation of TE properties as a function of \(T\) for a set of given \(n\) values is performed, noting that the thermally activated carrier excitations from the CBM and the VBM, i.e., the bipolar effect, are self-consistently considered within this framework.
It will be shown that the above treatment is far from accurate and a remarkable discrepancy of the calculated $S(T)$, $\sigma(T)$, and $\kappa_e(T)$ from the measured one will appear, as presented below.

III. Computational results

3.1. Calculated TE properties

The calculated electronic band structure and densities of states (DOSs, including the total DOS and projected DOS) are shown in Fig. 2. Clearly, CaMg$_2$Bi$_2$ is a semiconductor with a direct gap of $\Delta \sim 0.41$ eV at the $\Gamma$ point. The estimated band gap from the relationship $E_g = 2eS_{\max}T_{\max}$ is $\sim 0.45$ eV if the measured Seebeck coefficient $S$ as a function of $T$ is used. It is seen that the profiles near the VBM and the CBM are roughly mirror-symmetric with each other. At the same time, the total DOS and projected DOS (PDOS) data suggest that the VBM near the Fermi level is mainly contributed from p electrons of Bi atoms, noting the big DOS scale differences in Fig. 2(c–e). The Ca and Mg atoms have little contributions due to the low density of states. It is also suggested that the TE properties should be sensitive to the electron distribution of the Bi atom.

The calculated phonon band structures and PDOSs for each type of atoms are plotted in Fig. 3(a) and (b). One sees that all the phonon dispersion frequencies are positive without an imaginary part, indicating that the structure at zero temperature is stable. In the low frequency range (0–3.0 THz), the maximum contribution in terms of the acoustic branches and the lowest frequency optical branches is again from Bi atoms. The Ca atoms make the largest contribution to the DOS in the intermediate range (3.0–5.0 THz), while the high frequency modes (> 5.0 THz) are from the Mg atoms. The major reason for these features is simply due to the fact that the Bi atom is the heaviest, followed by Ca and Mg atoms. In these respective frequency ranges, the vibration mode couplings between these atoms are weak, possibly responsible for the low lattice thermal conductivity of CaMg$_2$Bi$_2$. At the same time, a phonon band gap within the 2.0–3.0 THz range implies the phonon forbiddance, a property favorable for TE performance.

Given the details of the calculation procedure and discussion reported earlier, the calculated TE properties of CaMg$_2$Bi$_2$ as a function of carrier (hole) concentration $n$ are obtained, and as a summary the data at three different $T$ (300 K, 600 K, and 900 K) are plotted in Fig. 4. Only a brief discussion on these data will be given here, and the focus is on the bipolar effect. It is indicated that $\sigma$ at $T = 300$ K increases linearly over the whole $n$-range, while at $T = 600$ K and 900 K it exhibits a platform in the low-$n$ range and then increases linearly in the...
high-\(n\) range, a signature of strong bipolar effect in the low-\(n\) range. The \(S(n)\) dependences are opposite to the \(\sigma(n)\) dependences, as shown in Fig. 4(b).

The value of \(S\) decreases linearly with increasing \(n\) at \(T = 300\) K but evolves into a single-peaked pattern at \(T = 600\) K and 900 K due to the enhanced bipolar effect too. The \(\kappa_e(n)\) dependences are qualitatively similar to \(\sigma(n)\), as shown in Fig. 4(d), which is reasonable considering the well-known Wiedemann–Franz relation \(\kappa_e = L\sigma T\), where \(L\) is the Lorenz number. The calculated \(\kappa_{\text{tot}}\) as shown in Fig. 4(e), exhibits a broad platform over the \(n\)-range from \(\sim 10^{16}\) cm\(^{-3}\) to \(\sim 10^{20}\) cm\(^{-3}\), beyond which \(\kappa_{\text{tot}}\) increases rapidly. It is noted that \(\kappa_e\) is only a minor part of \(\kappa_{\text{tot}}\) with \(\kappa_e \ll \kappa_L\). The predicted \(\kappa_{\text{tot}}\) of CaMg\(_2\)Bi\(_2\) is relatively low with respect to most TE materials. Eventually, the evaluated PF and \(ZT\) are shown in Fig. 4(c) and (f) respectively. Both of them show a single-peaked pattern as a function of \(n\) for a given \(T\). The peaked PF values for different \(T\) are roughly similar and the \(ZT\)-peaks appear roughly at \(n = 10^{18}\) cm\(^{-3}\) with \(ZT \sim 0.6\) at \(T = 900\) K.

3.2. Inconsistencies between calculated and measured TE properties

The present computations based on a combination of the first-principles calculations and semi-classical Boltzmann transport theory can indeed predict all the TE parameters at a given \(n\). However, the calculated values are inconsistent with the measured results, which is a serious issue, as shown in Fig. 5, where the measured \(S(T)\) data are shown in blue dots. Clearly, serious inconsistency between the measured and calculated \(S(T)\) data is seen, suggesting that the assumption of constant carrier concentration does not work at all.

Here, several features of these data deserve a further discussion on the bipolar effect. First, the measured \(S(T)\) dependence is not strong and only a variation of \(\sim 40\%\) over the whole \(T\)-range. This single-peaked \(T\)-dependence is very broad. Second, all the calculated \(S(T)\) curves under the low-\(n\) conditions show a gradual upward variation and then a rapid downward variation with increasing \(T\), generating a sharp and asymmetric peak pattern. For extremely low \(n\) (<10\(^{18}\) cm\(^{-3}\)), a sign reverse of \(S\) in the high-\(T\) range is predicted. This sign-reversal effect remains until \(n\) is enhanced up to \(\sim 2.5 \times 10^{19}\) cm\(^{-3}\) within the \(T\)-range covered here. These are clear indications of the strong bipolar effect in CaMg\(_2\)Bi\(_2\), suggesting that the bipolar effect cannot be suppressed unless the doped hole concentration is sufficiently high. Above \(n \sim 4 \times 10^{19}\) cm\(^{-3}\), one observes a roughly linear growth of positive \(S\) with increasing \(T\), a typical behavior for a single-polar semiconductor. By the way, similar inconsistencies between the calculated and measured results can be found for other two electro-transport parameters \(\sigma\) and \(\kappa_e\).

In short, these results provide evidence for the argument that CaMg\(_2\)Bi\(_2\) does show a strong bipolar effect, which on the other hand may partially explain the discrepancy of the calculated properties from the measured ones. Here, the central issue is related to the carrier concentration \(n\) that is strongly \(T\)-dependent due to the bipolar effect, but the computations are based on the constant \(n\) assumption. A self-consistent computation of all the TE parameters becomes impossible if this \(T\)-dependent \(n\) is unknown.

IV. Modified approach and discussion

4.1. Effective carrier concentration \(n_{\text{eff}}\)

For a p-type TE compound, one assumes that the externally doped carrier concentration is \(n_{\text{p0}}\), which is treated as a constant over the \(T\)-range here. For the bipolar effect, the concentration of intrinsically excited holes at a given \(T\) is \(n_p\), and the concentration of the excited electrons at this \(T\) is \(n_n\), satisfying \(n_p = n_n\). The corresponding Seebeck coefficients are \(S_{\text{p0}}, S_p,\) and \(S_n\). As a result, the total Seebeck coefficient \(S_{\text{tot}}\) can be written as:

\[
S_{\text{tot}} = \frac{S_{\text{p0}} \sigma_{\text{p0}} + S_p \sigma_p + S_n \sigma_n}{\sigma_{\text{p0}} + \sigma_p + \sigma_n},
\]

where \(\sigma_{\text{p0}}, \sigma_p,\) and \(\sigma_n\) are the corresponding electrical conductivities contributed by doping induced holes, excited holes, and excited electrons, respectively. For a TE semiconductor, the following relationship should be satisfied:

\[
n_p \cdot n_n = A_0 T^3 \exp \left( \frac{E_x}{k_B T} \right) = C(T),
\]

where \(A_0\) is a pre-factor, \(E_x\) is the thermal excitation related band gap, and \(k_B\) is the Boltzmann constant. Therefore, the majority carriers have a concentration \(n_p = n_{\text{p0}} + n_p\). Assuming that the impurities are fully ionized, one has \(n_n = n_{n0}\). In this case, eqn (2) can be re-written as:

\[
n_p(n_p - n_{p0}) = C(T),
\]

\[
n_p = \frac{1}{2} n_{p0} \pm \frac{1}{2} \sqrt{n_{p0}^2 + 4C(T)},
\]

It is seen that the intrinsic excitation can be ignored at low \(T\), leading to \(n_p = n_{p0}\). For a quite high \(T\), the thermally
excited carriers are sufficient, allowing a negligible $n_{p0}$. One thus has:

$$n_p = \frac{1}{2} \sqrt{4C(T)} = A_0^{1/2} T^{3/2} \exp \left(-\frac{E_g}{k_B T}\right). \quad (4)$$

For an intermediate $T$, one may approximately formulate the majority carrier concentration as:

$$n_p \sim n_{p0} + AT^{3/2} \exp \left(-\frac{E_g}{2k_B T}\right). \quad (5)$$

where $A$ is another pre-factor. The strong bipolar effect allows us to question the current computational framework based on the assumption of constant carrier concentration. As discussed above, the bipolar effect makes the carrier concentration to be $T$-dependent. Any discussion on the TE properties as a function of $T$ at a fixed carrier concentration is misleading. This approximation can be applicable only in cases of $n_{p0} \gg n_e$, which seems to be not true for CaMg$_2$Bi$_2$ that we are dealing with in this study.

As an approximation, we propose an effective carrier concentration $n_{\text{eff}}$ which follows:

$$n_{\text{eff}}(T) \sim n_{p0} + AT^{3/2} \exp \left(-\frac{E_g}{2k_B T}\right). \quad (6)$$

and it will be shown that this approximation does work for accounting of the bipolar effect. Here, the excited electrons (with concentration $n_e$) and their contributions are completely ignored, which seems to be unreasonable. However, in the Boltzmann transport calculations, the carrier (hole) concentration $n$ is obtained by shifting the Fermi level, and this action is somehow equivalent to suppressing the concentration of opposite carriers (electrons), i.e., ignoring the electron carriers.

To proceed, we re-calculate the data presented in Fig. 5 by considering the $T$-dependent carrier concentration. Using the band structure obtained from the first principles calculations, we set up a series of concentration values as the input carrier concentrations (doping levels) in the BoltzTraP code to calculate the transport properties. In the calculations, the input parameters $n$ (carrier concentration) have been carefully adjusted so that the calculated $S(n, T)$ curve can pass across one data point of the measured $S(T)$ curve.\(^{34}\) Consequently, the input $n$ is treated as $n_{\text{eff}}$ as shown in Fig. 6(a).

For a purpose of comparison, we assume that the electrotransport is solely contributed from electrons or holes as carriers, and then calculate the electrical conductivity for electrons $\sigma_e$ and that for holes $\sigma_h$ as a function of $T$ respectively. Similarly, the calculated results are compared with measured data so that the evaluated $\sigma_e(T)$ can be obtained, as shown in Fig. 6(a). We can see that in the lower temperature region ($T < 600$ K), the $\sigma_e(T)$ curves obtained from $S$, $\sigma_h$, and $\sigma_e$, respectively, have quite similar tendencies, while there is indeed a slight discrepancy in the effective carrier concentration between the results obtained from different parameters in the high temperature region ($T > 600$ K). This discrepancy is mainly due to the fact that both $n$-type and $p$-type carriers have contributions to the electrical conductivity. However, they will deteriorate the total Seebeck coefficient due to the opposite carrier signs. Therefore, the coexistence of two types of carriers leads to the discrepancy in $n_{\text{eff}}$ in the high temperature region.

### 4.2. Bipolar effect

Subsequently, the evaluated $n(T)$ data from the $S(T)$ data are fitted using eqn (6) and the fitted curve is presented in Fig. 6(b). The fitting generated parameters are $n_{p0} = 5.7 \times 10^{18}$ cm$^{-3}$, $A = 1.6257 \times 10^{-17}$ cm$^{-3}$, and $E_g = 0.56$ eV. First, the value of $E_g$ (≈0.56 eV) is consistent with the predicted band gap $\Delta = 0.41$ eV and the measured value of ≈0.45 eV, noting that the first-principles calculation based on the MBJ potential\(^{45,46}\) gives a gap of ≈0.70 eV.\(^{13}\) Second, the evaluated $n_{p0} = 5.7 \times 10^{18}$ cm$^{-3}$ is also roughly consistent with the measured carrier concentration of ≈2.38 \times 10^{18}$ cm$^{-3}$ at room temperature ($T = 300$ K) reported by Shuai et al.\(^{31}\) and the experimental data between $\sim 1.0 \times 10^{18}$ cm$^{-3}$ and $\sim 1.95 \times 10^{19}$ cm$^{-3}$ at room temperature ($T = 300$ K) reported by May et al.\(^{31,33}\) considering that the
The dependence of $n$ below 300 K is quite weak. In other words, the value of $n_{po}$ would be on the order of magnitude of $10^{18}$–$10^{19}$ cm$^{-3}$.

From the fitting data, we can safely make a conclusion that the experimental data are in line with eqn (6), confirming that our approximation is physically reasonable. This allows us to discuss the consequence of the bipolar effect. The significance of the bipolar effect in terms of carrier concentration may be measured by a dimensionless factor $x$:

$$x = \frac{A T^{3/2} \exp\left(-\frac{E_g}{2k_BT}\right)}{n_{po}} (x > 0),$$

and its dependence on $T$ is plotted in Fig. 6(b). It is seen that the bipolar effect is weak below $T \sim 600$ K and becomes remarkable above 600 K. One may recollect that: (1) a higher $n_{po}$ benefits from the suppression of the bipolar effect, (2) a bigger $E_g$ is favorable for a weaker bipolar effect, and (3) a smaller carrier mass is appreciated for a weaker bipolar effect since the pre-factor $A$ is smaller with a smaller mass.

Supported by the above results, one can plot the evaluated $S(T)$ curve in Fig. 6(c), which exhibits a broad peak centered at around $T \sim 480$ K. The measured $S(T)$ data are inserted too for a comparison, which shows a good consistency between them. Subsequently, the evaluated $n_{eff}$ as a function of $T$ is used as the input carrier concentration to re-calculate the TE parameters. The results are presented in Fig. 7. Here, it should be mentioned that for calculating the carrier relaxation time and mobility, we take the effective mass estimated from experimental measurements in ref. 34 in order to better analyze the bipolar effect in the thermoelectric material $\text{CaMg}_2\text{Bi}_2$. Since we concentrate on the bipolar effect in this work, no details of the carrier relaxation time and mobility will be given here, and the calculated data as a function of $T$ are presented in Fig. 7 of the ESI for reference. In Fig. 7(a), the calculated electrical resistivity $\rho(T)$ and the measured data show similar $T$-dependences although a discrepancy between them in the low-$T$ range is displayed. The broad single-peaked pattern is essentially ascribed to the bipolar effect which enables the thermally excited carriers to dominate the electrical transport in the high-$T$ range in competing with the metal-like transport behavior in the low-$T$ range due to the externally doped carriers. The calculated and measured PF data as a function of $T$ are plotted in Fig. 7(b), exhibiting quite similar $T$-dependences and the values are on the same order of magnitude.

The evaluated $\kappa_e(T)$, $\kappa_l(T)$, and $\kappa_{tot}(T)$ are presented in Fig. 7(c), where the measured $\kappa_{tot}(T)$ data are inserted for a comparison. It is seen again that the predicted and measured $\kappa_{tot}(T)$ data show similar $T$-dependences and their difference over the whole-$T$ range is relatively small. Furthermore, the $\kappa_e(T)$ is only a minor part of $\kappa_{tot}(T)$ in the low-$T$ range but its contribution increases with increasing $T$, obviously due to the bipolar effect. Consequently, the predicted and measured $ZT$ are plotted in Fig. 7(d), demonstrating good consistency between them with some discrepancy in the high-$T$ range.

4.3. Discussion

The calculated results and comparisons with experimental data presented above allow us to conclude that the consequence of the bipolar effect in terms of the TE properties can be seen as an effective carrier concentration $n_{eff}$ which increases exponentially with increasing $T$ following the bipolar excitation mechanism. The bipolar effect, at least for $\text{CaMg}_2\text{Bi}_2$ here, is large and imposes a significant influence on the TE performance. Besides the influences on the electro-transport and Seebeck effect, its impact on the thermal transport can be discussed too even if $\kappa_e(T)$ is only a small part of $\kappa_{tot}(T)$ for $\text{CaMg}_2\text{Bi}_2$ in the $T$-range covered here. As mentioned in the Introduction, we believe that the bipolar effect would carry more energy from the hot-end to the cold-end. In this sense, the modified $\kappa_{e}(T)$ should be higher than that $(\kappa_{tot}(T))$ without counting the bipolar effect. The calculated $\kappa_{tot}(T)$ by setting $n_{eff} = n_{po}$ together with the modified data $(\kappa_{e}(T))$ are plotted in Fig. 8, note that no measured $\kappa_{e}(T)$ data are available unfortunately. While $\kappa_{e}(T) > \kappa_{tot}(T)$ is always true, their difference $(\kappa_{bp})$ is small in the low-$T$ range but

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**Fig. 7** Calculated and measured TE parameters: (a) $\rho$, (b) PF, (c) $\kappa$ $(\kappa_e$, $\kappa_l$, $\kappa_{tot})$, and (d) $ZT$. The blue dots are measured data from ref. 34.

**Fig. 8** Calculated electronic thermal conductivity $\kappa_{tot}(T)$ by setting $n_{eff} = n_{po}$ = $5.7 \times 10^{18}$ cm$^{-3}$ and $\kappa_{e}(T)$ by taking $n_{eff}$ from eqn (6) with $A = 1.6257 \times 10^{12}$ cm$^{-3}$ and $E_g = 0.56$ eV. The difference between $\kappa_{e}(T)$ and $\kappa_{tot}(T)$ reflects the influence of the bipolar effect.
increases with increasing $T$, accounting for more contribution from the excited electrons and holes to $\kappa_{\text{tot}}(T)$.

Finally, we discuss the discrepancies of the calculated TE parameters from the measured ones. All the measured data are from polycrystalline CaMg$_2$Bi$_2$ samples synthesized by a hot-pressing technique, and the typical grain size varies from 100 to 500 nm.\textsuperscript{34} Inevitably, the grain boundaries and microstructural imperfections would definitely induce scattering to carrier transport and phonon transport, while the dependence of the Seebeck effect on microstructural details is relatively weak. This is the reason why the measured $S(T)$ data are utilized for model fitting. These side-effects reasonably explain the fact that the predicted $\rho(T)$ is smaller than the measured $\rho(T)$, and the predicted $\kappa_{\text{tot}}(T)$ is higher than the measured one. In particular, suppression of the $\kappa_{\text{tot}}$ by microstructural details in the nanoscale is significant, making the predicted $ZT$ factor slightly lower than the measured values in the high-$T$ range.

V. Conclusion

In this work, by choosing the compound CaMg$_2$Bi$_2$ as an object, we have investigated the influence of the bipolar effect on the TE properties, especially the Seebeck coefficient, using the full-scale computational scheme based on the first-principles method combined with semi-classical Boltzmann theory. It has been suggested that the bipolar effect makes the current computational scheme inapplicable for properly predicting the TE properties due to the fact that the majority carrier concentration is obtained by shifting the Fermi level in this scheme. We have proposed an effective carrier concentration ($n_{\text{eff}}$) to take into account of the bipolar effect. The computation based on the same scheme using the effective carrier concentration can predict the TE properties fairly consistently with the measured results. Since the bipolar effect is inevitable and may be strong in the concerned temperature range for TE materials with narrow band gap and low external doping concentration, the present work presents an alternative scenario to quantify the bipolar effect in TE materials.

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