Electron transport modeling and energy filtering for efficient thermoelectric 
Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions

Je-Hyeong Bahk, Zhixi Bian, and Ali Shakouri

1Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907, USA
2Department of Electrical Engineering, University of California, Santa Cruz, California 95064, USA

(Received 28 June 2013; revised manuscript received 22 January 2014; published 5 February 2014)

We present a comprehensive electron transport model to analyze thermoelectric properties of both $n$- and $p$-type bulk Mg$_2$Si$_{1-x}$Sn$_x$ ($0 \leq x \leq 1$) solid solutions. A temperature-dependent multiparabolic bands model is used to describe the band structures of the alloys, and the transport properties are calculated using the linearized Boltzmann transport equations under the relaxation time approximation. A variety of experimental data from literature are fitted very well by this model and analyzed for further material optimization.

Thermoelectric properties of Bi-doped $n$-type Mg$_2$Si have been extensively studied. Tani and Kido [12] studied a variety of Bi contents in the spark-plasma-sintered Mg$_2$Si and found 2% Bi-doped Mg$_2$Si showed a maximum $zT \sim 0.86$ at 862 K. Akasaka et al. [13] used the vertical Bridgman method to grow Bi-doped Mg$_2$Si; they obtained $zT \sim 0.65$ at 840 K for 1% Bi:Mg$_2$Si. Bux et al. [7] used the mechnochemical synthesis method to enhance the crystal quality of Bi-doped Mg$_2$Si and obtained $zT \sim 0.7$ at 775 K with Bi content as low as 0.15% in Mg$_2$Si. Yi et al. [14] studied Bi-doped Mg$_2$Si/Si nanocomposites and observed the reduction of lattice thermal conductivity by 5 to 10% along with a negative effect on the power factor to obtain a maximum $zT \sim 0.7$ at 775 K, with 0 and 2.5% excess Si. Dasgupta et al. [15] used Sn as another $n$-type dopant in Mg$_2$Si and found that electron concentration increases to $1.4 \times 10^{20}$ cm$^{-3}$, as Sn content increases to 2.5%, and then remains almost constant due to vacancy formation. Further incorporation of Sn helped to reduce the lattice thermal conductivity significantly, and thus a maximum $zT \sim 0.55$ at 750 K was obtained for Mg$_2$Si$_{0.9}$Sn$_{0.1}$. Typically, $p$-type dopants, such as Ag$^{13}$ and Ga$^{16}$ in Mg$_2$Si, are less efficient than their $n$-type counterparts since hole concentration has been limited to $\sim 10^{19}$ cm$^{-3}$. Thus, ambipolar transport becomes significant at high temperatures in $p$-type Mg$_2$Si materials, which limits their maximum figure of merit to $zT \sim 0.1$ at 550 to 600 K for both 1% Ag and 0.4 to 0.8% Ga in $p$-type Mg$_2$Si [13,16].

Zaitsev et al. [17] explored the Sn alloys of magnesium silicide, $n$-type Mg$_2$Si$_{1-x}$Sn$_x$, focusing on $x = 0.4$ and 0.6, and achieved a significantly enhanced maximum $zT \sim 1.1$ at $\sim 800$ K. In these solid solutions, the thermal conductivity was drastically reduced to 2 to 2.5 W/mK due to the strong alloy phonon scattering induced by the large molecular mass difference between Mg$_2$Si and Mg$_2$Sn. At the same time, the electronic density of states (DOS) was increased by the use of well-known bulk materials that have shown the highest figures of merit (zT) in recent years for various nanostructured materials [3,4].

In the numerator, $S^2\sigma$ is called the power factor, which is related to charge-carrier transport. Significant enhancements of the thermoelectric figure of merit have been reported in recent years for various nanostructured materials [3,4]. However, most high-performance thermoelectric materials involve a complicated synthesis procedure that is expensive and nonscalable for large quantity production, and many are based on toxic or expensive elements. These factors impede large-scale commercial applications.

Magnesium silicide and related alloys are promising candidates for waste heat recovery applications in the midtemperature range 500 to 900 K [6,7]. PbTe-based bulk materials [8,9], CoSb$_3$-based filled skutterudites [10], and clathrates [11] are well-known bulk materials that have shown the highest figures of merit ($zT > 1$) in this temperature range. Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions are an emerging thermoelectric material that has a comparable figure of merit to those conventional materials in the same temperature range with their own advantages; these compounds are environmentally friendly with no toxic elements, such as Pb, and cost-effective with no expensive elements, such as Te or rare earths.

1*jbahk@purdue.edu

DOI: 10.1103/PhysRevB.89.075204

PACS number(s): 72.20.Pa, 84.60.Rb

I. INTRODUCTION

Recently, thermoelectric power generation has drawn significant attention as a candidate technology for waste heat recovery in vehicles and industrial processes [1,2]. Thus far, the applications of thermoelectric devices have been limited due to their relatively low-energy conversion efficiency. The efficiency of a thermoelectric device is determined by the material’s dimensionless figure of merit, $zT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $\kappa$ is the thermal conductivity. In the numerator, $S^2\sigma$ is called the power factor, which is related to charge-carrier transport. Significant enhancements of the thermoelectric figure of merit have been reported in recent years for various nanostructured materials [3,4]. However, most high-performance thermoelectric materials involve a complicated synthesis procedure that is expensive and nonscalable for large quantity production, and many are based on toxic or expensive elements. These factors impede large-scale commercial applications.

Magnesium silicide and related alloys are promising candidates for waste heat recovery applications in the midtemperature range 500 to 900 K [6,7]. PbTe-based bulk materials [8,9], CoSb$_3$-based filled skutterudites [10], and clathrates [11] are well-known bulk materials that have shown the highest figures of merit ($zT > 1$) in this temperature range. Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions are an emerging thermoelectric material that has a comparable figure of merit to those conventional materials in the same temperature range with their own advantages; these compounds are environmentally friendly with no toxic elements, such as Pb, and cost-effective with no expensive elements, such as Te or rare earths.

Thermoelectric properties of Bi-doped $n$-type Mg$_2$Si have been extensively studied. Tani and Kido [12] studied a variety of Bi contents in the spark-plasma-sintered Mg$_2$Si and found 2% Bi-doped Mg$_2$Si showed a maximum $zT \sim 0.86$ at 862 K. Akasaka et al. [13] used the vertical Bridgman method to grow Bi-doped Mg$_2$Si; they obtained $zT \sim 0.65$ at 840 K for 1% Bi:Mg$_2$Si. Bux et al. [7] used the mechnochemical synthesis method to enhance the crystal quality of Bi-doped Mg$_2$Si and obtained $zT \sim 0.7$ at 775 K with Bi content as low as 0.15% in Mg$_2$Si. Yi et al. [14] studied Bi-doped Mg$_2$Si/Si nanocomposites and observed the reduction of lattice thermal conductivity by 5 to 10% along with a negative effect on the power factor to obtain a maximum $zT \sim 0.7$ at 775 K, with 0 and 2.5% excess Si. Dasgupta et al. [15] used Sn as another $n$-type dopant in Mg$_2$Si and found that electron concentration increases to $1.4 \times 10^{20}$ cm$^{-3}$, as Sn content increases to 2.5%, and then remains almost constant due to vacancy formation. Further incorporation of Sn helped to reduce the lattice thermal conductivity significantly, and thus a maximum $zT \sim 0.55$ at 750 K was obtained for Mg$_2$Si$_{0.9}$Sn$_{0.1}$. Typically, $p$-type dopants, such as Ag$^{13}$ and Ga$^{16}$ in Mg$_2$Si, are less efficient than their $n$-type counterparts since hole concentration has been limited to $\sim 10^{19}$ cm$^{-3}$. Thus, ambipolar transport becomes significant at high temperatures in $p$-type Mg$_2$Si materials, which limits their maximum figure of merit to $zT \sim 0.1$ at 550 to 600 K for both 1% Ag and 0.4 to 0.8% Ga in $p$-type Mg$_2$Si [13,16].

Zaitsev et al. [17] explored the Sn alloys of magnesium silicide, $n$-type Mg$_2$Si$_{1-x}$Sn$_x$, focusing on $x = 0.4$ and 0.6, and achieved a significantly enhanced maximum $zT \sim 1.1$ at $\sim 800$ K. In these solid solutions, the thermal conductivity was drastically reduced to 2 to 2.5 W/mK due to the strong alloy phonon scattering induced by the large molecular mass difference between Mg$_2$Si and Mg$_2$Sn. At the same time, the electronic density of states (DOS) was increased by the
convergence of two conduction bands at these Sn content levels, which led to the enhancement of the Seebeck coefficient without significantly reducing the mobility. The favorable effect of band convergence on power factor has also been investigated in PbTe alloys [18]. Recently, Liu et al. [19] performed a systematic study on the various compositions of n-type Sb-doped Mg2Si1-xSnx of 0.2 <= x <= 0.8 and found that the compositions with x = 0.6 to 0.7 showed a maximum zT ~ 1.3 at ~750 K via the enhanced power factor by the band convergence along with the thermal conductivity reduction by alloying.

In recent years, there have been several theoretical studies based on the first-principle band calculations and the Boltzmann transport theory for Mg2Si1-xSnx solid solutions [13,20–24]. Other Mg2Si-based alloys, such as Mg2Si1-xGex and Mg2Si1-xSbx, have also been studied theoretically [16,25–27]. Akasaka et al. [13] used the first-principle calculations to obtain the band structure of Mg2Si and fitted their experimental Seebeck coefficients for both n-type and p-type Mg2Si. They found that the temperature-dependent band gap must be used to fit the Seebeck coefficient data, particularly at high temperatures where the two-type carrier transport becomes significant. Similarly, Wang et al. [20] used the first-principle band calculations for Mg2Si and solved the Boltzmann transport equations to calculate the thermoelectric properties. Satyala and Vashaee [21] modeled both electron and thermal transport in Mg2Si based on the multiple nonparabolic band model to predict a maximum zT ~ 0.8 for both n-type and p-type Mg2Si.

Recently, Tan et al. [22] calculated the band structures of various compositions of Mg2Si1-xSnx with 0.25 <= x <= 0.875 using the first-principles pseudopotential method. They confirmed the enhancement of the power factor by the convergence of the two conduction bands at x = 0.625 and predicted a maximum zT ~ 1.1 at 800 K. Pulikkotil et al. [23] reported theoretical prediction on the thermoelectric power factors of the binaries and x = 0.5 for Mg2Si1-xSnx with the first-principle band calculations based on the modified Becke-Johnson potential, which yielded band gaps in good agreement with experiments. Kutorasinski et al. [24] used the Korringa-Kohn-Rostocker method with coherent potential approximation to study the band structure and the Fermi surface of Mg2Si1-xSnx. In these theoretical studies based on the first-principle full band calculations, however, they assumed that the calculated band structure is invariant with temperature, although it is well-known that the band structure of Mg2Si1-xSnx has a strong temperature dependence [6,13,28]. Using a larger band gap based on low-temperature calculations can severely underestimate the bipolar effect at high temperatures. Also, the constant relaxation time was assumed in these studies, which is not a good assumption since the energy-dependent acoustic phonon scattering is dominant [12,14]. Therefore, limited comparisons of the theoretical calculations with experimental data have been presented.

In this paper, we present a comprehensive transport model for both n- and p-type bulk Mg2Si1-xSnx (0 <= x <= 1) solid solutions over a wide temperature range from 300 to 900 K, with the temperature-dependent multeparabolic band structure model and the energy-dependent relaxation time taken into account. We find that at high Sn compositions, where the band gap is small, and at low doping levels, the bipolar transport effects are very important to accurately predict all of the thermoelectric properties (Seebeck coefficient, electrical conductivity, and electronic contribution to thermal conductivity). In Sec. II, we describe the temperature-dependent band structures, material properties, and scattering parameters used in our model for Mg2Si1-xSnx. The Boltzmann transport theory is discussed in Sec. III. We verify our model by comparing it to various experimental data from the literature in Sec. IV and in the Appendix. In Sec. V, both n-type and p-type Mg2Si1-xSnx materials are optimized with doping density and composition based on our model to find the maximum figure of merit that could be achieved. In Sec. VI, we study the impact of the electron energy filtering [29] and quantify the potential improvement in the figure of merit. Finally, conclusions are given in Sec. VII.

II. BAND STRUCTURES AND MATERIAL PARAMETERS

Intermetallic compounds Mg2Si and Mg2Sn have the antifluorite-type crystal structure in the fcc lattice with the lattice constants of 6.338 and 6.765 Å, respectively [6]. Mg2Si is an indirect band gap semiconductor with a forbidden band gap of Eg = 0.78 eV at 0 K [28]. The band gap was reported to decrease with temperature almost linearly. There are a range of different values reported for the temperature coefficient of the band gap (dEg/dT) between ~3.5 \times 10^{-4} and ~6.0 \times 10^{-4} eV/K for Mg2Si [6,13,28]. A value of ~4.0 \times 10^{-4} eV/K was chosen for this work. The valence band maximum is located at the Γ point in the Brillouin zone, whereas the conduction band minimum is located at the X point, as shown schematically in Fig. 1. The X point conduction band consists of two nondegenerate bands, X3 and X1, separated by a distance EO = 0.4 eV for Mg2Si [17]. The band separation between the two X conduction bands remains constant with temperature, while the separation between the valence band edge and the principal conduction band edge constantly decreases with temperature at a rate of ~4.0 \times 10^{-4} eV/K. The Γ point valence band has two degenerate bands denoted as light-hole (LH) and heavy-hole (HH), with no separation between the bands. In the case of Mg2Sn, the band

![FIG. 1. (Color online) (a) A schematic of the band structures for Mg2Si1-xSnx solid solutions. (b) The band gap between the X3 conduction band edge and the Γ valence band (ExΓ) at 0 K and the separation between the X1 and X3 conduction bands, showing the convergence of the two bands for x ~ 0.7.](image URL)
structure is almost similar, but the $X_1$ conduction band edge is lower than that of the $X_3$ band by 0.165 eV, i.e., $E_0 = -0.165$ eV [17]. Therefore, in Mg$_2$Sn, a forbidden gap occurs between the $\Gamma$ valence band edge and the $X_1$ conduction band edge. As with Mg$_2$Si, the band gap of Mg$_2$Sn also decreases constantly with temperature at a rate of $-3.0$ to $-3.5 \times 10^{-4}$ eV/K [6,17]. We chose a slightly smaller rate of $-2.8 \times 10^{-4}$ eV/K for better fitting to experimental data.

The material parameters of Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions are obtained by linear interpolations between the two parameters for Mg$_2$Si and Mg$_2$Sn, except for the acoustic phonon deformation potential for electrons, which is modeled as a parabolic function of Sn content $x$. As shown in Fig. 1(b), the separation of the $X_1$ and $X_3$ conduction bands decreases linearly with increasing Sn content $x$, and the complete convergence of the two bands occurs at $x \sim 0.7$ [17]. The band gap between the $\Gamma$ valence band edge and the $X_3$ conduction band edge also decreases almost linearly with $x$ [6]. Note that Fig. 1(b) shows the $\Gamma$-$X_3$ band gap at 0 K. The band gap of Mg$_2$Si decreases with temperature a little more quickly than that of Mg$_2$Sn. Therefore, at higher temperatures, the decreasing rate of the band gap with Sn content, $x$, is slower. Table I summarizes the material parameters for Mg$_2$Si$_{1-x}$Sn$_x$, solid solutions used for transport calculations throughout the paper as a function of temperature $T$ and Sn content $x$.

### III. ELECTRON TRANSPORT THEORY

#### A. Two-carrier transport equations

The transport properties of Mg$_2$Si$_{1-x}$Sn$_x$ can be calculated using the linearized Boltzmann transport equations under the relaxation time approximation. The Fermi level is determined first with a given doping density by the charge neutrality,

$$n + N_A^+ = p + N_D^-, \quad (1)$$

where $N_D^-$ is the total ionized donor density and $N_A^+$ is the total ionized acceptor density in the material. For an $n$-type material, $(N_D^- - N_A^+)$ is called the doping density, whereas $(N_A^+ - N_D^-)$ is the doping density for a $p$-type material. This doping density is experimentally measured using the Hall effect.

The Fermi level is found numerically by an iterative search until (1) is satisfied. The $n$ and $p$ are calculated using the Fermi-Dirac distribution and the DOS obtained from the band structure information. We use parabolic dispersion relations for all of the bands in Mg$_2$Si$_{1-x}$Sn$_x$. Typically, thermoelectric materials are highly doped in order to maintain a sufficiently high electrical conductivity; therefore, the doping density is much greater than the intrinsic carrier density. The intrinsic carrier density, however, increases exponentially with temperature, while the doping density remains constant if there are no additional carriers activated from deep-level donors or acceptors. Therefore, the effects of minority carriers can become significant at high temperatures.

Once the Fermi level has been determined for a given doping density at a given temperature, the thermoelectric transport properties for each type of carrier can be calculated by the linearized Boltzmann transport equation. All the transport properties are expressed as an integral function of the differential conductivity defined by [30]

$$\sigma_{d,i}(E) = e^2 \tau(E) v^2(E) \rho_{DOS}(E) \left( \frac{\partial f_0}{\partial E} \right), \quad (2)$$

where $E$ is the carrier energy, $e$ is the electron charge, $\tau$ is the total relaxation time of the carrier, $v$ is the carrier velocity in one direction, $\rho_{DOS}$ is the DOS, and $f_0$ is the Fermi-Dirac distribution function. The electrical conductivity, the Seebeck coefficient, and the electronic thermal conductivity for one type of carrier are given, respectively, by [30]

$$\sigma = \sum_i \int \sigma_{d,i}(E) \, dE, \quad (3)$$

$$S = \sum_i \frac{1}{qT} \int \frac{\sigma_{d,i}(E)(E - E_{F,i})^2}{\sigma} \, dE \quad \sigma, \quad (4)$$

$$\kappa_{\text{elect}} = \sum_i \frac{1}{q^2T} \int \frac{(E - E_{F,i})^2}{\sigma} \sigma_{d,i}(E) \, dE - S^2 \sigma T, \quad (5)$$

where $\sigma_{d,i}$ is the differential conductivity of the $i$th band of the specific type of carrier, $q$ is $+e$ for holes, and $-e$ for electrons, and $E_{F,i}$ is the relative position of the Fermi level from the $i$th band edge. Note that the energy integrals in Eqs. (3)–(5) are performed for each band with energy referenced to the corresponding band edge, from 0 energy to infinity. So, the

### TABLE I. Material parameters used for transport calculations of Mg$_2$Si$_{1-x}$Sn$_x$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy gap $E_{g,3}$ (eV)</td>
<td>$(0.78 - 4.0 \times 10^{-4} \times T) \times (1 - x) + (0.38 - 2.8 \times 10^{-4} \times T) \times x$</td>
</tr>
<tr>
<td>Conduction band offset $E_0$ (eV)</td>
<td>$0.4 \times (1 - x) + (-0.165) \times x$</td>
</tr>
<tr>
<td>$X_3$ valley effective mass $m_{x3}^*$ $(m_0)$</td>
<td>$0.38$</td>
</tr>
<tr>
<td>$X_1$ valley effective mass $m_{x1}^*$ $(m_0)$</td>
<td>$0.49 + 2.0 \times 10^{-4} \times T$</td>
</tr>
<tr>
<td>HH effective mass $m_{hh}^*$ $(m_0)$</td>
<td>1.0</td>
</tr>
<tr>
<td>LH effective mass $m_{lh}^*$ $(m_0)$</td>
<td>1.5</td>
</tr>
<tr>
<td>Static permittivity $\varepsilon_0$ (F/m)</td>
<td>$(20 \times (1 - x) + 23.75 \times x) \times 8.85 \times 10^{-12}$</td>
</tr>
<tr>
<td>High-frequency permittivity $\varepsilon_{\infty}$ (F/m)</td>
<td>$(13.3 \times (1 - x) + 17 \times x) \times 8.85 \times 10^{-12}$</td>
</tr>
<tr>
<td>Optical phonon energy $\hbar\omega_0$ (meV)</td>
<td>$40 \times (1 - x) + 28.8 \times x$</td>
</tr>
<tr>
<td>Lattice constant $a$ (Å)</td>
<td>$6.338 \times (1 - x) + 6.765 \times x$</td>
</tr>
<tr>
<td>Mass density $\rho$ (kg/m$^3$)</td>
<td>$1.88 \times 10^3 \times (1 - x) + 3.59 \times 10^3 \times x$</td>
</tr>
<tr>
<td>Acoustic phonon deformation potential $D_a$ (eV)</td>
<td>$9.0 - 1.5 \times x^2$</td>
</tr>
<tr>
<td>Elastic constants $C_i$ (N/m$^2$)</td>
<td>$4.15 \times 10^{10} \times (1 - x) + 3.22 \times 10^{10} \times x$</td>
</tr>
</tbody>
</table>
Fermi level needs to be converted to the relative position for the specific band in the integrals. The contributions from all the bands are added to obtain the transport properties for the multiband structure.

Subsequently, the total electrical conductivity and the total Seebeck coefficient in the two-type carrier transport are obtained by

$$\sigma = \sigma_e + \sigma_h,$$

$$S = \frac{\sigma_e S_e + \sigma_h S_h}{\sigma_e + \sigma_h},$$

where the subscripts $e$ and $h$ denote the partial properties of electrons and holes, respectively.

The total electronic thermal conductivity is not only the sum of the partial electronic thermal conductivities of electrons and holes. Another term from the bipolar thermoeffect must be added. The bipolar electronic thermal conductivity is given by [31]

$$\kappa_{bi} = \frac{\sigma_e \sigma_h}{\sigma_e + \sigma_h} (S_e - S_h)^2 T.$$  (8)

The bipolar electronic thermal conductivity can be quite large, particularly at high temperatures, even if the intrinsic carrier densities are much lower than the doping density, because the Seebeck coefficients of the two types have opposite signs; they are added and then squared in Eq. (8). $\kappa_{bi}$ also increases with temperature. The total electronic thermal conductivity is then obtained as

$$\kappa_e = \kappa_{elect,e} + \kappa_{elect,h} + \kappa_{bi}.$$  (9)

The total thermal conductivity that is experimentally measured is the sum of the lattice thermal conductivity and the electronic thermal conductivity such that

$$\kappa = \kappa_l + \kappa_e.$$  (10)

The electronic thermal conductivity can limit $zT$ at high temperatures and at high doping densities, especially when the lattice thermal conductivity is significantly reduced by nanostructuring or alloying. The lattice thermal conductivity is not calculated in this work. We extract the lattice thermal conductivity from the measured total thermal conductivity and the calculated electronic thermal conductivity using (10). The obtained lattice thermal conductivity is then assumed to be constant to analyze the variation of the figure of merit with doping density.

### B. Scattering mechanisms

The predominant electron scattering mechanism in Mg$_2$Si$_{1-x}$Sn$_x$ from 300 K and above is the acoustic phonon deformation potential scattering [12,14]. The energy-dependent scattering time by acoustic phonon deformation potential for a parabolic band is given by [32]

$$\tau_{AC}(E) = \frac{\pi \hbar^4 C_l}{2^{1/2}(m^*_e)^{3/2} D^*_e k_B T \sqrt{E}},$$  (11)

where $C_l$ is the elastic constant, $m^*_e$ is the DOS effective mass for a single valley, and $D_a$ is the acoustic phonon deformation potential.

In addition to the acoustic phonon scattering, the polar optical phonon (POP) scattering and the ionized impurity scattering have been included in the total scattering time, although it turns out that they are still much weaker than the acoustic phonon scattering over the temperature range and the doping density range of interest. The scattering times by POPs and ionized impurities (II) for a parabolic band are given, respectively, by [33,34]

$$\tau_{POP}(E) = \frac{\hbar^2 E^{1/2}}{(2m^*_e)^{1/2} \epsilon^2 k_B T (\epsilon^{-1} - \epsilon_0^2)} \times \left[1 - \delta_\infty \ln \left(1 + \delta_\infty^{-1}\right)\right]^{-1},$$  (12)

$$\tau_{II}(E) = \frac{16 \sqrt{2 m^*_e \epsilon^2 E^{3/2}}}{N_0 e^4 \left[\ln \left(1 + \delta_0^{-1}\right) - \frac{\delta_0}{1 + \delta_0}\right]}.$$

With the assumption that the different scattering events are independent of each other, the total energy-dependent scattering time can be obtained by

$$\frac{1}{\tau(E)} = \frac{1}{\tau_{AC}(E)} + \frac{1}{\tau_{POP}(E)} + \frac{1}{\tau_{II}(E)}.$$  (14)

This total scattering time is plugged into (2) to calculate the differential conductivity as a function of energy, which is then used to calculate the thermoelectric properties of Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions using (3) through (10).

### IV. FITTING AND ANALYSIS OF EXPERIMENTAL DATA

We present the material parameters of Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions used for the transport calculations in Table I. As some of the parameters are not well-known, and there are conflicting reports on the values for the several parameters, we have determined some of the material parameters by fitting the experimental data available in the literature. The material parameters adjusted in this work are the effective masses of the two conduction bands and the two valence bands and the acoustic phonon deformation potential. In particular, the effective mass of the $X_1$ conduction band is found to best fit the experimental data for high Sn compositions when it is temperature dependent, increasing with temperature at a rate of $2 \times 10^{-4} \times m_0 \text{kg/K}$, where $m_0$ is the stationary electron mass. It is possible that other parameters are also temperature dependent. However they have not been thoroughly studied, so in this paper we tried to minimize the number of adjustable parameters since they could result in additional uncertainties in the calculations.

First, we fitted the properties of the binary materials, Mg$_2$Si and Mg$_2$Sn, to determine their material parameters, and then
FIG. 2. (Color online) Calculated (a) electrical conductivities, (b) Seebeck coefficients, (c) power factors, and (d) electronic thermal conductivities as a function of doping density for \( n \)-type Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) with varying \( x = 0/223 \) to 1.0 at 700 K.

The material parameters of Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) solid solutions are obtained by linear interpolations between those of the two binary materials, except for the acoustic phonon deformation potential. We used the experimental data of \( n \)-type Mg\(_2\)Si from Tani and Kido [12] and the data of \( n \)-type Mg\(_2\)Sn from Chen and Savvides [35] for the fitting. The experimental data of both \( n \)-type and \( p \)-type Mg\(_2\)Si\(_{0.58}\)Sn\(_{0.42}\) \((x = 0.6)\) were extracted from Zaitsev et al. [17] and Akasaka et al. [13], respectively, and fitted over a wide temperature range. Finally, the experimental data of various compositions of \( n \)-type Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) \((x = 0.4, 0.6, 0.7, \) and 0.8) were obtained from Liu et al. [19] and successfully fitted by the theory. In particular, the experimental thermal conductivity data from this paper was extensively analyzed, and the electronic contribution of thermal conductivity was separated from the lattice contribution for each sample of the paper using the Boltzmann transport theory presented in Sec. III. It is found that the \( n \)-type Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) samples in Liu et al. [19] exhibit the lattice thermal conductivity of 1.0 to 1.2 W/mK at 800 K. Detailed fitting analysis of all the experimental data is presented in Appendix.

V. MATERIAL OPTIMIZATION OF Mg\(_2\)Si\(_{1-x}\)Sn\(_x\)

We have successfully fitted several key experimental data for a variety of Sn compositions in Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) solid solutions reported in literature as shown in the Appendix. The set of material parameters determined throughout the fitting can now be used to simulate the transport properties of the materials over a wider range of material conditions. We selected 700 K, a value within the working temperature range for Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) solid solutions and calculated the transport properties over a wide range of doping densities from 10\(^{19}\) to 10\(^{21}\) cm\(^{-3}\) for several different Sn contents between \( x = 0 \) to 1. The simulation results for \( n \)-type Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) are presented in Fig. 2. The electrical conductivity shown in Fig. 2(a) typically increases with doping density, while the mobility changes as a function of doping. However, at low dopings the electrical conductivity is much higher than the linearity line between the electrical conductivity and the doping density due to the contribution from the minority carriers, which, in this case, are holes. Since the band gap is smaller at higher Sn content, the bipolar transport becomes more significant. At high doping levels, this bipolar effect becomes negligible. In this one-type carrier transport regime, the electrical conductivity is larger for lower Sn content material, because the higher the Sn content, the heavier the average effective mass of electrons; therefore, the mobility is lower at the same doping level.

The Seebeck coefficients at 700 K are also affected significantly by the bipolar transport at low doping levels as shown in Fig. 2(b). The magnitude of the Seebeck coefficient drops as the doping density decreases since the two partial
FIG. 3. (Color online) Calculated figure of merit \( zT \) as a function of doping density for \( n \)-type \( \text{Mg}_2\text{Si}_{1-x}\text{Sn}_x \) with varying \( x = 0 \sim 1.0 \) at 700 K. The lattice thermal conductivity is assumed to be 1.0 W/mK for all the compositions.

Seebeck coefficients of electrons and holes are subtracted from one another to yield the total Seebeck coefficient according to (7). This detrimental effect of ambipolar transport shows up at a doping level as high as \( 10^{20} \) cm\(^{-3} \) for \( x = 0.8 \) at this temperature, so the optimal doping density for this composition must be much higher than this doping level.

However, if the doping level is too high, the magnitude of the Seebeck coefficient remains low due to the well-known trade-off relationship between the Seebeck coefficient and the electrical conductivity. As a result, the maximum power factor for \( x = 0.8 \) is obtained at a doping level of \( \sim 5 \times 10^{20} \) cm\(^{-3} \) at 700 K, as shown in Fig. 2(c). For \( x = 0.6 \) and 0.7, the optimal doping levels that maximize the power factor are similar, \( \sim 4 \times 10^{20} \) cm\(^{-3} \) at 700 K. To maximize the figure of merit, however, the thermal conductivity must be also considered. As one can see in Fig. 2(d), the electronic thermal conductivity is actually very high at the doping levels that maximize the power factor. Therefore, the optimal doping level for maximum \( zT \) is lower than these doping levels. The contribution of the bipolar thermal conductivity is also apparent in the low doping region for high Sn compositions. For example, for \( x = 0.7 \), the electronic thermal conductivity is higher than 1 W/mK and even increases with decreasing doping density in the low doping region due to the bipolar transport effect. Thus, a minimum value for the electronic thermal conductivity for \( x = 0.7 \) is found to be 0.95 W/mK at around \( 7 \times 10^{19} \) to \( 1 \times 10^{20} \) cm\(^{-3} \) doping densities, above which the one-type carrier electronic thermal conductivity increases quickly with doping density. For \( x = 0.6 \), the minimum electronic thermal conductivity is found to be 0.7 W/mK at \( 5 \times 10^{19} \) cm\(^{-3} \) doping density.

The resulting figure of merit as a function of doping density at 700 K is shown in Fig. 3. Here, we assume a constant

![Graph showing figure of merit as a function of doping density.](image)

FIG. 4. (Color online) Calculated (a) electrical conductivities, (b) Seebeck coefficients, (c) power factors, and (d) electronic thermal conductivities as a function of doping density for \( p \)-type \( \text{Mg}_2\text{Si}_{1-x}\text{Sn}_x \) with varying \( x = 0 \sim 1.0 \) at 700 K.
lattice thermal conductivity of 1.0 W/mK since this value was obtained in the analysis of the thermal conductivity data for the $x = 0.6$ sample from Liu et al. [19] in the Appendix. In fact, the lattice thermal conductivity for lower Sn content or higher Sn content would be higher due to the weaker alloy phonon scattering. Therefore, the figure of merit for the very low or high Sn contents can be lower than the predicted values in Fig. 3. As shown in Fig. 3, the maximum $zT$ of 1.2 is obtained for $x = 0.6$ at 700 K. Even though the conduction band is converged completely near $x = 0.7$, the figure of merit was slightly higher for $x = 0.6$ than for $x = 0.7$, due to the lower electronic thermal conductivity with the slightly larger band gap for $x = 0.6$. The optimal doping density for maximum $zT$ at 700 K lies at $1 \times 10^{20}$ cm$^{-3}$ for $x = 0.6$ to 0.7 compositions. At a higher temperature, i.e., 800 K, we find that the maximum $zT \approx 1.2$ can be obtained at $2 \times 10^{20}$ cm$^{-3}$ doping density for $x = 0.6$. Even though the temperature has increased and the power factor is slightly higher at the optimal doping than that at 700 K, the maximum figure of merit is similar to that at 700 K because the thermal conductivity has also increased by the increased electronic contribution of thermal conductivity at the elevated temperature.

Next, we calculated the transport properties of $p$-type Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions at 700 K. The resulting transport properties are presented as a function of doping density in Fig. 4. Similar to their $n$-type counterparts, the bipolar transport contribution is significant at low dopings so that large power factors are found at relatively high doping above $1 \times 10^{20}$ cm$^{-3}$. However, a distinctive feature for $p$-type materials is shown in the Seebeck coefficient plot in Fig. 4(b). Unlike the case of $n$-type materials, the Seebeck coefficients for lower Sn content materials are higher than those of $x = 0.6$ to 0.8 for $p$-type materials at high doping levels outside the bipolar transport region because there is no band convergence effect in $p$-type materials. As a result, the power factor is higher for lower Sn content and, thus, the maximum power factor is obtained for the lowest Sn content, i.e., $x = 0$, as shown in Fig. 4(c). However, the differences between the power factors of the compositions between $x = 0$ and 0.8 are actually small, only within 20%. Therefore, the thermal conductivity is actually the factor that determines the highest figure of merit among the $p$-type materials. As shown in Fig. 4(d), the electronic thermal conductivity is lower for lower Sn content since the band gap is smaller. The bipolar thermal conductivity is significantly larger for high Sn content even at very high doping levels. The electronic thermal conductivity is very low for $x = 0$ and as low as 0.3 W/mK over a wide doping range below $1 \times 10^{20}$ cm$^{-3}$.

Therefore, the figure of merit for $p$-type Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions is maximized for $x = 0$, i.e., Mg$_2$Si without Sn, because the bipolar thermal conductivity is lowest. The maximum $zT$ is found to be ~0.9 at $2 \times 10^{20}$ cm$^{-3}$ doping density at 700 K, as shown in Fig. 5 when the lattice thermal conductivity is assumed to be 1.0 W/mK. In the binary Mg$_2$Si, however, the phonon alloy scattering can be smaller than the compositions of $x > 0$, so the lattice thermal conductivity can be higher than others. We also plotted the estimated figure of merit for Mg$_2$Si ($x = 0$) with a more realistic lattice thermal conductivity of 2.0 W/mK in Fig. 5. In general, a low Sn content of $x < 0.4$ can possess the highest figure of merit at this temperature as long as the doping density is as high as $2 \times 10^{20}$ cm$^{-3}$, and it can be achieved without significant reduction of electrical conductivity. The electronic thermal conductivity at this optimal doping level for $x = 0$ for $p$-type is as low as 0.5 W/mK, which, along with the lattice thermal conductivity of 1.0 W/mK, amounts to 1.5 W/mK total thermal conductivity. Recall that the total thermal conductivity for the $n$-type material that has a maximum $zT$ at 700 K was 1.86 W/mK, including the lattice thermal conductivity of 1.0 W/mK. The thermal conductivity of the optimal $p$-type material, therefore, is lower than that of the $n$-type optimal. However, the power factor of the $p$-type is lower than that of the $n$-type under the optimal condition because it does not benefit from the band convergence effect on the power factor. Therefore, it is concluded that the convergence of the conduction bands in $n$-type Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions is of great importance for the material optimization.

**VI. IMPACT OF ELECTRON ENERGY FILTERING**

In the previous sections, it has been shown that the contribution from bipolar transport is significant in both the power factor and the electronic thermal conductivity at low dopings and at high temperatures in Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions. At high doping levels, the electronic thermal conductivity by one-carrier carriers is so significant that the optimal doping level for maximum $zT$ is shifted to a lower level from the optimal doping that maximizes the power factor. If the electronic thermal conductivity is suppressed sufficiently in the high doping region, then the figure of merit can be further increased.

Recently, we conducted a theoretical study of the electron energy filtering scheme, and found that both the power factor enhancement and the electronic thermal conductivity reduction are simultaneously possible when an appropriate cutoff energy level is introduced in the electron transport, i.e., when electrons having energies below this cutoff energy are...
effectively prevented from participating in the transport [29]. According to the paper, a power factor enhancement of about 90% is possible for \( n \)-type bulk PbTe at 600 K if a cutoff energy level as high as 0.4 eV is introduced in the material with a doping density higher than \( 2 \times 10^{20} \) cm\(^{-3}\). At the same time, electron energy filtering gives an electronic thermal conductivity as low as 0.5 W/mK at this high doping density, which otherwise would increase to 5 W/mK or higher. As a result of the combined effects, a figure of merit for \( zT \sim 1.66 \) can be achieved for \( n \)-type PbTe at 600 K, with the assumption of lattice thermal conductivity of 1.0 W/mK. This \( zT \) value can be even higher if the lattice thermal conductivity is reduced further by nanostructuring. In fact, recently a lattice thermal conductivity as low as \( \sim 0.5 \) W/mK has been reported at 900 K in \( p \)-type bulk Na-doped PbTe:SrTe [36].

Similarly, we study the impact of electron filtering on \( \text{Mg}_2\text{Si}_{1-x}\text{Sn}_x \) solid solutions and calculate the figure of merit. The details of the electron filtering theory and the transport calculations with a cutoff energy can be found in Ref. [29]. Figure 6 shows the impact of electron filtering on the transport properties of \( n \)-type \( \text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6} \) (\( x = 0.6 \)) solid solutions as a function of doping density at 700 K. This material composition is selected as it has the highest figure of merit at this temperature, according to the material optimization performed in the previous section. A constant lattice thermal conductivity of 1.0 W/mK is used. In this study, the optimal cutoff energy level that maximizes the figure of merit is obtained for each doping density, and they are shown in Fig. 6(c), along with the Fermi level on the right \( y \) axis. The optimal cutoff energy level for maximum \( zT \) is found to be slightly higher than the optimal cutoff energy level for maximum power factor since the higher cutoff energy reduces the electronic thermal conductivity sufficiently to more than offset the reduction of the power factor. The optimal cutoff energy level is found to be about \((2.1 \text{ to } 2.3) \times k_B T\) higher than the Fermi level at each doping density.

As shown in Fig. 6(a), the magnitude of the Seebeck coefficient is still very high (>300 \( \mu \)V/K) even at very high doping densities due to the electron filtering effect. In comparison, the bulk Seebeck coefficient is also shown in Fig. 6(a) to decrease significantly with increasing doping density. The electrical conductivity is reduced at the same time by the filtering effect, but the power factor can be enhanced over the maximum bulk value as the enhancement of the Seebeck coefficient overcomes the reduction of the electrical conductivity, as shown in Fig. 6(b). Here, the enhancement of the power factor is, in fact, not so high; at the \( 1 \times 10^{21} \) cm\(^{-3}\) doping level, the power factor is increased to \( 66 \) \( \mu \)W cm\(^{-1}\) K\(^{-2}\), which is about a 60% enhancement over the maximum bulk value of \( 41 \) \( \mu \)W cm\(^{-1}\) K\(^{-2}\). However, the electronic thermal conductivity is reduced considerably by the optimal filtering effect, as shown on the right \( y \) axis in Fig. 6(b). Even if the doping density increases, the electronic thermal conductivity remains as low as \( 0.5 \) W/mK with optimal filtering. It is possible to even decrease the electronic thermal conductivity with increased doping with an appropriate cutoff energy filtering. As a result, the figure of merit can be drastically enhanced over the bulk maximum of 1.2 and reach \( zT = 3.0 \) at a doping density of \( 1 \times 10^{21} \) cm\(^{-3}\) with a cutoff energy level of 0.4 eV at 700 K.

**VII. CONCLUSIONS**

In this paper, we have presented a comprehensive electron transport model for \( \text{Mg}_2\text{Si}_{1-x}\text{Sn}_x \) \((0 \leq x \leq 1)\) solid solutions. This model fits the experimental data from literature for various compositions very well. Throughout the analysis of the experimental data, it has been found that the bipolar transport effect can be significant at low doping densities for low Sn content alloys at high temperatures. We also quantify that the convergence of the two \( X \) valley conduction bands plays an important role in enhancing the Seebeck coefficient and
thus the power factor for the $n$-type Mg$_2$Si$_{1-x}$Sn$_x$ materials. In $p$-type materials, the bipolar thermal conductivity is a major factor determining the figure of merit at high temperatures. The composition for $x = 0.6$ to 0.7 has the highest figure of merit in the midtemperature range for $n$-type Mg$_2$Si$_{1-x}$Sn$_x$, and the low Sn content of $x = 0$ to 0.4 has the highest figure of merit for $p$-type Mg$_2$Si$_{1-x}$Sn$_x$ at this temperature. Finally, in order to simultaneously enhance the power factor and reduce the electronic thermal conductivity, we propose the use of the electron energy filtering for this material.

**ACKNOWLEDGMENT**

We gratefully acknowledge the financial support by the National Science Foundation and the Department of Energy Partnership Grant No. CBET-1048801.

**APPENDIX: DETAILED FITTING RESULTS OF EXPERIMENTAL DATA**

Figure 7 shows the experimental data of the electrical conductivities and Seebeck coefficients for $n$-type Mg$_2$Si from Tani and Kido [12] and for $n$-type Mg$_2$Sn from Chen and Savvides [35], along with our calculated curves. The four samples of different Bi doping content, 0.1 to 1.0% Bi, in Mg$_2$Si from Tani and Kido were successfully fitted over the wide temperature range from 300 to 900 K by our model. Bi is well-known as an efficient $n$-type dopant in Mg$_2$Si, and its content increases the electron concentration in this material almost linearly until 1.0%, beyond which the electron concentration is saturated [12]. Since there can be additional electron scatterings by agglomeration of Bi atoms and compensated ionized atoms, which is difficult to model, we only focused on the Bi content up to 1.0%. The doping densities used for curve fitting are $1 \times 10^{19}$, $3.3 \times 10^{19}$, $4.5 \times 10^{19}$, and $8 \times 10^{19}$ cm$^{-3}$, respectively, for 0.1, 0.3, 0.5, and 1.0% Bi samples from Tani and Kido. These doping densities are slightly smaller than the carrier densities measured by the Hall effect in the paper by less than 20%. This small deviation is plausible considering the uncertainties in the Hall effect measurements for large-size samples. Both the electrical conductivity and the Seebeck coefficients are in excellent agreement with the experimental data over the entire temperature range, with the exception of the Seebeck coefficient data for the 0.1% Bi:Mg$_2$Si sample. However, the sudden drop in the magnitude of the Seebeck coefficient beyond 750 K for this sample is clearly observed in the theoretical curve, as shown in Fig. 7(b). This is due to the contribution from the intrinsic holes that are thermally excited at these high temperatures, particularly for the low doping density. This bipolar effect also shows up in the electrical conductivity, which slightly increases with temperature beyond 750 K for this sample.

Since Mg$_2$Sn has a much smaller band gap than Mg$_2$Si, the bipolar contribution can show up at much lower temperatures. Indeed, as shown in Fig. 7, the 1.0% Bi-doped Mg$_2$Sn sample from Chen and Savvides [35] showed a sudden increase in the electrical conductivity and a sudden decrease in the magnitude of the Seebeck coefficient as early as at 470 K. This sample has a very high electron concentration of $9.5 \times 10^{19}$ cm$^{-3}$, and the hole concentration is much smaller, $\sim 5 \times 10^{18}$ cm$^{-3}$ at 300 K, according to our calculation. However, at 470 K, the hole concentration increases about two orders of magnitude to $\sim 6 \times 10^{20}$ cm$^{-3}$, while the electron concentration increases slightly to $\sim 1 \times 10^{20}$ cm$^{-3}$. The hole contribution to the electrical conductivity of this sample becomes as large as 15% of the total electrical conductivity by 600 K. As a result, the magnitude of the Seebeck coefficient decreases substantially from 160 $\mu$V/K at 400 K to 120 $\mu$V/K at 600 K and keeps decreasing with temperature, as shown in Fig. 7(b).

For the solid solutions composed of the two binary materials, we chose the experimental data for the three samples with composition $x = 0.6$ from Zaitsev et al. [17] and one sample of the same composition from Zhang et al. [37] for curve fitting. They are all $n$-type materials. The fitting results for those samples are shown in Fig. 8. The samples 1 to 3 from Zaitsev et al. have varying electron concentrations, $5.9 \times 10^{19}$, $2.52 \times 10^{20}$, and $2.99 \times 10^{20}$ cm$^{-3}$, respectively, measured at room temperature by the Hall effect measurements in the paper. We fitted the properties of the these three samples with the room-temperature electron concentration of $3.0 \times 10^{19}$, $1.25 \times 10^{20}$, and $1.75 \times 10^{20}$ cm$^{-3}$, respectively, which are all

![FIG. 7. (Color online) Fitting results of (a) electrical conductivities and (b) Seebeck coefficients; experimental data of $n$-type Bi-doped Mg$_2$Si from Tani and Kido [12], and of $n$-type Bi-doped Mg$_2$Sn from Chen and Savvides [35]. The symbols are the experimental data, and the curves are the theoretical fitting.](image)
about 50% smaller than the measured concentrations. A further investigation of the carrier densities is necessary as the 50% difference between the theoretical and experimental values seems too large in Hall effect measurements. Note that all the other experimental carrier densities used for fitting in this work agreed reasonably well with our theoretically estimated values.

The calculated curves match closely with the experimental data for all of the samples, as shown in Fig. 8. The higher the electron concentration, the higher the electrical conductivity and the magnitude of the Seebeck coefficient for these samples. For sample 1 of Zaitsev et al., the doping density was so low that the bipolar contribution started to show up at around 600 K, which caused the electrical conductivity to increase and the magnitude of the Seebeck coefficient to decrease beyond that temperature. The experimental data clearly shows this behavior in Fig. 8. The 0.75% Sb-doped \( \text{Mg}_2 \text{Si}_{0.4} \text{Sn}_{0.6} \) sample from Zhang et al. \cite{37} lies between samples 1 and 2 of Zaitsev et al. in terms of the doping density, which is \( 1.03 \times 10^{20} \text{ cm}^{-3} \); hence, both the electrical conductivity and Seebeck coefficients also lie between the curves of the two samples. The electron concentration from Hall effects (\( 1.03 \times 10^{20} \text{ cm}^{-3} \)) matches very closely with the value used for the theoretical curve, which is \( 9.5 \times 10^{19} \text{ cm}^{-3} \).

Although the available experimental data for high temperatures is limited, it is important to note that the theoretical calculations predict that all the samples in Fig. 8 will show the bipolar transport effects at higher temperatures. The theory clearly indicates, therefore, that if this material is to be used at higher temperatures, one needs to either increase the doping density in order to delay the bipolar effect or use a lower Sn content (\( x < 0.6 \)) material that has a larger band gap.

We also curve-fitted experimental data for \( p \)-type Ag-doped \( \text{Mg}_2 \text{Si}_{0.4} \text{Sn}_{0.6} \) (\( x = 0.6 \)) solid solutions from Akasaka et al. \cite{13}. Figure 9 shows the fitting results for the Ag-I and Ag-II samples from the paper. The doping efficiency of Ag as a \( p \)-type dopant in \( \text{Mg}_2 \text{Si}_{0.4} \text{Sn}_{0.6} \) looks lower than Bi as an \( n \)-type dopant in the same matrix, as 1.0% Ag doping achieved only up to \( 7.42 \times 10^{18} \text{ cm}^{-3} \) hole concentration. We used room-temperature hole concentrations of \( 7.0 \times 10^{18} \text{ cm}^{-3} \) for the fitting of Ag-I and Ag-II samples, respectively. The Ag-I sample has a higher electrical conductivity and a slightly smaller Seebeck coefficient than the Ag-II sample as it has a higher hole concentration. But both samples are overwhelmed by the strong bipolar transport effects at temperatures as low as 600 K, and the Seebeck coefficient in these samples is significantly reduced due to the bipolar effect.
coefficients sign changes to \( n \)-type above 700 K. This is clearly indicated by the theoretical curves shown in Fig. 9. According to our calculations, the electron concentration rises to \( 1.2 \times 10^{18} \) cm\(^{-3} \) by 700 K in the Ag-II sample, which is comparable to the hole concentration of \( 3.2 \times 10^{18} \) cm\(^{-3} \) at the same temperature. Since the electron mobility is higher than the hole mobility due to the smaller effective mass, the contribution of electrons to the electrical conductivity accounts for 60% of the total electrical conductivity at 700 K in this sample. The electron’s contribution to the Seebeck coefficient is also increased according to (7); thus, the sign of the Seebeck coefficient turns negative, and the value reaches \(-125 \) \( \mu \)V/K based on the calculations. In the experimental data, the Seebeck coefficient increases and becomes positive again at higher temperatures. This is not possible if the doping density remains the same. This may be due to the activation of other deep-level acceptors or the redistribution of impurities by increased kinetics to give up more holes to the matrix at these high temperatures.

Now, we turn to the more recently published experimental data by Liu et al. [19] for curve fitting. Figure 10 shows the measured electrical conductivities and Seebeck coefficients for four different compositions (\( x = 0.4, 0.6, 0.7, 0.8 \)) of \( n \)-type Mg\(_2\)Si\(_{1-x}\)Sn\(_x\) solid solutions from the paper, along with our calculations. We used the same set of material parameters obtained from the previous fittings here. We slightly modified the room-temperature electron concentrations from the measured ones reported in the paper in order to obtain improved curve fitting. Since electrical conductivity and the Seebeck coefficient of bulk materials are closely coupled at different dopings, fitting temperature-dependent Seebeck and electrical conductivity data are another way to extract the carrier concentration. For the \( x = 0.4, 0.6, 0.7, 0.8 \) samples, electron concentrations of \( 9.5 \times 10^{19}, 1.4 \times 10^{20}, 1.6 \times 10^{20}, \) and \( 2.3 \times 10^{20} \) cm\(^{-3} \), were assumed for better fitting of electrical conductivity, while the measured values reported in the paper were \( 1.8 \times 10^{20}, 1.7 \times 10^{20}, 1.7 \times 10^{20}, \) and \( 1.8 \times 10^{20} \) cm\(^{-3} \), respectively. These differences may be explained considering the uncertainties in the Hall effect measurements as well as potential nonuniform doping distribution in the sample as the Hall effect is often done on a different piece of material. It is also possible, however, that the mobilities in these samples were reduced from the bulk values due to
the presence of nanostructures and impurities. As shown in Fig. 10(b), the experimental Seebeck coefficients are also in good agreement with the calculated curves except for the $x = 0.8$ sample above 600 K and the $x = 0.7$ sample over the entire temperature range. For the $x = 0.8$ sample, the calculations predicted a lower magnitude for the Seebeck coefficients at high temperatures due to the bipolar effect, which has been confirmed by the previous fittings of the other papers and may be due to the uncertainty in the carrier concentration for this sample. For the $x = 0.7$ sample, the electrical conductivities match almost perfectly, but the magnitudes of the calculated Seebeck coefficients are lower than the measured counterparts by almost a constant value over the entire temperature range. Since the electrical conductivities and the electron concentrations of the $x = 0.6$ and $x = 0.7$ samples are almost the same, the theory also predicted about the same Seebeck coefficients between the two samples. Even though complete band convergence occurs at $x \approx 0.7$, $x = 0.6$ is also still very close, and the continuous changes of material parameters from $x = 0.6$ to 0.7 could not explain such a big shift in Seebeck coefficients between the two samples.

Detailed analysis of the thermal conductivity data in Liu et al. [19] highlights important conclusions that can be extracted from the Boltzmann transport model. As can be seen in Fig. 11, the measured total thermal conductivities of all the samples in the paper showed significant increases at high temperatures beyond 600 K. The paper claimed that this can be due to the bipolar effect on thermal conductivity but could not extract the bipolar thermal conductivity from the lattice thermal conductivity. Our transport model calculated the bipolar thermal conductivities using (8) without any further adjustment of parameters after fitting the electrical conductivities with adjusted doping densities, as shown in Fig. 11(b). The bipolar thermal conductivity increases significantly beyond 600 K, and it is larger for higher Sn content $x$ since the band gap is smaller. The bipolar thermal conductivity reaches $1.0 \, \text{W/mK}$ at 800 K for the $x = 0.8$ sample according to the calculations, which raises the electronic thermal conductivity obtained from (9) to 2.1 W/mK at 800 K. This significant increase of the electronic thermal conductivity clearly shows up in the measured total thermal conductivity in Fig. 11(a). Considering the total thermal conductivity of 3.2 W/mK for the $x = 0.8$ sample at 800 K, the electronic thermal conductivity accounts for about 66%, and the remainder, which amounts to 1.1 W/mK, is attributed to the lattice thermal conductivity. Similarly, the $x = 0.6$ sample is found to have the lattice thermal conductivity of $\sim 0.9 \, \text{W/mK}$ at this temperature, and all the other samples have similar values, between 1.0 ~ 1.2 W/mK at 800 K. The extracted lattice thermal conductivities for all four samples steadily decreases with temperature, as shown in Fig. 11(a). This trend looks reasonable as the predominant phonon scattering mechanisms in this temperature range, such as the Umklapp scattering, become stronger as the temperature increases [38].


