The effect of shallow vs. deep level doping on the performance of thermoelectric materials

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**Detailed Terms**
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The effect of shallow vs. deep level doping on the performance of thermoelectric materials

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It is well known that the efficiency of a good thermoelectric material should be optimized with respect to doping concentration. However, much less attention has been paid to the optimization of the dopant’s energy level. Thermoelectric materials doped with shallow levels may experience a dramatic reduction in their figures of merit at high temperatures due to the excitation of minority carriers that reduces the Seebeck coefficient and increases bipolar heat conduction. Doping with deep level impurities can delay the excitation of minority carriers as it requires a higher temperature to ionize all dopants. We find through modeling that, depending on the material type and temperature range of operation, different impurity levels (shallow or deep) will be desired to optimize the efficiency of a thermoelectric material. For different materials, we further clarify where the most preferable position of the impurity level within the bandgap falls. Our research provides insight on why different dopants often affect thermoelectric transport properties differently and directions in searching for the most appropriate dopants for a thermoelectric material in order to maximize the device efficiency. Published by AIP Publishing.

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Solid-state thermoelectric devices can be used in power generation by converting heat into electricity.1 The maximum efficiency of thermoelectric power generator is determined by the dimensionless figure of merit $zT = \sigma S^2 T / (\kappa_e + \kappa_h + \kappa_{bg} + \kappa_l)$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $T$ is the temperature, $\kappa_e$ and $\kappa_h$ are the unipolar thermal conductivities of electrons and holes, respectively, $\kappa_{bg}$ is the bipolar thermal conductivity, and $\kappa_l$ is the lattice thermal conductivity.2 To optimize the efficiency of thermoelectric energy conversion devices, materials with a high $zT$ is preferable. Many efforts have been made to enhance $zT$, including reducing the lattice thermal conductivity $\kappa_l$,3–5 and optimizing the power factor $\sigma S^2$.6–9 Specifically, doping is an indispensable step to have a significant electrical conduction, and selecting dopants has become the essential part in optimizing the thermoelectric performance.9

Introducing dopants into thermoelectric materials usually creates impurity levels within the material’s energy bandgap. Impurity levels close to the band edge (either conduction band minimum or valence band maximum) are called “shallow” levels, while those far away from the band edge are called “deep” levels.10 The fraction of dopants ionized to create electrons or holes depends on temperature and the position of the impurity level measured from the Fermi level. In a material doped with shallow levels, it is expected that at a moderate temperature, the donors (acceptors) are nearly all ionized. However, at a higher temperature, minority carriers emerge due to direct thermal excitation across the bandgap, which increases the bipolar thermal conductivity11 and reduces the Seebeck coefficient due to cancellation of electron and hole currents,12 thus causing a dramatic reduction of $zT$. A material doped with deep levels, on the other hand, requires high thermal energy and thereby a high temperature to ionize the impurities. Therefore, the minority carriers can only be excited at an even higher temperature, i.e., the deep levels suppress the thermal excitation of minority carriers. For thermoelectric devices under a large temperature gradient, deep levels delay the undesired bipolar effect to higher temperatures and may help to improve the maximum efficiency. There has been continuous interest in optimizing thermoelectric performance through carefully designing the doping, such as blocking minority carriers by heterostructure barriers,12 preferential scattering of minority carriers,13 stabilizing the optimal carrier concentration.14 Experiments show that doping deep levels (indium) in PbTe$_{1-x}$S$_x$ alloy is an effective way to enhance the thermoelectric efficiency.15 There has not been, however, a systematic study on the effect on thermoelectric performance of different impurity energy levels.

Deep levels can mitigate the bipolar effect and delay the reduction of $zT$ to higher temperatures. The tradeoff, however, is that deep levels provide fewer free carriers than shallow levels at the same dopant concentration. As a result, a higher dopant concentration is required for the deep levels to have a comparable performance with shallow levels. Moreover, an inappropriate dopant concentration of deep levels makes the Fermi level deviate from its optimal position. In this letter, using theoretical modeling, we answer the

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following question: Under what conditions are deep/shallow levels preferred? We find that a material with a narrow bandgap working under a large temperature difference, for which the bipolar effect can be induced easily, requires deep levels to maximize the efficiency. Besides, a large material parameter $B$, usually a signature of good thermoelectrics, also implies a significant bipolar contribution to the total thermal conduction and therefore deep levels are desired.

To have a general understanding of the role of deep levels in thermoelectrics, we take parabolic and isotropic conduction and valence bands assuming a rigid band formalism and the band curvature is characterized by single-valley density-of-state effective mass $m^*_g$. Assuming that the effective masses and band degeneracies of electrons and holes are equal, the density of majority and minority carriers is written as\(^{16}\)

$$n = \frac{N_e}{2\pi^2} \left( \frac{2m^*_e k_B T}{\hbar^2} \right)^{3/2} F_{1/2}(\alpha) ,$$

$$p = \frac{N_e}{2\pi^2} \left( \frac{2m^*_h k_B T}{\hbar^2} \right)^{3/2} F_{1/2}(\beta) ,$$

where $N_e$ is the band degeneracy, $\hbar$ is the reduced Plank constant, $\alpha = (E_f - E_c)/k_B T$, $\beta = (E_v - E_f)/k_B T$ are the reduced Fermi level measured from conduction band minimum and valence band maximum, respectively. The complete Fermi-Dirac integral of $j$th order is defined as $F_{j}(\alpha)$ $= \int_0^\infty \frac{\xi^{j-1}}{1 + e^{\xi - \alpha}} d\xi$, where $\xi$ is the reduced carrier energy $\xi = (E - E_c)/k_B T$, $E$ is the energy of carriers, and $k_B$ is the Boltzmann constant. In this paper, the $n$-type thermoelectric material is studied. The normalized Fermi level $z$ is obtained by solving the charge neutrality equation $n = p + N_d^+$, where $N_d^+ = N_d / (1 + \beta_p e^{(E_f - E_v)/k_B T})$ is the ionized impurity density, $N_d$ is the doping concentration, and $\beta_p$ is the donor degeneracy (assuming $\beta_d = 2$). Note that the statistics of the deep levels can be complicated,\(^{17}\) but here we still adopt the effective-mass approximation used in shallow levels to treat deep levels, which gives reasonable results compared with experiments\(^{18}\) and serves as a starting point to study the effect of different impurity levels.

In Eq. (6), the material-dependent dimensionless parameter is written as $B(T) = \kappa^* / \kappa_i$,\(^{22}\) which has been widely used to identify materials with good thermoelectric performance.\(^{23}\) The transport properties of thermoelectric materials vary greatly with temperature. To accurately compare the effect of shallow levels and deep levels, we calculate the device efficiency under different operating temperatures. The maximum efficiency is obtained as $\eta_{\text{max}} = \eta_c \left( \sqrt{1 + \frac{zT_{\text{eng}}^2 \eta_c^2 - 1}{z_2}} \right)$ and the definition of $zT_{\text{eng}}$ and $z_2$ can be found in the literature.\(^{24}\)

The relaxation time approximation is adopted to solve the linearized Boltzmann transport equation to calculate the transport properties.\(^{19}\) The major scattering mechanism for carriers is assumed to be acoustic deformation potential scattering.\(^{20}\) The electrical conductivity can then be expressed as

$$\sigma = \frac{2}{3} N_e \frac{\hbar c^2}{\pi m^*_e \Xi} \left[ F_0(\alpha) + F_0(\beta) \right] ,$$

where $C_1$ is the average longitudinal elastic modulus and $\Xi$ is the deformation potential constant. The Seebeck coefficient is written as

$$S = \frac{k_B}{e} \left[ zF_0(\alpha) - \beta F_0(\beta) - 2(F_1(\alpha) - F_1(\beta)) \right] .$$

The electronic contribution to thermal conductivity of electrons and holes is equal to

$$\kappa_e = \kappa^* \left[ 3F_2(\alpha) - \frac{4(F_1(\alpha))^2}{F_0(\alpha)} \right] ,$$

$$\kappa_h = \kappa^* \left[ 3F_2(\beta) - \frac{4(F_1(\beta))^2}{F_0(\beta)} \right] .$$

And the bipolar thermal conductivity can be described by

$$\kappa_{bp} = \kappa^* \frac{F_0(\alpha) F_0(\beta)}{F_0(\alpha) + F_0(\beta)} \left[ \frac{\xi_g + 2F_1(\alpha)}{F_0(\alpha) + 2F_1(\beta)} \right] ,$$

where $\xi_g = E_g / k_B T$ is the reduced bandgap. Here, the physical quantity $\kappa^*$, which has the same units as thermal conductivity [W/mK], is defined to be $\kappa^* = \frac{2}{3} N_e \frac{\hbar c^2 T}{\pi m^*_e \Xi}$ and $\kappa^*$ of selected thermoelectric materials is listed in Table I. As we see in Eqs. (4) and (5), $\kappa^*$ scales the magnitude of the electronic thermal conductivity and the bipolar thermal conductivity as well. In our model, the lattice thermal conductivity $\kappa_l$ is assumed to be temperature-independent.\(^{21}\) Accordingly, the figure of merit $zT$ is

$$zT = \frac{1}{B(T)} + \left[ \frac{zF_0(\alpha) - \beta F_0(\beta) - 2(F_1(\alpha) + 2F_1(\beta))}{3F_2(\alpha) + 3F_2(\beta) - \frac{4F_1^2(\alpha)}{F_0(\alpha)} - \frac{4F_1^2(\beta)}{F_0(\beta)} + F_0(\alpha) F_0(\beta)} \right] \left[ \frac{\xi_g + 2F_1(\alpha)}{F_0(\alpha) + 2F_1(\beta)} \right] .$$

We first study the general trend of the dependence of a thermoelectric material’s performance on temperature by doping successively deeper levels. In a narrow-bandgap thermoelectric material, the optimal Fermi level (corresponds to the optimal doping concentration that maximize $zT$ at certain $T$) initially lies below the conduction band minimum and then rises above the conduction band minimum with increasing temperature in Fig. 1(a). This behavior occurs because at low temperatures a high Seebeck coefficient is preferable, which requires the Fermi level to lie slightly lower than the
conduction band, while at higher temperatures, the optimal Fermi level should avoid approaching the middle of the bandgap to prevent large concentrations of minority carriers that would reduce \(zT\) through the bipolar effect. Starting with the same carrier concentration at 300 K, we want to explore how the temperature mediates the dopant ionization for different impurity levels and how the Fermi level evolves with temperature relative to the optimal Fermi level. For the shallow levels (green dashed-dotted line), at room temperature, most of the donors are ionized. With increasing temperature, the donors all become ionized and thermally excited electron-hole pairs become dominant. Accordingly, in Fig. 1(b), \(zT\) drops dramatically after experiencing a peak value and the efficiency starts to decrease at \(T_h = 1000\) K in Fig. 1(c). A similar scenario showing delayed bipolar effect has also been reported in experiment. For the case of doping with deeper levels (black dotted line), the temperature dependence of \(zT\) is further weakened such that we do not observe a dramatic drop of \(zT\) at high temperature in Fig. 1(b). However, the \(zT\) falls below the other two curves. This is because for much deeper levels, a higher doping concentration is required to reach the same carrier concentration at room temperature and the Fermi level rises up into the conduction band as the temperature becomes high since the gradually ionized dopant centers release more and more electrons into the system, shown in Fig. 1(a). When the Fermi level is deep inside the conduction band, the Seebeck coefficient is much smaller, leading to a reduced \(zT\) over the whole temperature range. In Fig. 1(c), for the case of doping with deeper levels, the efficiency is the lowest in most temperature ranges and keeps increasing as \(T_h\) increases. Whereas for a wide-bandgap thermoelectric material, the shallow levels lead to the highest efficiency over the whole temperature range and introducing deeper levels will only reduce the efficiency, shown in Fig. 1(f), due to the fact that a large band gap intrinsically suppresses the excitation of minority carriers, and the optimal choice of dopant is not deep levels.

<table>
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<tr>
<th>Material</th>
<th>(E_g) (eV)</th>
<th>(\kappa^*) (W/mK)</th>
<th>(\kappa) (W/mK)</th>
<th>Note</th>
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<td>PbS(^{25})</td>
<td>0.42</td>
<td>0.18</td>
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<td>n-type</td>
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<td>PbSe(^{25})</td>
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<td>0.28</td>
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<td>PbTe(^{25})</td>
<td>0.31</td>
<td>0.32</td>
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<td>Bi(_2)Te(_3)(^{31})</td>
<td>0.13</td>
<td>0.60</td>
<td>1.7</td>
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<td>Bi(_2)Se(_3)(^{32–34})</td>
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<td>0.12</td>
<td>2.8</td>
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<td>Sb(_2)Te(_3)(^{35–37})</td>
<td>0.24</td>
<td>3.18</td>
<td>1.0</td>
<td>p-type</td>
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<tr>
<td>SiGe(^{38})</td>
<td>0.96</td>
<td>1.57</td>
<td>8.8</td>
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<tr>
<td>Mg(_2)Si(^{39–41})</td>
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<td>9.25</td>
<td>7.9</td>
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<td>Mg(_2)Ge(^{39–41})</td>
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<tr>
<td>Mg(_2)Sn(^{39–41})</td>
<td>0.35</td>
<td>0.50</td>
<td>5.9</td>
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<tr>
<td>CoSb(^{42–44})</td>
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<td>5.43</td>
<td>10</td>
<td>p-type</td>
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<tr>
<td>ZrNiSn(^{35})</td>
<td>0.51</td>
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<td>6.0</td>
<td>n-type</td>
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The efficiency is defined by \(zT\) at different hot-side temperature and the same cold-side temperature (300 K). Here, \(E_r - E_d\) is defined to be the distance between the impurity level and the conduction band minimum. The case of a narrow-bandgap thermoelectric material (0.4 eV) and the case of a wide-bandgap thermoelectric material (0.9 eV). The dopant concentration for \(E_r - E_d = 0.04\) eV, \(0.09\) eV, \(0.14\) eV are \(2.5 \times 10^{20}\) cm\(^{-3}\), \(1.6 \times 10^{20}\) cm\(^{-3}\), \(1.1 \times 10^{19}\) cm\(^{-3}\), respectively, and \(\kappa^* = 0.5\) W/mK, \(\kappa = 2\) W/mK.
Having discussed the general feature of the effects of dopants with different energy levels on the thermoelectric performance, we now discuss how one should select the dopants from the perspective of their energy levels. Practically, there are two variables that can be controlled: the doping concentration \( N_d \) and the dopant element, the latter of which determines the energy level \( E_d \) of the dopant. To better characterize these dopant properties, we introduce two corresponding dimensionless parameters,

\[
N_d^* = \ln\left( \frac{2N_e\pi^2k^2}{N_d}(2\pi\hbar^2k^2T_c^2) \right)
\]

and

\[
\xi_d^* = \frac{E_c - E_d}{kBT_c},
\]

where \( T_c \) is the cold-side temperature. For a given temperature difference, the thermoelectric efficiency is determined by \( N_d^* \) and \( \xi_d^* \) as shown in Fig. 2(a). There exists an optimal \( \xi_d^* \) corresponding to the maximum efficiency for a fixed temperature difference. The origin of this optimum stems from the fact that either too large or too small \( \xi_d^* \) will place the Fermi level far away from the position of optimum efficiency while a suitable one should keep the Fermi level relatively close to this optimum across the whole temperature range. Changing from doping with shallow levels \((E_c - E_d = 0.01 \text{ eV})\) to deep levels \((E_c - E_d = 0.12 \text{ eV})\), there is a 10% relative improvement in efficiency, when the highest efficiency of each level is compared.

In Fig. 2(b), the optimal \( \xi_d^* \) and \( N_d^* \) are presented, from which we first notice that \( \xi_d^* \) and \( N_d^* \) follow the same trend, i.e., a higher value of \( \xi_d^* \) requires a higher value of \( N_d^* \) to reach higher efficiency, meaning that deeper levels need a higher doping concentration. The non-dimensional parameter \( \xi_d^* \) is a measure of the difficulty of donor excitation and \( N_d^* \) describes the amount of donors provided in the material. A larger \( \xi_d^* \) corresponds to a higher binding energy indicating that it is more difficult to ionize the donors; thus, more donors are required to reach the optimal number of free carriers determined by the optimal Fermi level. We also note that deeper levels are preferred under a larger temperature difference. This is due to the fact that bipolar thermal conductivity increases rapidly with rising temperature. To counteract the stronger bipolar effect, it is desirable to have donors with deeper levels that will not ionize until higher temperatures. When the temperature difference is small \((\Delta T < 100 \text{ K})\), there is no obvious optimal \( \xi_d^* \), as the Fermi level can be tuned to close to the optimal position with both deep levels and shallow levels without introducing a significant bipolar effect.

Fig. 2(c) shows the optimal \( E_c - E_d \) as a function of bandgap and hot-side temperature with respect to different \( \kappa^* \), from which we can conclude that impurities with deep levels are preferable to impurities with shallow levels in narrow-bandgap materials. In wide-bandgap materials, the distance required between the impurity level and the conduction band minimum is smaller. If the bandgap is even larger, the position of optimal impurity level converges because the bandgap is large enough to suppress minority carrier excitation. For the same \( E_c \) and \( T_c \), impurities with deeper levels are more preferable as \( \kappa^* \) is larger. In the meantime, when \( \kappa_j \) becomes smaller (not shown here), a deeper level is also favorable. This is because either a large \( \kappa^* \) or a low \( \kappa_j \) means that bipolar thermal conduction will dominate. This indicates that a material with large elastic modulus, large band degeneracy, small effective mass, small deformation potential, and low lattice thermal conductivity benefits from deep level doping in particular, which is also consistent with the definition of a good thermoelectric material. In other words, a good thermoelectric material demands more attention in choosing the appropriate impurity level.

![FIG. 2. (a) Given the cold-side (300 K) and hot-side temperatures (1200 K), the efficiency of a thermoelectric material as a function of \( \xi_d^* \) and \( N_d^* \) \((E_c = 0.4 \text{ eV})\), (b) \( \xi_d^* \) and \( N_d^* \) required by the optimum efficiency at different hot-side temperatures. In the calculation, \( \kappa^* = 0.5 \text{ W/mK}, \kappa_j = 1 \text{ W/mK} \). (c) Optimal impurity level as a function of band gap and hot-side temperature with different \( \kappa^* \). In the calculation, \( \kappa_j = 1 \text{ W/mK} \). (d) Optimal impurity level of PbTe as a function of hot-side temperature \( T_h \), obtained by the simple model and the full model, plotted with the impurity level of indium doped PbTe and iodine doped PbTe. \( T_c = 300 \text{ K} \) and \( T_h \) ranges from 400 K to 900 K.](image-url)
We wish to examine the effect of deep level doping in real material systems. PbTe is chosen as the example material considering it has a narrow bandgap and small effective mass as well as a low lattice thermal conductivity. As can be seen in Fig. 2(d), the green line shows the optimal impurity level of PbTe from the abovementioned simple model. The red line shows the optimal impurity level of PbTe as a function of temperature, obtained by a full model that applies the Kane-band model to calculate the band structure, acoustic/optical deformation potential scattering, polar scattering, and impurity scattering to calculate mobility. Callaway model including phonon-phonon scattering in the lattice thermal conductivity calculation and incorporates the temperature dependence of the effective mass and band gap, which does not deviate much from the simple model. As the temperature difference increases, the impurity level required becomes deeper. Indium (black dashed line) has been shown to be a deep level dopant substituting for Pb in PbTe, while iodine (blue dashed-dot line) is a shallow level dopant substituting for Te. For the case of high $T_d$, we expect that indium doped PbTe has a higher efficiency than iodine doped due to the suppression of the bipolar effect. In fact, if phonon-impurity scattering is included in the full model, the relative improvement in efficiency from iodine doped to indium doped can be as high as 11% (6% by simple model), due to the extra benefit that the large mass difference between indium and lead gives a reduced $\kappa_f$.\(^{26}\)

In summary, we have studied the effect of different impurity levels on the thermoelectric figure of merit $zT$ and efficiency using a two-parabolic-band model and relaxation time approximation. We find that deep levels can improve the thermoelectric performance by delaying the bipolar effect, depending on the material's characteristics including the bandgap and material parameter $B$, as well as the operating temperature. Moreover, when the temperature difference is large and the bandgap is small, deep levels are desired to increase the efficiency. For different materials, the optimized position of impurity level varies depending on their transport properties. For thermoelectric materials with a large material parameter $B$, doping with deep level impurities results in much larger benefits. It should be noted that it is generally difficult to predict the impurity energy levels, which might also changes with temperature. Our results are thus more helpful for understanding the effects of different dopants on thermoelectric properties and for pointing out the ideal positions of the dopant energy level for dopant search.

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21. In the current formalism, a temperature-dependent $\kappa_f$ instead changes the figure of merit $zT$, yet makes no notable differences in the relative improvement in efficiency after optimization.
46. It should be noted the difficulty of finding the exact relationship between the impurity level and the dopant element, as well as the exact solubility limits of different dopants, which is excluded in our model.