The optimal Seebeck coefficient for obtaining the maximum power factor in thermoelectrics

P. Pichanusakorn and P. R. Bandaru
Department of Mechanical Engineering, Materials Science Program, University of California, San Diego, La Jolla, California 92039-0411, USA

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We propose the existence of an optimal Seebeck coefficient ($S_{opt}$) for three-, two-, and one-dimensional thermoelectric materials. This assertion is supported by an exhaustive comparison with experimental data of well characterized bulk thermoelectrics, all of which have shown that the power factor is maximized when $S_{opt}$ in the range of 130–187 $\mu$V/K. Our study serves as a quick guideline for the optimization of thermoelectric materials, and makes the point that efforts should be focused on increasing the electrical conductivity ($\sigma$) at the given $S_{opt}$. © 2009 American Institute of Physics. [DOI: 10.1063/1.3147186]

In order to increase the efficiency of thermoelectric materials, a wide range of bulk and nanostructured materials has been investigated. The extensive scope of this research has led to increased complexity and introduction of many variables such as alloy composition, carrier concentration, temperature, and relevant length scales. Since the thermoelectric figure of merit at a particular temperature $T$, $ZT = (S^2\sigma)/k_r + \kappa_lT$, is composed of the Seebeck coefficient ($S$), electrical conductivity ($\sigma$), and thermal conductivity from electrons ($\kappa_e$) and the lattice ($\kappa_l$), each of which responds differently to the variables, the maximization of $ZT$ could be quite a complex task. It would then be necessary and useful to take stock of the situation and identify optimization criteria.

In this paper, we present the conditions under which the power factor ($S^2\sigma$) is maximized in any material, at any temperature and for any given electron gas dimensionality using the reduced Fermi potential, $\eta = E_F - E_F/k_BT$, as the dependent variable. The $\eta$ is correlated with the carrier concentration, $n$, determined by both the $E_F$ (Fermi energy), measured from a ground state energy level $E_F$, and the $T$. Such a criterion allows us to establish the universal and optimal Seebeck coefficient where power factor is maximized. Our conclusions are valid for systems that can be described by the Boltzmann transport equation (BTE), assuming (a) parabolic band structure, (b) single band/subband approximation, and (c) power-law relaxation time of the form $r(E) = \tau_0 E^r$, where $r$ and $\tau_0$ are the scattering constants. Such assumptions are satisfied in most materials, and any slight deviations will not affect the results presented here much.

In most materials, the $\sigma$ and the $S$ are manifestation of carrier (i.e., electrons/holes) diffusion along a concentration gradient, which is established by a gradient of the $E_F$ or $T$, (we neglect other possible contributions, e.g., phonon drag). The transport coefficients are given by the steady-state solution to the BTE as

$$S = \frac{k_B}{e} \left[ \frac{r + D/2 + 1}{D/2} F_{rs(D/2)}(\eta) - \eta \right], \tag{1}$$

where $\sigma = ne\mu$, (2)

where the carrier concentration ($n$) and the electron mobility ($\mu$) are

$$n = \frac{N}{g_D} \frac{(2k_BTm_e)^{D/2}}{\hbar^2} F_{(D/2)-1}(\eta), \quad \text{where } g_D = 2\pi^2 (\text{for } D = 3); \quad D\pi (\text{for } D = 2, 1), \tag{3}$$

$$\mu = \frac{e}{m_\sigma} \eta \frac{r_0(k_BT)^2}{F_{rs(D/2)-1}(\eta)} \frac{F_{rs(D/2)-1}(\eta)}{F_{(D/2)-1}(\eta)}. \tag{4}$$

Here, $F_j(\eta) = \int_0^\infty [x^j \exp(x-\eta+1)] dx$ is the $j$th order Fermi integral and is evaluated numerically. $N$, $m_e$, and $m_\sigma$ refer to number of conduction valleys, density of states (DOS) effective mass, and conductivity effective mass, intrinsic to the material. $D$ and $a$ are the electron gas dimensionality factor ($D=3, 2, 1$ for bulk material, quantum well, and nanowire) and relevant length scale (e.g., quantum well/nanowire thickness) pertinent to the device under consideration, respectively. $k_B$ and $\hbar$ are the Boltzmann and the reduced Planck constants, while $e$ is the unit of elementary charge.

The variation of $S$ and $\sigma$ with $\eta$ is represented through Figs. 1(a)–1(c). From Eq. (1), $S$ as a function of $\eta$ is independent of intrinsic material parameters and temperature, and Fig. 1(a) is universal for a given $D$ and $r$. Since the Seebeck voltage is proportional to the difference of the average electron energy and the lowest energy level (e.g., $E_F$ at 0 K), $|S|$ always increases as $\eta$ is decreased, i.e., if either $T$ is increased or $E_F$ is decreased. Similarly, while both $n$ and $\mu$, from Eqs. (3) and (4), are dependent on material parameters and temperature, their normalized forms, $\eta$ in Fig. 1(b) and $\mu$ in Fig. 1(c), are universally applicable to any material at any temperature. In most instances, $\sigma$ tends to increase with increased $E_F$ (i.e., increased $\eta$ and $n$) and/or increased $T$ (i.e., $n \approx T^{D/2}$). Consequently, when both $n$ and $\sigma$ are increased by doping or biasing, which increases $E_F$ and $\eta$, $|S|$ is decreased. Consolidating the above results, the power factor ($S^2\sigma$) is seen to always increase with increasing $T$ assuming a constant $E_F$ but exhibits a peak at an optimal $E_F$ when constant $T$ is assumed. Now, considering that (i) $S^2\eta\mu$ will be maximized at a unique optimal value of reduced Fermi potential

\[ S^2\eta\mu = \text{maximized at a unique optimal value of reduced Fermi potential} \]
r > 0, i.e., when weakly screened ionized impurity scattering is dominant, the $S^2 \sigma$ may increase without limit due to combined increase in $n$ and $\mu$ being larger than the reduction in $S^2$ as $\eta$ is increased. However, this is not observed in practice as strongly screened scattering, with $r < 0$, dominates at high value of $\eta$ and $n$. When multiple scattering processes are concurrent, $r$ may take intermediate values to those listed in Table I. As the Fermi integral changes gradually with incremental changes in its indices (i.e., $r$), the value of $\eta_{opt}$ will also change gradually and should follow the trend set forth in Table I. Our results now show that for any material, the maximum $S^2 \sigma$ at a given temperature is expected when the $|S|$ is in the range of $130–187 \ \mu\text{V/K}$.

Literature surveys confirm our expectation of maximum $S^2 \sigma$ when $|S|$ approaches $S_{opt}$ in cases where there is sufficient data. An example is shown for a number of $p$- and $n$-Bi$_2$Te$_3$ and $n$-PbTe alloys with various dopant concentrations in Fig. 2. In the range of 75–150 K for Bi$_2$Te$_3$ and at

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**TABLE I.** The value of $\eta_{opt}$ (top line) and $S_{opt}$ (bottom line) for maximum power factor ($S^2 \sigma$) as a function of the scattering constant ($r$) and dimensionality ($D$). $S$ is indeterminate for $D=1$ and $r=-\frac{3}{2}$. For $r=\pm\frac{3}{2}$ ($D=3, 2, 1$) and $r=\pm\frac{1}{2}$ ($D=3$), the $S^2 \sigma$ increases without limit as $\eta$ is increased. The $r$ changes with $D$ for acoustic and optical phonon deformation potential scattering (i.e., ADP and ODP) and strongly screened ionized impurity scattering, as indicated through grouping, as the scattering rate for these processes is proportional to the DOS.

<table>
<thead>
<tr>
<th>$D$</th>
<th>$r$</th>
<th>$S_{opt}$ (\text{\mu V/K})</th>
<th>$\eta_{opt}$ (\text{cm}^3/\text{V}^2\text{K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>$-\frac{3}{2}$</td>
<td>0.67 167</td>
<td>no limit</td>
</tr>
<tr>
<td>3</td>
<td>$+\frac{3}{2}$</td>
<td>2.47 130</td>
<td>no limit</td>
</tr>
</tbody>
</table>

| 2   | $-\frac{1}{2}$ | 0.37 187 | no limit |
|     | $+\frac{1}{2}$ | 2.47 167 | no limit |
| 1   | $\frac{1}{2}$  | $\mu$/$\mu$ | $\mu$/$\mu$ |

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FIG. 1. The variation of (a) the Seebeck coefficient, $|S|$, (b) normalized carrier concentration, $\bar{n}$, and (c) normalized mobility, $\mu$, as a function of the reduced Fermi potential, $\eta$. The equivalent $E_F$ at 300 K is labeled on the top horizontal axis. In the inset table to (a), the $|S|$ is similar for several combinations of $r$ and $D$. In the inset to (b), the carrier concentration normalization constant, $\bar{n}$, is defined. $a'^*$ is the width (in nm) of quantum well or nanowire.

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FIG. 2. The variation of $|S|$ and power factor ($S^2 \sigma$), with temperature (T), for bulk $p$- and $n$-Bi$_2$Te$_3$ (see Ref. 8) and $n$-PbTe (see Ref. 9). The magnitude of $S^2 \sigma$ is indicated by the size and shading of each data point, i.e., a larger size and darker shade indicates larger $S^2 \sigma$. The carrier concentrations are indicated in units of $10^{16}$ cm$^{-3}$. The solid lines serve as a guide for the eye, and connect data of one sample over range of temperature (Bi$_2$Te$_3$ based samples) or of different samples at a particular temperature (PbTe). The inset indicates the maximization of $S^2 \sigma$ at values close to $S_{opt}$. 

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By plotting $S^2 \bar{n} \bar{\mu}$ as a function of $\eta$, the $\eta_{opt}$ has been identified for several values of $D$ and $r$, as listed in Table I. While $\eta_{opt}$ generally increases as $r$ or $D$ is increased, when
300 K for PbTe, respectively, it is clear that the $S^2 \sigma$ is maximized for samples doped such that $|S|$ is close to 130–167 $\mu$V/K. For Bi$_2$Te$_3$, at $T > 150$ K, it is evident that $S^2 \sigma$ increases as $|S|$ decreases toward $S_{\text{opt}}$, and our results predict an even higher $S^2 \sigma$ as the dopant concentration is increased until $|S| > S_{\text{opt}}$. At $T > 250$ K, the onset of bipolar conduction leads to a reduction of both $|S|$ and $S^2 \sigma$ for the Bi$_2$Te$_3$ alloys.

At high temperature, the intrinsic carrier concentration may be comparable to the dopant concentration, and significant electrical conduction could occur by both electrons and holes. Since the $S$ for the electrons (holes) is negative (positive), the average $|S|$ is decreased, which then limits the power factor. The onset temperature of bipolar conduction is lower for materials with a smaller band gap, but increases slightly for samples with larger dopant concentration and lower $|S|$ as observed in Fig. 2. Since bipolar conduction violates our single band assumption, its onset temperature is considered the upper limit for our model. Incidentally, the maximum $S^2 \sigma$ in a particular material would be achieved just below this onset temperature, and when $|S| = S_{\text{opt}}$.

Our ideas are also applicable to other materials such as SiGe, manganese silicide, and metal oxides, e.g., SrTiO$_3$. Similar analysis of $p$-Si$_{x}$Ge$_{1-x}$ data in the 400–600 K range shows maximization of $S^2 \sigma$ as $|S|$ approaches $S_{\text{opt}}$ ($\sim 167$ $\mu$V/K), while $n$-Si$_{x}$Ge$_{1-x}$ also shows increasing $S^2 \sigma$ as $|S|$ is reduced toward $S_{\text{opt}}$. In Fig. 3, the maximum $S^2 \sigma$ of the silicides also occurs at $S_{\text{opt}} \sim 167$ $\mu$V/K, with bipolar conduction above 600 K, while both La- and Nb-doped SrTiO$_3$ also exhibit a maximum $S^2 \sigma$ near $S_{\text{opt}} \sim 167$ $\mu$V/K, at 300 K (Ref. 13) and 1000 K, respectively.

Currently, the highest $S^2 \sigma$ achieved in bulk materials, as seen from Figs. 2 and 3, is approximately 40–45 $\mu$W/cm K$^2$. Such values are consistent with the fact that these materials have similar values of $ZT$ (in the range of 0.8–1) and $\kappa$ ($\sim 1$–4 W/m K). As $|S|$ should be close to $S_{\text{opt}} \sim 167$ $\mu$V/K, we estimate an $\sigma \sim 1800$ $\Omega^{-1}$ cm$^{-1}$ for these materials when optimized for maximum $S^2 \sigma$. However, while the $|S|$ and $\sigma$ are similar, the constituent $n$ and $\mu$ can vary significantly. For example, Bi$_2$Te$_3$ and PbTe possess small $n$ and large $\mu$ due to their small carrier masses, while Si$_{1-x}$Ge$_x$ and SrTiO$_3$ have large $n$ and small $\mu$ due to large carrier mass. Larger power factors exceeding 100 $\mu$W/cm K$^2$ have been reported in PbTe quantum wells and SrTiO$_3$ superlattices, where the enhancement has been ascribed to the increased DOS due to electron confinement. Our predictions of $\eta_{\text{opt}}$ and $S_{\text{opt}}$ should also hold for nanostructures and other modified materials to which a BTE based approach may be applicable, although we were unable to find sufficient experimental data on the variation of $n$ and $E_F$ in these structures.

In conclusion, we have demonstrated, the existence of a universal optimal reduced Fermi potential ($\eta_{\text{opt}}$) and the corresponding optimal Seebeck coefficient ($S_{\text{opt}}$), in the range of 130–187 $\mu$V/K, where the power factor is maximized at any given temperature. Our findings might help to dispel the notion that good thermoelectrics should have very large $|S|$. Instead, it would help to refocus efforts on increasing the $S^2 \sigma$ through an increase in the $\sigma$ while maintaining $|S| \sim S_{\text{opt}}$. Additionally, the identification of $\eta_{\text{opt}}$ will enable easy determination of the optimal carrier concentration, along with minimum quantum well/nanowire thickness required for an enhancement of the power factor over the bulk values.

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