GENERAL EFFICIENCY THEORY OF THERMOELECTRIC CONVERSION

BYUNGKI RYU, JAYWAN CHUNG, AND SUDONG PARK

ABSTRACT. In this Letter, we show thermoelectric conversion efficiency is exactly determined by three independent material parameters $Z_{\text{gen}}$, $\tau$, and $\beta$. Each parameter is a figure of merit hence improving $\tau$ or $\beta$ is an additional way to increase the efficiency. The $Z_{\text{gen}}$ generalizes the traditional figure of merit $zT$. Two degrees of freedom $\tau$ and $\beta$ reflect the temperature gradients of the material properties and are crucial to evaluate the heat current altered by non-zero Thomson heat and asymmetric Joule heat escape. Physical insights on high $\tau$ or $\beta$ materials explain why the single parameter approaches can be inaccurate for efficiency prediction.

A thermoelectric module utilizing the thermoelectric effect for direct conversion of thermal energy into electrical energy is a heat engine [1]. Hence its conversion efficiency is the fraction of input heat current $Q_h$ into the electrical power $P$ delivered to an external load. The power $P$ is simply determined by the electrical device parameters as $P = I(V - IR)$ where $I$, $V$, and $R$ are electric current, total generated voltage, and internal electrical resistance. However the heat current has no such expression due to the nonlinearity of the thermoelectric equation [2, 3, 4, 5] caused by temperature-dependent thermoelectric material properties. As a result, the thermoelectric efficiency $\eta = \frac{P}{Q_h}$ has no analytical expression in terms of the device parameters.

When the material properties are temperature-independent, the single parameter $zT$ suggested by Ioffe [1, 3] is a figure of merit for the thermoelectric efficiency. Its generalization for temperature-dependent material properties, several single average parameters have been suggested [5, 3, 6, 7, 4, 8] but their efficiency prediction can be significantly different from exact numerical one for some practical material curves [5, 3, 6, 7, 4, 9, 8, 10, 11, 12].

In this Letter, we show the input heat current $Q_h$ of a one-dimensional thermoelectric generator model with temperature- and position-dependent material properties is determined by the device parameters and two additional material parameters $\tau$ and $\beta$. As a consequence, the efficiency $\eta$ is determined by three material parameters $Z_{\text{gen}}$, $\tau$, and $\beta$. Here the $Z_{\text{gen}}$ is a generalization of the figure of merit $zT$ and is written by the device parameters; see (6). Although the three material parameters depend on the electrical current $I$, the dependence is negligible when the maximum power or maximum efficiency is considered; see Fig. 2. Treating the $Z_{\text{gen}}$, $\tau$, and $\beta$ as constants, we have an analytical formula for the maximum thermoelectric efficiency as a natural generalization of the constant material property case; see (8). Furthermore, each of our $\tau$ and $\beta$ is a dimensionless figure of merit, hence its improvement is a novel approach to enhance the efficiency, different from improving the $zT$. While the definitions of $\tau$ and $\beta$ in (5) are

1 B.R. and J.C. contributed equally to this work
E-mail addresses: byungkiryu@keri.re.kr, jchung@keri.re.kr.
Date: October 25, 2019.
involved, their approximations give clear insights to improve the $\tau$ and $\beta$, and explain why the single parameter generalizations of $zT$ fail for some materials, as discussed later.

Before deriving the $\tau$ and $\beta$, first we observe the necessity of them. Let $\alpha$, $\rho$, $\kappa$ be temperature-dependent Seebeck coefficient, electrical resistivity, and thermal conductivity of a thermoelectric material, respectively. For a single thermoelectric leg module with length $L$ and cross-sectional area $A$ in one spatial dimension, we may define average parameters of the material properties as $\overline{\alpha} := \frac{1}{A} \int_0^L \alpha \, dx$, $\overline{\rho} := \frac{1}{L} \int_0^L \rho \, dx$, and $\overline{\kappa} := \frac{1}{A} \int_0^L \kappa \, dx$. Here $\Delta T$ is the given temperature difference between the two ends of the generator, $x$ is the spatial coordinate inside the module, $T = T(x)$ is the temperature distribution inside the module, and $1/K$ is the thermal resistance of the module. If the material properties do not depend on $T$, the hot-side input heat current at temperature $T_h$ and the cold-side output heat current at temperature $T_c$ are determined by the average parameters as $Q_h = K \Delta T + I \overline{\alpha}(T_h - \tau \Delta T) - \frac{1}{2} I^2 R(1 + \beta)$ and $Q_c = K \Delta T + I \overline{\alpha}(T_c - \tau \Delta T) + \frac{1}{2} I^2 R(1 - \beta)$.

To derive the $\tau$ and $\beta$, we examine the thermoelectric equation. The thermoelectric effect is expressed in terms of electric current density $J := I/A$ and heat current density $J^Q := Q/A$ as $J = \sigma(E - \alpha \nabla T)$ and $J^Q = \alpha T J - \kappa \nabla T$ where $E$ is the electric field. Applying the charge and energy conservation laws to $J$ and $J^Q$, we can obtain the thermoelastic differential equation of temperature $T$ in a one-dimensional thermoelectric leg without radiative and convective losses:

\[ \frac{d}{dx} \left( \kappa \frac{dT}{dx} \right) - T \frac{d\alpha}{dx} \frac{dT}{dx} J + \rho J^2 = 0, \]

where $x$ is the spatial coordinate inside the leg. The left-hand side of the equation is composed of thermal diffusion, Thomson heat generation, and Joule heat generation. Let $f_T$ be the heat source term of the equation as $f_T(x) := -\frac{dx}{dx} \frac{dT}{dx} J + \rho J^2$. Assuming the $\kappa(x)$ and $f_T(x)$ are known, the linear equation with a Dirichlet boundary condition $T(0) = T_h$, $T(L) = T_c$ can be solved to find an integral equation for $T$ and $\frac{dT}{dx}$:

\begin{align*}
T(x) &= \left( T_h - \frac{K \Delta T}{A} \int_0^x \frac{1}{\kappa(s)} \, ds \right) \\
&\quad + \left( - \int_0^x \frac{F(s)}{\kappa(s)} \, ds + \frac{K \delta T}{A} \int_0^x \frac{1}{\kappa(s)} \, ds \right), \\
\frac{dT}{dx}(x) &= \left( - \frac{K \Delta T}{A} \frac{1}{\kappa(x)} \right) + \left( \frac{F(x)}{\kappa(x)} + \frac{K \delta T}{A} \frac{1}{\kappa(x)} \right),
\end{align*}
where \( F(x) := \int_0^x f_T(s) \, ds \) and \( \delta T := \int_0^L \frac{F(x)}{\kappa(x)} \, dx \). Note that the first equation is of the form \( T = \varphi[T] \) where \( \varphi \) is an integral operator. With this relation, the exact \( T \) can be obtained via fixed-point iteration \( T_{n+1} = \varphi[T_n] \) in most practical cases.

Using the second equation in (3) for \( \frac{dT}{dx}(x) \), we derive an integral equation of the heat currents as

\[
Q_h = I_0 \alpha h T_h - A K_h \left( \frac{dT}{dx} \right)_h = I_0 \alpha h T_h + K (\Delta T - \delta T),
\]

(4)

\[
Q_c = I_0 \alpha c T_c - A K_c \left( \frac{dT}{dx} \right)_c = Q_h - P.
\]

The \( \delta T \) has two contribution terms of \( I \) and \( I^2 \) from double integration of Thomson and Joule heat: since

\[
F_T(x) = I^2 \int_0^x \frac{1}{A \kappa(x)} \, ds - I \int_0^x \frac{1}{A} T(s) \frac{dT}{dT}(T(s)) \, \frac{dT}{dx}(s) \, ds
\]

\[
=: I^2 F_T^{(2)}(x) - I F_T^{(1)}(x),
\]

we have

\[
\delta T = I^2 \int_0^L \frac{F_T^{(2)}(s)}{\kappa(s)} \, ds - I \int_0^L \frac{F_T^{(1)}(s)}{\kappa(s)} \, ds
\]

\[
=: I^2 \delta T^{(2)} - I \delta T^{(1)}.
\]

Rewriting the \( Q_h \) in (4) into the form of (1), we obtain

\[
\tau := 1 - \frac{1}{\bar{\alpha} \Delta T} [2 (\bar{\alpha} - \alpha_h) T_h - K \delta T^{(1)}],
\]

(5)

\[
\beta := 2 R K \delta T^{(2)} - 1.
\]

For \( T \)-independent material properties, \( \delta T^{(2)} = \frac{1}{2 R} \) and \( \delta T^{(1)} = 0 \) so that \( \tau \equiv 0 \) and \( \beta \equiv 0 \), which implies \( Q_h = \frac{Q_c}{\gamma} = K \Delta T + I \bar{\alpha} T_h - \frac{1}{2} I^2 R \), as expected.

Next we define the \( Z_{gen} \) as a generalization of the figure of merit \( zT \). For a given load resistance \( R_L \), the electric current is \( I = \frac{V}{R_L + \gamma} \gamma \) where \( \gamma := R_L/R \). Hence the power delivered to the load is \( P = I^2 R_L = I (V - IR) = \frac{\pi^2 (\Delta T)^2}{\bar{\rho} K} \frac{\gamma}{(1+\gamma)^2} \). With this observation, we define the general device power factor as \( PF_{gen} := \frac{\pi^2}{\bar{\rho}} \) and the general device figure of merit as

\[
Z_{gen} := \left( \frac{V}{\Delta T} \right)^2 R K = \frac{\bar{\alpha}^2}{\bar{\rho} K}.
\]

When the \( PF_{gen} \) is slowly varying on \( I \), the power \( P \) is maximized near \( \gamma = 1 \). The \( Z_{gen} \) is adopted for the simplification of the efficiency formula as in (7). Furthermore, the \( Z_{gen} \) is a generalization of the previous single average parameters. The \( Z_{gen} \) is reduced to the average figure of merit \( z_{av} := \frac{\langle \alpha \rangle^2}{\langle \rho \rangle} \) by Ioffe and Borrego \([1, 11, 12, 13, 14]\) under the constant heat approximation. Here the bracket \( \langle \cdot \rangle \) indicates the averaging over \( T \). The \( Z_{gen} \) is reduced to the engineering figure of merit \( Z_{eng} := \frac{\langle \alpha \rangle^2}{\langle \rho \rangle} \) by Kim et al. \([8]\) under the linear-\( T \) approximation. Similarly, the \( PF_{gen} \) is reduced to the effective power factor \( \frac{\langle \alpha \rangle^2}{\langle \rho \rangle} \) under the constant heat approximation \([11]\).

Finally we consider the thermoelectric conversion efficiency \( \eta := \frac{Q_h - Q_c}{Q_h} \). Using (1), we can verify that the dimensionless heat currents \( Q_h/K \Delta T, Q_c/K \Delta T \), and the efficiency are determined by five parameters \( \Delta T, Z_{gen}, \tau, \beta, \) and \( I \) (or the resistance ratio \( \gamma \)). Thereby,
Given external thermal and electrical condition, the efficiency is exactly determined by three parameters as

\[
\eta(Z_{\text{gen}}, \tau, \beta|T_h, T_c, \gamma) = \frac{\Delta T \gamma}{1 + \frac{1}{1+\gamma}} - \frac{\Delta T}{2} \left(\frac{1}{1+\gamma}\right)^2 (1 + \beta).
\]

Note that the \(\eta\) is monotonically increasing with respect to \(\Delta T, Z_{\text{gen}}, \tau\), and \(\beta\). The monotone increasing property on \(\tau\) and \(\beta\) is easily observed from \(Q_h\) in (1); since \(Q_h\) is monotonically decreasing with respect to \(\tau\) and \(\beta\), the \(\eta = \frac{P}{Q_h}\) is monotonically increasing. Therefore each of \(Z_{\text{gen}}, \tau\), and \(\beta\) is a figure of merit; see Fig. 1.

The efficiency formula (7) is applicable to segmented- and graded-material devices with contact resistance. This is because the computation of \(Z_{\text{gen}}, \tau\), and \(\beta\) in (6) and (5) is based on the integral formulation of temperature distribution in (3): the derivative of \(\alpha\) can be replaced with an integral by part on the Thomson heat as \(\frac{d\alpha}{dT} = d(\alpha T) - \alpha dT\), hence the choice of \(\alpha(x), \rho(x), \kappa(x)\) for such general cases is straightforward. Moreover, as each of \(p\)- and \(n\)-legs performance is simulated, the formula can be extended to compute the thermoelectric efficiency of the module with \(p\)- and \(n\)-leg pairs: \(\eta_{\text{module}} = \frac{P(p) + P(n)}{Q_h(p) + Q_h(n)}\), where \(p\) and \(n\) in parenthesis indicates \(p\)- and \(n\)-type legs, respectively.

The three average parameters \((\overline{\pi}, \overline{\rho}, \overline{\kappa})\) and the three degrees of freedom \((Z_{\text{gen}}, \tau, \beta)\) are slowly varying on \(I\) and \(\gamma\). For the SnSe [15] single-element leg module working at \(T_h = 970.1K\) and \(T_c = 302.7K\), the relative absolute variations for the six parameters is less than 0.1% near the maximum efficiency condition; see Fig. 2. Even for the
segmented leg composed of 0.4 mm low-temperature side segment of BiSbTe \[15\] and 0.6 mm high-temperature side segment of SnSe \[15\] and operating between 970 K and 300 K, calculations reveal that the six parameters are still robust against the change of $I$: the variation is about 5% for $\gamma$ in the range of maximum power case and maximum efficiency case.

The maximum efficiency can be predicted using the three degrees of freedom ($Z_{\text{gen}}$, $\tau$, $\beta$). As the thermoelectric parameters are robust against $I$ and $\gamma$, the $Z_{\text{gen}}$, $\tau$ and $\beta$ can be assumed to be constants. To find an approximate value of the maximum efficiency, we maximize the $\eta$ for $\gamma$ fixing $Z_{\text{gen}}$, $\tau$, $\beta$. Then we have a general maximum efficiency formula:

$$\eta_{\text{max}}^{\text{gen}} := \frac{\Delta T}{T_h} \sqrt{1 + \frac{Z_{\text{gen}} T_m'}{T_m} - \frac{1}{2}},$$

where $T_h := T_h - \tau \Delta T$, $T_c' := T_c - (\tau + \beta) \Delta T$, and $T_m' := (T_h + T_c')/2$. The maximum efficiency occurs when $\gamma$ is near the $\gamma_{\text{opt}} := \sqrt{1 + \frac{Z_{\text{gen}} T_m'}{T_m}}$. The computed efficiency results for 276 published thermoelectric material properties with available temperature ranges [see §1-4 in Supporting Material (SM)] in Fig. 3(a) and (b) validate our general maximum efficiency formula \[8\]. It shows the error in efficiency prediction by the single parameter $zT$ is due to the neglect of the hidden parameters $\tau$ and $\beta$. The general efficiency formula $\eta_{\text{max}}^{\text{gen}}$ in \[8\] is a natural generalization of the traditional efficiency formula of constant property model $\eta_{\text{max}}^{\text{const}} := \frac{\Delta T}{T_h} \sqrt{1 + \frac{Z_{\text{gen}} T_m'}{T_m} - \frac{1}{2}}$, where $z := \frac{\alpha^2}{\rho \kappa}$ and $T_m = (T_h + T_c)/2$. Just replacing the $z, T_m, T_h, T_c$ in $\eta_{\text{max}}^{\text{const}}$ by $Z_{\text{gen}}, T_m', T_h', T_c'$, respectively, our $\eta_{\text{max}}^{\text{gen}}$ is obtained. When material properties are constant ($\tau = \beta = 0$), both formulas are the same.

The compatibility factor \[17\] can be also generalized. The optimal current for maximum efficiency $I_{\text{opt}}$ is close to $I_{\text{opt}}^{\text{gen}} := \frac{V}{R + \frac{1}{\eta_{\text{max}}^{\text{gen}}}}$. The compatibility factor $s = \frac{\sqrt{1 + z T - 1}}{1 + \frac{1}{\eta_{\text{max}}^{\text{gen}}}}$ describes the optimal relative current for maximum efficiency at a given $T$. Hence, a general compatibility factor can be derived as $s_{\text{gen}} := \frac{I_{\text{opt}}}{\Delta T} = \frac{\sqrt{1 + z T - 1}}{\eta_{\text{max}}^{\text{gen}} - 1}$.

A maximum efficiency formula using the dimensionless weight factors of Joule and Thomson heat $W_J$ and $W_T$ is suggested by Kim et al. \[8\]. However, their formula is not a generalization of the traditional efficiency formula; the $W_T = \int_{T_h}^{T_c} \frac{\alpha'\tau}{\alpha T \kappa} \frac{dT'}{dT}$ is not defined when the $\alpha$ is constant because the numerator and denominator vanishes. Also the $W_T$ is not a figure of merit.

While the exact computation of $Z_{\text{gen}}, \tau, \beta$ require temperature distribution inside the module, an accurate one-shot approximation of them is also available (see §5 in SM):

$$Z_{\text{gen}} \approx Z_{\text{gen}}^{(0)} := \frac{\left( \int_{T_h}^{T_c} \alpha(T) \frac{dT}{dT} \right)^2}{\Delta T \int_{T_h}^{T_c} \rho(T) \kappa(T) \frac{dT}{dT}}, \tag{9}$$

$$\tau \approx \tau_{\text{lin}}^{(0)} := -\frac{1}{3} \frac{\alpha_h - \alpha_c}{\alpha_h + \alpha_c},$$

$$\beta \approx \beta_{\text{lin}}^{(0)} := \frac{1}{3} \frac{(\rho \kappa)_{\text{lin}} - (\rho \kappa)_{\text{lin}}}{(\rho \kappa)_{\text{lin}} + (\rho \kappa)_{\text{lin}}}.$$

Here the subscripts $h$ and $c$ denote the evaluation of the function at $T_h$ and $T_c$ respectively. The formulas for $Z_{\text{gen}}^{(0)}, \tau_{\text{lin}}^{(0)}, \beta_{\text{lin}}^{(0)}$ in \[9\] can be derived using two assumptions: (i) $T = T^{(0)}$ where $T^{(0)}$ is the temperature distribution for the $J = 0$ case, i.e. $T^{(0)}$ is a solution of $-\kappa(T^{(0)}) \frac{dT^{(0)}}{dx} = \text{const}$. The superscript (0) means we use the $J = 0$ case. (ii)
the material properties $\alpha$ and $\rho \times \kappa$ are linear with respect to $T$. The subscripts in $\tau_{\text{lin}}^{(0)}$ and $\beta_{\text{lin}}^{(0)}$ emphasize the linearity. In Fig. 3(c)–(e), the strong correlation between the one-shot approximation values and exact numerical values is verified for the 276 thermoelectric material properties from literature. The approximation fails only when the Seebeck coefficient is small and sign-changing with temperature.

The one-shot approximation clarifies the effect of temperature-dependent material properties on the efficiency. For example, because $\tau \approx -\frac{1}{3} \frac{\alpha_h - \alpha_c}{\alpha_h + \alpha_c}$, the efficiency can be enhanced if the $\alpha(T)$ declines more rapidly on $T$, i.e. the Thomson effect as a heat sink becomes stronger. Hence the Thomson effect in efficiency estimation is important as reported previously.

The one-shot approximation also explains why the single parameter generalizations of the $zT$ fail for efficiency prediction of some materials. For example, the peak $zT$ of SnSe materials is significantly greater than that of BiSbTe materials (SnSe has the highest peak $zT$ of 2.6 at 923 K), but the efficiency of BiSbTe is significantly greater than that of the SnSe. This extreme failure of $zT$ can be explained by the figure of merit $\tau$. Consider three imaginary materials imitating BiSbTe-like, SnSe-like, and constant-$z$ materials. For simplicity, we impose two assumptions on their material properties: (i) the $\rho$ and $\kappa$ of them are $T$-independent and they have the same $\bar{\tau}$. (ii) the $\alpha$ of them is linear on temperature; the BiSbTe-like material has linearly decreasing $\alpha$, the SnSe-like material has linearly increasing $\alpha$, and the constant-$z$ material has the constant $\alpha$. Then, as shown in Fig. 4, the peak $zT$ of the SnSe-like material is very high as the $zT$ is proportional to $T^3$. However, due to the temperature-dependent profile of $\alpha$, the $\tau$ of the SnSe-like material is negative while the $\tau$ of BiSbTe-like material is positive; see (5).
Figure 3. Efficiency estimation methods using $\eta_{\text{gen}}^{\text{max}}(zT)$, $\eta_{\text{gen}}^{\text{max}}(Z_{\text{gen}}^{(0)})$, $\eta_{\text{gen}}^{\text{max}}(Z_{\text{gen}}^{(0)}, \tau_{\text{lin}}^{(0)}, \beta_{\text{lin}}^{(0)})$, and $\eta_{\text{gen}}^{\text{max}}(Z_{\text{gen}}, \tau, \beta|I_{\text{opt}})$ are tested for 276 published materials under available temperature range. (a) Comparison of the efficiency estimation methods and numerically computed maximum efficiency. (b) Relative absolute errors between the efficiency estimation methods and the numerical maximum efficiency. (c),(d),(e) Comparison of the one-shot approximation values $Z_{\text{gen}}^{(0)}$, $\tau_{\text{lin}}^{(0)}$, $\beta_{\text{lin}}^{(0)}$ in (9) and the numerical $Z_{\text{gen}}$, $\tau$, $\beta$ when the maximum efficiency is attained.

and [9]. Since the $Z_{\text{gen}}$ is the same for the three materials, the $\tau$ is the main figure of merit which concludes that the BiSbTe-like material has higher maximum efficiency than the SnSe-like material. This example shows a single average parameter is not enough for efficiency prediction and the gradient of material properties can be important.

In summary, three degrees of freedom $Z_{\text{gen}}$, $\tau$ and $\beta$ exactly determine the thermoelectric conversion efficiency. Each degree of freedom is a figure of merit hence improving $\tau$ or $\beta$ is a complementary way to increase the efficiency. The physical insights on high $\tau$ or $\beta$ materials explain why single parameter approaches are not enough for some materials, and can be used to evaluate and optimize the thermoelectric materials and devices.
Figure 4. (a) The $zT$, (b) the $z$, (c) the maximum efficiency and $\tau$ for three imaginary materials which imitates BiSbTe-like, SnSe-like, and constant-$z$ materials. The $\alpha$ of the materials is linear while the $\rho$ and $\kappa$ of them are constant. The materials have the same $\bar{\sigma}$ and $Z_{\text{gen}}$. For working temperature range from 300K to 900K, the highest maximum efficiency is found in the BiSbTe-like material due to the positive $\tau$.

Acknowledgement

B.R. and J.C. contributed equally to this work. This work was supported by KERI primary research program through the NST funded by the MSIT of the Republic of Korea (ROK): grant No. 19-12-N0101-22. It was also supported by the KETEP and the MOTIE of the ROK: grant Nos. 2016200000910, 2017201000830, 2018855000290.

References

[1] Ioffe, A. F. *Semiconductor thermoelements and thermoelectric cooling* (Infosearch, London, 1957).
[2] Chung, J. & Ryu, B. Nonlocal problems arising in thermoelectrics. *Mathematical Problems in Engineering* **2014**, 909078 (2014).
[3] Borrego Larralde, J. M. Optimum impurity concentration in semiconductor thermoelements. Ph.D. thesis, Massachusetts Institute of Technology (1961).
[4] Sherman, B., Heikes, R. & Ure Jr, R. Calculation of efficiency of thermoelectric devices. *Journal of Applied Physics* **31**, 1–16 (1960).
[5] Goupil, C. *Continuum theory and modeling of thermoelectric elements* (John Wiley & Sons, 2015).
[6] Borrego, J. M. Carrier concentration optimization in semiconductor thermoelements. *IEEE Transactions on Electron Devices* **10**, 364–370 (1963).
[7] Borrego, J. M. Approximate analysis of the operation of thermoelectric generators with temperature dependent parameters. *IEEE Transactions on Aerospace* **2**, 4–9 (1964).
[8] Kim, H. S., Liu, W., Chen, G., Chu, C.-W. & Ren, Z. Relationship between thermoelectric figure of merit and energy conversion efficiency. *Proceedings of the National Academy of Sciences* **112**, 8205–8210 (2015).
[9] Sunderland, J. E. & Burak, N. T. The influence of the Thomson effect on the performance of a thermoelectric power generator. *Solid-State Electronics* **7**, 465–471 (1964).
[10] Kim, H. S., Liu, W. & Ren, Z. Efficiency and output power of thermoelectric module by taking into account corrected Joule and Thomson heat. *Journal of Applied Physics* **118**, 115103 (2015).
[11] Armstrong, H. *et al.* Estimating energy conversion efficiency of thermoelectric materials: Constant property versus average property models. *Journal of Electronic Materials* **46**, 6–13 (2017).
[12] Wee, D. Analysis of thermoelectric energy conversion efficiency with linear and nonlinear temperature dependence in material properties. *Energy Conversion and Management* **52**, 3383–3390 (2011).
[13] Burden, R. L. & Faires, J. D. *Numerical analysis* (Brooks/Cole, Cengage Learning, 2010), 9th edn.
[14] Zabrocki, K., Seifert, W. & Müller, E. Effective power factor and thermoelectric figure of merit. In *AIP Conference Proceedings*, vol. 1449, 427–430 (AIP, 2012).
[15] Zhao, L.-D. *et al.* Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals. *Nature* **508**, 373–377 (2014).
[16] Kim, S. I. et al. Dense dislocation arrays embedded in grain boundaries for high-performance bulk thermoelectrics. *Science* **348**, 109–114 (2015).

[17] Snyder, G. J. & Ursell, T. S. Thermoelectric efficiency and compatibility. *Physical Review Letters* **91**, 148301 (2003).

[18] Ybarrondo, L. & Sunderland, J. E. Influence of spatially dependent properties on the performance of a thermoelectric heat pump. *Advanced Energy Conversion* **5**, 383–405 (1965).

[19] Min, G., Rowe, D. & Kontostavlakis, K. Thermoelectric figure-of-merit under large temperature differences. *Journal of Physics D: Applied Physics* **37**, 1301 (2004).
Supplementary Material for “General Efficiency Theory of Thermoelectric Conversion”

ABSTRACT. This Suppelmentary Material (SM) is prepared to support the paper for publication in the Applied Physics Letters, entitled General Efficiency Theory of Thermoelectric Conversion. This SM is composed of following sections. In §1, we give information on full reference list for 276 thermoelectric materials from 263 literatures, which were used for efficiency prediction (Fig. 3) In §2, we describe how to compute numerical ideal maximum efficiency for thermoelectric conversion of single-leg materials in Fig. 3. In §3, we give a statistical analysis for the predicted efficiency of 276 materials (Fig. 3). In §4, we give an efficiency analysis data for selective 18 thermoelectric materials. In §5, we give a full derivation of one-shot approximation forms for $Z_{gen}$, $\tau$, and $\beta$.

§1 Thermoelectric Property (TEP) Data used in Figure 2

In this work, we constructed a dataset of TEPs of 276 materials gathered from 263 literatures [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263] to test our method. To digitize the TEP data, we use the Plot Digitizer [264]. The dataset consists of Seebeck coefficient $\alpha$, electrical resistivity $\rho$ (or electrical conductivity $\sigma$), and thermal conductivity $\kappa$ at measured temperature $T$. For the numerical computation of efficiency, we use the available temperature ranges of the given material: the $T_c$ is defined as the maximum of the lowest measured temperature and $T_h$ is defined as the minimum of the highest measured temperature for given materials.

As shown in Table 1, the 276 materials in our dataset have various base-material groups: 59 Bi$_2$Te$_3$-related materials, 55 PbTe-related materials, 40 skutterudite (SKD), 23 Mg$_2$Si-based materials, 18 GeTe materials, 14 M$_2$Q antifluorite-type chalcogenide materials (where M = Cu, Ag, Au and Q = Te, Se), 12 SnTe-related materials, 11 ABQ$_2$-type materials (where A=Group I, B=Bi, Sb, Q=Te, Se), 8 SnSe-related materials, 7 PbSe-related materials, 7 half-Heusler (HH) materials, 6 SiGe-related materials, 3 In$_4$Se$_3$-related materials, 3 PbS-related materials, 2 oxide materials, 2 clathrate materials, and 6 others. Here the base-material denotes the representative material, not the exact composition. Also note that for the categorizatoin of base materials, the doping element is ignored. For examples, Bi$_2$Te$_3$, Sb$_2$Te$_3$, Bi$_2$Se$_3$ binary and their ternary alloys are categorized as Bi$_2$Te$_3$-related materials. The material doping composition is not denoted in the composition of the base material.
Table 1. TEP Dataset of 276 materials with various material groups. 'Group' and '#mat.' columns represent the group of base material and the number of materials inside the Group.

| Group  | #mat. | Group  | #mat. |
|--------|-------|--------|-------|
| Bi$_2$Te$_3$ | 59 | SnSe | 8 |
| PbTe | 55 | PbSe | 7 |
| SKD | 40 | HH | 7 |
| Mg$_2$Si | 23 | SiGe | 6 |
| GeTe | 18 | In$_4$Se$_3$ | 3 |
| MnQ | 14 | PbS | 3 |
| SnTe | 12 | Oxide | 2 |
| ABQ$_2$ | 11 | clathrate | 2 |
| etc. | 6 | Total | 276 |

§2 Numerical Efficiency Calculation in Figure 3

Thermoelectric phenomena in power module is governed by the thermoelectric differential equation as below:

\[
\frac{d}{dx} \left( \kappa \frac{dT}{dx} \right) - T \frac{d\alpha}{dT} \frac{dT}{dx} J + \rho J^2 = 0.
\]

Numerical maximum efficiencies of ideal thermoelectric modules without thermal loss by radiation or air convection are computed for 276 materials and compared with the peak $zT$ values. The thermoelectric properties are fitted using the piecewise linear interpolation at intermediate temperatures. The exact temperature distribution $T(x)$ of steady state is determined by solving the differential equations of thermoelectricity (see equation-(10)) with Dirichlet boundary conditions; the end point temperature is determined from the available temperature range. Then the thermoelectric performances of a thermoelectric leg with length $L$ and cross sectional area $A$ are calculated as a function of current density $J$ given as $\eta(J) = P/A = \frac{\int_{L}^{h} \rho dx - J \int_{0}^{L} \rho dx}{-\kappa_h \nabla T_h + J \alpha_h L_h}$, where the $P$ and $Q_h$ are the power delivered outside and the hot-side heat current respectively. Then, the maximum of numerical efficiency ($\eta_{\text{max}}$) is calculated, which satisfies the relation $\eta(J) \leq \eta_{\text{max}}$. The reduced efficiency $\eta_{\text{red}}$ is obtained as $\eta_{\text{red}} = \frac{\eta_{\text{max}}}{\eta_{\text{Carnot}}}$, where $\eta_{\text{Carnot}} = \frac{T_h - T_c}{T_h}$. 

§3 Maximum efficiency prediction using $\eta_{\text{gen}}^\text{max}$ in Figure 3

In Figure 3(b), we can observe that the maximum efficiency estimation formula $\eta_{\text{gen}}^\text{max}(Z_{\text{gen}}, \tau, \beta)$ in equation (8) is highly accurate. In Table 2, various statistics on the relative error of maximum efficiency ($\frac{\eta_{\text{gen}}^\text{max} - \eta_{\text{max}}}{\eta_{\text{max}}}$) are given.

Table 2. Statistics on the relative error (RelErr) of the maximum efficiency estimation formula $\eta_{\text{gen}}^\text{max}(Z_{\text{gen}}, \tau, \beta)$. Average (Avg), root mean square (RMS RelErr or StdErr), maximum (max), and minimum (min) of the relative errors are estimated for 276 materials for thermoelectric power generator working at their available temperature.

| 276 materials for power module | Relative error in maximum efficiency formula | $\eta_{\text{gen}}^\text{max}$ | $\eta_{\text{max}}$ | peak $zT$ |
|--------------------------------|--------------------------------------------|-------------------------------|------------------|---------|
| Avg RelErr                     | 0.02%                                      | 1.11%                        | 1.08%            | 1.42%   | 2.29%   | 235%    |
| StdErr (RMS RelErr)            | 0.09%                                      | 1.38%                        | 1.38%            | 1.52%   | 2.47%   | 1854%   |
| max RelErr                     | 1.15%                                      | 5.45%                        | 5.23%            | 5.80%   | 9.96%   | 28835%  |
| min RelErr                     | -0.61%                                     | -1.92%                       | -1.76%           | -1.78%  | -2.48%  | -4%     |

If we use the exact $Z_{\text{gen}}, \tau, \beta$, the standard error (=root mean square of relative errors) of $\eta_{\text{gen}}^\text{max}$ is $9.60 \times 10^{-4}$. Actually, these small value is generated during numerical analysis.

If we use $Z_{\text{gen}}^{(0)}, \tau_{\text{lin}}^{(0)}, \beta_{\text{lin}}^{(0)}$, the standard error is $1.75 \times 10^{-2}$. For the single crystalline SnSe with peak $zT$ of 2.6, the relative error of one shot method is found to be only $6.82 \times 10^{-3}$. However, when we use the different approximation such as linear $T(x)$ or different average scheme for $z$, the error becomes larger than ours due to the non-linearity of $T$ for this material [8].

If we only use the $Z_{\text{gen}}^{(0)}$ with zero $\tau$ and $\beta$, the efficiency is still well predicted with the standard error of $3.37 \times 10^{-2}$. But, in some materials, the error is relatively large due to the neglect of the $\tau$ and $\beta$. The largest relative error of 10% is found for [011], due to the non-vanishing gradient parameters ($\tau = -0.222 \approx \tau^{(0)} = -0.177 \approx \tau_{\text{lin}}^{(0)} = -0.204$, $\beta = 0.2085 \approx \beta^{(0)} = 0.228 \approx \beta_{\text{lin}}^{(0)} = 0.185$, when $T_h = 918K$ and $T_c = 304K$).

§4 Efficiency analysis for selective 18 TE materials

As the representative, we consider 18 thermoelectric materials showing high peak $zT$ values exceeding 1. The TEP curves for temperature dependent Seebeck coefficient, electrical conductivity, and thermal conductivity can be found in the additional excel SM file. The full $zT$ curves of them are shown in Figure 5. Table 3, 4 and 5 contain more information of the materials, including available temperature range, peak $zT$, numerical efficiency, formula efficiency, and the thermoelectric degrees of freedom.
**Selected 18 candidates for segmented-leg TE Material, p-type, chalcogenides +**

**Figure 5.** The $zT$ curves for 18 selected materials. The ‘ref-#' is the reference number.

**Table 3.** Information of 18 selected materials: available temperature range $T_c$ and $T_h$, $\Delta T = T_h - T_c$, peak $zT$, temperature of the peak $zT$.

| ID-# | Material or Process                  | [Reference] | $T_c$ (K) | $T_h$ (K) | peak-$zT$ @T   |
|------|-------------------------------------|-------------|-----------|-----------|----------------|
| ID-1 | (PbTe)(SrTe):Na                     | 1           | 251       | 818       | 1.7 @800K     |
| ID-2 | (PbTe)(SrTe):Na                     | 2           | 302       | 915       | 2.2 @915K     |
| ID-4 | FeNbSb                              | 3           | 301       | 1200      | 1.5 @1200K    |
| ID-5 | Ge$_{0.87}$Pb$_{0.13}$Te            | 4           | 329       | 713       | 2 @673K       |
| ID-6 | Cu$_2$S$_{0.52}$Te$_{0.48}$         | 5           | 299       | 997       | 2.1 @1000K    |
| ID-9 | Bi$_{0.3}$Sb$_{1.7}$Te$_{3}$        | 8           | 298       | 479       | 1.3 @380K     |
| ID-10| (PbTe)$_{(0.96)(MgTe)}_{0.02}$Na$_{0.04}$ | 9         | 307       | 900       | 1.8 @810K     |
| ID-12| BST dislocation                     | 10          | 300       | 480       | 1.86 @320K    |
| ID-17| PbTe$_{0.85}$Se$_{0.15}$            | 13          | 300       | 847       | 1.8 @850K     |
| ID-18| PbTeNa                              | 16          | 300       | 750       | 1.4 @750K     |
| ID-19| BST nanobulk                        | 17          | 300       | 525       | 1.4 @373K     |
| ID-23| PbTeNa, quenching (PNAS)            | 19          | 321       | 759       | 2 @773K       |
| ID-27| sc-SnSe, $b$-axis                  | 22          | 303       | 970       | 2.6 @923K     |
| ID-28| Sn$_{0.985}$Na$_{0.015}$Se          | 23          | 304       | 773       | 2 @773K       |
| ID-34| Bi$_{0.4}$Sb$_{1.6}$Te$_{3}$        | 24          | 303       | 513       | 1.8 @316K     |
| ID-43| KERI BSTAg, HP                     | 36          | 323       | 573       | 1.2 @373K     |
| ID-85| (PbTe)$_{0.8}$Pb$_{0.2}$ + 3at% Na | 73          | 302       | 922       | 2.3 @923K     |
| ID-292| Cu$_{1.94}$Al$_{0.02}$Se (APL)     | 255         | 327       | 1019      | 2.62 @1029K   |
Table 4. Information of 18 selected materials: (a) maximum efficiencies computed using exact numerical method ($T$ is computed by fixed-point iteration, then power, heat and efficiency are computed), maximum efficiencies computed from general maximum efficiency formula $\eta_{\text{max}}^{\text{gen}}$ (see equation (8) in the Manuscript) (b) using exact thermoelectric degrees of freedom (DOFs) with exact $T$ ($Z_{\text{gen}}, \tau, \beta$), (c) using DOFs with $T^{(0)}$ ($Z_{\text{gen}}^{(0)}, \tau^{(0)}, \beta^{(0)}$), (d) using DOFs with one-shot approximation ($Z_{\text{gen}}^{(0)}, \tau_{\text{lin}}^{(0)}, \beta_{\text{lin}}^{(0)}$), (e) using DOFs with only $Z_{\text{gen}}$ while $\tau = \beta = 0$, (f) using DOFs with only $Z_{\text{gen}}^{(0)}$ while $\tau = \beta = 0$, and (g) using the classical efficiency formula for constant TEP using peak $zT$. Note that when we computing the numerical maximum efficiency we calculate the $T$ using the fixed-point iteration with integral equation of $T$ for given $J$. Then $J$ is optimized to maximize the efficiency. To compute $Z_{\text{gen}}$, $\tau$, and $\beta$, we used the $T$ distribution of the $J$ of the maximum efficiency condition. For one shot approximations, we use the equation (9) in the Manuscript.

| ID-#   | (a) exact | $\eta_{\text{max}}$ | $\eta_{\text{gen}}_{\text{max}}$ | $\eta_{\text{const}}_{\text{max}}$ | peak $zT$ |
|--------|-----------|----------------------|-------------------------------|--------------------------------------|-----------|
| ID-1   | 13.7%     | 13.7%                | 14.3%                         | 14.3%                                | 22.9%     |
| ID-2   | 15.9%     | 15.9%                | 16.2%                         | 16.6%                                | 24.9%     |
| ID-4   | 15.3%     | 15.3%                | 15.8%                         | 15.8%                                | 23.8%     |
| ID-5   | 12.5%     | 12.6%                | 12.9%                         | 13%                                  | 18%       |
| ID-6   | 10.5%     | 10.5%                | 10.7%                         | 11.1%                                | 25.9%     |
| ID-9   | 8.4%      | 8.4%                 | 8.4%                          | 8.4%                                 | 9.2%      |
| ID-10  | 13.8%     | 13.8%                | 14.2%                         | 14.6%                                | 22%       |
| ID-12  | 9.1%      | 9.1%                 | 9.1%                          | 9.1%                                 | 11.2%     |
| ID-17  | 12.6%     | 12.7%                | 13%                           | 12.9%                                | 21.5%     |
| ID-18  | 10.4%     | 10.4%                | 10.8%                         | 10.9%                                | 16.9%     |
| ID-19  | 9.9%      | 9.9%                 | 10%                           | 10%                                  | 11.1%     |
| ID-23  | 11.6%     | 11.6%                | 12.1%                         | 12.2%                                | 19.6%     |
| ID-27  | 7.1%      | 7.1%                 | 7.1%                          | 7.1%                                 | 27.9%     |
| ID-28  | 16.2%     | 16.2%                | 16.9%                         | 16.7%                                | 20.9%     |
| ID-34  | 10.1%     | 10.1%                | 10.1%                         | 10%                                  | 12.2%     |
| ID-43  | 8.2%      | 8.2%                 | 8.2%                          | 8.1%                                 | 10.3%     |
| ID-85  | 17.6%     | 17.6%                | 18.1%                         | 18.5%                                | 25.6%     |
| ID-292 | 14.3%     | 14.3%                | 14.9%                         | 14.9%                                | 27.5%     |
Table 5. Information of 18 selected materials: exact value and one-shot approximation of thermoelectric degrees of freedom.

| ID-#  | $Z_{\text{gen}}$ | $\tau$  | $\beta$  | $Z_{\text{gen}}^{(0)}$ | $\tau_{\text{lin}}^{(0)}$ | $\beta^{(0)}_{\text{lin}}$ |
|-------|------------------|---------|---------|--------------------------|----------------------------|--------------------------|
| ID-1  | 0.0015           | -0.253  | 0.192   | 0.0016                   | -0.207                     | 0.199                    |
| ID-2  | 0.0018           | -0.186  | 0.068   | 0.0018                   | -0.152                     | 0.074                    |
| ID-4  | 0.0010           | -0.164  | 0.197   | 0.0011                   | -0.141                     | 0.203                    |
| ID-5  | 0.0022           | -0.227  | 0.094   | 0.0023                   | -0.168                     | 0.105                    |
| ID-6  | 0.0008           | -0.253  | 0.027   | 0.0008                   | -0.208                     | 0.028                    |
| ID-9  | 0.0029           | -0.019  | 0.135   | 0.0029                   | -0.017                     | 0.136                    |
| ID-10 | 0.0015           | -0.192  | 0.102   | 0.0015                   | -0.161                     | 0.107                    |
| ID-12 | 0.0033           | 0.030   | 0.177   | 0.0033                   | 0.032                      | 0.178                    |
| ID-17 | 0.0014           | -0.231  | 0.109   | 0.0015                   | -0.189                     | 0.112                    |
| ID-18 | 0.0014           | -0.271  | 0.167   | 0.0014                   | -0.214                     | 0.172                    |
| ID-19 | 0.0028           | -0.015  | 0.189   | 0.0028                   | -0.013                     | 0.190                    |
| ID-23 | 0.0017           | -0.254  | 0.138   | 0.0017                   | -0.194                     | 0.142                    |
| ID-27 | 0.0005           | 0.082   | -0.379  | 0.0005                   | 0.086                      | -0.382                   |
| ID-28 | 0.0025           | -0.154  | 0.217   | 0.0026                   | -0.118                     | 0.225                    |
| ID-34 | 0.0032           | 0.033   | 0.164   | 0.0032                   | 0.036                      | 0.166                    |
| ID-43 | 0.0019           | 0.028   | 0.186   | 0.0019                   | 0.029                      | 0.187                    |
| ID-85 | 0.0021           | -0.179  | 0.079   | 0.0021                   | -0.146                     | 0.095                    |
| ID-292| 0.0013           | -0.211  | 0.178   | 0.0014                   | -0.166                     | 0.187                    |
§5 One-shot approximation $Z_{\text{gen}}^{(0)}$, $\tau_{\text{lin}}^{(0)}$ and $\beta_{\text{lin}}^{(0)}$

The exact forms of $Z_{\text{gen}}$, $\tau$ and $\beta$ are written as

\begin{align}
Z_{\text{gen}} &:= \frac{(V/\Delta T)^2}{RK} = \frac{\pi^2}{\rho \kappa}, \\
\tau &:= \frac{1}{\alpha \Delta T} \left[ (\overline{\alpha} - \alpha_h) T_h - K \delta T^{(1)} \right], \\
\beta &:= \frac{2}{R} K \delta T^{(2)} - 1.
\end{align}

The computation of $Z_{\text{gen}}$, $\tau$ and $\beta$ requires the exact temperature distribution. But they can be estimated directly from the material properties. In this section we derive an approximate formula for $Z_{\text{gen}}$, $\tau$ and $\beta$. The idea is to use the temperature distribution for $J = 0$, which is similar to the exact temperature distribution because most devices induce small $J$ due to the small $\varepsilon T$. Let $T^{(0)}$ be the temperature distribution for $J = 0$ and define

\begin{align}
\rho^{(0)} &:= \frac{1}{L} \int_0^L \rho(T^{(0)}(x)) \, dx = \frac{A}{L} R^{(0)}, \\
\kappa^{(0)} &:= \frac{1}{L} \int_0^L \frac{1}{\kappa(T^{(0)}(x))} \, dx = \frac{A}{L} \frac{1}{K^{(0)}}.
\end{align}

From the thermoelectric differential equation (10) with $J = 0$, we can check that

\begin{equation}
-\kappa(T^{(0)}(x)) \frac{dT^{(0)}}{dx}(x) = \kappa^{(0)} \Delta T \frac{1}{L}.
\end{equation}

Hence

\begin{align*}
\int_{T_c}^{T_h} \rho(T) \kappa(T) \, dT &= \int_{T_c}^{T_h} \rho(T^{(0)}(x)) \left( -\frac{\Delta T}{L} \kappa^{(0)} \right) \frac{dx}{dT^{(0)}} \, dT^{(0)} \\
&= \frac{\Delta T}{L} \int_0^L \rho(T^{(0)}(x)) \kappa^{(0)} \, dx \\
&= \Delta T \frac{1}{R} \rho^{(0)} \kappa^{(0)}.
\end{align*}

Replacing $T$ with $T^{(0)}$ in $Z_{\text{gen}} = \frac{\pi^2}{\rho \kappa}$, we have an one-shot approximation for $Z_{\text{gen}}$:

\begin{equation}
Z_{\text{gen}} \approx \frac{\alpha^2}{\rho^{(0)} \kappa^{(0)}} = \frac{\left( \int \alpha \, dT \right)^2}{\Delta T \int \rho \kappa \, dT} =: Z_{\text{gen}}^{(0)}.
\end{equation}

To approximate $\tau$, we assume the Seebeck coefficient is a linear function of $T$:

$$\alpha(T) \approx \alpha_{\text{lin}}(T) := \alpha_h + \left( \frac{\alpha_c - \alpha_h}{T_c - T_h} \right) (T - T_h).$$

In this way we can observe the effect of the gradient of $\alpha$ on $\tau$ more clearly. Since the $\tau$ in (12) has $K \delta T^{(1)}$ term, we estimate a relevant term:

\begin{align*}
F_{(1)}^{(s)}(s) \approx & \int_0^s \frac{1}{A} T \frac{d\alpha_{\text{lin}}}{dT}(T(x)) \frac{dT}{dx} \, dx = \int_{T_h}^{s} \frac{1}{A} T \frac{\alpha_c - \alpha_h}{T_c - T_h} \, dT \\
&= \frac{1}{2} \frac{\alpha_c - \alpha_h}{T_c - T_h} (T(s)^2 - T_h^2) =: F_{(1)}(T(s)).
\end{align*}
Using \(-\kappa \frac{dT}{dx} \approx \overline{\kappa}^{(0)} \frac{\Delta T}{L}\) from \([14]\),

\[
\delta T^{(1)} = \int_0^L \frac{F_T^{(1)}(x)}{\kappa(x)} \, dx \approx - \int_0^L \frac{\overline{F}^{(1)}(T(x))}{\overline{\kappa}(0)} \frac{L}{\Delta T} \frac{dT}{dx} \, dx
\]

\[
= \frac{1}{\overline{\kappa}(0)} \Delta T \int_{T_h}^{T_c} \overline{F}^{(1)}(T) \, dT
\]

\[
= \frac{1}{2 \overline{K}^{(0)} \Delta T} \frac{1}{T_c - T_h} \frac{1}{3} (\Delta T)^2 (-3T_h + \Delta T)
\]

\[
= \frac{\alpha_c - \alpha_h}{6 \overline{K}^{(0)}} (-3T_h + \Delta T) =: \delta \overline{T}^{(1)}
\]

where \(\overline{K}^{(0)} := \frac{4}{L} \overline{\kappa}^{(0)}\). Therefore we have an one-shot approximation for \(\tau\):

\[
\tau \approx - \frac{1}{3 \alpha_h + \alpha_c} \cdot \gamma_{\text{lin}}^{(0)}.
\]

To approximate \(\beta\), we assume the \(\rho \kappa\) is a linear function of \(T\):

\[
(\rho \kappa)(T) \approx (\rho \kappa)_{\text{lin}}(T) := (\rho \kappa)_h + \left( \frac{(\rho \kappa)_c - (\rho \kappa)_h}{T_c - T_h} \right) (T - T_h).
\]

Using \(-\kappa \frac{dT}{dx} \approx \overline{\kappa}^{(0)} \frac{\Delta T}{L}\) from \([14]\), we approximate relevant terms for \(\beta\):

\[
F_T^{(2)}(s) = \int_0^s \frac{1}{A^2} (\rho \kappa)(T(x)) \frac{1}{\kappa(x)} \, dx \approx - \frac{L}{A^2 \overline{\kappa}(0) \Delta T} \int_0^s (\rho \kappa)_{\text{lin}}(T(x)) \frac{dT}{dx} \, dx
\]

\[
= - \frac{L}{A^2 \overline{\kappa}(0) \Delta T} \int_{T_h}^{T(s)} (\rho \kappa)_{\text{lin}}(T) \, dT
\]

\[
= - \frac{L}{A^2 \overline{\kappa}(0) \Delta T} \left[ (\rho \kappa)_h(T(s) - T_h) + \frac{1}{2} \frac{(\rho \kappa)_c - (\rho \kappa)_h}{T_c - T_h} (T(s) - T_h)^2 \right]
\]

\[
=: F^{(2)}(T(s))
\]

hence

\[
\delta T^{(2)} = \int_0^L \frac{F_T^{(2)}(x)}{\kappa(x)} \, dx \approx \int_0^L \frac{\overline{F}^{(2)}(T(x))}{\overline{\kappa}(0)} \left( - \frac{L}{\overline{\kappa}(0) \Delta T} \right) \frac{dT}{dx} \, dx
\]

\[
= - \frac{L}{\overline{\kappa}(0) \Delta T} \int_{T_h}^{T_c} \overline{F}^{(2)}(T) \, dT
\]

\[
= \frac{1}{6 \overline{K}^{(0)}^2} (2(\rho \kappa)_h + (\rho \kappa)_c) =: \delta \overline{T}^{(2)}.
\]

Therefore we have an one-shot approximation for \(\beta\):

\[
\beta \approx \frac{2}{A^2 \overline{\kappa}^{(0)}} \overline{K}^{(0)} \delta \overline{T}^{(2)} - 1 = \frac{1}{3 \overline{\rho}^{(0)} \overline{\kappa}^{(0)}} (2(\rho \kappa)_h + (\rho \kappa)_c) - 1
\]

\[
\approx \frac{1}{2} \frac{((\rho \kappa)_h + (\rho \kappa)_c)}{2(\rho \kappa)_h + (\rho \kappa)_c} (2(\rho \kappa)_h + (\rho \kappa)_c) - 1
\]

\[
= \frac{1}{3} \frac{(\rho \kappa)_h - (\rho \kappa)_c}{(\rho \kappa)_h + (\rho \kappa)_c} =: \beta_{\text{lin}}^{(0)}.
\]
In summary, we have one-shot approximations as following:

$$Z_{\text{gen}} \approx Z_{\text{gen}}^{(0)} = \left( \frac{\int \alpha dT}{\Delta T} \right)^2, \quad \rho \tau \approx \rho \tau^{(0)} \equiv -\frac{1}{3} \frac{\alpha_h - \alpha_c}{\alpha_h + \alpha_c}, \quad \beta \approx \beta^{(0)} \equiv \frac{1}{3} \frac{\rho_h \kappa_h - \rho_c \kappa_c}{\rho_h \kappa_h + \rho_c \kappa_c}.$$  

The one-shot approximation derived above is accurate enough for many cases. See Figure 6, where we compare the exact $Z_{\text{gen}}$, $\rho \tau$, $\beta$ with their one-shot approximations for 276 materials.

Furthermore, these one-shot approximations can be used to predict the performance of segmented devices. In Figure 7, we consider a two-stage segmented leg with no contact resistance. The segmented leg consists of SnSe [22] for hot side and BiSbTe [17] for cold side. The exact temperature distribution $T$ inside the leg shows a jump of the gradient at $x = 0.6$ due to the inhomogeneity of the material; see Figure 7(b). Despite the nonlinearity of the $T$, the one-shot approximation using $Z_{\text{gen}}^{(0)}$, $\rho \tau^{(0)}$, and $\beta^{(0)}$, which does not use the exact $T$, shows high accuracy in prediction of thermoelectric performances; see Figure 7(c)-(f). The relative error is high near $\gamma = 0$, where the reaction term is large due to the large electric current and thereby large Joule heat. For large $\gamma$, the error is negligible. Near the $\gamma = 1$, the error is acceptable; the relative error is less than 5%. The one-shot approximation predicts the maximum efficiency to be 7.68% while the exact value is 7.53%. 
Figure 6. Estimation of thermoelectric degrees of freedom for 276 materials. Numerical $Z_{\text{gen}}$, $\tau$, $\beta$ are computed using the exact $T$ at the maximum efficiency. One-shot approximations $Z_{\text{gen}}^{(0)}$, $\tau^{(0)}$, $\beta^{(0)}$ are computed using the $T^{(0)}$ for $J = 0$. Going further, the $\tau_{\text{lin}}^{(0)}$ and $\beta_{\text{lin}}^{(0)}$ are computed by assuming the linearity of $\alpha$ and $\rho\kappa$; see [9] for their explicit formula.
Figure 7. The thermoelectric performances of a two-stage segmented leg predicted by the one-shot approximation. The numerical exact values are computed by fixed-point iteration and the one-shot values are computed using \( Z_{\text{gen}}^{(0)}, \tau_{\text{lin}}^{(0)}, \) and \( \beta_{\text{lin}}^{(0)} \); see [9] for the explicit one-shot formula. (a) The geometry of the segmented leg: SnSe \[22\] and BiSbTe \[17\] are used for hot and cold-side materials. \( T_h = 970K \) and \( T_c = 300K \) are used. (b) Exact temperature distribution obtained by solving the integral equation (??) of \( T \) with fixed-point iteration. (c) Power delivered outside, (d) heat current at the hot side, (e) efficiency, and (f) relative errors in power, heat current, efficiency between the numerical value and the one-shot approximation.
ACKNOWLEDGEMENT

B.R. and J.C. contributed equally to this work. The most of the work is already reported in arXiv:1810.11148, entitled “Thermoelectric Efficiency has Three Degrees of Freedom”.

REFERENCES

[1] Biswas, K. et al. Strained endotaxial nanostructures with high thermoelectric figure of merit. Nat Chem 3, 160–166 (2011).
[2] Biswas, K. et al. High-performance bulk thermoelectrics with all-scale hierarchical architectures. Nature 489, 414–418 (2012).
[3] Fu, C. et al. Realizing high figure of merit in heavy-band $p$-type half-Heusler thermoelectric materials. Nat Commun 6, 8144 (2015).
[4] Gelbstein, Y., Davidow, J., Girard, S. N., Chung, D. Y. & Kanatzidis, M. Controlling metallurgical phase separation reactions of the Ge$_{0.87}$Pb$_{0.13}$Te alloy for high thermoelectric performance. Adv. Energy Mater. 3, 815–820 (2013).
[5] He, Y. et al. Ultrahigh thermoelectric performance in mosaic crystals. Adv. Mater. 27, 3639–3644 (2015).
[6] Heremans, J. P. et al. Enhancement of thermoelectric efficiency in PbTe by distortion of the electronic density of states. Science 321, 554–557 (2008).
[7] Hsu, K. F. et al. Cubic AgPb$_{m}$SbTe$_{2+m}$: Bulk thermoelectric materials with high figure of merit. Science 303, 818–821 (2004).
[8] Hu, L.-P. et al. Shifting up the optimum figure of merit of $p$-type bismuth telluride-based thermoelectric materials for power generation by suppressing intrinsic conduction. NPG Asia Mater 6, e88 (2014).
[9] Hu, X. et al. Power generation from nanostructured PbTe-based thermoelectrics: comprehensive development from materials to modules. Energy Environ. Sci. 9, 517–529 (2016).
[10] Kim, S. I. et al. Dense dislocation arrays embedded in grain boundaries for high-performance bulk thermoelectrics. Science 348, 109–114 (2015).
[11] Lin, S. et al. Tellurium as a high-performance elemental thermoelectric. Nat Commun 7, 10287 (2016).
[12] Liu, W.-S. et al. Thermoelectric property studies on Cu-doped $n$-type Cu$_{2}$Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ nanocomposites. Advanced Energy Materials 1, 577–587 (2011).
[13] Liu, W. et al. Convergence of conduction bands as a means of enhancing thermoelectric performance of $n$-type Mg$_{2}$Si$_{1−x}$Sn$_{x}$ solid solutions. Phys. Rev. Lett. 108, 166601 (2012).
[14] Pan, Y. & Li, J.-F. Thermoelectric performance enhancement in $n$-type Bi$_{2}$Te$_{3}$ alloys owing to nanoscale inhomogeneity combined with a spark plasma-textured microstructure. NPG Asia Mater 8, e275 (2016).
[15] Pei, Y. et al. Convergence of electronic bands for high performance bulk thermoelectrics. Nature 473, 66–69 (2011).
[16] Pei, Y., LaLonde, A., Iwanaga, S. & Snyder, G. J. High thermoelectric figure of merit in heavy hole dominated PbTe. Energy Environ. Sci. 4, 2085–2089 (2011).
[17] Poudel, B. et al. High-thermoelectric performance of nanostructured bismuth antimony telluride bulk alloys. Science 320, 634–638 (2008).
[18] Rhyee, J.-S. et al. Peierls distortion as a route to high thermoelectric performance in In$_4$Se$_{3−δ}$ crystals. Nature 459, 965–968 (2009).
[19] Wang, H. et al. Right sizes of nano-and microstructures for high-performance and rigid bulk thermoelectrics. Proceedings of the National Academy of Sciences 111, 10949–10954 (2014).
[20] Zhao, L.-D. et al. Raising the thermoelectric performance of $p$-type PbS with endotaxial nanostructuring and valence-band offset engineering using CdS and ZnS. J. Am. Chem. Soc. 134, 16327–16336 (2012).
[21] Zhao, L.-D. et al. Thermoelectrics with earth abundant elements: High performance $p$-type PbS nanostructured with SrS and CaS. J. Am. Chem. Soc. 134, 7902–7912 (2012).
[22] Zhao, L.-D. et al. Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals. Nature 508, 373–377 (2014).
[23] Zhao, L.-D. et al. Ultrahigh power factor and thermoelectric performance in hole-doped single-crystal SnSe. Science 347(6219), 561–565 (2015).

[24] Cui, J. L. et al. Thermoelectric properties of Ag-doped n-type (Bi$_2$Te$_3$)$_{0.9}$(Bi$_{2-x}$Ag$_x$Se$_3$)$_{0.1}$ (x=0–0.4) alloys prepared by spark plasma sintering. Journal of Solid State Chemistry 180, 1158–1162 (2007).

[25] Cui, J. L. et al. Crystal structure analysis and thermoelectric properties of p-type pseudo-binary (Al$_2$Te$_3$)$_{1-x}$Bi$_{3-x}$Sb$_x$Te$_3$)$_{1-x}$ (x=0–0.2) alloys prepared by spark plasma sintering. Journal of Alloys and Compounds 460, 426–431 (2008).

[26] Eum, A.-Y. et al. Transport and thermoelectric properties of Bi$_2$Te$_2$S$_{0.3}$ prepared by mechanical alloying and hot pressing. Journal of the Korean Physical Society 66, 1726–1731 (2015).

[27] Fan, S. et al. p-type Bi$_0.4$Sb$_{1.6}$Te$_3$ nanocomposites with enhanced figure of merit. Applied Physics Letters 96, 182104 (2010).

[28] Han, M.-K., Kim, S., Kim, H.-Y. & Kim, S.-J. An alternative strategy to construct interfaces in bulk thermoelectric material: nanostructured heterophase Bi$_2$Te$_3$/Bi$_2$S$_3$. RSC Adv. 3, 4673–4679 (2013).

[29] HSU, H. C., HUANG, J.-Y. & HUANG, T.-K. Enhancing figure of merit of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ through nano-composite approach. China Steel Technical Report 27, 57–63 (2014).

[30] Zheng, Y. et al. Mechanically robust BiSbTe alloys with superior thermoelectric performance: A case study of stable hierarchical nanostructured thermoelectric materials. Adv. Energy Mater. 5, 1401391 (2014).

[31] Hu, L. et al. Tuning multiscale microstructures to enhance thermoelectric performance of n-type bismuth-telluride-based solid solutions. Adv. Energy Mater. 5, 1500411 (2015).

[32] Hwang, S. et al. Enhancing the thermoelectric properties of p-type bulk Bi-Sb-Te nanocomposites via solution-based metal nanoparticle decoration. Journal of Elec Materi. 42, 1411–1416 (2013).

[33] Ko, J. et al. Nanostructured thermoelectric Bi$_2$Te$_2$S$_{0.3}$ with ultralow phonon transport prepared from chemically exfoliated nanoplatelets. Journal of Materials Chemistry A 1, 12791 (2013).

[34] Zhang, Q. et al. Improved thermoelectric performance of silver nanoparticle-dispersed Bi$_2$Te$_3$ composites deriving from hierarchical two-phased heterostructure. Adv. Funct. Mater. 25, 966–976 (2015).

[35] Zhao, X. B. et al. Bismuth telluride nanotubes and the effects on the thermoelectric properties of nanotube-containing nanocomposites. Applied Physics Letters 86, 062111 (2005).

[36] Lee, J. K. et al. Control of thermoelectric properties through the addition of Ag in the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ alloy. Electron. Mater. Lett. 6, 201–207 (2010).

[37] Lee, K.-H. et al. Enhancement of the thermoelectric performance of Bi$_{0.4}$Sb$_{1.6}$Te$_3$ alloys by In and Ga doping. Journal of Elec Materi. 42, 1617–1621 (2013).

[38] Lee, D. S. et al. Crystal structure, properties and nanostructuring of a new layered chalcogenide semiconductor, Bi$_2$MnTe$_4$. CrystEngComm 15, 5532–5538 (2013).

[39] Yan, X. et al. Experimental studies on anisotropic thermoelectric properties and structures of n-type Bi$_2$Te$_2$S$_{0.3}$. Nano Lett. 10, 3373–3378 (2010).

[40] Lee, G.-E. et al. Preparation and thermoelectric properties of doped Bi$_2$Te$_3$-Bi$_2$Se$_3$ solid solutions. Journal of Elec Materi. 43, 1650–1655 (2013).

[41] Lee, G.-E. et al. Preparation and thermoelectric properties of Bi$_2$Te$_3$-Bi$_2$Se$_3$ solid solutions. Journal of the Korean Physical Society 64, 1416–1420 (2014).

[42] Lee, G.-E. et al. Preparation and thermoelectric properties of iodine-doped Bi$_2$Te$_3$-Bi$_2$Se$_3$ solid solutions. Journal of the Korean Physical Society 65, 696–701 (2014).

[43] Lee, G.-E. et al. Preparation and thermoelectric properties of n-type Bi$_2$Te$_2$S$_{0.3}$Dm. Journal of Elec Materi. 44, 1579–1584 (2014).

[44] Lee, G.-E. et al. Thermoelectric properties of I-doped Bi$_2$Te$_2$S$_{0.3}$Se$_{0.15}$ solid solutions. Journal of the Korean Physical Society 64, 1692–1696 (2014).

[45] Sumithra, S. et al. Enhancement in thermoelectric figure of merit in nanostructured Bi$_2$Te$_3$ with semimetal nano’inclusions. Adv. Energy Mater. 1, 1141–1147 (2011).

[46] Lukas, K. C., Liu, W. S., Ren, Z. F. & Opeil, C. P. Transport properties of Ni, Co, Fe, Mn doped Cu$_{0.01}$Bi$_2$Te$_2$S$_{0.3}$ for thermoelectric device applications. Journal of Applied Physics 112, 054509 (2012).

[47] Min, Y. et al. Surfactant-free scalable synthesis of Bi$_2$Te$_3$ and Bi$_2$Se$_3$ nanoflakes and enhanced thermoelectric properties of their nanocomposites. Advanced Materials 25, 1425–1429 (2013).
Puneet, P. et al. Ovsyannikov, S. V. et al. Dong, Y., McGuire, M. A., Malik, A.-S. & DiSalvo, F. J. Transport properties of undoped and Br-
Bali, A., Wang, H., Snyder, G. J. & Mallik, R. C. Thermoelectric properties of indium doped
Bali, A., Kim, I.-H., Rogl, P. & Mallik, R. C. Thermoelectric properties of two-phase PbTe with
Androulakis, J., Lee, Y., Todorov, I., Chung, D.-Y. & Kanatzidis, M. High-temperature thermo-
Wang, S., Li, H., Lu, R., Zheng, G. & Tang, X. Metal nanoparticle decorated
Ahn, K. et al. Improvement in the thermoelectric figure of merit
Androulakis, J. et al. Preparation and thermoelectric transport properties of high-performance p-type Bi$_2$Te$_3$ with layered nanostructure. Applied Physics Letters 90, 012102 (2007).
Wang, S., Li, H., Lu, R., Zheng, G. & Tang, X. Metal nanoparticle decorated n-type Bi$_2$Te$_3$-based materials with enhanced thermoelectric performances. Nanotechnology 24, 285702 (2013).
Wu, F. et al. Thermoelectric properties of Ce-doped n-type Ce$_x$Bi$_{2−x}$Te$_2$Sb$_y$Se$_{0.3}$ nanocomposites. Phys. Status Solidi A 210, 1183–1189 (2013).
Yelgel, ¨O. C. & Srivastava, G. P. Thermoelectric properties of n-type Bi$_2$(Te$_{0.85}$Se$_{0.15}$)$_3$ single crystals doped with CuBr and Sb$_3$. Phys. Rev. B 85, 125207 (2012).
Zhang, G. et al. Rational synthesis of ultrathin n-type Bi$_2$Te$_3$ nanowires with enhanced thermoelectric properties. Nano Lett. 12, 56–60 (2012).
Wei, P. et al. Minimum thermal conductivity in weak topological insulators with bismuth-based stack structure. Adv. Funct. Mater. 26, 5360–5367 (2016).
Lan, J., Lin, Y.-H., Liu, Y., Xu, S. & Nan, C.-W. High thermoelectric performance of nanostructured In$_2$O$_3$-based ceramics. Journal of the American Ceramic Society 95, 2465–2469 (2012).
Yu, C. et al. Preparation and thermoelectric properties of inhomogeneous bismuth telluride alloyed nanorods. Journal of Alloys and Compounds 570, 86–93 (2013).
Kosuña, A. et al. Enhanced thermoelectric performance of In-substituted GeSb$_6$Te$_{10}$ with homologous structure. APL Materials 2, 086102 (2014).
Schoele, M. et al. Thermoelectric properties of lead halogenide core shell nanostructures. ACS Nano 5, 8541–8551 (2011).
Ahn, K., Li, C., Uher, C. & Kanatzidis, M. G. Improvement in the thermoelectric figure of merit by La/Ag cosubstitution in PbTe. Chemistry of Materials 21, 1361–1367 (2009).
Ahn, K. et al. Exploring resonance levels and nanostructuring in the PbTe-CdTe system and enhancement of the thermoelectric figure of merit. J. Am. Chem. Soc. 132, 5227–5235 (2010).
Ahn, K. et al. Enhanced thermoelectric properties of p-type nanostructured PbTe-MTe (M = Cd, Hg) materials. Energy Environ. Sci. 6, 1529–1537 (2013).
Androulakis, J. et al. Thermoelectric enhancement in PbTe with K or Na codoping from tuning the interaction of the light- and heavy-hole valence bands. Phys. Rev. B 82, 115209 (2010).
Androulakis, J., Lee, Y., Todorov, I., Chung, D.-Y. & Kanatzidis, M. High-temperature thermoelectric properties of n-type PbSe doped with Ga, In, and Pb. Physical Review B 83 (2011).
Bali, A., Kim, I.-H., Rogl, P. & Mallik, R. C. Thermoelectric properties of two-phase PbTe with indium inclusions. Journal of Electronic Materials (2013).
Bali, A., Wang, H., Snyder, G. J. & Mallik, R. C. Thermoelectric properties of indium doped PbTe$_{1−x}$Se$_x$ alloys. Journal of Applied Physics 116, 033707 (2014).
Wu, D. et al. Superior thermoelectric performance in PbTe-PbS pseudo-binary: Extremely low thermal conductivity and modulated carrier. Energy & Environmental Science 8, 2056 (2015).
Dong, Y., McGuire, M. A., Malik, A.-S. & DiSalvo, F. J. Transport properties of undoped and Br-doped PbTe sintered at high-temperature and pressure ≥ 4.0 GPa. Journal of Solid State Chemistry 182, 2602–2607 (2009).
Dow, H. S. et al. Effect of Ag or Sb addition on the thermoelectric properties of PbTe. Journal of Applied Physics 108, 113709 (2010).
Falkenbach, O., Hartung, D., Klar, P. J., Koch, G. & Schlecht, S. Thermoelectric properties of nanostructured bismuth-doped lead telluride Bi$_x$(PbTe)$_{1-x}$ prepared by co-ball-milling. *Journal of Electronic Materials* **43**, 1674–1680 (2014).

Fan, H. *et al.* Enhanced thermoelectric performance of PbSe co-doped with Ag and Sb. *Journal of Alloys and Compounds* **639**, 106–110 (2015).

Fang, H., Feng, T., Yang, H., Ruan, X. & Wu, Y. Synthesis and thermoelectric properties of compositional-modulated lead telluride bismuth telluride nanowire heterostructures. *Nano Letters* **13**, 2058–2063 (2013).

Jaworski, C. M. *et al.* Valence-band structure of highly efficient $p$-type thermoelectric PbTe-PbS alloys. *Phys. Rev. B* **87**, 045203 (2013).

Jian, Z. *et al.* Significant band engineering effect of YbTe for high performance thermoelectric PbTe. *J. Mater. Chem. C* **3**, 12410–12417 (2015).

Keiber, T., Bridges, F., Sales, B. & Wang, H. Complex role for thallium in PbTe:Tl from local probe studies. *Physical Review B* **87** (2013).

Kim, M.-S., Lee, W.-J., Cho, K.-H., Ahn, J.-P. & Sung, Y.-M. Spinodally decomposed PbSe-PbTe nanoparticles for high-performance thermoelectrics: Enhanced phonon scattering and unusual transport behavior. *ACS Nano* **10**, 7197–7207 (2016).

Lee, J. K. *et al.* Improvement of thermoelectric properties through controlling the carrier concentration of Ag$_x$Pb$_{1-x}$Sb$_{20}$ alloys by Sb addition. *Electron. Mater. Lett.* **8**, 659–663 (2012).

Lee, Y. *et al.* Contrasting role of antimony and bismuth dopants on the thermoelectric performance of lead selenide. *Nat Commun* **5** (2014).

Li, X. *et al.* Enhanced thermoelectric properties of (PbTe)$_{0.88}$(PbS)$_{0.12}$ composites by Bi doping. *Journal of Alloys and Compounds* **547**, 86–90 (2013).

Li, Z.-Y. *et al.* PbTe-based thermoelectric nanocomposites with reduced thermal conductivity by SiC nanodispersion. *Applied Physics Letters* **104**, 113905 (2014).

Liu, J., Wang, X. & Peng, L. Effect of annealing on thermoelectric properties of eutectic PbTeSi$_2$Te$_3$ composite with self-assembled lamellar structure. *Intermetallics* **41**, 63–69 (2013).

Lo, S.-H., He, J., Biswas, K., Kanatzidis, M. G. & Dravid, V. P. Phonon scattering and thermal conductivity in $p$-type nanostructured PbTe-BaTe Bulk thermoelectric materials. *Adv. Funct. Mater.* **22**, 5175–5184 (2012).

Lu, P.-X., Qu, L.-B. & Cheng, Q.-H. Enhancement of thermoelectric figure of merit in binary-phased La$_{0.3}$Ce$_{0.37}$Fe$_{0.3}$Co$_{0.12}$-PbTe materials. *Journal of Alloys and Compounds* **558**, 50–55 (2013).

Pei, Y., Heinz, N. A., LaLonde, A. & Snyder, G. J. Combination of large nanostructures and complex band structure for high performance thermoelectric lead telluride. *Energy Environ. Sci.* **4**, 3640–3645 (2011).

Pei, Y., Lensch-Falk, J., Toberer, E. S., Medlin, D. L. & Snyder, G. J. High thermoelectric performance in PbTe due to large nanoscale Ag$_x$Te precipitates and La doping. *Advanced Functional Materials* **21**, 241–249 (2011).

Pei, Y., May, A. F. & Snyder, G. J. Self-tuning the carrier concentration of PbTe/Ag$_x$Te composites with excess Ag for high thermoelectric performance. *Advanced Energy Materials* **1**, 291–296 (2011).

Pei, Y. *et al.* Stabilizing the optimal carrier concentration for high thermoelectric efficiency. *Adv. Mater.* **23**, 5674–5678 (2011).

Pei, Y., LaLonde, A. D., Wang, H. & Snyder, G. J. Low effective mass leading to high thermoelectric performance. *Energy Environ. Sci.* **5**, 7963–7969 (2012).

Pei, Y., Wang, H., Gibbs, Z. M., LaLonde, A. D. & Snyder, G. J. Thermopower enhancement in Pb$_{1-x}$Mn$_x$Te alloys and its effect on thermoelectric efficiency. *NPG Asia Mater* **4**, e28 (2012).

Pei, Y. *et al.* Optimum carrier concentration in $n$-type PbTe thermoelectrics. *Adv. Energy Mater.* **4**, 1400486 (2014).

Poundeu, P. F. P. *et al.* High thermoelectric figure of merit and nanostructuring in bulk $p$-type Na$_{1-x}$Pb$_x$Bi$_2$Te$_3$$_{1+2}$. *Angewandte Chemische International Edition* **45**, 3835–3839 (2006).

Rawat, P. K., Paul, B. & Banerji, P. Thermoelectric properties of PbS$_{0.5}$Te$_{0.5}$$_{1.5}$ (PbI$_2$) with endotaxial nanostructures: a promising $n$-type thermoelectric material. *Nanotechnology* **24**, 215401 (2013).

Wang, H. *et al.* Large enhancement in the thermoelectric properties of Pb$_{0.98}$Na$_{0.02}$Te by optimizing the synthesis conditions. *Journal of Materials Chemistry A* **1**, 11269 (2013).

Wang, H., Gibbs, Z. M., Takagiwa, Y. & Snyder, G. J. Tuning bands of PbSe for better thermoelectric efficiency. *Energy Environ. Sci.* **7**, 804–811 (2014).
[101] Wu, H. J. et al. Broad temperature plateau for thermoelectric figure of merit $ZT > 2$ in phase-separated PbTe$_{0.7}$S$_{0.3}$. Nat Commun 5, 4515 (2014).

[102] Wu, H. et al. Strong enhancement of phonon scattering through nanoscale grains in lead sulfide thermoelectrics. NPG Asia Mater 6, e108 (2014).

[103] Yamini, S. A. et al. Heterogeneous distribution of sodium for high thermoelectric performance of $p$-type multiphase lead-chalcogenides. Adv. Energy Mater. 5, 1501047 (2015).

[104] Yang, H. et al. Enhanced thermoelectric properties in bulk nanowire heterostructure-based nanocomposites through minority carrier blocking. Nano Lett. 15, 1349 (2015).

[105] Zebarjadi, M. et al. Power factor enhancement by modulation doping in bulk nanocomposites. Nano Lett. 11, 2225–2230 (2011).

[106] Zhang, Q. et al. Enhancement of thermoelectric figure-of-merit by resonant states of aluminium doping in lead selenide. Energy & Environmental Science 5, 5246 (2012).

[107] Zhang, Q. et al. Heavy doping and band engineering by potassium to improve the thermoelectric figure of merit in $p$-type PbTe, PbSe, and PbTe$_{1-y}$Se$_y$. J. Am. Chem. Soc. 134, 10031–10038 (2012).

[108] Zhang, Q. et al. Effect of aluminium on the thermoelectric properties of nanostructured PbTe. Nanotechnology 24, 345705 (2013).

[109] Zhang, Q. et al. Enhancement of thermoelectric performance of $n$-type PbSe by Cr doping with optimized carrier concentration. Adv. Energy Mater. 5, 1401977 (2015).

[110] Al Rahal Al Orabi, R. et al. Band degeneracy, low thermal conductivity, and high thermoelectric figure of merit in SnTe-CaTe alloys. Chem. Mater. 28, 376–384 (2015).

[111] Banik, A., Shenoy, U. S., Anand, S., Waghmare, U. V. & Biswas, K. Mg alloying in SnTe facilitates valence band convergence and optimizes thermoelectric properties. Chem. Mater. 27, 581–587 (2015).

[112] Banik, A., Shenoy, U. S., Saha, S., Waghmare, U. V. & Biswas, K. High power factor and enhanced thermoelectric performance of SnTe-AgInTe$_2$: Synergistic effect of resonance level and valence band convergence. Journal of the American Chemical Society 138, 13068–13075 (2016).

[113] Banik, A. & Biswas, K. AgI alloying in SnTe boosts the thermoelectric performance via simultaneous valence band convergence and carrier concentration optimization. Journal of Solid State Chemistry 242, 43–49 (2016).

[114] Chen, C.-L., Wang, H., Chen, Y.-Y., Day, T. & Snyder, J. Thermoelectric properties of $p$-type polycrystalline SnSe doped with Ag. J. Mater. Chem. A 2, 11171–11176 (2014).

[115] Chen, Y.-X. et al. Understanding of the extremely low thermal conductivity in high-performance polycrystalline SnSe through potassium doping. Adv. Funct. Mater. 26, 6836–6845 (2016).

[116] Leng, H.-Q., Zhou, M., Zhao, J., Han, Y.-M. & Li, L.-F. The thermoelectric performance of anisotropic SnSe doped with Na. RSC Adv. 6, 9112–9116 (2016).

[117] Pei, Y. et al. Interstitial point defect scattering contributing to high thermoelectric performance in SnTe. Adv. Electron. Mater. 2, 1600019 (2016).

[118] Tan, G. et al. High thermoelectric performance of $p$-type SnTe via a synergistic band engineering and nanostructuring approach. J. Am. Chem. Soc. 136, 7006–7017 (2014).

[119] Tan, G. et al. Codoping in SnTe: Enhancement of thermoelectric performance through synergy of resonance levels and band convergence. J. Am. Chem. Soc. 137, 5100–5112 (2015).

[120] Tan, G. et al. Valence band modification and high thermoelectric performance in SnTe heavily alloyed with MnTe. J. Am. Chem. Soc. 137, 11507–11516 (2015).

[121] Tang, G. et al. Realizing high figure of merit in phase-separated polycrystalline Sn$_{1-x}$Pb$_x$Se. Journal of the American Chemical Society 138, 13647–13654 (2016).

[122] WANG, X. et al. Thermoelectric properties of Eu- and Na-substituted SnTe. Journal of Rare Earths 33, 1175–1181 (2015).

[123] Zhang, Q. et al. High thermoelectric performance by resonant dopant indium in nanostructured SnTe. Proceedings of the National Academy of Sciences 110, 13261–13266 (2013).

[124] Zhou, M. et al. Optimization of thermoelectric efficiency in SnTe: the case for the light band. Phys. Chem. Chem. Phys. 16, 20741–20748 (2014).

[125] Guan, X. et al. Thermoelectric properties of SnSe compound. Journal of Alloys and Compounds 643, 116–120 (2015).

[126] Suzuki, Y. & Nakamura, H. A supercell approach to the doping effect on the thermoelectric properties of SnSe. Phys. Chem. Chem. Phys. 17, 29647–29654 (2015).
[127] Fahrenbauer, F., Souchay, D., Wagner, G. & Oeckler, O. High thermoelectric figure of merit values of germanium antimony tellurides with kinetically stable cobalt germanide precipitates. J. Am. Chem. Soc. 137, 12633–12638 (2015).

[128] Gelbstein, Y., Dashevsky, Z. & Dariel, M. In-doped Pb0.5Sn0.5Te p-type samples prepared by powder metallurgical processing for thermoelectric applications. Physica B: Condensed Matter 396, 16–21 (2007).

[129] Gelbstein, Y., Dashevsky, Z. & Dariel, M. Powder metallurgical processing of functionally graded p-Pb1−mSn0.5Te materials for thermoelectric applications. Physica B: Condensed Matter 391, 256–265 (2007).

[130] Gelbstein, Y., Rosenberg, Y., Sadia, Y. & Dariel, M. P. Thermoelectric properties evolution of spark plasma sintered (Ge0.6Pb0.5Sn0.4)Te following a spinodal decomposition. The Journal of Physical Chemistry C 114, 13126–13131 (2010).

[131] Hazan, E. et al. Effective electronic mechanisms for optimizing the thermoelectric properties of GeTe-rich alloys. Adv. Electron. Mater. 1, 1500228 (2015).

[132] Kusz, B., Miruszelewski, T., Bochentyn, B., Lapiński, M. & Karczewski, J. Structure and thermoelectric properties of Te-Ag-Ge-Sb (TAGS) materials obtained by reduction of melted oxide substrates. Journal of Elec Materi 45, 1085–1093 (2016).

[133] Lee, J. K. et al. Influence of Mn on crystal structure and thermoelectric properties of GeTe compounds. Electron. Mater. Lett. 10, 813–817 (2014).

[134] Schröder, T. et al. Nanostructures in Te/Sb/Ge/Ag (TAGS) thermoelectric materials induced by phase transitions associated with vacancy ordering. Inorg. Chem. 53, 7722–7729 (2014).

[135] Schröder, T. et al. TAGS-related indium compounds and their thermoelectric properties—the solid solution series (GeTe)xAgIn5Sb1−yTe2 (x = 1–2; y = 0.5 and 1). J. Mater. Chem. A 2, 6384–6395 (2014).

[136] Williams, J. B., Lara-Curzio, E., Cakmak, E., Watkins, T. & Morelli, D. T. Enhanced thermoelectric performance driven by high-temperature phase transition in the phase change material Ge4SbTe5. Journal of Materials Research FirstView, 1–6 (2015).

[137] Wu, D. et al. Origin of the high performance in GeTe-based thermoelectric materials upon Bi2Te3 doping. J. Am. Chem. Soc. 136, 11412–11419 (2014).

[138] Aikebaier, Y., Kurosaki, K., Muta, H. & Yamanaka, S. Effect of (Pb,Ge)Te addition on the phase stability and the thermoelectric properties of AgSbTe2. MRS Online Proceedings Library 1267, 1267–DD04–11 (2010).

[139] Chen, Y., He, B., Zhu, T. J. & Zhao, X. B. Thermoelectric properties of non-stoichiometric AgSbTe2 based alloys with a small amount of GeTe addition. J. Phys. D: Appl. Phys. 45, 115302 (2012).

[140] Dow, H. S. et al. Thermoelectric properties of AgPb1−mSbTe1+m/2 (12 ≤ m ≤ 26) at elevated temperature. Journal of Applied Physics 105, 113703 (2009).

[141] Drymiotis, F., Day, T. W., Brown, D. R., Heinz, N. A. & Snyder, G. J. Enhanced thermoelectric performance in the very low thermal conductivity Ag2Se0.5Te0.5. Applied Physics Letters 103, 143906 (2013).

[142] Du, B., Li, H. & Tang, X. Effect of Ce substitution for Sb on the thermoelectric properties of AgSbTe2 compound. Journal of Electronic Materials 43, 2384–2389 (2014).

[143] Guin, S. N. & Biswas, K. Sb deficiencies control hole transport and boost the thermoelectric performance of p-type AgSbSe2. J. Mater. Chem. C 3, 10415–10421 (2015).

[144] Han, M.-K., Androulakis, J., Kim, S.-J. & Kanatzidis, M. G. Lead-free thermoelectrics: High figure of merit in p-type AgSb1−xSnxTe1−x/2. Adv. Energy Mater. 2, 157–161 (2012).

[145] He, Z. et al. Synthesis and thermoelectric properties of Mn-doped AgSbTe2 compounds. Chinese Phys. B 21, 106101 (2012).

[146] Hong, A. J. et al. Anomalous transport and thermoelectric performances of CuAgSe compounds. Solid State Ionics 261, 21–25 (2014).

[147] Liu, X., Jin, D. & Liang, X. Enhanced thermoelectric performance of n-type transformable AgBiSe2 polymorphs by indium doping. Applied Physics Letters 109, 133901 (2016).

[148] Mohanraman, R. et al. Influence of nanoscale Ag2Te precipitates on the thermoelectric properties of the Sn doped P-type AgSbTe2 compound. APL Materials 2, 096114 (2014).

[149] Pei, Y., Heinz, N. A. & Snyder, G. J. Alloying to increase the band gap for improving thermoelectric properties of Ag2Te. J. Mater. Chem. 21, 18256–18260 (2011).
[150] Wang, H., Li, J.-F., Zou, M. & Sui, T. Synthesis and transport property of AgSbTe$_2$ as a promising thermoelectric compound. *Applied Physics Letters* **93**, 202106 (2008).

[151] Wu, H.-j. *et al.* State of the art Ag$_{50-x}$Sb$_x$Se$_{50-y}$Te$_y$ alloys: Their high $zT$ values, microstructures and related phase equilibria. *Acta Materialia* **93**, 38–45 (2015).

[152] Zhang, S. N., Zhu, T. J., Yang, S. H., Yu, C. & Zhao, X. B. Improved thermoelectric properties of AgSbTe$_2$ based compounds with nanoscale Ag$_2$Te in situ precipitates. *Journal of Alloys and Compounds* **499**, 215–220 (2010).

[153] Aizawa, T., Song, R. & Yamamoto, A. Solid state synthesis of ternary thermoelectric magnesium alloy. *Materials Transactions* **47**, 1058–1065 (2006).

[154] Akasaka, M., Iida, T., Nishio, K. & Takanashi, Y. Composition dependent thermoelectric properties of sintered Mg$_{515-x-y}$Ge$_x$ (x=0 to 1) initiated from a melt-grown polycrystalline source. *Thin Solid Films* **515**, 8237–8241 (2007).

[155] Akasaka, M. *et al.* Non-wetting crystal growth of Mg$_5$Si by vertical Bridgman method and thermoelectric characteristics. *Journal of Crystal Growth* **304**, 196–201 (2007).

[156] Cheng, X., Farahi, N. & Kleinke, H. Mg$_5$Si-based materials for the thermoelectric energy conversion. *JOM* **68**, 2680–2687 (2016).

[157] Duan, X., Hu, K., Kuang, J., Jiang, Y. & Yi, D. Effects of Ag-doping on thermoelectric properties of Ca$_{2-x}$Ag$_x$Si alloys. *Journal of Electronic Materials* **46**, 2986–2989 (2016).

[158] Kajikawa, T. *et al.* Thermoelectric figure of merit of impurity doped and hot-pressed magnesium silicide elements. In *Seventeenth International Conference on Thermoelectrics. Proceedings ICT98 (Cat. No.98TH8365)*, 362–369 (1998).

[159] Liu, W. *et al.* n-type thermoelectric material Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ for high power generation. *PNAS* **112**, 3269–3274 (2015).

[160] Luo, W. *et al.* Fabrication and thermoelectric properties of Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions by solid state reaction and spark plasma sintering. *Materials Science and Engineering: B* **157**, 96–100 (2009).

[161] Mars, K., Ihou-Mouko, H., Pont, G., Tobola, J. & Scherrer, H. Thermoelectric properties and electronic structure of Bi- and Ag-doped Mg$_2$Si$_{1-x}$Ge$_x$ compounds. *Journal of Electronic Materials* **38**, 1360–1364 (2009).

[162] Noda, Y., Kon, H., Furukawa, Y., Nishida, I. A. & Masumoto, K. Temperature dependence of thermoelectric properties of Mg$_2$Si$_{0.6}$Ge$_{0.4}$. *Mater. Trans., JIM* **33**, 851–855 (1992).

[163] Tani, J.-i. & Kido, H. Thermoelectric properties of Bi-doped Mg$_2$Si semiconductors. *Physica B: Condensed Matter* **364**, 218–224 (2005).

[164] Tani, J.-i. & Kido, H. Thermoelectric properties of P-doped Mg$_2$Si semiconductors. *Japanese Journal of Applied Physics* **46**, 3309–3314 (2007).

[165] Tani, J.-i. & Kido, H. Thermoelectric properties of Sb-doped Mg$_2$Si semiconductors. *Intermetallics* **15**, 1202–1207 (2007).

[166] Yang, M. J., Luo, W. J., Shen, Q., Jiang, H. Y. & Zhang, L. M. Preparation and thermoelectric properties of Bi-doped Mg$_2$Si nanocomposites. *Advanced Materials Research* **66**, 17–20 (2009).

[167] Yin, K. *et al.* Optimization of the electronic band structure and the lattice thermal conductivity of solid solutions according to simple calculations: a canonical example of the Mg$_2$Si$_{1-x}$Sn$_{x}$Ge$_y$ ternary solid solution. *Chemistry of Materials* **28**, 5538–5548 (2016).

[168] Zhang, Q. *et al.* High figures of merit and natural nanostructures in Mg$_2$Si$_{0.4}$Sn$_{0.6}$ based thermoelectric materials. *Applied Physics Letters* **93**, 102109 (2008).

[169] Zhang, Q. *et al.* *In situ* synthesis and thermoelectric properties of La-doped Mg$_2$(Si, Sn) composites. *Journal of Physics D: Applied Physics* **41**, 185103 (2008).

[170] Zhang, L. *et al.* Suppressing the bipolar contribution to the thermoelectric properties of Mg$_2$Si$_{0.4}$Sn$_{0.6}$ by Ge substitution. *Journal of Applied Physics* **117**, 155103 (2015).

[171] Zhao, X. B. *et al.* Synthesis of nanocomposites with improved thermoelectric properties. *Journal of Electronic Materials* **38**, 1017–1024 (2009).

[172] Joshi, G. *et al.* Enhanced thermoelectric figure-of-merit in nanostructured p-type silicon germanium bulk alloys. *Nano Lett.* **8**, 4670–4674 (2008).

[173] Tang, J. *et al.* Holey silicon as an efficient thermoelectric material. *Nano Letters* **10**, 4279–4283 (2010).

[174] Wang, X. W. *et al.* Enhanced thermoelectric figure of merit in nanostructured n-type silicon germanium bulk alloy. *Applied Physics Letters* **93**, 193121 (2008).
Ahm, K. et al. Improvement in the thermoelectric performance of the crystals of halogen-substituted In₄Se₄-xHₓO₃ (H = F, Cl, Br, I): Effect of halogen-substitution on the thermoelectric properties in In₄Se₄, J. Mater. Chem. A 2, 5730–5736 (2012).

Bhatt, R. et al. Thermoelectric performance of layered Sr₂TiSe₂ above 300 K. J. Phys.: Condens. Matter 26, 445002 (2014).

Fu, C., Zhu, T., Liu, Y., Xie, H. & Zhao, X. Band engineering of high performance p-type FeNbSb based half-Heusler thermoelectric materials for figure of merit zT > 1. Energy & Environmental Science 8, 216–220 (2015).

Kraemer, D. et al. High thermoelectric conversion efficiency of MgAgSb-based material with hot-pressed contacts. Energy Environ. Sci. 8, 1299–1308 (2015).

Krez, J. et al. Long-term stability of phase-separated half-Heusler compounds. Phys. Chem. Chem. Phys. 17, 29854–29858 (2015).

Liu, W.-S., Zhang, B.-P., Li, J.-F. & Zhao, L.-D. Thermoelectric property of fine-grained CoSb₃ skutterudite compound fabricated by mechanical alloying and spark plasma sintering. J. Phys. D: Appl. Phys. 40, 566 (2007).

Mudryk, Y. et al. Thermoelectricity of clathrate I Si and Ge phases. J. Phys.: Condens. Matter 14, 7991 (2002).

Shi, X. et al. Low thermal conductivity and high thermoelectric figure of merit in n-type BaₓYbₓCo₄Sb₁₂ double-filled skutterudites. Applied Physics Letters 92, 182101 (2008).

Bai, S. et al. Enhanced thermoelectric performance of dual-element-filled skutterudites BaₓCeₓCo₄Sb₁₂. Acta Materialia 57, 3135–3139 (2009).

Bao, S., Yang, J., Fan, X. & Duan, X. Effect of processing parameters on formation and thermoelectric properties of La₀.₄Fe₀.₄Co₀.₄Sb₁₂ skutterudite by MA-HP method. Journal of Alloys and Compounds 476, 802–806 (2009).

Chitroub, M., Besse, F. & Scherrer, H. Thermoelectric properties of semi-conducting compound CoSb₃ doped with Pd and Te. Journal of Alloys and Compounds 467, 31–34 (2009).

Dong, N. et al. HPHT synthesis and thermoelectric properties of CoSb₃ and Fe₀.₆Co₀.₄Sb₁₂ skutterudites. Journal of Alloys and Compounds 480, 882–884 (2009).

Duan, B., Zhai, P., Liu, L., Zhang, Q. & Ruan, X. Synthesis and high temperature transport properties of Te-doped skutterudite compounds. Journal of Materials Science: Materials in Electronics 23, 1817–1822 (2012).

Dyck, J. S. et al. Thermoelectric properties of the n-type filled skutterudite Ba₀.₃Co₀.₇Sb₁₂ doped with Ni. Journal of Applied Physics 91, 3698–3705 (2002).

He, Z. et al. Thermoelectric properties of hot-pressed skutterudite CoSb₃. Journal of Applied Physics 101, 053713 (2007).

He, Q. et al. The great improvement effect of pores on ZT in Co₁₋ₓNiₓSb₃ system. Applied Physics Letters 93, 042108 (2008).

Laufek, F., Navratil, J., Plášil, J., Plecháček, T. & Drašar, Č. Synthesis, crystal structure and transport properties of skutterudite-related CoSn₁₋ₓSe₁₋ₓ. Journal of Alloys and Compounds 479, 102–106 (2009).

Li, X. Y. et al. Thermoelectric properties of Te-doped CoSb₃ by spark plasma sintering. Journal of Applied Physics 98, 083702 (2005).

Liang, T. et al. Ultra-fast synthesis and thermoelectric properties of Te doped skutterudites. J. Mater. Chem. A 2, 17914–17918 (2014).

Liu, W.-S., Zhang, B.-P., Li, J.-F., Zhang, H.-L. & Zhao, L.-D. Enhanced thermoelectric properties in CoSb₃₋ₓTeₓ alloys prepared by mechanical alloying and spark plasma sintering. Journal of Applied Physics 102, 103717 (2007).

Mallick, R. C. Transport properties of Sn-filled and Te-doped CoSb₃ skutterudites. Metals and Materials International 14, 615–620 (2008).

Mallick, R. C. et al. Thermoelectric properties of Fe₀.₂Co₀.₈Sb₁₂₋ₓTeₓ skutterudites. Acta Materialia 61, 6698–6711 (2013).

Mi, J. L., Zhao, X. B., Zhu, T. J. & Tu, J. P. Thermoelectric properties of Yb₀.₁₅Co₀.₈Sb₁₂ based nanocomposites with CoSb₃ nano-inclusion. Journal of Physics D: Applied Physics 41, 205403 (2008).

Pei, Y., Bai, S., Zhao, X., Zhang, W. & Chen, L. Thermoelectric properties of Eu₀.₅Co₀.₅Sb₁₂ filled skutterudites. Solid State Sciences 10, 1422–1428 (2008).
[199] Qiu, P. F. et al. High-temperature electrical and thermal transport properties of fully filled skutterudites RFe$_4$Sb$_{12}$ (R = Ca, Sr, Ba, La, Ce, Pr, Nd, Eu, and Yb). *Journal of Applied Physics* **109**, 063713 (2011).

[200] Rogl, G., Grytsiv, A., Bauer, E., Rogl, P. & Zehetbauer, M. Thermoelectric properties of novel skutterudites with didymium: DD$_y$(Fe$_{1-x}$Co$_x$)$_4$Sb$_{12}$ and DD$_y$(Fe$_{1-x}$Ni$_x$)$_4$Sb$_{12}$. *Intermetallics* **18**, 57–64 (2010).

[201] Rogl, G., Grytsiv, A., Rogl, P., Bauer, E. & Zehetbauer, M. A new generation of p-type didymium skutterudites with high ZT. *Intermetallics* **19**, 546–555 (2011).

[202] Rogl, G. et al. n-type skutterudites (R,Ba,Yb)$_y$Co$_4$Sb$_{12}$ (R = Sr, La, Mn, DD, SrMm, SrDD) approaching ZT $\approx$ 2.0. *Acta Materialia* **63**, 30–43 (2014).

[203] Rogl, G. et al. New bulk p-type skutterudites DD$_{0.7}$Fe$_{2.7}$Co$_{1.3}$Sb$_{12}$–x$_2$ (X = Ge, Sn) reaching ZT $>$ 1.3. *Acta Materialia* **91**, 227–238 (2015).

[204] Sales, B. C., Mandrus, D. & Williams, R. K. Filled skutterudite antimonides: A new class of thermoelectric materials. *Science* **272**, 1325–1328 (1996).

[205] Shi, X. et al. Multiple-filled skutterudites: High thermoelectric figure of merit through separately optimizing electrical and thermal transports. *Journal of the American Chemical Society* **133**, 7837–7846 (2011).

[206] Stiewe, C. et al. Nanostructured Co$_{1-x}$Ni$_x$(Sb$_{1-y}$Te$_y$)$_3$ skutterudites: Theoretical modeling, synthesis and thermoelectric properties. *Journal of Applied Physics* **97**, 044317 (2005).

[207] Su, X. et al. Structure and transport properties of double-doped CoSb$_{2.75}$Ge$_{0.25}$–xSb$_x$ (x = 0.125–0.20) with in situ nanostructure. *Chem. Mater.* **23**, 2948–2955 (2011).

[208] Tang, X. F., Chen, L. D., Goto, T., Hirai, T. & Yuan, R. Z. Synthesis and thermoelectric properties of filled skutterudite compounds Ce$_y$Fe$_2$Co$_{4-x}$Sb$_{12}$ by solid state reaction. *Journal of Materials Science* **36**, 5435–5439 (2001).

[209] Xu, C., Duan, B., Ding, S., Zhai, P. & Zhang, Q. Thermoelectric properties of skutterudites Co$_4$–xNi$_x$Sb$_{11.9–y}$Te$_y$Se$_{0.1}$, Journal of Electronic Materials **43**, 2224–2228 (2014).

[210] Yang, K. et al. Synthesis and thermoelectric properties of double-filled skutterudites Ce$_y$Yb$_{0.5–x}$Co$_{2.5}$Sb$_{12}$. *Journal of Alloys and Compounds* **467**, 528–532 (2009).

[211] Zhang, J. et al. High-pressure synthesis of phonon-glass electron-crystal featured thermoelectric Li$_x$Co$_3$Sb$_{12}$. *Acta Materialia* **60**, 1246–1251 (2012).

[212] Zhao, W. et al. Enhanced thermoelectric performance in barium and indium double-filled skutterudite bulk materials via orbital hybridization induced by indium filler. *Journal of the American Chemical Society* **131**, 3713–3720 (2009).

[213] Zhou, L., Qiu, P., Uher, C., Shi, X. & Chen, L. Thermoelectric properties of p-type Yb$_2$La$_{0.5}$Fe$_{2.5}$Co$_{0.5}$Sb$_{12}$ double-filled skutterudites. *Intermetallics* **32**, 209–213 (2013).

[214] Bali, A. et al. Thermoelectric properties of In and I doped PbTe. *Journal of Applied Physics* **120**, 175101 (2016).

[215] Ding, G., Si, J., Yang, S., Wang, G. & Wu, H. High thermoelectric properties of n-type Cd-doped PbTe prepared by melt spinning. *Scripta Materialia* **122**, 1–4 (2016).

[216] Jo, S. et al. Simultaneous improvement in electrical and thermal properties of interface-engineered BiSbTe nanostructured thermoelectric materials. *Journal of Alloys and Compounds* **689**, 899–907 (2016).

[217] Joo, S.-J. et al. Thermoelectric properties of Bi$_2$Te$_2.7$Se$_{0.3}$ nanocomposites embedded with MgO nanoparticles. *Journal of the Korean Physical Society* **69**, 1314–1320 (2016).

[218] Li, Y. Y. et al. Enhanced thermoelectric performance of Cu$_2$Se/Bi$_{0.4}$Sb$_{1.6}$Te$_3$ nanocomposites at elevated temperatures. *Appl. Phys. Lett.* **108**, 062104 (2016).

[219] Li, Y., Liu, G., Qin, X. & Shan, F. Inhibition of minority transport for elevating the thermoelectric figure of merit of CuO/Bi$_3$SbTe nanocomposites at high temperatures. *RSC Adv.* **6**, 112050–112056 (2016).

[220] Liu, W. et al. Enhanced thermoelectric properties of n-type Mg$_{2.16}$(Si$_{0.4}$Sn$_{0.6}$)$_{1–y}$Sb$_y$ due to nano-sized Sn-rich precipitates and an optimized electron concentration. *Journal of Materials Chemistry A* **22**, 13653 (2012).

[221] Zhou, Y. M. et al. Strategy to optimize the overall thermoelectric properties of SnTe via compositing with its property-counter CuInTe$_2$. *Acta Materialia* **125**, 542–549 (2017).

[222] Zhou, C. et al. Scalable solution-based synthesis of component-controllable ultrathin PbTe$_{1–x}$Se$_x$ nanowires with high n-type thermoelectric performance. *J. Mater. Chem. A* **5**, 2876–2884 (2017).
Toberer, E. S., Xiong, Z., Chen, X., Huang, X., Bai, S. & Chen, L. High thermoelectric performance of Yu, C. et al. 
Zhao, X. Y., Zhao, L.-D., Yamanaka, S., Kobayashi, H. & Kurosaki, K. Thermoelectric properties of layered rare earth copper 
Salvador, J. R., Yang, J., Shi, X., Wang, H. & Wereszczak, A. Transport and mechanical prop-
Sharp, J. W. Some properties of GeTe-based thermoelectric alloys. In Thermoelectrics, 2003
Zhou, M., Li, J.-F. & Kita, T. Nanostructured AgPb
Zhu, T. J., Cao, Y. Q., Yan, F. & Zhao, X. B. Nanostructuring and thermoelectric properties of
Pei, Y. et al. Multiple converged conduction bands in KxBi2Se13: A promising thermoelectric material with extremely low thermal conductivity. J. Am. Chem. Soc. 138, 16364–16371 (2016).
Park, K. et al. Extraordinary off-stoichiometric bismuth telluride for enhanced n-type thermoelectric power factor. J. Am. Chem. Soc. 138, 14458–14468 (2016).
Moon, S. P. et al. Tunable thermoelectric transport properties of Cu0.086Bi2Te2.75Sb0.3 via control of the spark plasma sintering conditions. Journal of the Korean Physical Society 69, 811–815 (2016).
Zhu, T. J., Cao, Y. Q., Yan, F. & Zhao, X. B. Nanostructuring and thermoelectric properties of semiconductors tellurides. In Thermoelectrics, 2007. ICT 2007. 26th International Conference on, 8–11 (IEEE, 2007.
Choi, J.-S. et al. Thermoelectric properties of n-type (Pb1–xGe)2Te fabricated by hot pressing method. In XVI International Conference on Thermoelectrics, 1997. Proceedings ICT ’97, 228–231 (1997).
Yamanaka, S., Kosuga, A. & Kurosaki, K. Thermoelectric properties of Tb3BiTe6. Journal of Alloys and Compounds 352, 275–278 (2003).
Yang, S. H. et al. Nanostructures in high-performance (GeTe)x(AgSbTe2)100−x thermoelectric materials. Nanotechnology 19, 245707 (2008).
Yang, S. H., Zhu, T. J., Zhang, S. N., Shen, J. J. & Zhao, X. B. Natural microstructure and thermoelectric performance of (GeTe)x80(AgSb2−xTe3−x)20. Journal of Electronic Materials 39, 2127–2131 (2010).
Zhang, S. N. et al. Effects of ball-milling atmosphere on the thermoelectric properties of TAGS-85 compounds. Journal of Electronic Materials 38, 1142–1147 (2009).
Zhou, M., Li, J.-F. & Kita, T. Nanostructured AgPb\textsubscript{m}SbTe\textsubscript{m+2} system bulk materials with enhanced thermoelectric performance. Journal of the American Chemical Society 130, 4527–4532 (2008).
Sharp, J. W. Some properties of GeTe-based thermoelectric alloys. In Thermoelectrics, 2003 Twenty-Second International Conference on-ICT, 267–270 (IEEE, 2003).
Salvador, J. R., Yang, J., Shi, X., Wang, H. & Wereszczak, A. Transport and mechanical property evaluation of (AgSbTe1−x)(GeTe)x (x=0.80, 0.82, 0.85, 0.87, 0.90). Journal of Solid State Chemistry 182, 2088–2095 (2009).
Levin, E. M. et al. Analysis of Ce- and Yb-Doped TAGS-85 materials with enhanced thermoelectric figure of merit. Advanced Functional Materials 21, 441–447 (2011).
Yamanaka, S., Kobayashi, H. & Kurosaki, K. Thermoelectric properties of layered rare earth copper oxides. Journal of alloys and compounds 349, 321–324 (2003).
Zhao, L.-D. et al. Thermoelectric and mechanical properties of nano-SiC-dispersed Bi2Te3 fabricated by mechanical alloying and spark plasma sintering. Journal of Alloys and Compounds 455, 259–264 (2008).
Zhao, X. Y. et al. Synthesis and thermoelectric properties of Sr-filled skutterudite Sr\textsubscript{5}Co\textsubscript{4}Sb\textsubscript{12}. Journal of Applied Physics 99, 053711 (2006).
Yu, C. et al. High-performance half-Heusler thermoelectric materials Hf1−xZrxNiSnu−ySb\textsubscript{p} prepared by levitation melting and spark plasma sintering. Acta Materialia 57, 2757–2764 (2009).
Xiong, Z., Chen, X., Huang, X., Bai, S. & Chen, L. High thermoelectric performance of Yb0.26Co4Sb12/yGaSb nanocomposites originating from scattering electrons of low energy. Acta Materialia 58, 3995–4002 (2010).
Toberer, E. S. et al. Traversing the metal-insulator transition in a Zintl phase: Rational enhancement of thermoelectric efficiency in Yb14Mn1−xAl2Sb11. Advanced Functional Materials 18, 2795–2800 (2008).
[247] Chung, D.-Y. et al. CsBi$_4$Te$_6$: A high-performance thermoelectric material for low-temperature applications. *Science* **287**, 1024–1027 (2000).

[248] Tang, X., Li, P., Deng, S. & Zhang, Q. High temperature thermoelectric transport properties of double-atom-filled clathrate compounds Yb$_{12}$Ba$_{8-x}$Ga$_{16}$Ge$_{30}$. *Journal of Applied Physics* **104**, 013706 (2008).

[249] Mi, J. L., Zhao, X. B., Zhu, T. J. & Tu, J. P. Improved thermoelectric figure of merit in n-type CoSb$_3$ based nanocomposites. *Applied Physics Letters* **91**, 172116 (2007).

[250] Liu, W.-S., Zhang, B.-P., Zhao, L.-D. & Li, J.-F. Improvement of thermoelectric performance of CoSb$_3$–xTe$_x$ skutterudite compounds by additional substitution of IVB-group elements for Sb. *Chemistry of Materials* **20**, 7526–7531 (2008).

[251] Li, H., Tang, X., Su, X. & Zhang, Q. Preparation and thermoelectric properties of high-performance Sb additional Yb$_{0.2}$Co$_4$Sb$_{12+y}$ bulk materials with nanostructure. *Applied Physics Letters* **92**, 202114 (2008).

[252] Chen, L. D., Huang, X. Y., Zhou, M., Shi, X. & Zhang, W. B. The high temperature thermoelectric performances of Zr$_{0.5}$Hf$_{0.5}$Ni$_{0.8}$Pd$_{0.2}$Sn$_{0.99}$Sb$_{0.01}$ alloy with nanophase inclusions. *Journal of Applied Physics* **99**, 064305 (2006).

[253] Zhong, B. et al. High superionic conduction arising from aligned large lamellae and large figure of merit in bulk Cu$_{1.94}$Al$_{0.02}$Se. *Applied Physics Letters* **105**, 123902 (2014).

[254] Yu, B. et al. Thermoelectric properties of copper selenide with ordered selenium layer and disordered copper layer. *Nano Energy* **1**, 472–478 (2012).

[255] Liu, H. et al. Ultra high thermoelectric performance by electron and phonon critical scattering in Cu$_{3}$Se$_{1-x}$I$_{x}$. *Advanced Materials* **25**, 6607–6612 (2013).

[256] Liu, H. et al. Copper ion liquid-like thermoelectrics. *Nature Materials* **11**, 422–425 (2012).

[257] He, Y., Zhang, T., Shi, X., Wei, S.-H. & Chen, L. High thermoelectric performance in copper telluride. *NPG Asia Mater* **7**, e210 (2015).

[258] Gahtori, B. et al. Giant enhancement in thermoelectric performance of copper selenide by incorporation of different nanoscale dimensional defect features. *Nano Energy* **13**, 36–46 (2015).

[259] Day, T. W. et al. High-temperature thermoelectric properties of Cu$_{1.97}$Ag$_{0.03}$Se$_{1+y}$. *Materials for Renewable and Sustainable Energy* **3** (2014).

[260] Ballikaya, S., Chi, H., Salvador, J. R. & Uher, C. Thermoelectric properties of Ag-doped Cu$_2$Se and Cu$_2$Te. *J. Mater. Chem. A* **1**, 12478–12484 (2013).

[261] Bailey, T. P. et al. Enhanced ZT and attempts to chemically stabilize Cu$_2$Se via Sn doping. *J. Mater. Chem. A* **4**, 17225–17235 (2016).

[262] Li, W. et al. Promoting SnTe as an eco-friendly solution for $p$-PbTe thermoelectric via band convergence and interstitial defects. *Advanced Materials* **29**, 1605887 (2017).

[263] Liang, D.-D., Ge, Z.-H., Li, H.-Z., Zhang, B.-P. & Li, F. Enhanced thermoelectric property in superionic conductor Bi-doped Cu$_{1.8}$S. *Journal of Alloys and Compounds* **708**, 169–174 (2017).

[264] Plot Digitizer description. http://plotdigitizer.sourceforge.net/. Accessed: 2018-10-05.

[265] Ryu, Byungki, Chung, Jaywan, Park, Su Dong Thermoelectric Efficiency has Three Degrees of Freedom. *arXiv*:1810.11148. (2018).