Efficiency as a performance metric for material optimization in thermoelectric generators

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Abstract

The optimization of thermoelectric (TE) materials with respect to carrier concentration, chemical composition, microstructure, etc. is inevitable for maximizing the performance of TE devices. Theoretical performance prediction can speed up this process dramatically as the synthesis and experimental characterization of all relevant combinations is practically impossible. Conventionally, the dimensionless figure of merit (\(zT\)) is considered as a measure of TE energy conversion capability. However, \(zT\) could mislead the search for optimized materials as it is only an intermediate parameter. To resolve this issue, we combined a device performance calculation routine (one-dimensional continuum theory-based, with fully temperature dependent TE properties) with a band structure-based material model. As an example, a study was conducted on p-type Mg\(_{2}\)Si\(_{1-x}\)Sn\(_x\) solid solutions for which optimization of carrier concentration (\(n\)) and composition (\(x\)) is required. Here, according to previous findings, a single parabolic band (SPB) model was assumed, with an effective mass linearly dependent on composition and carrier concentration, and acoustic phonon and alloy scattering of the charge carriers. It was found that for a cold side temperature of 300 K and a hot side temperature of 500 K (which is well within the validity limits of a SPB model), the optimum \(n\) for Mg\(_{2}\)Si\(_{1-x}\)Sn\(_x\) based on efficiency was found to be at 4.5 \(\times 10^{19}\) cm\(^{-3}\), while based on \(zT\)\(_{\text{max}}\) it was found to be about 20% higher. Additionally, the usage of the temperature average of \(zT\) (\(zT_{\text{Av}}\)) for finding the optimum parameters is also analysed. For p-Mg\(_{2}\)(Si,Sn), \(zT_{\text{Av}}\) predicts the optimum composition and carrier concentration close to the exact efficiency calculation, despite the fact that the efficiency predicted by \(zT_{\text{Av}}\) can be quite off from exact efficiency. The usage of \(zT_{\text{Av}}\) was further tested for common TE materials such as n-type Mg\(_{2}\)Si\(_{1-x}\)Sn\(_x\) and PbTe and a similar conclusion is obtained. Finally, the reason for this closeness and the importance of using exact efficiency plots is discussed.

1. Introduction

Devices made of thermoelectric (TE) materials convert a certain fraction of the heat passed through them into useful electrical power or, vice versa, can pump heat from cold to hot, driven by an electric current \cite{1}. A good TE generator material needs to be able to maintain the temperature (\(T\)) difference (i.e. should have low thermal conductivity \(\kappa\)) while being able to transport the generated electric power to the external load at low internal loss (high electrical conductivity \(\sigma\)). The Seebeck coefficient (\(\alpha\)), which is proportional to the output voltage, is inversely related to electrical conductivity (more specifically to the number of charge carriers) \cite{2}. Due to this inherent, partially reverse coupling, an optimum between these TE properties has to
be found for best performance [2]. Materials have to be engineered to meet this optimum, resulting in exploration of several adjustable parameters such as base composition, ratios of the constituting elements, doping level, dopants species, etc, affecting the electronic band structure and thermal transport. For example, tuning the doping species and concentrations in Skutterudites [3], Mg₃Sb₂ [4, 5] or tuning of x in PbTe₁₋₅Se [6], Bi₂₋₅Sb₂Te₃ [7], Sn₁₋₅Se [8], Mg₂Si₁₋₅Snₓ [9] and changing the Zr or Hf concentration in half-Heuslers [10, 11] are some strategies to optimize performance.

In order to reduce time-consuming experimental efforts to study the effect of each of the free parameters, modelling material properties and thereby predicting TE device performance is a convenient approach. Conventionally, a dimensionless figure of merit \( \eta \) defined as \( \frac{\Delta T}{k} \) \( \int_0^{T_{Av}} \alpha F_0(\eta_c) dT \) derived under the constant property model (CPM) assumptions, whereas in reality, the material properties are temperature dependent. Constant averaged material properties entering the CPM model (obtained by averaging the temperature dependent data) must be chosen such that they reflect the actual material behaviour in the device as good as possible. Despite the use of appropriate averages, the efficiency prediction is inaccurate due to asymmetry in distribution of Joule heat to the hot and cold side of the device and assumption of magnitude and distribution of Peltier–Thomson heat in CPM compared to reality [12–17]. Additionally, the Carnot efficiency [16, 18, 19] is not taken into account when considering just the figure of merit \( z \). Therefore, \( zT \) alone can be quite misleading for performance estimation [16–20].

To overcome this, here, we analyse the device efficiency (for temperature dependent properties) directly to estimate the optimum parameters. This is done by a custom-made 1D performance calculation tool (based on the solution of the 1D heat balance) that was developed in [17]. The material properties can be obtained from electronic band structure models such as the single parabolic band (SPB) model [21, 22], a multiband model [23–25] or similar models which give simplified expressions for material properties based on the solution of the Boltzmann transport equation (BTE). The 1D device performance routine is combined with the BTE-based models in a single calculation routine such that the fundamental material parameters are directly coupled to the predicted device efficiency.

As an example for the implementation of the technique, p-type Mg₃Si₁₋₅Snₓ has been chosen as Mg₃(Si,Sn) solid solutions have gained popularity due to the high performance of the n-type materials [26, 27], availability, low cost and progress in contact development [28, 29]. However, the p-type suffers from still limited performance with a maximum reported \( zT \) of about 0.5 [9, 30] and hence, the performance needs to be improved. Previously, several authors [9, 31–34] have shown the capability of an SPB model to closely describe the behaviour of p-type Mg₃Si₁₋₅Snₓ. In a recent study [31], the SPB model was successfully applied to the whole compositional range of p-type Mg₃Si₁₋₅Snₓ, involving acoustic phonon and alloy scattering as dominant scattering mechanisms. This allowed for an approximate identification of the optimum carrier concentration \( n_{opt} \) and optimum composition \( x_{opt} \). However, the optimum was determined based on \( zT_{max} \) which is not exact as stated before. Here, we would like to identify refined optimum parameters for p-Mg₃Si₁₋₅Snₓ using the actual efficiency and compare the results with those obtained kusing averaged \( zT_{T0} \) as an indicator of optimum parameters.

2. Method

The basic SPB model equations describing the three main TE transport properties (\( \alpha, \sigma \) and \( \kappa \)) are given below [22]:

\[
|\alpha| = \frac{k_B}{e} \left( \frac{2 F_i(\eta_c)}{F_0(\eta_c)} - \eta_c \right)
\]

\[
\sigma = n \mu \eta_c
\]

\[
\kappa = \kappa_1 + \sigma T
\]

\[
n = 4 \pi \left( \frac{2m_i^* k_B T}{\hbar^2} \right)^{1.5} F_{0.5}(\eta_c)
\]

where \( F_i = \int_0^\infty \frac{e^i d\epsilon}{1 + e^{\frac{\epsilon - \mu_c}{k_B T}} - \eta_c} \) is the Fermi integral of the order \( i \), \( k_B \) is the Boltzmann constant, \( e \) is the electronic charge, \( \eta_c = \frac{\mu_c}{k_B T} \) is the reduced chemical potential of the charge carriers and \( E_F \) is the Fermi energy. \( n \) is the
charge carrier concentration given by equation (4) where \( n_F \) is the density of states effective mass, \( h \) is Planck’s constant, and \( \mu \) is the mobility. In contrast to the original publication where the experimental data is discussed and a linear fit for \( n_F \) is used [31] we have introduced here a bilinear equation for \( n_F \) with a dependence both on \( n \) and \( x \). The additional weak dependence on \( n \) improves the agreement between experimental data and model as discussed in [31]; the best fit is given by \( n_F(x, n) = (2.14 - 1.39x + 0.16 \times 10^{-20} \text{cm}^3 \text{n}^{-1}) m_0 \), where \( m_0 \) is the electron rest mass. The fitted 2D plot and the comparison of a purely linear fit of \( n_F(x) \) and \( n_F(x, n) \) with \( n_F \) obtained by comparing the SPB model with experimental data is given in the supplementary information (SI) in figure S1 available online at stacks.iop.org/JPENERGY/3/044006/mmedia. In p-type MgSi_{1-x}Sn\(_x\), the mobility is assumed to be governed by acoustic phonon and alloy scattering mechanisms [31]. The exact equations for these scattering mechanisms and the scattering potentials used (from [31] which were obtained by comparing the SPB model with experimental data) are given in the SI.

For predicting the properties using the SPB model, for each \( n \) (taken as a free parameter), the chemical potential is calculated from the Fermi integral and with this, \( \alpha(T) \) is calculated. The electrical conductivity \( \sigma(T) \) is calculated according to equation (2). The thermal conductivity \( \kappa \) consists of the lattice thermal conductivity \( \kappa_L \) and the conductivity associated with the charge transport given by \( L \sigma T \), where \( L \) is the Lorenz number \( L = \left( \frac{h^2}{4\pi k_e^2(\eta_2(\eta_3) - 4\eta_3(\eta_4)^2)} \right) \) [35]. \( \kappa_L(T) \) is an input parameter for an SPB model and, for the considered case, it is obtained from experimental data as in [31]. A 2D polynomial fit function \( \kappa_L(x, T) \) covering the whole compositional range as described in [31] was used.

From all of these temperature dependent parameters the TE properties are obtained. Employing \( x \) and \( n \) as independent variables matches the experimental reality as a change in \( x \) corresponds to an isovalent substitution of Si by Sn and \( n \) is adjusted by adding small amounts of dopants (Li substituting Mg in this case); hence \( x \) and \( n \) can be adjusted basically independent of each other [30]. While applying the SPB model, the validity of the assumptions should be discussed. The SPB assumption fails above the temperature at which bipolar conduction becomes relevant i.e. where more than one band contributes significantly to conduction. Conventionally, the validity range of the SPB model can be judged by visual examination of the Pisarenko plot [21] or by comparing experimental results and calculated SPB model output. Here we have used the shape of the \( zT(T) \) curve as a criterion to estimate the validity range as it is related to efficiency. An example \( zT(T) \) curve calculated using the SPB model (solid lines) for a composition of \( x = 1 \), and \( n \ [10^{20} \text{cm}^{-3}] = 1.51, 2.47 \) and 2.68 is compared to the experimental data (dotted lines) in figure 1. For simplicity, the \( zT \) maximum, i.e. the point where \( \frac{dzT}{dT} = 0 \) was chosen as the validity limit of the SPB model. \( \frac{dzT}{dT} \) was analysed for comparison and it was found that the results are very similar, with \( \frac{dzT}{dT} \) being the more conservative limit on average, see figure S2 in SI. Such data were obtained for a number of samples available from literature [31, 36–38] and the validity limit was interpolated over the whole compositional range. In order to avoid unphysical extrapolation, the maximum validity limit outside the known experimental points was set to 700 K.

Considering a single TE leg with a hot side temperature \( T_H \) and a cold side temperature \( T_L \), the device performance, i.e. efficiency and output power, is calculated [17, 35] using the material properties obtained employing the SPB. In the steady-state, the exact temperature profile \( T(x) \) obtained by solving the TE heat balance equation [39, 40] (equation (3)) is used for accurate performance calculation of the TEG. In 1D, the heat balance equation is written as [35],

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

(5)

where \( j \) is the current density. The term \( \frac{d}{dx} \left( \frac{\kappa}{\rho c_p} \right) \) corresponds to the Fourier heat flux which also compensates for the locally appearing Joule heat \( \rho(T)j^2 \) and Peltier–Thomson heat \( \frac{\partial q}{\partial T} T \). The exact solution of equation (5) is obtained using the iterative procedure described in [17]. From the temperature profile, the exact power and efficiency are obtained as follows:

\[
p = V \cdot j
\]

(6)

where \( V = V_0 - RI \), and \( V_o = \int_{T_L}^{T_H} \alpha(T) \text{d}T \). Here, \( p \) is the electrical output power density given by the product of output voltage \( V \) and the current density \( j \left( \frac{1}{A} \right) \). \( V \) consists of the generated Seebeck voltage \( V_0 \) and the voltage drop due to the internal resistance \( R_i = \int_0^1 \rho(T(x)) \text{d}x \) where \( A \) is the cross-sectional area, \( l \) the length of the TE leg and \( \rho(T) \) the resistivity of the TE material. The efficiency (\( \eta \)) is the ratio of output
Figure 1. Comparison of the interpolated experimental figure of merit and the figure of merit calculated by the SPB model for different carrier concentrations \( n = 1.51, 2.47, \) and \( 2.68 \times 10^{20} \text{ cm}^{-3} \) in p-type MgSn. The temperature corresponding to the peak (marked) of the experimental \( zT \) curves is taken as the validity limit of the SPB model.

3. Results

The validity limit was obtained as explained in section 2 (figure 1) using the experimental data available in literature \([31, 36, 38]\). The full data used is given in table S1 in the supplementary info. The data was interpolated using the Thin Plate Spline algorithm available in the Origin software \([41]\) and is shown in figure 2. As expected, as we move from MgSi to MgSn, the maximum temperature up to which the SPB model is valid reduces for a fixed \( n \), due to the decreasing band gap, and as we move from lower carrier concentrations to higher, the validity limit increases as the contribution of the minority carriers decreases \([31, 42]\). The partially wavy form of the temperature contour lines is due to the input data, which was obtained from different sources and shows the usual experimental scatter.

3.1. Optimum carrier concentration

Contour plots showing the calculated maximum efficiency for a hot side temperature \( (T_h) \) of 500 K and a cold side temperature \( (T_c) \) of 300 K as a function of \( x \) and \( n \) are shown in figure 3(a). For comparison to \( zT_{\text{max}} \) (figure 3(b)), \( zT_{\text{TAv}} \) contours are also plotted in figure 3(c), where \( zT_{\text{TAv}} = \frac{T_h}{\Delta T} \int_0^{\Delta T} zT(T) \, dT \) (a physically appropriate temperature average for Seebeck coefficient suggested by Ioffe) \([1]\). Since minority carrier effects are not considered in an SPB model, \( zT \) increases monotonously with \( T \) and therefore \( zT_{\text{max}} \) is the result of the SPB model at the considered hot side temperature (here 500 K). The line for the chosen \( T_h \) of 500 K from the validity plot in figure 2 is superimposed onto these plots (the area with SPB valid only up to less than...
Figure 2. Contour plot indicating the temperatures up to which the SPB was applied as function of $x$ and carrier concentration $n$ for p-type Mg$_2$Si$_{1-x}$Sn$_x$.

Figure 3. (a) Maximum calculated efficiency for $T_h = 500$ K and $T_c = 300$ K; (b) $zT$ at 500 K ($zT_{\text{max}}$); (c) $zT_{\text{Tav}}$ for $T_h = 500$ K and $T_c = 300$ K, for different $n$ and $x$ for p-type Mg$_2$Si$_{1-x}$Sn$_x$; the SPB approximation does not hold in the shaded region on the graphs as discussed by figure 2. (d) Optimum $n$ with respect to the calculated maximum efficiency ($x = 0.64$), $zT_{\text{max}}$ ($x = 0.65$), and $zT_{\text{Tav}}$ ($x = 0.64$), all curves normalized to their maximum values.

500 K indicated by the dimmed region) to clarify what part of the modelling results is physically interpretable. Note that the performance maximum near $x = 1$ is thus not accessible. It arises due to the low $m^*_{\text{f}}$ for low $n$ and high $x$ and overcompensates the effect of increasing lattice thermal conductivity for $x \rightarrow 1$, but is outside the validity range for the SPB model; practically $zT$ is lower here than predicted by the SPB model due to the influence of minority carriers.
As can be seen from figure 3(d), the optimum carrier density \( n_{opt} \) differs between the calculated efficiency and \( zT_{n} \) plots, while \( n_{opt} \) from the \( zT_{h} \) plot coincides approximately with that from the efficiency plot. For efficiency, the maximum is found at \( n = 0.44 \times 10^{29} \text{ cm}^{-3} \) for \( zT_{h} \), while for \( zT_{n} \) the maximum occurs at \( n = 0.54 \times 10^{29} \text{ cm}^{-3} \).

4. Discussion

The necessity to define a validity range is due to employing an SPB model for the efficiency calculation, which naturally fails at higher temperatures due to bipolar contributions. This could be overcome by a multiband description, but so far no multiband model with a good agreement of experimental and modelling data has been published. To date, most modelling approaches were focused on n-type Mg\(_2\)Si\(_3\)Sn\(_{0.6}\) for which the SPB model is usually valid for a larger temperature range, partially because of the higher mobility of the electrons compared to the holes [4, 24, 43, 44]. Previous approaches to estimate the validity range of an SPB model were based on the analysis of the temperature dependence of the calculated electrochemical potential [31] or approximate two-band modelling [45]; using \( \frac{d(\eta)}{dT} \) as a criterion is a more pragmatic approach. As \( \frac{d(\eta)}{dT} \) decreases towards higher \( T \), the \( zT \) of the model will usually be higher than that of the real sample; hence the efficiency from the SPB model will be too high if the chosen temperature interval includes a range close to the experimental \( zT_{n} \). However, we estimate this maximum relative difference in efficiency to about 10%. From figure 4, it can be seen that the possibility to predict \( n_{opt} \), \( x_{opt} \) and the efficiency at the optimum fails beyond a hot side temperature of 610 K, since for higher \( T_{h} \) the optimum lies outside the valid region of the employed SPB model. Nevertheless, with an expected maximum application \( T_{h} \) of \( \approx 700 \text{ K} \), the SPB model can be applied to a significant fraction of the relevant temperature range and the modelling results are of practical relevance.

From figure 3, it can be seen that the maximum efficiency plot and the \( zT_{n} \) plot do not result in the same optimum region. This is because \( zT_{n} \) is one of the less suitable methods of representing the performance of the TE material [17, 19, 20] and overestimates performance [12]. For \( T_{h} = 500 \text{ K} \), the optimum \( n \) determined by \( zT_{n} \) is off from the efficiency prediction by 21% as seen from figure 3.

Figures 5(a) and (b) shows the changes in optimum \( n \) and \( x \), respectively, for \( T_{h} = 400 \text{ K}, 500 \text{ K}, 600 \text{ K} \) with \( T_{h} = 300 \text{ K} \). It can be seen that the optimum \( n \) using \( zT_{n} \) is always overestimated and that the discrepancy can be > 20%. Also, as expected, the discrepancy reduces as the temperature interval gets smaller, i.e. tending towards the CPM. A similar trend but much weaker in magnitude is observed in the case of \( zT_{h} \). There is no significant difference in optimum \( x \) with respect to the exact efficiency and \( zT_{h} \) and \( zT_{n} \) as seen from figure 4(b). Analysing figures 5(a) and 3(d) it can be concluded that the shift in the optimum \( n \) with \( T_{h} \) is for p-Mg\(_2\)Si\(_3\)Sn\(_{0.6}\) of minor practical relevance. The maximum of \( \eta(n) \) is wide, and hence a deviation from \( n_{opt} \) by even 20% will mean a performance loss of only about 1.5%. Similar for \( \eta(x) \), a mean composition near 0.635 would be suitable for all \( T_{h} \) for p-Mg\(_2\)Si\(_3\)Sn\(_{0.6}\).

The optimum parameters obtained with \( zT_{h} \) plots almost coincide with those from the efficiency plots. This is because the basic input SPB parameters (\( m^*_\), deformation potential constant (\( E_{dep}, \kappa_s \)) do not vary erratically with \( n \) and \( x \) for the considered material. However, to see if the optimum position \( (x, n) \) predicted by CPM (using \( zT_{h} \) or \( zT_{n} \) in the efficiency formula) is different from that of exact efficiency, it is important to see how the parameters that determine this discrepancy between CPM and exact calculation vary with \( n \) and \( x \), rather than considering the discrepancy in the obtained efficiency value between CPM and the exact calculation. This is because even though the discrepancy between the CPM and exact efficiency might be quite large, the change of the factors that determine this discrepancy, for different \( n \) and \( x \), might be constant or negligibly varying, leading to the same optimum position \( (x, n) \) in both cases. This means that the parameters to be optimized \( (n \text{ and } x \text{ in our case}) \) can often nevertheless be obtained with high accuracy using CPM. A large discrepancy might be expected if the difference between CPM and exact efficiency is itself a strong function of \( n \) and \( x \).

Additionally, as a comparison, the optimum parameters obtained for n-type Mg\(_2\)Si\(_3\)Sn\(_{0.6}\) [46] and PbTe [47] using \( zT_{h} \) and exact efficiency are shown along with p-type Mg\(_2\)Si\(_3\)Sn\(_{0.6}\) in figure S3 of the SI (normalized efficiency and \( zT_{h} \) are presented). As can be seen, the width of the \( \eta \) and \( zT_{h} \) curves vs \( n \) varies from case to case, and \( zT_{h} \) predicts the optimum \( n \) very similar to exact efficiency in all cases.

If an SPB model is employed to describe the TE properties, it is presumably rare to see a material case where \( zT_{h} \) cannot be used to predict optimum parameters since it does not include any intrinsic carrier effects. The accuracy of efficiency prediction by CPM varies with a qualitative change in the slope and curvature of the TE properties on \( T \). In particular, these vary with the relative relevance of bipolar effects [12, 16, 17]. With constant or moderately changing parameters of a SPB model there will not be qualitative changes in the curve shape of the TE properties: \( \alpha(\text{T}) \) and \( \rho(\text{T}) \) will rise approximately linearly and \( \kappa(\text{T}) \).
Figure 4. Calculated maximum efficiency contours for a cold side temperature of $T_c = 300$ K and hot side temperature $T_h$ of $610$ K with the black line showing the validity limit of the SPB model. With increasing distance from the black line into the dimmed region the predicted efficiency is increasingly overestimated as the (detrimental) influence of the minority carriers is not taken into account by the employed SPB model.

Figure 5. (a) Change in optimum carrier density $n$ and (b) optimum composition $x$, for different hot side temperatures, estimated using $zT_{max}$, $zT_{TAv}$ and exact efficiency.

will decrease approximately as $\kappa \propto T + c_2$ [22, 48]. The relation between the chosen mode of $zT$ definition and the physically justified Ioffe $ZT$ (from the adequate averages of Seebeck and resistivities) will be quite stable under these conditions and also the distribution of Joule and Thomson heat, as discussed, will not vary a lot, as it is more the change of slope of the properties with $T$ rather than their absolute magnitude which makes the effects here. With that there is good reason to trust in that if $zT_{TAv}$ gives a very good match in two examples it would do so for many more materials; $zT_{TAv}$ can thus be a convenient alternative if the SPB model can be employed. However, in order to achieve higher efficiency, higher temperatures where bipolar conduction occurs are usually employed for applications and hence the SPB assumption and therefore $zT_{TAv}$ can prove to be ineffective due to the stronger change of temperature dependence of the transport properties. Note also, that even though $zT_{TAv}$ apparently can be used to identify the optimum carrier concentration, it can show quite some inaccuracy for the calculation of efficiency itself [12, 16, 17]. Finally, the approach shown here can relatively easily be upgraded to a p–n couple [22] and electrical and thermal contact resistances can be implemented. Then the approach shown here helps for an accurate estimation of device efficiency and optimized material properties under realistic application conditions. Employing the efficiency derived from the temperature dependent properties (equation (8)) allows for an optimization with respect to $n$ in scenarios when the area adjustment [18] to accommodate for different currents in p and n leg cannot be done for some practical reason or when contact resistances play a large role.
5. Summary and outlook

A simple and efficient tool to predict the exact optimum composition of the solid solution and optimum carrier density has been shown using p-Mg$_x$Si$_1-x$Sn$_x$ as an example. This approach is applicable to any material for which a description of the TE properties is given. This is demonstrated exemplarily by figure S3 in the supporting material, where the efficiency (normalized) vs $n$ curves for PbTe and n-Mg$_{0.8}$Sb$_{0.2}$Sn$_{0.6}$ have been provided. The difference in optimum carrier concentration obtained using commonly used indicators such as $zT_{\text{max}}$ or $zT_{\text{Av}}$ vs the optimum obtained considering the locally varying TE properties for p-Mg$_2$X has been discussed. Even though the discrepancy in calculated efficiency between CPM and exact calculations exists, for some materials like the one considered here, $zT_{\text{Av}}$ can be used to find optimum carrier concentration and composition with good accuracy for practical use.

In practice, to reach maximum efficiency, hot side temperatures entering the range of bipolar conduction are important, and to model such cases, multi band models are necessary. With the shown TEG calculation routine, the effect of having metal contacts and its effect on optimum parameters can be easily implemented and studied. The combination of a semiconductor physics model such as SPB and continuum theoretical efficiency calculation can also be employed to optimize material grading or segmentation for further performance enhancement.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Ioffe A E, Stil’Bans L, Iordanishvili E, Stavitskaya T, Gellbtuch A and Vineyard G J P 1959 Semiconductor thermoelements and thermoelectric cooling  *Physics Today* 12 42
[2] Snyder G J and Toberer E S 2011 Complex thermoelectric materials  *Materials for Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group* (Singapore: World Scientific) pp 101–10
[3] Rogl G and Rogl P 2017 Skutterudites, a most promising group of thermoelectric materials  *Curr. Opin. Green Sust* 4 50–57
[4] Mao J, Wu Y X, Song S W, Zhu Q, Shuai J, Liu Z H, Pei Y and Ren Z 2017 Defect engineering for realizing high thermoelectric performance in n-type Mg$_x$Sb$_{1-x}$Sn$_x$-based materials  *ACS Energy Lett.* 2 2245–50
[5] Wang X, Zhang X, Liu Y Q, Wang Y Z, Zheng J X and Yue M 2020 Optimizing the thermoelectric performance of p-type Mg$_x$Sb$_2$ by Sn doping  *Vacuum* 177 109388
[6] Pei Y, Shi X, LaLonde A, Wang H, Chen L and Snyder G J 2011 Convergence of electronic bands for high performance bulk thermoelectrics  *Nature* 473 66–69
[7] Goldsmid H J 2014 Bismuth telluride and its alloys as materials for thermoelectric generation  *Materials* 7 2577–92
[8] Chen Z G, Shi X L, Zhao L D and Zou J 2018 High-performance SnSe$_x$ thermoelectric materials: progress and future challenge  *Prog. Mater. Sci.* 97 283–346
[9] de Boor J, Dasgupta T and Müller E 2015 Thermoelectric Properties of Magnesium Silicide Based Solid Solutions and Higher Half-Heusler Structures  *Mater. Today Phys.* 7 69–76
[10] Hu C, Xia K, Chen X, Zhao X and Zhu T 2018 Transport mechanisms and property optimization of p-type (Zr, Hf) CoSb$_2$ half-Heusler thermoelectric materials  *Mater. Today* 22 1128–34
[11] Zeier W G, Schmitt J, Hautier G, Aydemir U, Gibbs Z M, Felser C and Snyder G J 2016 Engineering half-Heusler thermoelectric materials using Zintl chemistry  *Nat. Rev. Mater.* 1 1–10
[12] Ponnusamy P, de Boor J and Muller E 2020 Discrepancy between constant properties model and temperature-dependent material properties for performance estimation of thermoelectric generators  *Entropy* 22 1128
[13] Sherman B, Heikes R and Ure J R 1960 Calculation of efficiency of thermoelectric devices  *J. Appl. Phys.* 31 1–16
[14] Sunderland J E and Burak N T 1964 The influence of the Thomson effect on the performance of a thermoelectric power generator  *J. Solid-State Electron.* 7 465–71
[15] Wee D 2011 Analysis of thermoelectric energy conversion efficiency with linear and nonlinear temperature dependence in material properties  *Energy Convers. Manage.* 52 3383–90
Ryu B, Chung J and Park S 2018 Thermoelectric efficiency has three degrees of freedom (arXiv: 11148)

Ponnusamy P, de Boor J and Müller E 2020 Using the constant properties model for accurate performance estimation of thermoelectric generator elements Appl. Energy 262 114587

Goupil C 2015 Continuum Theory and Modeling of Thermoelectric Elements (NY: Wiley)

Kim H S, Liu W S and Ren Z F 2017 The bridge between the materials and devices of thermoelectric power generators Energy Environ. Sci. 10 69–85

Lau P G and Buist R J (ed) 1997 Calculation of thermoelectric power generation performance using finite element analysis XVI ICT’97 Proc. ICT’97 16th Int. Conf. on Thermoelectrics (Cat No. 97TH8291) (IEEE)

Naithani H and Dasgupta T 2019 Critical analysis of single band modeling of thermoelectric materials ACS Appl. Energy Mater. 2 2200–13

Rowe D M 2018 Thermoelectrics and Its Energy Harvesting, 2-Volume Set (Boca Raton, FL: CRC press)

Bulusu A and Walker D G 2008 Review of electronic transport models for thermoelectric materials Superlattices Microstruct. 44 1–36

Zhang L, Xiao P, Shi L, Henkelman G, Goodenough J B and Zhou J 2015 Suppressing the bipolar contribution to the thermoelectric properties of Mg$_2$Si$_{0.8}$Sn$_{0.2}$ by Ge substitution J. Appl. Phys. 117 155103

Mao J, Liu W and Ren Z 2016 Carrier distribution in multi-band materials and its effect on thermoelectric properties J. Mater. 2 203–11

Sankhla A, Patil A, Kamila H, Yasseri M, Farahi N, Mueller E and de Boor J 2018 Mechanical alloying of optimized Mg$_x$(Si,Sn) solid solutions: understanding phase evolution and tuning synthesis parameters for thermoelectric applications ACS Appl. Energy Mater. 1 531–42

Goyal G K, Mukherjee S, Mallik R C, Vitta S, Samajdar I and Dasgupta T 2019 High thermoelectric performance in Mg$_x$(Si,Sn) solid solutions: understanding phase evolution and tuning synthesis parameters for thermoelectric applications ACS Appl. Energy Mater. 1 1043–54

Pham N H, Farahi N, Kamila H, Sankhla A, Ayachi S, Muller E and de Boor J 2019 Ni and Ag electrodes for magnesium silicide based thermoelectric generators Mater. Today Energy 11 97–105

Kamila H et al 2019 Synthesis of p-type Mg$_x$Si$_{1−x}$Sn$_x$ with $x = 0$ to 1 and optimization of the synthesis parameters Mater. Today Proc. 8 546–55

Kamila H, Sahu P, Sankhla A, Yasseri M, Pham H-N, Dasgupta T, Mueller E and de Boor J 2019 Analyzing transport properties of p-type Mg$_x$(Si,Sn) solid solutions: optimization of thermoelectric performance and insight into the electronic band structure J. Mater. Chem. A 7 10453–54

Bux S K, Yeung M T, Toberer E S, Snyder G J, Kaner R B and Fleurial J-P 2011 Mechanochemical synthesis and thermoelectric properties of Mg$_2$Si$_{0.8}$Sn$_{0.2}$ by Ge substitution J. Appl. Phys. 117 155103

Liu W, Chi H, Sun H, Zhang Q, Yin K, Tang X, Zhang Q and Uher C 2014 Advanced thermoelectrics governed by a single parabolic band: Mg$_2$Si$_{0.8}$Sn$_{0.2}$, a canonical example Phys. Chem. Chem. Phys. 16 6893–7

de Boor J, Dasgupta T, Saparamadu U, Müller E and Ren Z 2017 Recent progress in p-type thermoelectric magnesium silicide based solid solutions Mater. Today Energy 4 105–21

Rowe D M 2005 Thermoelectrics Handbook: Macro to Nano (Boca Raton, FL: CRC press)

Liu W, Yin K, Su X, Li H, Yan Y, Tang X and Uher C 2013 Enhanced hole concentration through Ga doping and excess of Mg and thermoelectric properties of p-type Mg$_2$(1 + $z$)(Si$_x$Sn$_{1−x}$)$_2$Ga$_2$ Intermetallics 32 592–61

Isoda Y, Tada S, Nagai T, Fujii H and Shinohara Y 2010 Thermoelectric properties of p-type Mg$_2$(Ga$_{0.8}$Si$_{0.25}$Sn$_{0.75}$) with Li and Ag double doping J. Electron. Mater. 39 1531–5

Isachenko G, Samunin A Y, Gurieva E, Fedorov M, Pshenay-Severin D, Konstantinov P and Kamolova M D 2016 Thermoelectric properties of nanostructured p-Mg$_x$Si$_{1−x}$Sn$_x$ ($x = 0.2$–0.4) solid solutions J. Electron. Mater. 45 1982–6

Domenicali C A 1994 Stationary temperature distribution in an electrically heated conductor J. Appl. Phys. 25 1310–1

Domenicali C A 1993 Irreversible thermodynamics of thermoelectric effects in inhomogeneous, anisotropic media J. Phys. Rev. 92 877

Donato G and Belongie S J 2003 Approximation Methods for Thin Plate Spline Mappings and Principal Warps (San Diego: Citeseer)

Zhang Q, Cheng L, Liu W, Zheng Y, Su X, Chi H, Liu H, Yan Y, Tang X and Uher C 2014 Low effective mass and carrier concentration optimization for high performance p-type Mg$_2$(1−$z$)Li$_2$Si$_{1−z}$Sn$_z$ solid solutions Phys. Chem. Chem. Phys. 16 23576–83

Bahk J-K, Bian Z X and Shokouri A 2014 Electron transport modeling and energy filtering for efficient thermoelectric Mg$_2$Si$_{1−x}$Sn$_x$ solid solutions Phys. Rev. B 89 075204

Satyala N and Vashae D 2012 Modeling of thermoelectric properties of magnesium silicide (Mg$_x$Si) J. Electron. Mater. 41 1785–91

de Boor J, Berche A and Jund P 2020 Density of states effective mass for p-type Mg$_x$Si$_{1−x}$Sn$_x$ solid solutions: comparison between experiments and first principles calculations J. Phys. Chem. C 124 14987–96

Sankhla A, Kamila H, Kehr K, Mueller E and de Boor J 2020 Analyzing thermoelectric transport in n-type Mg$_2$Si$_{1−y}$Sn$_y$ and correlation with microstructural effects: an insight on the role of Mg Acta Mater. 199 85–95

Pei Y, LaLonde A, Iwanaga S and Snyder G J 2011 High thermoelectric figure of merit in heavy hole dominated PbTe Energy Environ. Sci. 4 2085–9

Uher C 2016 Materials Aspect of Thermoelectricity (Boca Raton, FL: CRC press)