Supplemental Materials

Advanced Thermoelectrics Governed by Single Parabolic Band Model:

Mg$_2$Si$_{0.3}$Sn$_{0.7}$, a Canonical Example

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In the Single Parabolic Band (SPB) model, with an energy dependent relaxation time

\[ \tau = \tau_0 e^{-\epsilon \tau}, \quad (S1) \]

all transport coefficients can be obtained by solving the Boltzmann transport equation \(^1\text{-}^3\).

Specifically, the Seebeck coefficient is given by

\[ \left( \frac{r + \frac{1}{2}}{r + \frac{1}{2}} \right) F_{r+\frac{1}{2}}(\eta) \right] \]

where \( k_B \) is the Boltzmann constant, \( q = -e \) is the electron charge, \( \eta \) (=\( E_F/k_BT \)) is the reduced Fermi level measured from the conduction band minimum, \( r = -1/2 \) for any scattering mechanism whose mean-free path \( \ell \) is independent of energy (MFPIE), such as acoustic phonon (AP) scattering and alloy scattering (AS) found relevant in this research, and \( F_n(\eta) \) is the Fermi integral given by:

\[ F_n(\eta) = \int_0^{\infty} \frac{1}{e^{\xi}\eta + 1} \xi^n d\xi. \quad (S3) \]

The experimentally accessible \( n_H (= 1/qR_H, \) where \( R_H \) is the Hall coefficient) is related to the free carrier density \( n \) via the Hall factor \( r_H \):

\[ n_H = n/r_H, \quad (S4) \]

where

\[ r_H = \frac{3 \left( 2r + \frac{1}{2} \right) F_{2r+\frac{1}{2}}(\eta)F_{r+\frac{1}{2}}(\eta)}{2 \left( r + \frac{3}{2} \right)^2} \left( r + \frac{1}{2} \right)^2 \frac{F_{2r+\frac{1}{2}}(\eta)}{F_{r+\frac{1}{2}}(\eta)}, \quad (S5) \]

and
Here \( m^* \) is the density-of-states effective mass given as a function of the single valley effective mass \( m_s^* \) and the associated valley degeneracy \( N_v \) as

\[
m^* = N_v^{2/3} m_s^*.
\] (S7)

Considering only the dominant scattering mechanisms of AP and AS, the overall \( \mu_H \) is given by the Matthiessen’s rule

\[
\frac{1}{\mu_H} = \frac{1}{\mu_H^{AS}} + \frac{1}{\mu_H^{AP}}.
\] (S8)

Noting that

\[
\mu_{H}^{s} = \mu_{d,0}^{s} \Psi_{r}(\eta),
\] (S9)

where \( \Psi_{r}(\pi) \) is given by

\[
\Psi_{r}(\eta) = \frac{3\sqrt{\pi}}{4} \frac{2r + \frac{1}{2}}{r + \frac{1}{2}} \frac{1}{\Gamma(r + \frac{5}{2})} \frac{F_{2r+\frac{1}{2}}(\eta)}{F_{r+\frac{3}{2}}(\eta)},
\] (S10)

with \( s \) (= AS, AP) indicating different scattering mechanisms. \( \mu_{d,0}^{s} \) represents the drift mobility in the non-degenerate limit which can be calculated, for the MFPIE case, with the knowledge of the corresponding mean-free path \( \ell_{d,0}^{MFPIE} \) from

\[
\mu_{d,0}^{MFPIE} = \frac{4}{3} \frac{q\ell_{d,0}^{MFPIE}}{(2\pi m^* k_B T)^{3/2}}.
\] (S11)

The literature result\(^4\) for AS is

\[
\mu_{d,0}^{AS} = \frac{64 e h^4 N_0}{9(2\pi)^{3/2} x (1-x) E_a^2 (m_s^*)^{3/2} (k_B T)^{1/2}},
\] (S12)

\[
n = \frac{4\pi (2m^* k_B T)^{3/2}}{\hbar^3} F_{\frac{1}{2}}(\eta).
\] (S6)
where \( x (= 0.7 \text{ for Mg}_2\text{Si}_{0.3}\text{Sn}_{0.7}) \) is the Sn fraction in the solid solution, \( N_0 \) is the number of atoms per unit volume, and \( E_a \) is the parameter characterizing the alloy potential fluctuation in \( \text{Mg}_2\text{Si}_{0.3}\text{Sn}_{0.7} \). The result for AP is: \(^5\)

\[
\mu_{d,0}^{AP} = \frac{(8\pi)^{1/2} e^4 \rho v_l^2}{3 E_d^2 (m_v^*)^5/2 (k_B T)^{3/2}}
\]  
(S13)

where \( v_l \) is the longitudinal velocity of sound and \( \rho \) is the density. \( E_d \) is the deformation potential.

The electronic thermal conductivity \( \kappa_e \) can be determined by using the Wiedemann-Franz law, \( \kappa_e = L \sigma T \), where \( L \) is the Lorenz number, \( \sigma \) is the electrical conductivity and \( T \) the absolute temperature. \( L \) and its temperature dependence are given by: \(^6\)

\[
L = \left( \frac{k_B}{q} \right)^2 \left\{ \left( \frac{r + \frac{3}{2}}{r + \frac{5}{2}} \right) F_{r+\frac{3}{2}} \left( \eta \right) - \left( \frac{r + \frac{5}{2}}{r + \frac{3}{2}} \right) F_{r+\frac{5}{2}} \left( \eta \right) \right\}^2
\]  
(S14)
Figure S1: (a) XRD patterns and (b) DSC curves of Mg$_2$(Si$_{0.3}$Sn$_{0.7}$)$_{1-y}$Bi$_y$ (0 ≤ y ≤ 0.04) solid solutions. Results indicate that, similar to the other Mg$_2$Si$_{1-x}$Sn$_x$-based solid solutions, all XRD patterns of Mg$_2$(Si$_{0.3}$Sn$_{0.7}$)$_{1-y}$Bi$_y$ can be indexed to the Mg$_2$Si$_{0.3}$Sn$_{0.7}$ solid solution with the cubic structure and space group of Fm3m, except for one slight peak belonging to MgO. In addition, DSC curves evolve gradually with temperature in the range of 350-820 K and no anomalous thermal effects are observed, attesting to Mg$_2$(Si$_{0.3}$Sn$_{0.7}$)$_{1-y}$Bi$_y$ being stable during measurements.
Figure S2: Back Scattering Image (a), elemental mapping distribution of Mg (b), Si (c), Sn (d) and Bi (e) for Mg$_2$(Si$_{0.3}$Sn$_{0.7}$)$_{0.97}$Bi$_{0.03}$. All the constituent elements distribute rather evenly in the micron size scale. We should note that, even Bi doping amount is as high as $y = 0.03$, we do not observe obvious segregation in the matrix of Mg$_2$(Si$_{0.3}$Sn$_{0.7}$)$_{0.97}$Bi$_{0.03}$. 
Figure S3: (a) correlation between the Seebeck coefficient $S$ and the Hall carrier density $n_H$ at room temperature for Mg$_2$Si$_{0.4}$Sn$_{0.6}$ (b), Mg$_2$Si$_{0.5}$Sn$_{0.5}$ (b), and Mg$_2$Si (c), respectively. The single parabolic band (SPB) model is utilized to generate the density-of-states effective mass $m^*$ from $S$ and $n_H$. The closer the composition of Mg$_2$Si$_{1-x}$Sn$_x$ to the band convergence at Mg$_2$Si$_{0.3}$Sn$_{0.7}$, the better is the coincidence between the experimental $S$ and the Pisarenko curve based on the SPB model, especially when $n_H > 8.4 \times 10^{19}$ cm$^{-3}$. 