Supporting Information

Computational prediction of high ZT of n-type Mg₃Sb₂-based compounds with isotropic thermoelectric conduction performance

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**Fig. S1** Calculated band structures (a) without and (b) with spin orbit coupling (SOC) in Mg₃Sb₂.

**Fig. S2** Calculated total DOS of Mg₃Sb₂. The back and red solid lines represent the calculated DOS without and with spin orbit coupling (SOC), respectively.

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Fig. S3 Calculated band-decomposed charge density of (a) conduction band minimum (CBM), isosurface value 0.0007 and (b) valence band maximum (VBM), isosurface value 0.0009. Purple, pink and green balls represent Mg1, Mg2, and Sb atoms, respectively.

Fig. S4 Effective band structure of (a) $2 \times 2 \times 2$ supercell of the primitive unit cell Mg$_3$Sb$_2$ (40 atoms) and (b) Mg$_3$Sb$_{1.5}$Bi$_{0.5}$ by PBE functional without SOC.

Estimation of carrier’s mobility and scattering time

Based on the deformation potential (DF) theory,$^1$ the carrier’s mobility $\mu$ and scatter time $\tau$ can be expressed as:

$$\mu = \frac{2\sqrt{2\pi} \hbar^4 c_j}{3(k_B T)^{3/2} m_i^{5/2} \Xi^2}$$  \hspace{1cm} (1)

$$\tau = \frac{\mu m_i^*}{e} = \frac{2\sqrt{2\pi} \hbar^4 c_j}{3(k_B T m_i^*)^{1/2} \Xi^2}$$  \hspace{1cm} (2)
where $c_{ii}$ is the lattice elastic constant ($i=1, 2, 3$), $\Xi$ is the deformation potential constant calculated as $\Xi = \partial E_{edge}/\partial (\Delta a/a)$, where $E_{edge}$ is the conduction band maximum (CBM), $a$ is the lattice constant and $\Delta a$, given by $\Delta a = a - a_0$, is the corresponding lattice distortion, and $m_i^*$ is the conductivity effective mass. Based on the band structure, we use the effective mass calculator (EMC)\textsuperscript{2} to calculate the effective mass tensor $m_j$ of a single valley, defined as:

$$m_j^* = h^2 (\partial^2 E(k)/\partial k_i \partial k_j)^{-1}, \quad i, j = x, y, z$$

(3)

The conductivity effective mass $m_i^*$ can be express as:

$$m_i^* = 3/[1/m_{xx}^* + 1/m_{yy}^* + 1/m_{zz}^*]$$

(4)

The effective masses of the K conduction band are estimated to be $m_{xx}^* = m_{yy}^* = 0.3580 m_e$, $m_{zz}^* = 0.2103 m_e$, which yield the conductivity effective mass at K point $m_{i,K}^* = 0.2899 m_e$, and the effective masses of the CB1 conduction band are estimated to be $m_{xx}^* = 0.1154 m_e$, $m_{yy}^* = 0.4786 m_e$, $m_{zz}^* = 0.1650 m_e$, leading to the conductivity effective mass at CB1 point $m_{i,CB1}^* = 0.1784 m_e$. Due to the energy difference between the K and the CB1 minimum is 0.1eV, smaller than $\sim 3k_B T$ at room temperature, so the conduction band minimum at K point and CB1 point can be considered as nearly converged at elevated temperature for n-type transport in Mg\textsubscript{3}Sb\textsubscript{2}. the conductivity effective mass $m_i^*$ is calculated using the average conductivity effective mass of two band ($m_{i,K}^*$ and $m_{i,CB1}^*$) described as:

$$m_i^* = 2/[1/m_{i,K}^* + 1/m_{i,CB1}^*]$$

(5)

Thus, the calculated conductivity effective mass $m_i^*$ of n-type Mg\textsubscript{3}Sb\textsubscript{2} is 0.22 eV. Using equation (1), the calculated $\mu$ are 101.8 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} along $\Gamma$ - M direction and 108.1 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} along $\Gamma$ - A direction at 300 K, and 27 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} along $\Gamma$ - M direction and 28.69 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} along $\Gamma$ - A direction at 725 K. Using equation (2), the
calculated $\tau$ are 12.62 $\text{fs}$ along $\Gamma - \text{M}$ direction and 13.39 $\text{fs}$ along $\Gamma - \text{A}$ direction at 300 K, and 3.333 $\text{fs}$ along $\Gamma - \text{M}$ direction and 3.539 $\text{fs}$ along $\Gamma - \text{A}$ direction at 725 K.

**Calculation of the minimum lattice thermal conductivity**

The minimum lattice thermal conductivity $\kappa_{\text{min}}$ is calculated using the Cahill’s formula as:\(^3,^4\)

$$\kappa_{\text{min}} = \frac{1}{2} \left( \frac{\pi}{6} \right)^{3/2} k_B (V)^{2/3} (2v_t + v_l)$$ (6)

where $V$ is the average volume per atom, $v_t$ is traverse elastic wave velocity and $v_l$ is longitudinal elastic wave velocity. $v_t$ and $v_l$ can be obtained using the following equations:\(^5,^6\)

$$v_t = \sqrt{\frac{G}{\rho}}$$ (7)

$$v_l = \sqrt{\frac{(B + \frac{4}{3} G)}{\rho}}$$ (8)

where $B$ is the bulk modulus, $G$ is the shear modulus and $\rho$ is the density. $B$ and $G$ are determined adopting the Voigt-Reuss-Hill averaging scheme in hexagonal system given by:\(^5,^6\)

$$B = (B_v + B_R)/2$$ (9)

$$G = (G_v + G_R)/2$$ (10)

$$B_v = \frac{1}{9} (2c_{11} + c_{12}) + 4c_{13} + c_{33})$$ (11)

$$B_R = \frac{4}{3} \frac{c_2}{M}$$ (12)

$$G_v = \frac{1}{30} (M + 12c_{44} + 12c_{66})$$ (13)
where \( c_{11}, c_{33}, c_{44}, c_{12}, \) and \( c_{13} \) are five independent elastic constants for hexagonal system. The calculated \( \kappa_{\text{min}} \) in Mg3Sb2 is 0.528 W m\(^{-1}\) K\(^{-1}\).

**Estimation of the lattice thermal conductivity**

According the Slack’s formula, the lattice thermal conductivity \( \kappa_L \) can be expressed as:

\[
\kappa_L = A \frac{M \Theta_D V_{\text{per}}^{1/3}}{\gamma n^{2/3} T}
\]  

(15)

where \( M \), \( \Theta_D \), \( V_{\text{per}} \), \( n \), and \( \gamma \) represent the average atomic mass, the Debye temperature, the volume per atom, the number of atoms in the primitive cell and the Grüneisen parameter, and \( A \) is a physical constant \( \approx 3.1 \times 10^{-6} \) when \( \kappa_L \) is in W m\(^{-1}\) K\(^{-1}\), \( M \) is in amu, and \( V_{\text{per}}^{1/3} \) is in Å. \( \Theta_D \) is proportional to the averaged sound velocity \( v_s \) and can be evaluated by:

\[
\Theta_D = \frac{\hbar}{k_B} (6\pi^2 n_s)^{1/3} v_s
\]  

(16)

where \( n_s \) is the number density of atoms. \( v_s \) can be calculated via:

\[
v_s = \left[ \frac{1}{3} \left( \frac{2}{v_p} + \frac{1}{v_l} \right) \right]^{-1/3}
\]  

(17)

\( \gamma \), determining the low \( \kappa_L \), is calculated using the combined density functional perturbation theory (DFPT) and the quasi-harmonic approximation (QHA), given by:

\[
G_k = \frac{5c^2 c_{44} c_{66}}{2(3B_4 c_{44} c_{66} + c^2 (c_{44} + c_{66}))}
\]  

(14)

\[
M = c_{11} + c_{12} + 2c_{33} - 4c_{13}
\]  

(15)

\[
c^2 = (c_{11} + c_{12}) c_{33} - 2c_{13}^2
\]  

(16)
where $\beta$, $B$, $V_m$ and $C_V$ represent the linear thermal expansion coefficient, the bulk modulus, the molar volume and the isometric heat capacity. $C_V$ is obtained from the phonon dispersion, expressed as:

$$C_V = \sum_n k_B \left( \frac{\hbar \omega_n(q)}{k_B T} \right)^2 \frac{e^{\hbar \omega_n(q)/k_B T}}{\left(e^{\hbar \omega_n(q)/k_B T} - 1\right)}$$

(19)

where $\omega_n(q)$ is the phonon frequency of the n-th branch with wave vector $q$. The volume changes in 3%, 2%, 1%, 0%, -1%, -2%, -3% are applied in QHA process. $\kappa_L$ in Mg$_3$Sb$_2$ is estimated to be 2.55 W m$^{-1}$ K$^{-1}$ at 300 K and 0.8 W m$^{-1}$ K$^{-1}$ at 725 K, which are small values derived from the large Grüneisen parameter $\gamma$ of 1.861 at 300 K and 2.148 at 725 K.

Reference: