# Supporting Information

# Computational prediction of high ZT of n-type Mg_3Sb_2-based compounds with isotropic thermoelectric conduction performance

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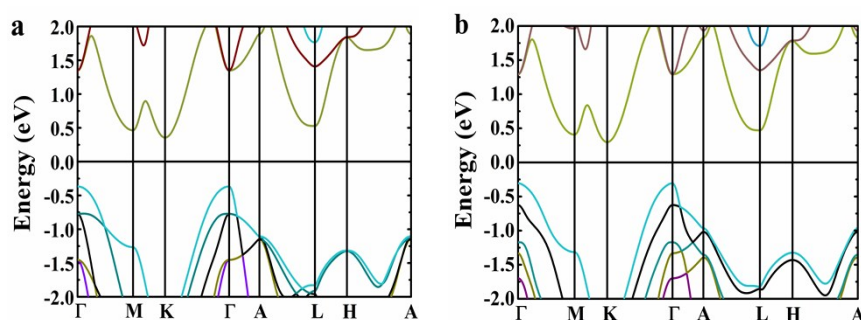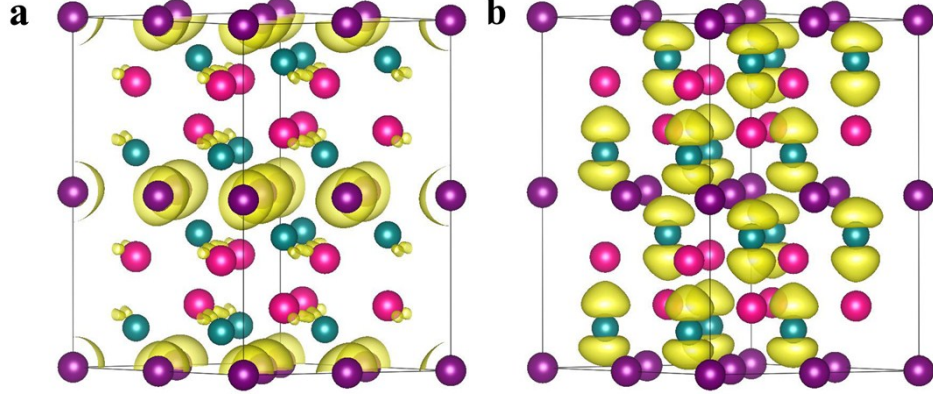

Fig. S1 Calculated band structures (a) without and (b) with spin orbit coupling (SOC) in Mg_3Sb_2.
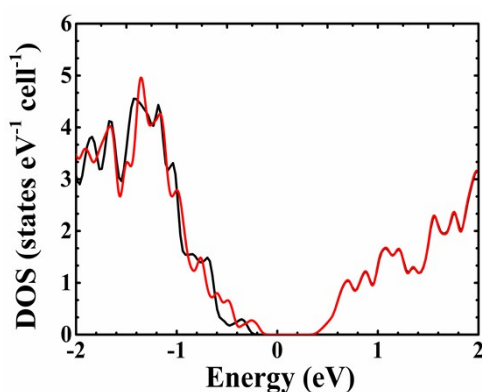
**Fig. S2** Calculated total DOS of Mg_3Sb_2. The back and red solid lines represent the calculated

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.
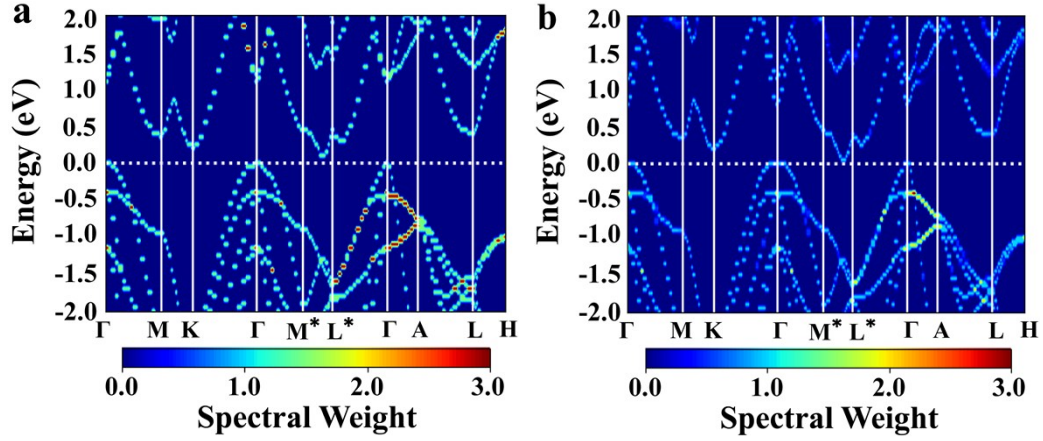
Fig. S4 Effective band structure of (a) $2 \times 2 \times 2$ supercell of the primitive unit cell Mg_3Sb_2 (40 atoms) and (b) $Mg_3Sb_{1.5}Bi_{0.5}$ by PBE functional without SOC.

Estimation of carrier's mobility and scattering time

Based on the deformation potential (DF) theory,[1] the carrier's mobility μ and scatter time τ can be expressed as:

$$\mu = \frac{2\sqrt{2\pi}\hbar^4 c_{ii}}{3(k_B T)^{3/2} m_I^{*5/2} \Xi^2} \tag{1}$$

$$\tau = \frac{\mu m_I^*}{e} = \frac{2\sqrt{2\pi}\hbar^4 c_{ii}}{3(k_B T m_I^*)^{3/2} \Xi^2} \tag{2}$$

where c_{ii} is the lattice elastic constant ($i=1, 2, 3$), Ξ 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 Δa, 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)[2] to calculate the effective mass tensor m_{ij} of a single valley, defined as:

$$m_{ij}^* = \hbar^2 (\partial^2 E(k)/\partial k_i \partial k_j)^{-1}, \quad i, j = x, y, z \tag{3}$$

The conductivity effective mass m_I^* can be express as:

$$m_I^* = 3/(1/m_{xx}^* + 1/m_{yy}^* + 1/m_{zz}^*) \tag{4}$$

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$_3$Sb$_2$. 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:

$$m_I^* = 2/(1/m_{I,K}^* + 1/m_{I,CB1}^*) \tag{5}$$

Thus, the calculated conductivity effective mass m_I^* of n-type Mg$_3$Sb$_2$ is 0.22 eV. Using equation (1), the calculated μ are 101.8 cm^2 V^{-1} s^{-1} along Γ - M direction and 108.1 cm^2 V^{-1} s^{-1} along Γ - A direction at 300 K, and 27 cm^2 V^{-1} s^{-1} along Γ - M direction and 28.69 cm^2 V^{-1} s^{-1} along Γ - A direction at 725 K. Using equation (2), the

calculated τ are 12.62 *fs* along Γ - M direction and 13.39 *fs* along Γ - A direction at 300 K, and 3.333 *fs* along Γ - M direction and 3.539 *fs* along Γ - A direction at 725 K.

Calculation of the minimum lattice thermal conductivity

The minimum lattice thermal conductivity κ_{min} is calculated using the Cahill's formula as:[3,4]

$$\kappa_{min} = \frac{1}{2}[(\frac{\pi}{6})^{1/3}]k_B(V)^{-2/3}(2v_t + v_l) \qquad (6)$$

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]

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

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

where B is the bulk modulus, G is the shear modulus and ρ is the density. B and G are determined adopting the Voigt-Reuss-Hill averaging scheme in hexagonal system given by:[5,6]

$$B = (B_V + B_R)/2 \qquad (9)$$

$$G = (G_V + G_R)/2 \qquad (10)$$

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

$$B_R = \frac{c^2}{M} \qquad (12)$$

$$G_V = \frac{1}{30}(M + 12c_{44} + 12c_{66}) \qquad (13)$$

$$G_R = \frac{5c^2 c_{44} c_{66}}{2(3B_V c_{44} c_{66} + c^2(c_{44} + c_{66}))} \tag{14}$$

$$M = c_{11} + c_{12} + 2c_{33} - 4c_{13} \tag{15}$$

$$c^2 = (c_{11} + c_{12})c_{33} - 2c_{13}^2 \tag{16}$$

where c_{11}, c_{33}, c_{44}, c_{12} and c_{13} are five independent elastic constants for hexagonal system. The calculated κ_{min} in Mg$_3$Sb$_2$ is 0.528 W m^{-1} K^{-1}.

Estimation of the lattice thermal conductivity

According the Slack's formula, the lattice thermal conductivity κ_L can be expressed as:[7]

$$\kappa_L = A \frac{\overline{M} \Theta_D^3 V_{per}^{1/3}}{\gamma^2 n^{2/3} T} \tag{15}$$

where $\overline{M}$, Θ_D, V_{per}, n and γ 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 κ_L is in W m^{-1} K^{-1}, $\overline{M}$ is in amu, and $V_{per}^{1/3}$ is in Å. Θ_D is proportional to the averaged sound velocity v_s and can be evaluated by:[3,7]

$$\Theta_D = \frac{h}{k_B} (6\pi^2 n_a)^{1/3} v_s \tag{16}$$

where n_a is the number density of atoms. v_s can be calculated via:[5,6]

$$v_s = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \tag{17}$$

γ, determining the low κ_L, is calculated using the combined density functional perturbation theory (DFPT) and the quasi-harmonic approximation (QHA), given by:[8]

$$\gamma = \frac{3\beta B V_m}{C_V} \qquad (18)$$

where β, 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:[8]

$$C_V = \sum_{n,q} k_B \left(\frac{\hbar\omega_n(q)}{k_B T} \right)^2 \frac{e^{\hbar\omega_n(q)/k_B T}}{\left(e^{\hbar\omega_n(q)/k_B T} - 1 \right)^2} \qquad (19)$$

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. κ_L in Mg_3Sb_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 γ of 1.861 at 300 K and 2.148 at 725 K.

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