Electronic Supplementary Information for

High thermoelectric performance in Te-free (Bi,Sb)₂Se₃ by structural transition induced band convergence and chemical bond softening

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Supplemental Note 1: Calculations of DOS effective masses and Lorenz numbers

On the basis of the Boltzmann transport equation and relaxation time approximation in a simplified single parabolic band, the Seebeck coefficient and carrier concentration of a degenerate semiconductor can be expressed as followed equations^{1,2}

$$\alpha = \frac{\kappa_B}{e} \left[\frac{(2+\lambda)F_{1+\lambda}(\xi_F)}{(1+\lambda)F_{\lambda}(\xi_F)} - \xi_F \right], \tag{1}$$

$$n_{\rm H} = \frac{4\pi (2k_{\rm B}Tm^*)^{3/2}}{h^3} F_{1/2}(\zeta_{\rm F}) , \qquad (2)$$

and
$$F_{j}(x) = \int_{0}^{\infty} \frac{\xi_{F}^{\ j} d\xi_{F}}{1 + \exp(\xi_{F} - x)} , \qquad (3)$$

where $F_j(x)$ is the Fermi integral, ξ_F the reduced Fermi level, m^* the effective mass, h the Planck constant, and k_B the Boltzmann constant, respectively. λ equates 0 for the acoustic phonon scattering, and then m^* can be calculated based on the results of α and p_H at 300 K. The Lorenz number can be calculated according to following equation ($\lambda = 0$),

$$L = \left(\frac{\kappa_{\rm B}}{e}\right)^2 \left[\frac{3F_0(\xi)F_2(\xi) - 4F_1^2(\xi)}{F_0^2(\xi)}\right]$$
(4)

Supplemental Note 2: Calculations of κ_L using the Klemens-Callaway theory

Considering only Umklapp and point defect phonon scattering processes, the ratio of κ_L of the crystal with disorder to that without disorder, κ_L^p , is

$$\frac{\kappa_L}{\kappa_L^p} = \frac{\tan^{-1}(u)}{u}, \quad u^2 = \frac{\pi^2 \theta_D \Omega}{h v^2} \kappa_L^p \Gamma_{\exp}, \tag{5}$$

where u, Ω , h, v, and Γ_{exp} are the disorder scaling parameter, the average volume per atom, the Planck constant, the average sound velocity, and the experimental disorder scattering parameter, respectively. The disorder scattering parameter, Γ_{calc} , is derived from the model of Slack³ and by Abeles⁴ by assuming $\Gamma_{cal}=\Gamma_{M}+\Gamma_{S}$, where the scattering parameters Γ_{M} and Γ_{S} are due to mass and strain field fluctuations, respectively. The composition of a compound can be expressed as $A1_{c1}A2_{c2}A3_{c3}...An_{cn}$, where the A*i* are crystallographic sublattices in the structure and the *ci* are the relative degeneracies of the respective sites. In general there will be several different types of atoms that occupy each sublattice, and the k_{th} atom of the i_{th} sublattice has mass M_i^k , radius r_i^k , and fractional occupation f_i^k . The average mass and radius of atoms on the *i*th sublattice are

$$\overline{M}_i = \sum_k f_i^k M_i^k, \quad \overline{r_i} = \sum_k f_i^k r_i^k.$$
(6)

The mass fluctuation scattering parameter is then given by

$$\Gamma_{M} = \frac{\sum_{i=1}^{n} c_{i} \left(\frac{M_{i}}{\overline{M}}\right)^{2} \Gamma_{M}^{i}}{\left(\sum_{i=1}^{n} c_{i}\right)}.$$
(7)

The mass fluctuation scattering parameter for the *i*th sublattice can be expressed as

$$\Gamma_M^i = \sum_k f_i^k (1 - \frac{M_i^k}{\overline{M}_i})^2, \tag{8}$$

and the average atomic mass of the compound is

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$$\overline{\overline{M}} = \frac{\sum_{i=1}^{n} c_i \overline{M}_i}{(\sum_{i=1}^{n} c_i)}.$$
(9)

For two different elements on each of the *i*th sublattice, i.e., k = 1, 2, we have masses M_i^1 and M_i^2 , fractional concentrations f_i^1 and f_i^2 , and, using $f_i^1 + f_i^2 = 1$ and $\overline{M}_i = f_i^1 M_i^1 + f_i^2 M_i^2$, Eqs. (7)–(9) become

$$\Gamma_{M} = \frac{\sum_{i=1}^{n} c_{i} (\frac{\overline{M}_{i}}{\overline{\overline{M}}})^{2} f_{i}^{1} f_{i}^{2} (\frac{M_{i}^{1} - M_{i}^{2}}{\overline{M}_{i}})^{2}}{(\sum_{i=1}^{n} c_{i})},$$
(10)

Impurity atoms in an ordered crystal lattice with different size and coupling forces from the lattice atoms, will create strain field fluctuation. Using an elastic continuum treatment, Steigmeier⁵ and Abeles⁴ derived a simplified expression for Γ_S that depends only on atomic radii relation between the change in stiffness constant and the change in size due to the presence of impurity atoms. For two different atoms on each of the *i*th sublattices, the Γ_S is given by

$$\Gamma_{S} = \frac{\sum_{i=1}^{n} c_{i} (\frac{\overline{M}_{i}}{\overline{\overline{M}}})^{2} f_{i}^{1} f_{i}^{2} \varepsilon_{i} (\frac{r_{i}^{1} - r_{i}^{2}}{\overline{r_{i}}})^{2}}{(\sum_{i=1}^{n} c_{i})}, \qquad (11)$$

where $\overline{r_i} = f_i^1 r_i^1 + f_i^2 r_i^2$, and ε_i is a phenomenological adjustable parameter for the *i*th sublattice. The parameter ε_i is a function of the Grüneisen parameter γ and elastic properties,⁴ and Ableses expressed ε_i as⁶

$$\varepsilon = \frac{2}{9} [(G + 6.4\gamma) \frac{1 + \delta}{1 - \delta}]^2,$$
(12)

where δ is the Poisson ratio which for most semiconducting compounds is found between 0.15 and 0.3. *G* is a ratio between the contrast in bulk modulus ($\Delta K/K$) and that in the local bonding length ($\Delta R/R$). *G* is materials dependent and not straightforward to calculate, and was taken as 4 for diamond structure. Here we taken $\delta = 0.25$ and G = 3 for the calculations, and used two different γ values of 1.5 and 2 which gives two different ε values of ~100 and ~150, respectively.

The other physical parameters used for calucaltions are averaged for Bi₂Se₃ and Sb₂Se₃, such as sound velocity, Debye temperature, atomic volume, etc.



Supplemental Figures

Figure S1. The backscattered electron images for $Bi_{2-x}Sb_xSe_3$ polycrystals.



Figure S2. The crystal structure of rhombohedral Bi₂Se₃, (a) hexagonal cell, (b) [BiSe₆] octahedron within quintuples. The quintuple layer (~1 nm) and van der Waals gap are shown in (a).



Figure S3. The crystal structure of orthorhombic Sb₂Se₃. (a) Unit cell, (b) chain-like structure projected on *ac* plane.



Figure S4. The thermoelectric transport properties of Bi_{2-x}Sb_xSe₃, (a) electrical conductivity, (b) Seebeck coefficient, (c) specific heat, (d) thermal conductivity, (e) power factor, and (f) *ZT*. The electrical properties of Sb₂Se₃ is unmeasurable in the ZEM-3 system.



Figure S5. The band gaps estimated by $E_g = 2e \alpha_{max} T_{max}$, and also compared with optical gaps of thin films.^{7,8}



Figure S6. Phonon dispersion of *O*-BiSbSe₃, enlarged in the low energy range.



Figure S6. Phonon dispersion of *R*-Bi₂Se₃.



Figure S7. Powder XRD of $Bi_{1,2}Sb_{0.8}(Se_{1-y}I_y)_3$ and $BiSb(Se_{1-y}I_y)_3$ (y = 0-0.03).



Figure 8. The BSE images of $Bi_{1.2}Sb_{0.8}(Se_{1-y}I_y)_3$ and $BiSb(Se_{1-y}I_y)_3$ (y = 0.01, 0.02, and 0.03).

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