Supplemental Information:

Synergistic optimization of the thermoelectric performance of $BiSbSe_3$ using doping and multi-scale defect engineering

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1.Calculation of Pisarenko curves.

The Boltzmann transport equation of the single parabolic band (SPB) model is used to calculate the Pisarenko curves, describing the relationship between S and n. The SPB model can be expressed by the following formula[123]:

$$S = \pm \frac{\kappa_B}{e}\left(\frac{(\lambda + 5/2)F_{\lambda + 3/2}(\eta)}{(\lambda + 3/2)F_{\lambda + 1/2}(\eta)} - \eta\right) \quad (1)$$

$$n = 4\pi\left(\frac{2m^* \kappa_B T}{h^2}\right)^{3/2} F_{1/2}(\eta) \quad (2)$$

$$F_n(\eta) = \int_0^\infty \frac{x^n}{1 + e^{x - \eta}} dx \quad (3)$$

where κ_B is the Boltzmann constant, e is the electron charge, η is the reduced Fermi energy, Fn(η) is the nth order Fermi integral, and h is the Planck constant. Acoustic phonon scattering is the dominant electron scattering mechanism with the scattering factor λ=-1/2. According to Equations (1)-(3), Pisarenko curves were plotted.

2. Calculation of Lorenz numbers.

The electronic thermal conductivity κ_e can be calculated by the Wiedemann-Franz law ($\kappa_e = L\sigma T$), where L is the Lorenz constant. Usually the degeneracy limit and non-degeneracy limit values of L are $L_0 \approx 2.45\times10^{-8}$ WΩK^{-2} and $L_1 \approx 1.5\times10^{-8}$ WΩK^{-2} respectively, while the values of L for thermoelectric materials are often in between. L can be calculated using the following formula[4]:

$$L = \left(\frac{\kappa_B}{e}\right)^2\left[\frac{(\lambda + 7/2)F_{\lambda + 5/2}(\eta)}{(\lambda + 3/2)F_{\lambda + 1/2}(\eta)} - \left(\frac{(\lambda + 5/2)F_{\lambda + 3/2}(\eta)}{(\lambda + 3/2)F_{\lambda + 1/2}(\eta)}\right)^2\right] \quad (4)$$

where the value of λ equates -1/2 for the acoustic phonon scattering, and the calculation formula of L is simplified as:

$$L = (\frac{\kappa_B}{e})^2 \frac{3F_0F_2 - 4F_1^2}{F_0^2} \quad (5)$$

3. Calculation of total heat capacity.

The total heat capacity of the samples is calculated using the heat capacity of the phonon harmonic term under the Debye model[5,6], which is basically consistent with the literature reports, the formula as follows:

$$C_p(T) = 9n_m\kappa_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (6)$$

$$\theta_D = \frac{h}{\kappa_B}\left(\frac{3N}{4\pi V}\right)^{1/3} v_s \quad (7)$$

$$V_s = \{\frac{1}{3}(\frac{1}{v_l^3} + \frac{2}{v_t^3})\}^{(-1/3)} \quad (8)$$

where C_p, n_m, θ_D, N, V, v_s are the heat capacity of harmonic phonon term, number of atoms per unit mass, Debye temperature, number of atoms per unit cell, volume per unit cell, average phonon velocity, respectively.

4. Supplemental figures.

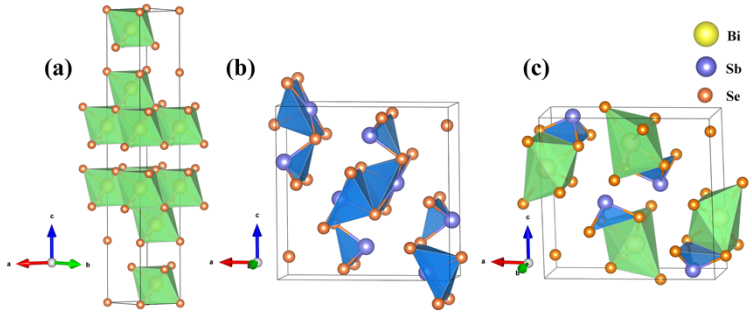

Fig.S1. Crystal structures of (a) Bi_2Se_3, (b) Sb_2Se_3, (c) $BiSbSe_3$.

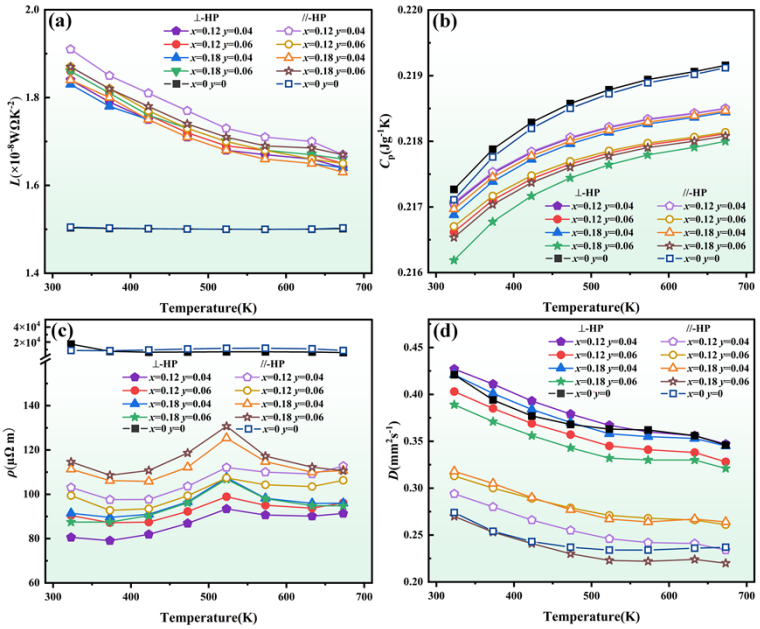

Fig.S2. Thermal transport properties as a function of temperature for $BiSbSe_{3-x-y}Br_xI_y$ (x=0, 0.12, 0.18; y=0, 0.04, 0.06): (a) Lorenz constant, (b) heat capacity, (c) electrical resistivity, (d) thermal diffusivity.

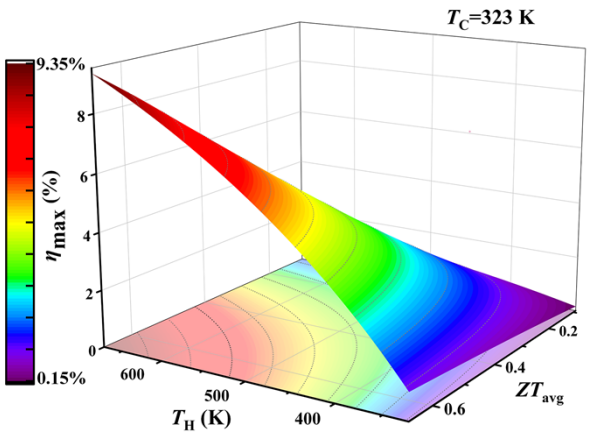

Fig.S3. The $BiSbSe_{2.78}Br_{0.18}I_{0.04}$ thermoelectric conversion efficiency η as a function of the hot-side temperature and average figure of merit ZT_{avg} at the clod side temperature T_C=323 K.

References

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