Supplementary Materials

Reduced bipolar conduction in bandgap-engineered *n*-type $Cu_{0.008}Bi_2(Te,Se)_3$ by sulfur doping

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S1. Single-parabolic-band model

In the single-parabolic-band model, the thermoelectric parameters of the VB and CB computed by using the Boltzmann transport equations [S1] can be substituted into the following equations (S1)–(S4),

$$\sigma_{tot} = \sum_i \sigma_i, \tag{S1}$$

$$S_{tot} = \frac{\sum_i S_i \sigma_i}{\sum_i \sigma_i}, \tag{S2}$$

$$R_{H\,total} = \frac{\sum_i R_{Hi} {\sigma_i}^2}{(\sum_i \sigma_i)^2}, \tag{S3}$$

$$\kappa_{bp} = \left(\sum_i {S_i}^2 \sigma_i - S_{total}^2 \sigma_{total}\right) T. \tag{S4}$$

The calculated σ_{tot} and S_{tot} of the samples were fitted to the experimental σ and S by adjusting the E_g, E_{def}, and m^* values for the VB and CB to estimate κ_{bp} (Table 1) [S1]. In the fitting, E_g estimated by using the Goldsmid–Sharp formula was employed [S2]. Owing to the symmetry of the $Bi_2(Sb,Te)_3$ crystal, more than one Fermi pocket contributes to m^* as $m^* = N_V^{2/3} m_b^*$, where N_V and m_b^* denote the valley degeneracy and band mass of a single valley, respectively. N_V for the VB and CB is 6. The Fermi level of an individual band calculated by using the experimental R_{Htot} was used to validate the values calculated by using S_p and S_n. The calculated R_{Hp} and R_H were used to estimate the hole and electron concentrations, shown in Table 1. κ_{bp} calculated by Equation (S4) with the parameters in Table 1 is shown in Figure 5(b).

S2. Debye–Callaway model

The effect of the S doping on κ_{latt} was analyzed by using the Debye–Callaway model [S3]. In substitutes are considered as additional point defects in the native cation disorder of $Te_{2.8}S_{0.2}$ in $Bi_2(Te_{2.8}S_{0.2})$. The thermal conductivity κ can be expressed by using the kinetic gas model,

$$\kappa = \frac{1}{3} C_V v l = \frac{1}{3} C_V v^2 \tau, \tag{S5}$$

where C_V, v, l, and τ denote the heat capacity, velocity, distance, and relaxation time between collisions, respectively. Equation (S5) can be used for phonons in solids as opposed to gas particles. The Callaway equation for κ_{latt} (Equation (S6)) is [S3]

$$\kappa_{latt} = \frac{1}{3} \int_0^{\omega_{max}} C_V(\omega) v_g(\omega)^2 \tau(\omega)\, \mathrm{d}\omega, \tag{S6}$$

where v_g denotes the phonon group velocity ($v_g = \mathrm{d}\omega/\mathrm{d}k$), equivalent to the speed of sound, v (Debye model). Thus, Equation (S6) can be expressed as Equation (S7), which corresponds to the Debye–Callaway model,

$$\kappa_{latt} = \frac{k_\mathrm{B}}{2\pi^2 v} \left(\frac{k_\mathrm{B} T}{\hbar}\right)^3 \int_0^{\theta_a/T} \frac{\tau_\mathrm{total}(z)\, z^4 e^z}{(e^z - 1)^2} \mathrm{dz}, \tag{S7}$$

where k_B, $\hbar$, θ, and z denote the Boltzmann constant, reduced Planck constant, Debye temperature θ_a, and $\hbar\omega/k_B T$, respectively. The Debye temperature θ_a (94 K) and average phonon velocity (2147 m s^{-1}) were obtained from the literature [S4,S5]. κ_{latt} was estimated by using Equation (S7), where the total relaxation time $\tau_{total}(z)$ is calculated by using the individual relaxation times (τ_i) of various scattering mechanisms based on the following relationship,

$$\tau_\mathrm{total}(z)^{-1} = \sum_i \tau_i(z)^{-1} = \tau_U(z)^{-1} + \tau_B(z)^{-1} + \tau_{PD}(z)^{-1}, \tag{S8}$$

where τ_U, τ_B, and τ_{PD} are the relaxation times of the Umklapp scattering, boundary scattering, and point-defect scattering, respectively. The point-defect scattering can be described by the scattering parameter

(Γ), which is related to the mass difference (ΔM) and lattice constant difference (Δa) between the two different constituents,

$$\tau_{PD}{}^{-1} = Pf(1-f)\omega^4 = \frac{V\omega^4}{4\pi v^3}\Gamma, \quad \text{(S9)}$$

$$\Gamma = f(1-f)\left[\left(\frac{\Delta M}{M}\right)^2 + \frac{2}{9}\left\{(G+6.4\gamma)\frac{1+r}{1-r}\right\}^2\left(\frac{\Delta a}{a}\right)^2\right], \quad \text{(S10)}$$

where P is a fitting parameter, f represents the fractional concentration of the substitutes, G is the ratio of the fractional change in bulk modulus to the local bond length, and γ and r are the Grüneisen parameter and Poisson's ratio, respectively. The same parameters used to calculate the individual relaxation times τ_U and τ_B were used for the fitting for the undoped sample.

To estimate τ_{PD} for the S-doped sample, we considered P in Equation (S9) as an adjusting parameter, where f is a fixed parameter, the determined factional concentration. For x = 0.05 and 0.15, the f values were 0.017 and 0.05, respectively. P was 83.1 × 10^{-41} s^3, fitted by using the experimental κ_{latt} values of the two doped samples. Thus, the $P_S f(1-f)$ values were 1.63 and 3.95 × 10^{-41} s^3 for x = 0.05 and 0.15, respectively. The fitted parameters are shown in Table S1. The lines in Figure 4(c) show the κ_{latt} values of the S-doped samples calculated with the fitted parameters.

Table S1. Point defect contributions to the total relaxation rates ($\tau_{\text{total}}{}^{-1}$) used to model the κ_{latt} values of the samples.

$Cu_{0.008}Bi_2Te_{2.8-x}Se_{0.2}S_x$	Fitting parameter, P_S ($10^{-41}s^3$)	$f(1-f)*P_S$ ($10^{-41}s^3$)
x=0 f=0	-	-
x=0.05 f=0.017	83.1	1.63
x=0.15 f=0.05	83.1	3.95

References

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