Supporting Information

High thermoelectric performance of p-type SnTe via a synergistic band engineering and nanostructuring approach

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Calculation of Lorenz number

The total thermal conductivity (κ_{tot}) of a material is composed of two contributions: the electronic component (κ_{ele}) and the lattice thermal conductivity (κ_{lat}). The electronic part κ_{ele} is proportional to the electrical conductivity σ through the Wiedemann-Franz equation $\kappa_{ele} = L\sigma T$ with *L* being the Lorenz number.¹ Usually, the values used for *L* are 2.45×10⁻⁸ V²/K² and 1.49×10⁻⁸ V²/K² for metals and non-degenerate semiconductors, respectively.² For typical thermoelectric materials, most of which are degenerate semiconductors, the Lorenz number depends on the scattering parameter *r* and will decrease as the reduced Fermi energy μ decreases with increasing temperature.³ The Lorenz number *L* can be expressed as:⁴

$$L = \left(\frac{k_{\rm B}}{e}\right)^2 \left[\frac{(r^{+7}/_2)F_{r^{+5}/_2}(\mu)}{(r^{+3}/_2)F_{r^{+1}/_2}(\mu)} - \left[\frac{(r^{+5}/_2)F_{r^{+3}/_2}(\mu)}{(r^{+3}/_2)F_{r^{+1}/_2}(\mu)}\right]^2\right]$$
(1)

Here, the Fermi energy η can be derived from the measured Seebeck coefficients by using the following relationship:

$$\alpha = \pm \frac{k_{\rm B}}{e} \left[\frac{(r^{+5}/_2)F_{r^{+3}/_2}(\mu)}{(r^{+3}/_2)F_{r^{+1}/_2}(\mu)} - \mu \right]$$
(2)

Where $F_n(\eta)$ is the Fermi integral,

$$F_n(\mu) = \int_0^\infty \frac{\varepsilon^n}{1 + e^{\varepsilon - \mu}} d\varepsilon$$
(3)

$$\mu = \frac{E_f}{k_B T} \tag{4}$$

In the above equations, $k_{\rm B}$ is the Boltzman constant, *e* the electron charge and $E_{\rm f}$ the Fermi energy. Meanwhile, acoustic phonon scattering has been assumed as the main carrier scattering mechanism,⁴ i.e., r = -1/2.⁵ The Lorenz number can be obtained by applying the calculated reduced Fermi energy μ and scattering parameter *r* into Eq. (1).

- [1]. Fitsul, V. I. Heavily Doped Semiconductors; Plenum Press: New York, 1969.
- [2]. Zhou, L.; Qiu, P.; Uher, C.; Shi, X.; Chen, L. Intermetallics 2013, 32, 209.
- [3]. Kumar, G. S.; Prasad, G.; Pohl, R. O.; J. Mater. Sci. 1993, 8, 4261.
- [4]. Zhao, L. D.; Lo, S. H.; He, J. Q.; Li, H.; Biswas, K.; Androulakis, J.; Wu, C. I.; Hogan, T. P.; Chung, D. Y.; Dravid, V. P.; Kanatzidis, M. G. J. Am. Chem. Soc. 2011, 133, 20476.
- [5]. Zhao, L. D., Zhang, B. P., Liu, W. S.; Li, J. F. J. Appl. Phys. 2009, 105, 023704.

Discussion on bipolar diffusion and band degeneracy

In semiconductors, bipolar diffusion is a complex phenomenon. In addition to band gap, carrier density is another influence factor that cannot be ignored.¹ Larger band gap and higher carrier concentration are beneficial to suppress the minority carriers. To make a meaningful comparison of bipolar diffusion between two samples, they should have similar carrier concentration. In this context we prepared a series of iodine doped SnTe and selected a sample with nominal composition $SnTe_{0.995}I_{0.005}$, the hole density of which (~7.01E10¹⁹ cm⁻³) is very close to that of 2 mol.% Cd-doped SnTe (~6.85E10¹⁹ cm⁻³) at room temperature. Importantly, the iodine dopant has been demonstrated to exert little influence on the electronic band structure of PbTe.² This is supported by the fact that the room temperature Seebeck coefficient of iodine doped SnTe agrees well with the Pisarenko plot expected by a VBM model, Figure S3. By comparing the electrical properties of iodine doped and Cd doped samples one can see how Cd alloying affects the band structure of SnTe, see Figure S4. From Figure S4(b), it is clear that the Cd-doped SnTe has a much larger Seebeck coefficient over the entire temperature range than iodine doped one despite the fact that the two samples have similar hole concentration at room temperature. This reveals that Cd alloying in SnTe has a higher hole density of states arising from the valence band degeneracy as suggested by the band structure calculations. Moreover, regardless of the magnitude of lattice thermal conductivity, one can see that iodine doped SnTe has a much lower onset temperature of bipolar diffusion with respect to cadmium doped one. It therefore verifies the gap opening by Cd doping. Without the two beneficial effects caused by Cd doping, under the same hole density, the maximum ZT value of iodine doped SnTe is only around ~ 0.6 , much lower than that of Cd-doped SnTe (~ 0.8).

[1] W. S. Liu et al, J. Appl. Phys. 102, 2007, 103717.

[2] A. D. LaLonde et al., Energy Environ. Sci., 4, 2011, 2090

Supporting Tables

Compositions	Densities, ρ (g/cm ³)	Compositions	Densities, ρ (g/cm ³)
SnTe	6.2	Sn _{0.98} Cd _{0.05} Te	6.1
Sn _{1.01} Te	6.2	Sn _{0.97} Cd _{0.06} Te	6.1
Sn _{1.02} Te	6.2	SnCd _{0.03} Te-1%CdS	6.1
Sn _{1.03} Te	6.1	SnCd _{0.03} Te-2%CdS	6.1
Sn _{1.04} Te	6.0	SnCd _{0.03} Te-3%CdS	6.2
Sn _{1.06} Te	5.9	SnCd _{0.03} Te-4%CdS	6.0
Sn _{1.08} Te	6.1	SnCd _{0.03} Te-5%CdS	6.1
Sn _{1.10} Te	5.9	SnCd _{0.03} Te-1%ZnS	6.2
$Sn_{1.02}Cd_{0.01}Te$	6.2	SnCd _{0.03} Te-2%ZnS	6.2
Sn _{1.01} Cd _{0.02} Te	6.1	SnCd _{0.03} Te-3%ZnS	6.1
$Sn_{1.00}Cd_{0.03}Te$	6.1	SnCd _{0.03} Te-4%ZnS	6.1
Sn _{0.99} Cd _{0.04} Te	6.1	SnCd _{0.03} Te-5%ZnS	6.1

Table S1. Densities of all samples investigated in this study.

Supporting Figures



Figure S1. (a) Thermal diffusivity D, (b) Heat capacity C_p , and (c) Lorenz number L as a function of temperature for Sn_{1+x} Te materials.



Figure S2. (a) Thermal diffusivity D, (b) Heat capacity C_p , and (c) Lorenz number L as a function of temperature for $Sn_{1.03-x}Cd_xTe$ samples.



Figure S3. Room temperature Seebeck coefficient as a function of hole density for iodine doped SnTe. The dotted line is Pisarenko plot expected by a VBM model.



Figure S4. A comparison of thermoelectric properties between cadmium doped and iodine doped SnTe with similar hole densities at room temperature: (a) electrical conductivity; (b): Seebeck coefficient; (c) power factor; (d) total thermal conductivity; (e) lattice thermal conductivity; and (f) *ZT* value.



Figure S5. TEM image of $SnCd_{0.03}$ Te-2%CdS taken along [110] direction. (a) Low magnification image of $SnCd_{0.03}$ Te-2%CdS. The inset is the SAD pattern taken along [110] direction, showing two sets of diffraction patterns from two grains separated by a grain boundary as shown in (a). (b) HRTEM image of a nanoprecipitate, highlighted by dashed white line.



Figure S6. TEM image of $SnCd_{0.03}$ Te-2%ZnS taken along [110] direction. (a) Low magnification image of $SnCd_{0.03}$ Te-2%ZnS. The inset is the SAD pattern taken along [110] direction. (b) HRTEM image of a nanoprecipitate, highlighted by dashed white line. (c) STEM-EDX results of the matrix and the precipitate. The spectra were acquired in the area shown in the inset STEM image. The precipitate (spot 1) has Zn and S signal, but the matrix (spot 2) has none



Figure S7. (a) Thermal diffusivity D, (b) Heat capacity C_p , and (c) Lorenz number L as a function of temperature for SnCd_{0.03}Te-x%CdS samples.



Figure S8. (a) Thermal diffusivity D, (b) Heat capacity C_p , and (c) Lorenz number L as a function of temperature for SnCd_{0.03}Te-x%ZnS samples.



Figure S9. Temperature dependent (a) electrical conductivity; (b) Seebeck coefficient; (c) total thermal conductivity; and (d) ZT values for SnCd_{0.03}Te-2%CdS samples of initially prepared one (black square), reproduced one (red circle), and the reproduced one (green triangle) after vacuum annealing at 723 K for 15 days.