Supplementary information

Atomic-Scale Structure and Thermoelectric Properties in Medium-Entropy PbSnTeSe Alloy

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Callaway model calculation

According to the Callaway model, the scattering caused by point defects derives from the mass fluctuation and stress field fluctuation between impurity atoms and matrix atoms. In this work, Callaway model is used to calculate the lattice thermal conductivity, where the chosen of matrix is based on the XRD results.

The ratio of the lattice thermal conductivity of a material containing defects to that of the parent material when the temperature is above the Debye temperature can be written as:

$$\frac{\kappa_{\mathrm{lat}}}{\kappa_{\mathrm{lat,\ p}}} = \frac{\tan^{-1}(u)}{u} \tag{1}$$

where κ_{lat} and $\kappa_{\mathrm{lat,\ p}}$ refers to the lattice thermal conductivity of the medium-entropy alloys and parent materials, and the parameter u is defined as:

$$u = \left(\frac{\pi^2 \theta_{\mathrm{D}} \Omega}{h v_{\mathrm{a}}^2} \kappa_{\mathrm{lat,\ p}} \Gamma \right)^{1/2} \tag{2}$$

where h and Ω are the Planck constant and average volume per atom, respectively, average sound velocity v_{a} can be extracted from:

$$v_{\mathrm{a}} = \left[\frac{1}{3} \left(\frac{1}{v_{\mathrm{l}}^3} + \frac{2}{v_{\mathrm{s}}^3} \right) \right]^{-1/3} \tag{3}$$

Longitudinal sound velocity (v_{l}) and shear sound velocity (v_{s}) can be measured experimentally. Debye temperature θ_{D} is defined by:

$$\theta_{\mathrm{D}} = \frac{h}{k_{\mathrm{B}}} \left[\frac{3N}{4\pi V} \right]^{1/3} v_{\mathrm{a}} \tag{4}$$

where k_{B} is Boltzmann parameter, the V is the unit-cell volume, N is the number of atoms in a unit cell. The imperfection scaling parameter Γ in Eq. (2) represents the strength of point defects phonon scattering, which includes two components, the scattering parameter due to mass fluctuations Γ_{M} and the scattering parameter due to strain field fluctuations Γ_{S}. A phenomenological adjustable parameter ε is always included because of uncertainty of Γ_{S}, one writes $\Gamma = \Gamma_{\mathrm{M}} + \varepsilon\Gamma_{\mathrm{S}}$. In this work, ε is directly estimated by following relationship:

$$\varepsilon = \frac{2}{9}\left(\frac{6.4\times\gamma\left(1+\upsilon_{\mathrm{p}}\right)}{1-\upsilon_{\mathrm{p}}}\right)^{2} \tag{5}$$

where υ_{p} the Poisson ratio, which can be calculated from the longitudinal (v_{l}) and transverse (v_{s}) sound velocities by the relationship as:

$$\upsilon_{\mathrm{p}} = \frac{1-2\left(v_{\mathrm{s}}/v_{\mathrm{l}}\right)^{2}}{2-2\left(v_{\mathrm{s}}/v_{\mathrm{l}}\right)^{2}} \tag{6}$$

Gruneisen parameter (γ) are calculated by using Poisson ratio (υ_{p}):

$$\gamma = \frac{3}{2}\left(\frac{1+\upsilon_{\mathrm{p}}}{2-3\upsilon_{\mathrm{p}}}\right) \tag{7}$$

Since solid solution occurs at both anionic and cationic locations of $(PbSe)_{1-x}(SnTe)_{x}$ (x = 0.1-0.9) alloys, Γ can be described as follow:

$$\Gamma_{(\mathrm{PbSe})_{1-x}(\mathrm{SnTe})_{x}} = \frac{1}{2}\left(\frac{M_{(\mathrm{Pb,\ Sn})}}{\overline{M}}\right)^{2}\Gamma_{(\mathrm{Pb,\ Sn})} + \frac{1}{2}\left(\frac{M_{(\mathrm{Se,\ Te})}}{\overline{M}}\right)^{2}\Gamma_{(\mathrm{Se,\ Te})} \tag{8}$$

$$\Gamma = \Gamma_{\mathrm{M}} + \varepsilon\Gamma_{\mathrm{S}} \tag{9}$$

$$\Gamma_{(\mathrm{Pb,\ Sn})} = \Gamma_{\mathrm{M}(\mathrm{Pb,\ Sn})} + \varepsilon\Gamma_{\mathrm{S}(\mathrm{Pb,\ Sn})} \tag{10}$$

$$\Gamma_{M_{(\mathrm{Pb,\ Sn})}} = x\left(1-x\right)\left(\frac{\Delta M_{(\mathrm{Pb,\ Sn})}}{M_{(\mathrm{Pb,\ Sn})}}\right)^{2} \tag{11}$$

$$\Gamma_{S_{(\mathrm{Pb,\ Sn})}} = x\left(1-x\right)\left(\frac{\Delta r_{(\mathrm{Pb,\ Sn})}}{r_{(\mathrm{Pb,\ Sn})}}\right)^{2} \tag{12}$$

in which $\Delta M = M_{\mathrm{Pb}} - M_{\mathrm{Sn}}$, $M_{(\mathrm{Pb,\ Sn})} = (1-x)M_{\mathrm{Pb}} + xM_{\mathrm{Sn}}$, $\Delta r = r_{\mathrm{Pb}} - r_{\mathrm{Sn}}$ and $r_{(\mathrm{Pb,\ Sn})} = (1-x)r_{\mathrm{Pb}} + xr_{\mathrm{Sn}}$. The parameter r_i stands for the cube root of the atomic volume of component i of the alloy.

Therefore, the Eq. (9) can be written as:

$$\Gamma_{(\mathrm{Pb,\ Sn})} = x\left(1-x\right)\left[\left(\frac{\Delta M_{(\mathrm{Pb,\ Sn})}}{M_{(\mathrm{Pb,\ Sn})}}\right)^{2} + \varepsilon\left(\frac{\Delta r_{(\mathrm{Pb,\ Sn})}}{r_{(\mathrm{Pb,\ Sn})}}\right)^{2}\right] \tag{13}$$

and the Eq. (8) can be described as:

$$\Gamma_{(PbSe)_{1-x}(SnTe)_x} = \frac{1}{2}\left(\frac{M_{(Pb,\,Sn)}}{\overline{M}}\right)^2 x(1-x)\left[\left(\frac{\Delta M_{(Pb,\,Sn)}}{M_{(Pb,\,Sn)}}\right)^2 + \varepsilon\left(\frac{\Delta r_{(Pb,\,Sn)}}{r_{(Pb,\,Sn)}}\right)^2\right] + \frac{1}{2}\left(\frac{M_{(Se,\,Te)}}{\overline{M}}\right)^2 x(1-x)\left[\left(\frac{\Delta M_{(Se,\,Te)}}{M_{(Se,\,Te)}}\right)^2 + \varepsilon\left(\frac{\Delta r_{(Se,\,Te)}}{r_{(Se,\,Te)}}\right)^2\right] \quad (14)$$

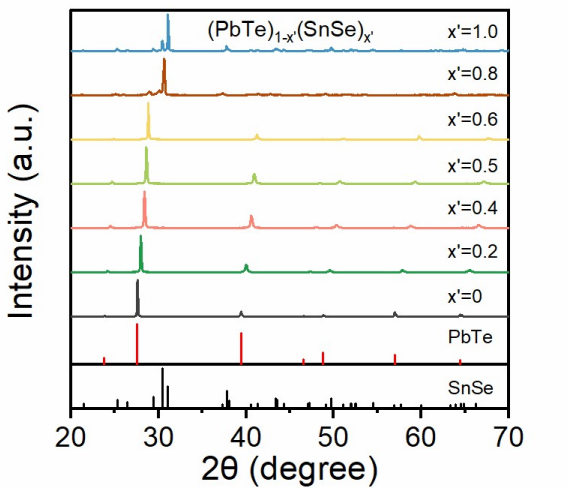

Fig. S1. Powder X-ray diffraction (XRD) patterns in $(PbTe)_{1-x'}(SnSe)_{x'}$ (x' = 0-1.0).

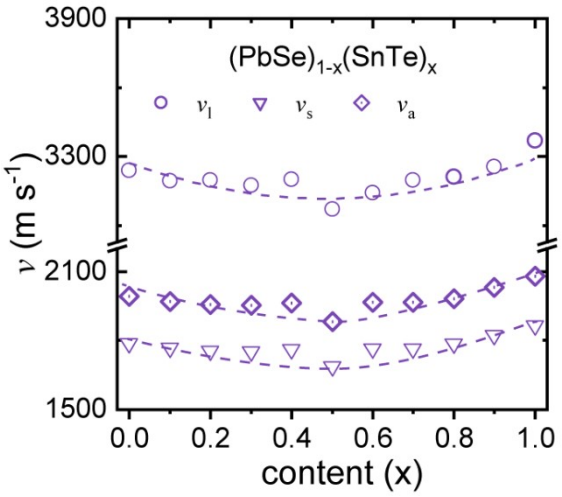

Fig. S2. Sound velocity of $(PbSe)_{1-x}(SnTe)_x$ (x = 0-1.0), where v_l, v_s and v_a refer to longitudinal, shear, and average sound velocity, respectively.

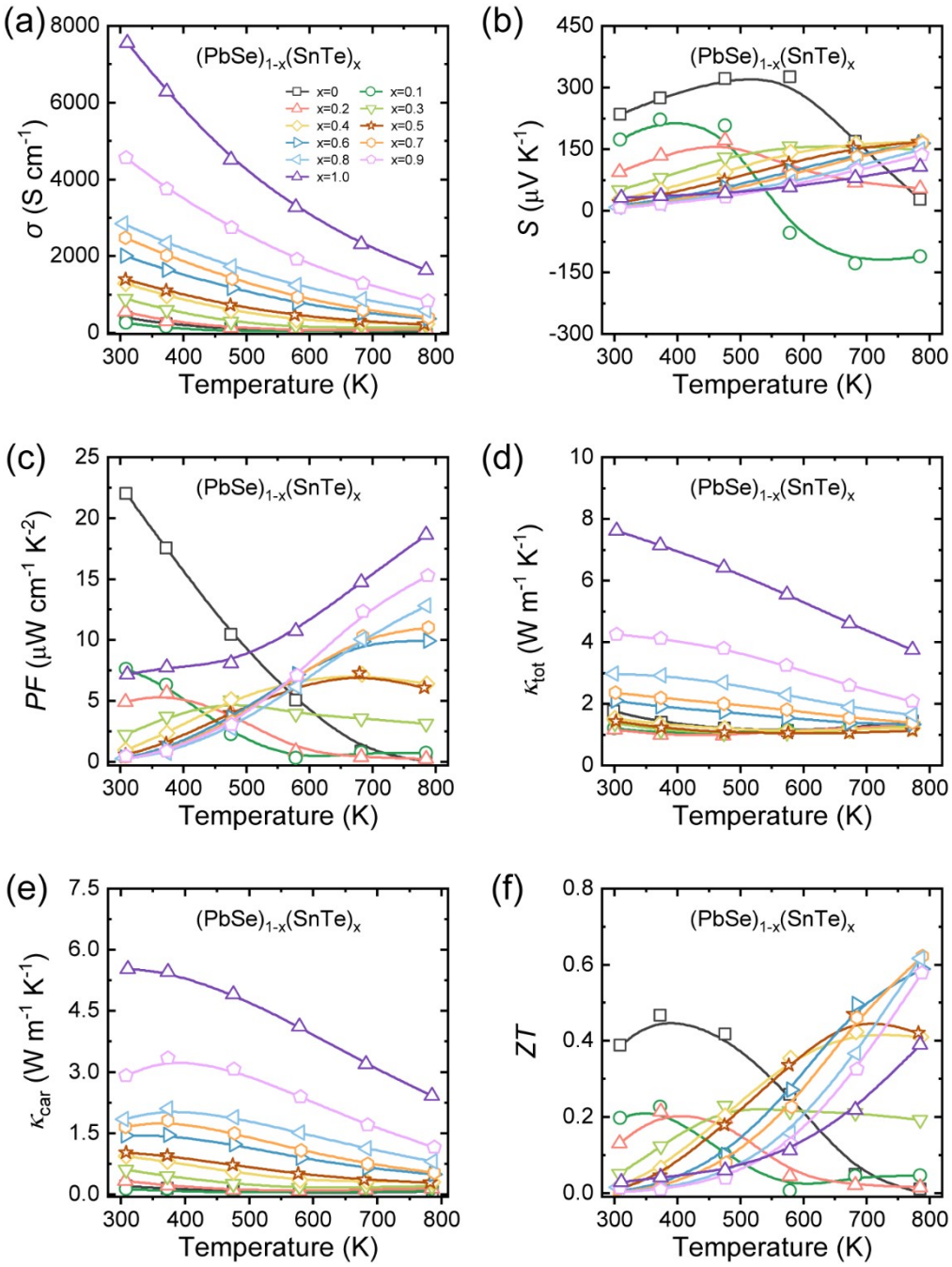

Fig. S3. Temperature-dependent thermoelectric properties in $(PbSe)_{1-x}(SnTe)_x$ (x = 0-1.0). (a) Electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) total thermal conductivity, (e) carrier thermal conductivity and (f) *ZT* values.

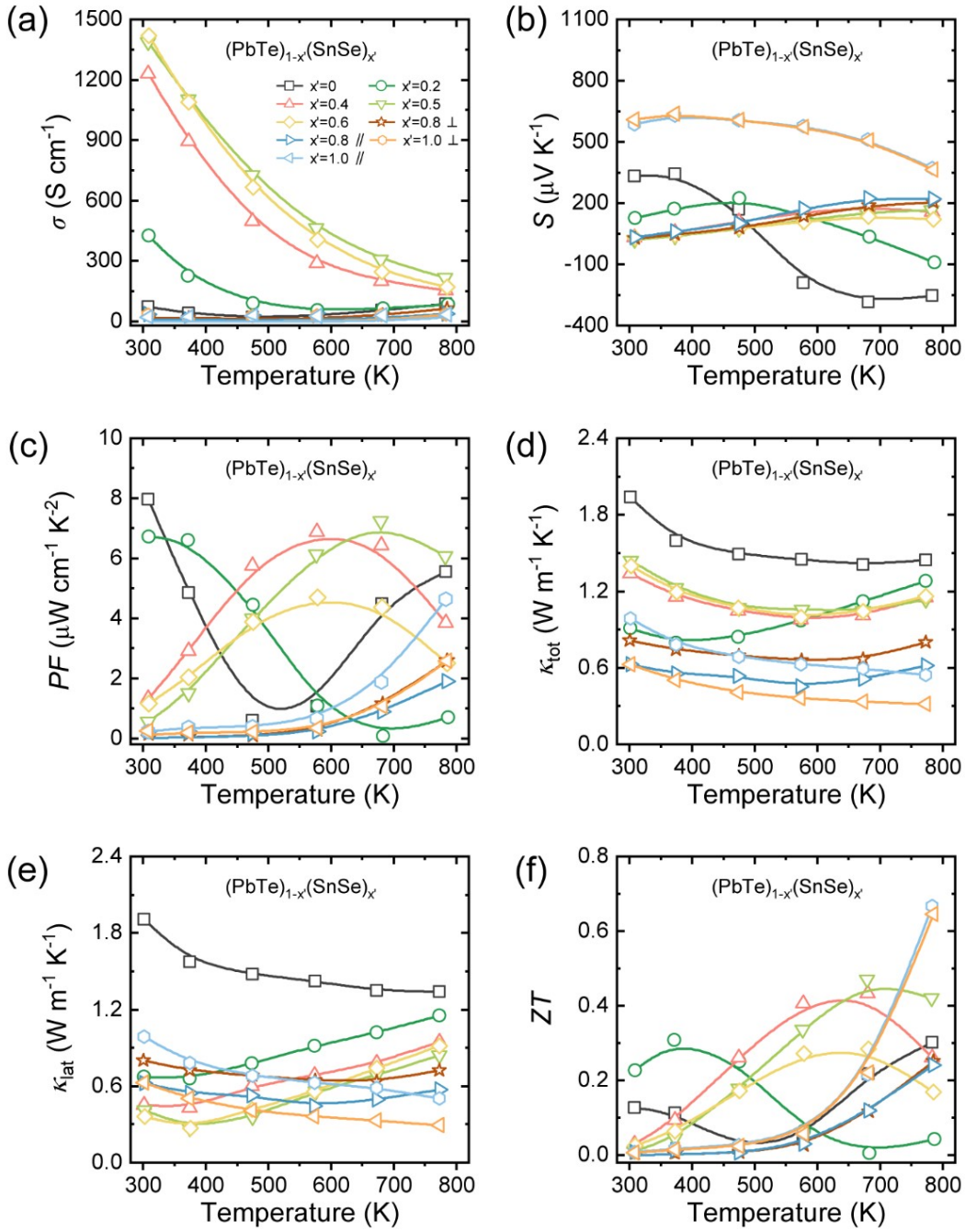

Fig. S4. Temperature-dependent thermoelectric properties in $(PbTe)_{1-x'}(SnSe)_{x'}$ (x' = 0-1.0). (a) Electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) total thermal conductivity, (e) lattice thermal conductivity and (f) *ZT* values.

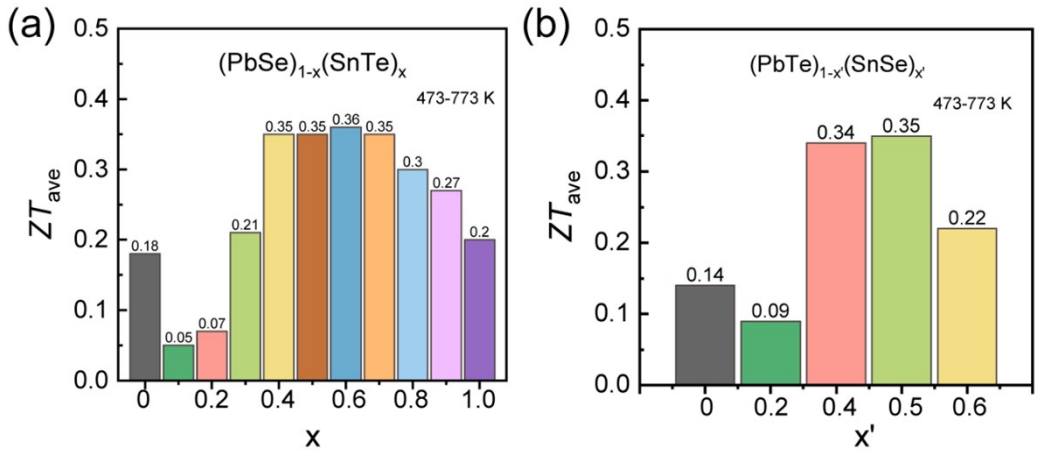

Fig. S5. Average *ZT* values in $(PbSe)_{1-x}(SnTe)_x$ (x = 0-1.0) and $(PbTe)_{1-x'}(SnSe)_{x'}$ (x' = 0-0.6) at 473-773 K.

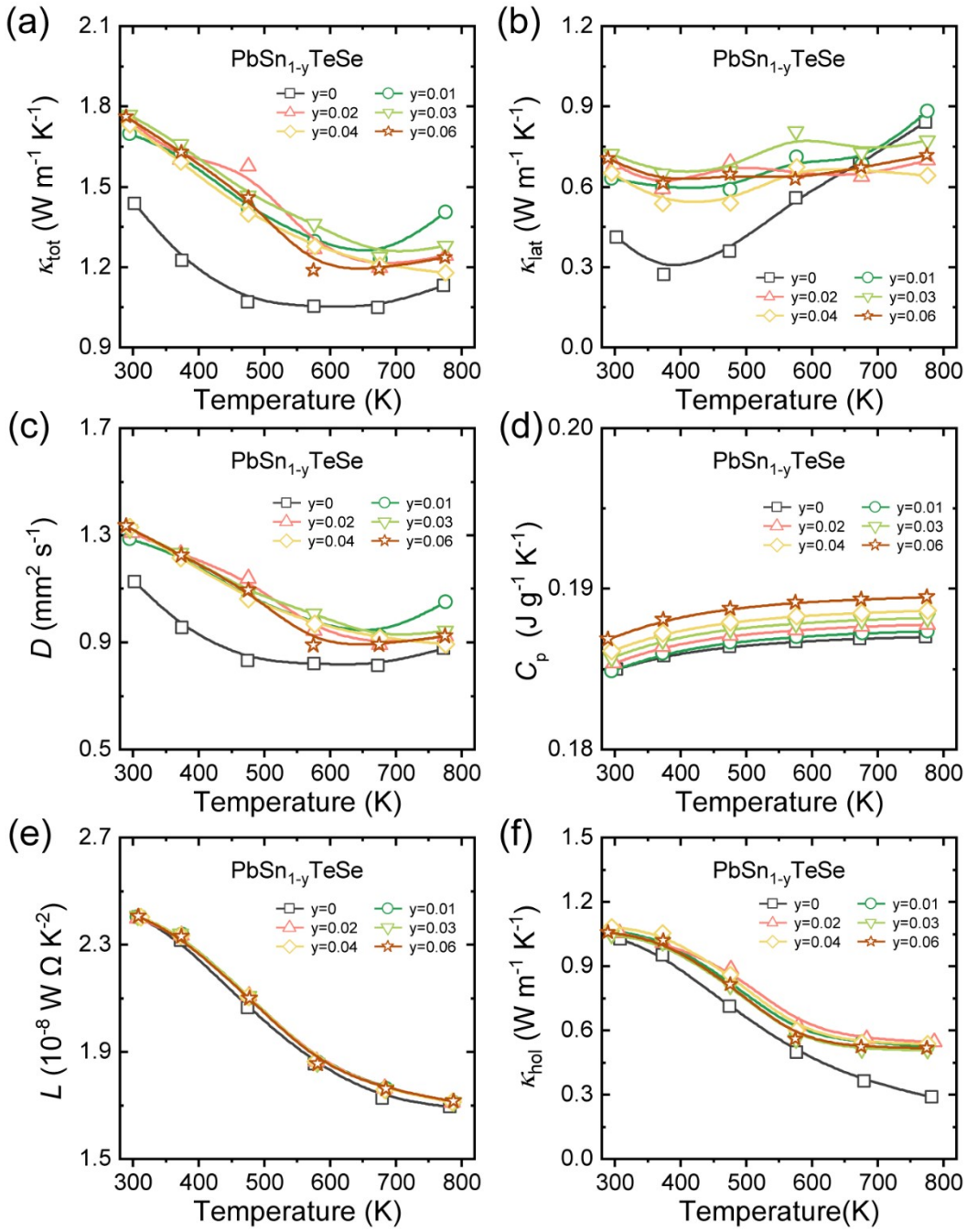

Fig. S6. Thermal transport properties in $PbSn_{1-y}TeSe$ (y = 0-0.06). (a) Total thermal conductivity, (b) lattice thermal conductivity, (c) thermal diffusivity, (d) heat capacity, (e) Lorenz number and (f) hole carrier thermal conductivity.

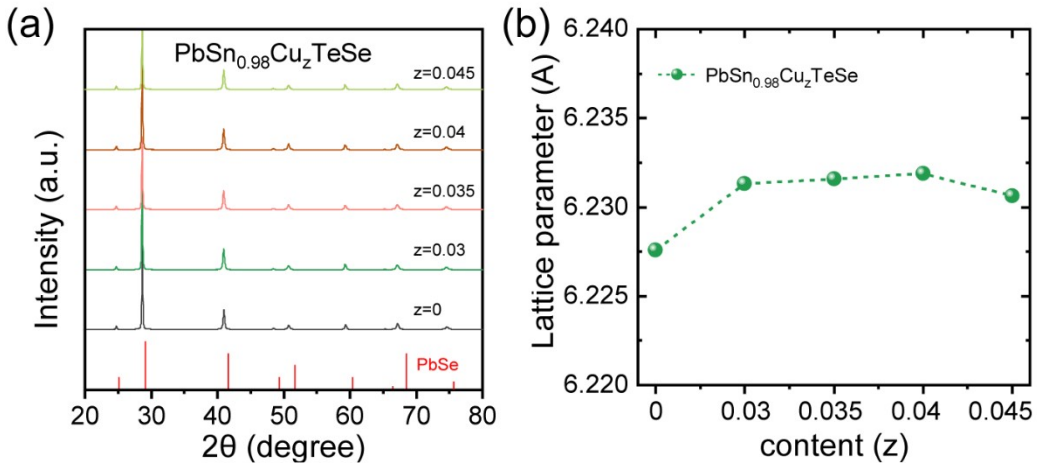

Fig. S7. (a) Powder X-ray diffraction (XRD) patterns in $PbSn_{0.98}Cu_zTeSe$ (z = 0-0.045). (b) Lattice parameter as a function of Cu content.

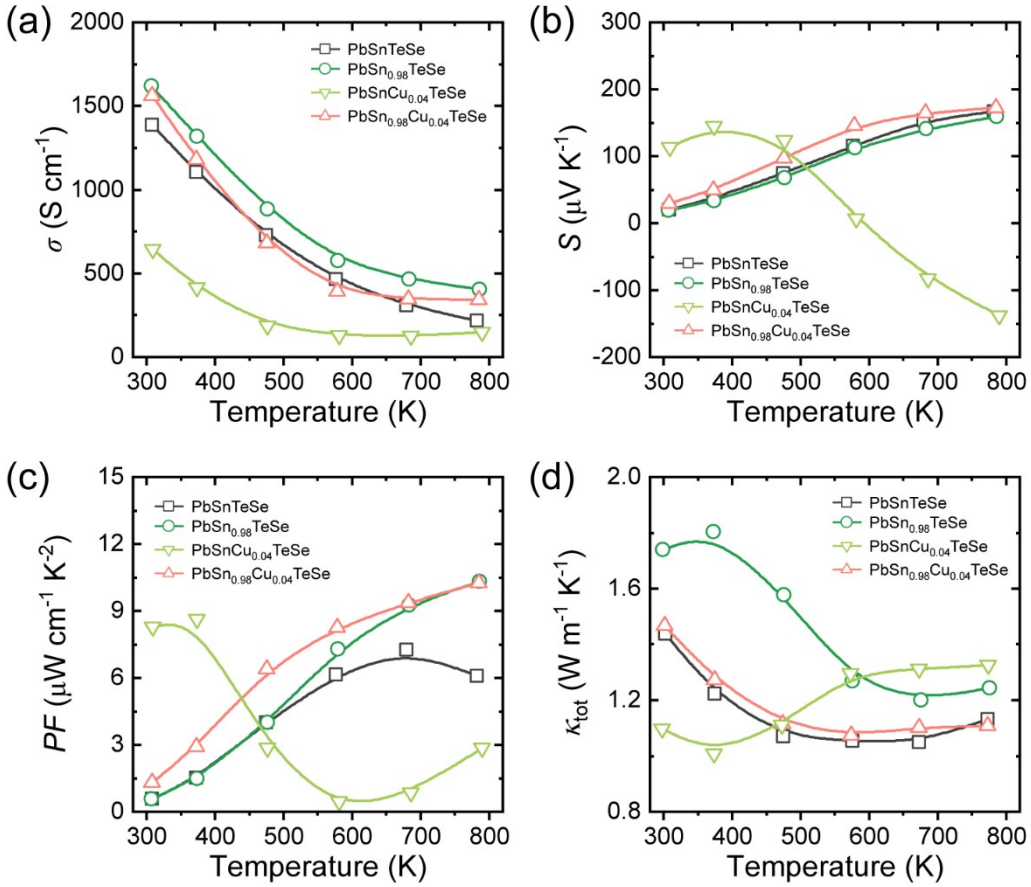

Fig. S8. Electrical transport properties and total thermal conductivity in PbSnTeSe, $PbSn_{0.98}TeSe$, $PbSnCu_{0.04}TeSe$ and $PbSn_{0.98}Cu_{0.04}TeSe$. (a) Electrical conductivity, (b) Seebeck coefficient, (c) power factor and (d) total thermal conductivity.

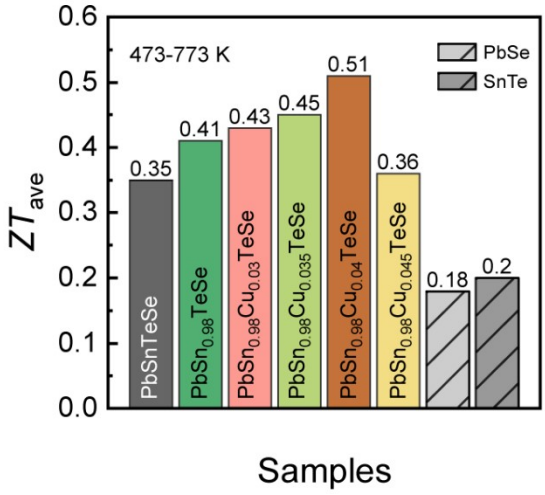

Fig. S9. Average *ZT* values in PbSe, SnTe, PbSnTeSe and $PbSn_{0.98}Cu_zTeSe$ (z = 0-0.045) at 473-773 K.

Table 1 Calculation results in $(PbSe)_{1-x}(SnTe)_x$ (x = 0-1.0) system based on Callaway model at 300 K.

Samples	v_a (m s^{-1})	Γ	u	Θ_D (K)	κ_{lat} (W m^{-1} K^{-1})
$(PbSe)_{0.9}(SnTe)_{0.1}$	1969.07	0.0100	0.670	191.08	0.930
$(PbSe)_{0.8}(SnTe)_{0.2}$	1956.12	0.0190	0.823	189.29	0.700
$(PbSe)_{0.7}(SnTe)_{0.3}$	1951.93	0.0253	0.918	187.94	0.623
$(PbSe)_{0.6}(SnTe)_{0.4}$	1963.33	0.0299	0.872	188.13	0.480
$(PbSe)_{0.5}(SnTe)_{0.5}$	1882.00	0.0325	0.774	179.98	0.345
$(PbSe)_{0.4}(SnTe)_{0.6}$	1965.16	0.0300	0.936	187.13	0.531
$(PbSe)_{0.3}(SnTe)_{0.7}$	1967.45	0.0280	0.931	186.74	0.561
$(PbSe)_{0.2}(SnTe)_{0.8}$	2013.00	0.0212	1.017	190.53	0.911
$(PbSe)_{0.1}(SnTe)_{0.9}$	2029.74	0.0126	0.854	191.62	1.087

Table 2 Sample density in $(PbSe)_{1-x}(SnTe)_x$ (x = 0-1.0) and $(PbTe)_{1-x'}(SnSe)_{x'}$ (x' = 0-1.0)

Samples	Density (g cm^{-3})	Samples	Density (g cm^{-3})
PbSe	8.18	PbTe	8.32
$(PbSe)_{0.9}(SnTe)_{0.9}$	7.92	$(PbTe)_{0.8}(SnSe)_{0.2}$	7.40
$(PbSe)_{0.8}(SnTe)_{0.2}$	7.77	$(PbTe)_{0.6}(SnSe)_{0.4}$	7.15
$(PbSe)_{0.7}(SnTe)_{0.3}$	7.59	$(PbTe)_{0.4}(SnSe)_{0.6}$	6.43
$(PbSe)_{0.6}(SnTe)_{0.4}$	7.38	$(PbTe)_{0.2}(SnSe)_{0.8}$	6.16
$(PbSe)_{0.5}(SnTe)_{0.5}$	7.10	SnSe	5.94
$(PbSe)_{0.4}(SnTe)_{0.6}$	6.93		
$(PbSe)_{0.3}(SnTe)_{0.7}$	6.62		
$(PbSe)_{0.2}(SnTe)_{0.8}$	6.50		
$(PbSe)_{0.1}(SnTe)_{0.9}$	6.34		
SnTe	6.38		