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Supporting Information

Anion exchanged Cl doping achieving the band sharpening and low lattice thermal conductivity for improving thermoelectric performance in SnTe

Quanxin Yang [a, 1], Tu Lyu [a, 1], Yuan Dong [a], Bohang Nan [a], Jian Tie [a], Xiaojing Zhou [a, b], Bin Zhang [a], Guiying Xu [a, *]

[a] Beijing municipal key lab of advanced energy materials and technology, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

[b] Micro-nano Fabrication Technology Department, Institute of Electrical Engineering, Chinese Academy of Sciences, Beijing 100190, China

[1] Equal contribution.

[*] Corresponding author. E-mail address: guiyingxu@126.com

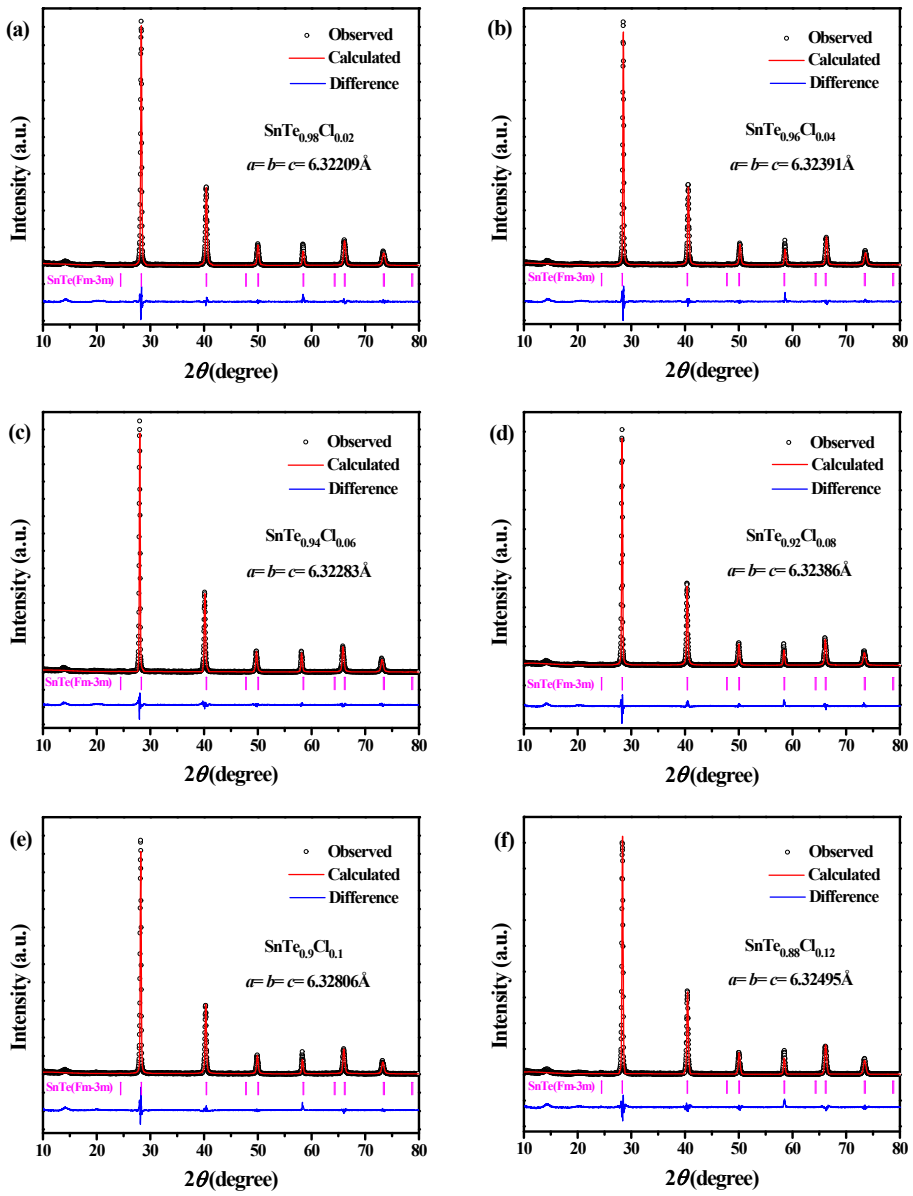

Fig. S1. The Rietveld refinements of XRD patterns for the $SnTe_{1-x}Cl_x$, (x= 0.02-0.12) samples.

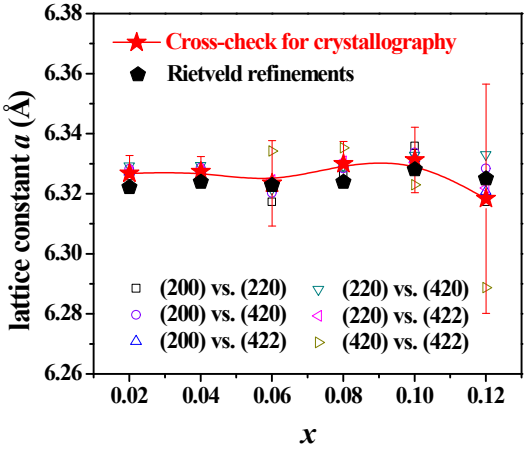

Fig. S2. The lattice parameter a as a function of the content of Cl.

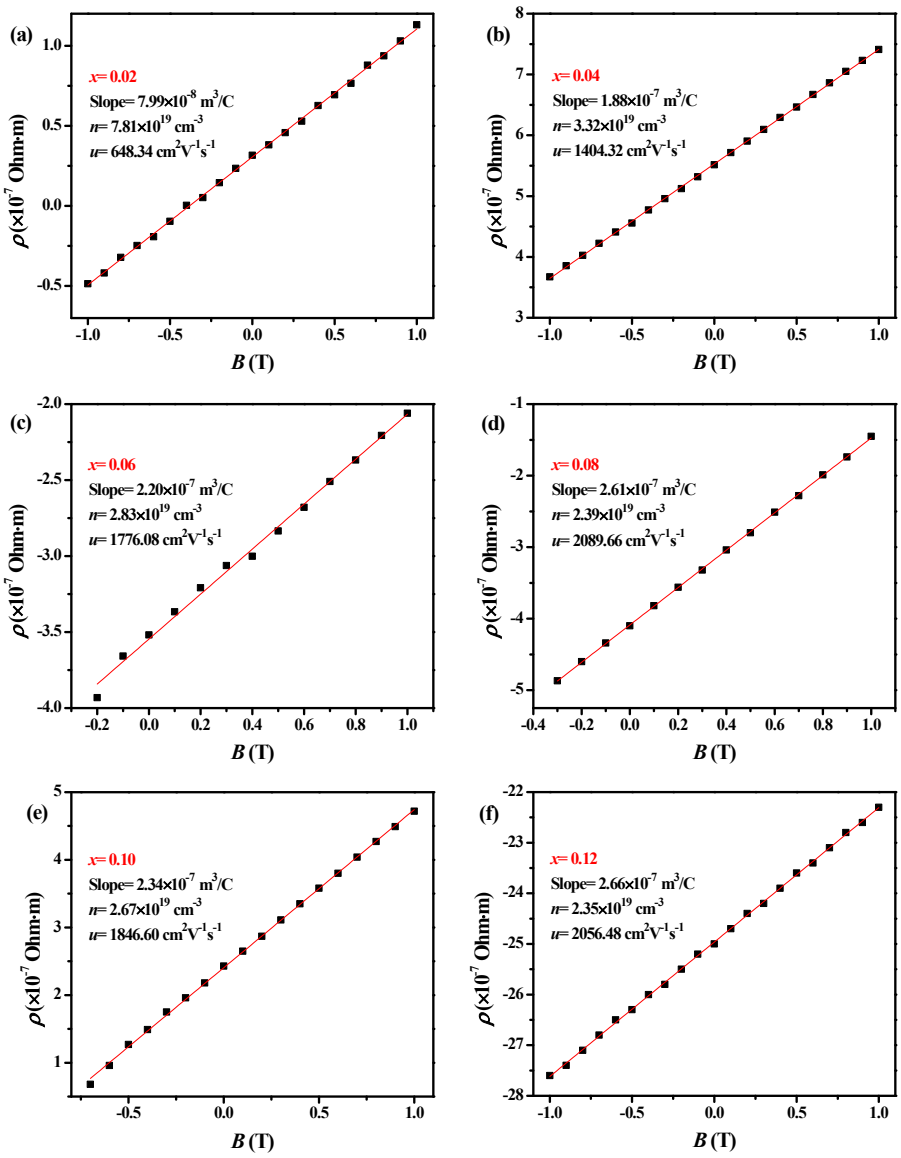

Fig. S3. The resistivity dependence on the magnetic strength, estimating the room-temperature Hall coefficient, carrier concentration and carrier mobility of the $SnTe_{1-x}Cl_x$, (x= 0.02-0.12) samples.

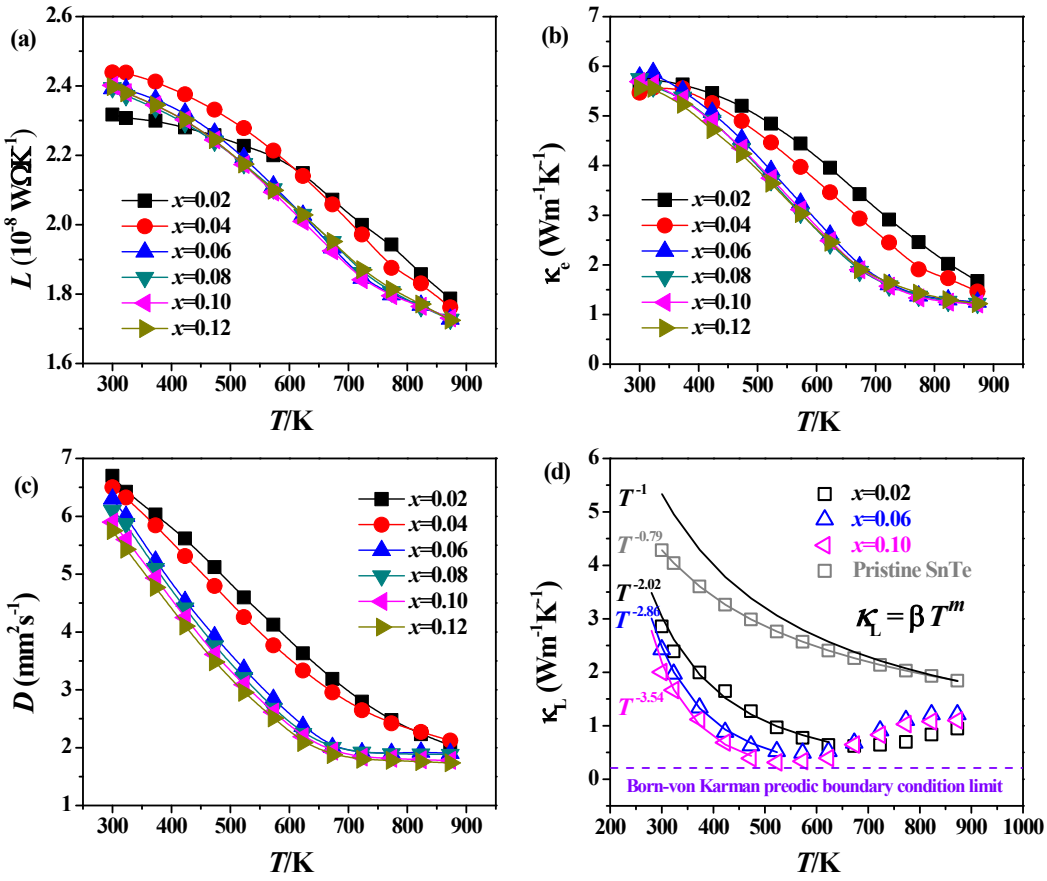

Fig. S4. Temperature dependence of (a) the Lorentz constant, (b) the electrical thermal conductivity, (c) the thermal diffusion coefficient and (d) the lattice thermal conductivity for the samples.

Tab. S1. The parameters of the samples at room temperature, where *a* is the lattice parameter, *n* is the Hall carrier concentration, *u* is the Hall carrier mobility and *d* is the volume density.

$SnTe_{1-x}Cl_x$	*a* (Å)	*n* ($\times 10^{19} cm^{-3}$)	*u* ($cm^2V^{-1}s^{-1}$)	*d* (gcm^{-3})
x=0.02	6.3221	7.81	648.34	6.39
x=0.04	6.3239	3.32	1404.32	6.37
x=0.06	6.3228	2.83	1776.08	6.34
x=0.08	6.3239	2.39	2089.66	6.31
x=0.10	6.3281	2.67	1846.60	6.25
x=0.12	6.3250	2.35	2056.48	6.28

Calculation methods

1. Crystallographic calculated lattice parameters

According to the rule of crystallography, the interplanar spacing d_{hkl} can be defined as:

$$2d_{hkl}sin\theta = \lambda \tag{S1}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{S2}$$

where θ is the Bragg diffraction angle, λ is the wavelength of the X-ray, a is the lattice parameter, as well as h, k, l are the crystal indices. Combining equations (S1) and (S2), we can obtain the lattice parameter a:

$$a = \frac{\lambda}{2sin\theta}\sqrt{h^2 + k^2 + l^2} \tag{S3}$$

Usually, the X-ray diffractometer inevitably introduce some instrumental errors (we called the zero offset) during per XRD measurement, which always leads to a shift of the angle. To eliminate the zero offset, two sets of diffraction peaks corresponding to the different lattice planes can be substituted into the equation (3) to solve the zero offset:

$$\frac{\sqrt{h_1^2 + k_1^2 + l_1^2}}{2sin(\theta_1 + zero\ offset)} = \frac{\sqrt{h_2^2 + k_2^2 + l_2^2}}{2sin(\theta_2 + zero\ offset)} \tag{S4}$$

When the zero offset is determined, the lattice parameter a can be obtained using the equation (3). We herein select four sets of the diffraction peaks corresponding to the lattice planes (200), (220), (420) and (422) respectively, to obtain a cross-check lattice parameter, and the results are exhibited in Fig. S2.

2. Two-band transport model

A special band structure for SnTe is that it has two main valence bands (L band for light hole valence band and ∑ band for heavy hole valence band) participating in electrical transport, L band

and ∑ band, which determines both the two bands should be considered in calculations. The two-band model is based on the Kane model[1]. The carrier scattering mechanism is assumed as the acoustic phonon scattering in calculations. Specifically, the physical parameters are defined by the Kane model as follows: [1-3]

the Seebeck coefficient:

$$S = \frac{k_B}{e}\left[\frac{{}^1F_{-2}^{1}}{{}^0F_{-2}^{1}} - \eta\right] \tag{S5}$$

the Hall factor:

$$A = \frac{3K(K+2)\,{}^0F_{-4}^{1/2} \cdot {}^0F_{0}^{3/2}}{(2K+1)^2 \quad ({}^0F_{-2}^{1})^2} \tag{S6}$$

the carrier concentration:

$$p_H = \frac{1}{eR_H} = \frac{N_v(2m_b^* k_B T)^{3/2}}{3\pi^2\hbar^3}\,{}^0F_0^{3/2} \tag{S7}$$

the carrier mobility:

$$\mu_H = \frac{2\pi\hbar^4 eC_l \qquad 3\,{}^0F_{-2}^{1}}{m_I^*(2m_b^* k_B T)^{3/2} E_{def}^{2}\;{}^0F_0^{3/2}} \tag{S8}$$

the electrical conductivity:

$$\sigma = p_H \mu_H e = \frac{2e^2 N_V \hbar C_l}{\pi m_I^* E_{def}^{2}}\,{}^0F_{-2}^{1} \tag{S9}$$

and the generalized Fermi intergral:

$${}^nF_k^m = \int_0^{+\infty}\left(-\frac{\partial f}{\partial \varepsilon}\right)\varepsilon^n(\varepsilon+\alpha\varepsilon^2)^m\left[(1+2\alpha\varepsilon)^2+2\right]^{k/2}d\varepsilon \tag{S10}$$

where k_B, $\hbar$ and e are Boltzmann constant, reduced Planck constant and electron charge respectively. η is the reduced Fermi level defined by $\eta = E_f / k_B T$, where E_f is Fermi level and T is absolute temperature. K is the anisotropic parameter defined by $K = m_{//}^* / m_{\perp}^*$, where $m_{//}^*$ and $m_{\perp}^*$ are the effective mass in different directions. Besides, N_v is the band degeneracy, m_b^* and m_I^* are the band

effective mass and inertial effective mass respectively, C_l is the elastic constant, and E_{def} is the deformation potential coefficient. ${}^{n}F_{k}^{m}$ is the generalized Fermi integral, α is the non-parabolic parameter defined as $\alpha=(k_B T)/E_g$ (E_g is the band gap), f is the Fermi distribution function, and ε is the reduced energy of electronic states.

After considering the effects of multi-bands, the total properties can be defined as:

the total electrical conductivity:

$$\sigma_{total} = \sigma_{lh} + \sigma_{hh} \tag{S11}$$

the total Seebeck coefficient:

$$S_{total} = \frac{S_{lh}\sigma_{lh} + S_{hh}\sigma_{hh}}{\sigma_{lh} + \sigma_{hh}} \tag{S12}$$

the total Hall coefficient:

$$R_{Htotal} = \frac{R_{Hlh}\sigma_{lh}^2 + R_{Hhh}\sigma_{hh}^2}{(\sigma_{lh} + \sigma_{hh})^2} \tag{S13}$$

the total carrier concentration:

$$p_{total} = \frac{1}{eR_{Htotal}} \tag{S14}$$

the total carrier mobility:

$$\mu_{total} = \sigma_{total} R_{Htotal} \tag{S15}$$

Noting that the subscripts “lh” and “hh” represent the light hole valence band (L band) and the heavy hole valence band (∑ band), respectively.

The parameters used in the room-temperature Pisarenko lines and the calculated carrier mobility dependence of the carrier concentration can be indexed in Tab. S2. The estimation of the temperature effect still depends on the two-band transport model and temperature-dependnet parameters used in the calculation can be found in Tab. S3.

Tab. S2. The parameters for the two bands used in calculation at room temperature.

Parameters	Light hole valence band	Heavy hole valence band
Band degeneracy N_v	4	12
Anisotropic parameter K[2,4]	4	1
Density of states effective mass m_d^* (m_e)[5]	0.168 for pristine SnTe, 0.06 for Cl doping SnTe	1.92
Band gap E_g (eV)[6]	0.18	-
Energy offset ΔE (eV)[4,5]	0.35	-
Reduced Fermi level η	η	η - ΔE / $k_B T$
Non-parabolic parameter α	$(k_B T) / E_g$	0
Deformation potential coefficient E_{def} (eV)[4,5]	50	25
Elastic constant C_l (Pa)[2,4]	5.8×10^{10}	5.8×10^{10}

Tab. S3. The parameters used in the calculation of the temperature effect.

Parameters	Temperature effect	Temperature driven band sharpening effect
m_d^* (m_e) for L band[2]	0.27	0.19
m_d^* (m_e) for $\sum$ band[2]	3.23	3.23
ΔE (eV)[2]	0.15	0.15
E_g (eV)[4]	0.42	0.42

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