Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information:

Investigating the thermoelectric performance of n-type SnSe: the synergistic effect of $NbCl_5$ doping and dislocation engineering

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1. Anisotropy Measurements

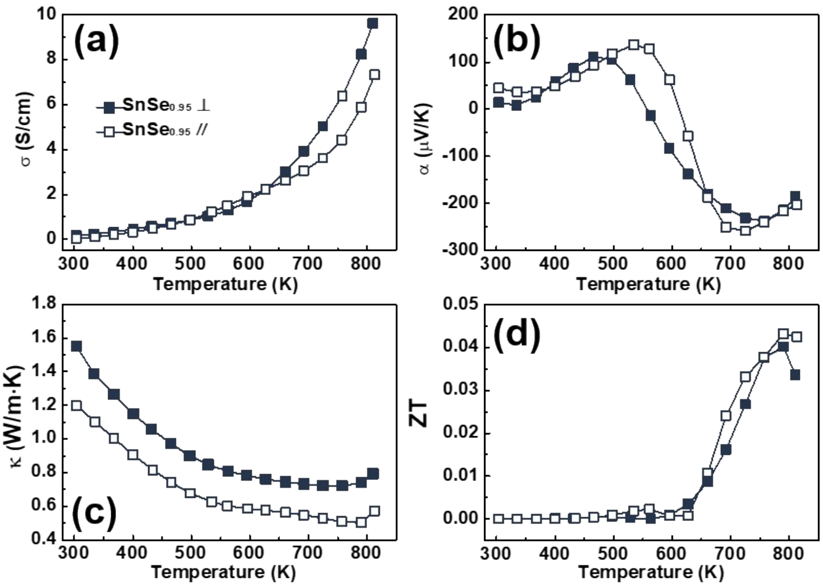

Figure S1. Temperature dependence of the (a) electrical conductivity and (b) Seebeck coefficient; (c) thermal conductivity; and (d) ZT of sample $SnSe_{0.95}$ measured along the direction parallel and perpendicular to the pressure.

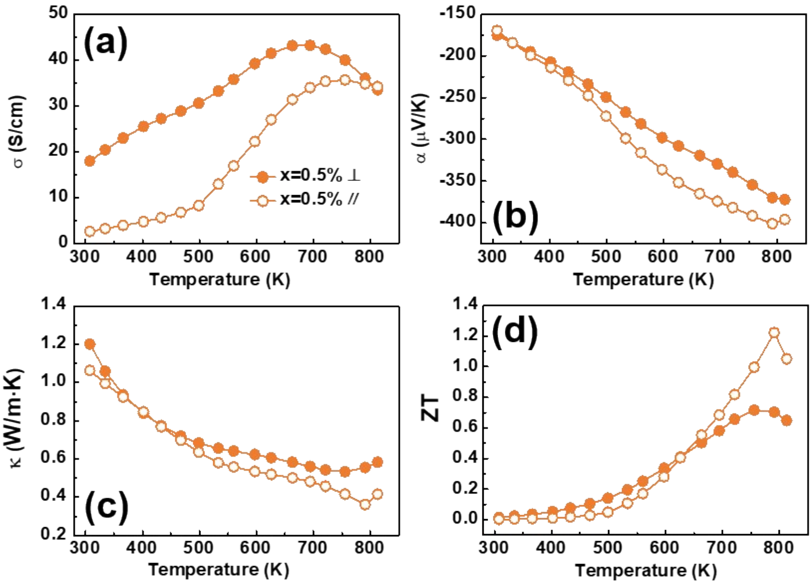

Figure S2. Temperature dependence of the (a) electrical conductivity and (b) Seebeck coefficient; (c) thermal conductivity; and (d) ZT of sample $SnSe_{0.95}$ + 0.5% $NbCl_5$ measured along the direction parallel and perpendicular to the pressure.

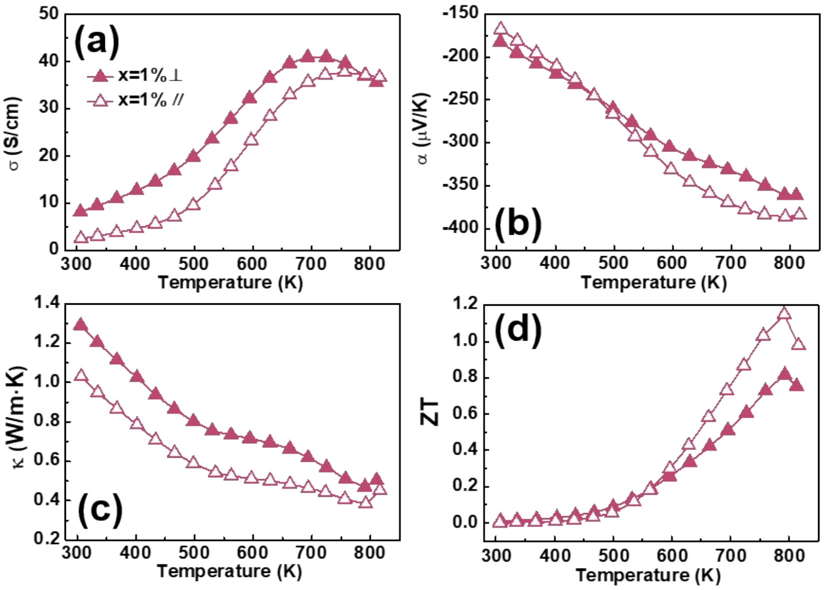

Figure S3. Temperature dependence of the (a) electrical conductivity and (b) Seebeck coefficient; (c) thermal conductivity; and (d) ZT of sample $SnSe_{0.95}$ + 1% $NbCl_5$ measured along the direction parallel and perpendicular to the pressure.

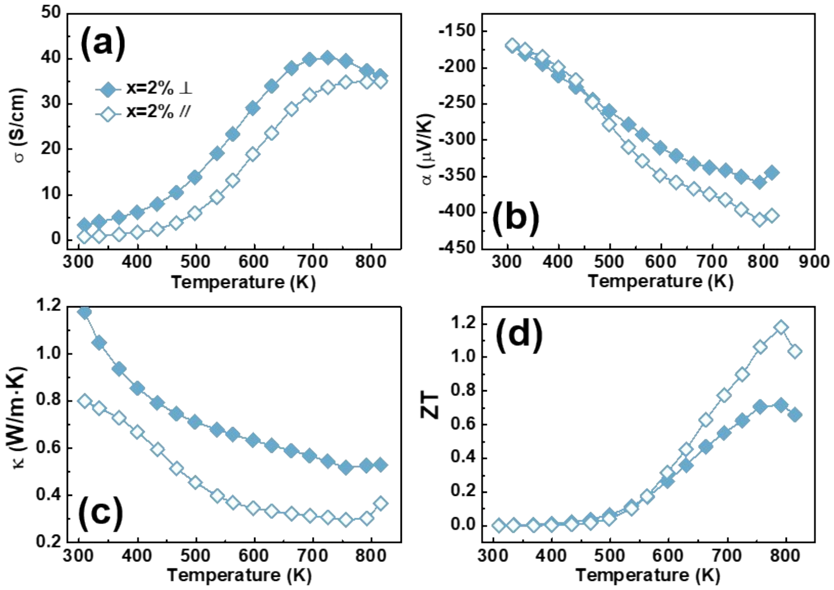

Figure S4. Temperature dependence of the (a) electrical conductivity and (b) Seebeck coefficient; (c) thermal conductivity; and (d) ZT of sample $SnSe_{0.95}$ + 2% $NbCl_5$ measured along the direction parallel and perpendicular to the pressure.

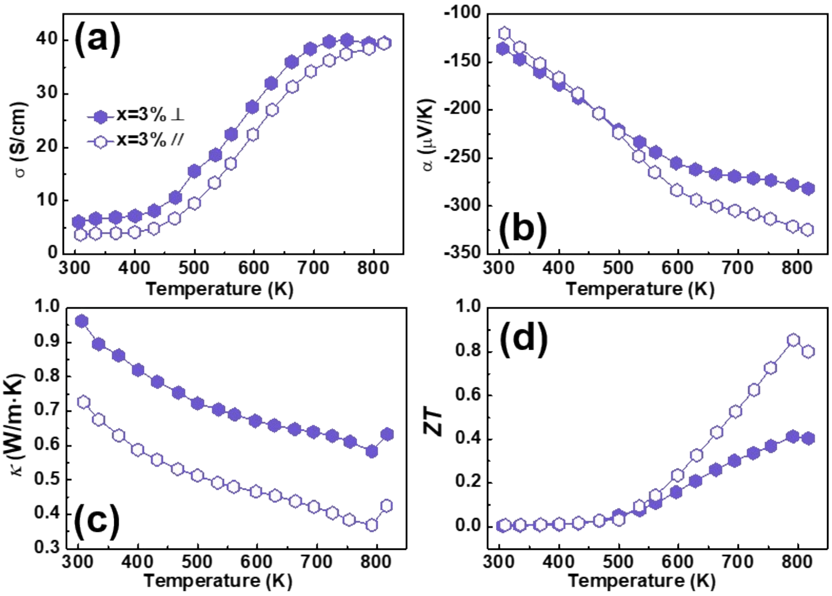

Figure S5. Temperature dependence of the (a) electrical conductivity and (b) Seebeck coefficient; (c) thermal conductivity; and (d) ZT of sample $SnSe_{0.95}$ + 3% $NbCl_5$ measured along the direction parallel and perpendicular to the pressure.

Table S1. Electrical conductivity, thermal conductivity, and ZT ratio of all the $SnSe_{0.95}$ + x mol% $NbCl_5$ (x = 0, 0.5, 1, 2and 3) bulk samples along the perpendicular to the pressure direction and the parallel to the pressure direction.

Sample Name	$\sigma_{\perp}/\sigma_{//}$ at 800 K	$\kappa_{\perp}/\kappa_{//}$ at 800 K	$ZT_{\perp}/ZT_{//}$ at 800 K
$x = 0$	1.40	1.48	0.93
$x = 0.5$	1.03	1.53	0.60
$x = 1$	1.05	1.30	0.71
$x = 2$	1.13	1.34	0.61
$x = 3$	1.03	1.58	0.49

2. Niobium doping effect

First-principle calculations are made to compare the formation energy of Nb doping at different lattice sites. Equations (1) and (2) represent the formation energy required for Nb ions to occupy the interstitial site and to substitute Sn ions, respectively:

$$E_{form} = E_{doped} - E_{pure} - \mu_{Nb} \,, \tag{1}$$

$$E_{form} = E_{doped} + \mu_{Sn} - E_{pure} - \mu_{Nb} \,, \tag{2}$$

where E_{form}, E_{doped} and E_{pure} is the formation energy of point defects, the total energy of the compound containing dopants, and that of the pure compound, respectively. The chemical potentials of Sn or Nb atoms are denoted by μ_i[1]. The calculation result of the defect formation energy ($\Delta H_{D,q}$) versus the Fermi energy (E_F) is shown in Figure S7 (a). Obviously, it is easier for niobium to replace Sn in the SnSe relative to enter the interstitial space. To experimentally evidence this, the $SnSe_{0.95}$ sample singly doped by 2.5 % Cl ions was prepared by the same fabrication procedures and the carrier concentrations were compared between this sample and the 0.5 % $NbCl_5$-doped $SnSe_{0.95}$ one. Both samples consisted of the same percentages of Cl ions so that we can examine the effect of Nb doping on the carrier concentrations of $SnSe_{0.95}$. The room-temperature Hall measurement results are shown in Figure S7 (b), where the carrier concentration of $NbCl_5$-doped sample (1.65×10^{19}cm^{-3}) is slightly higher than that of Cl-doped one (1.45×10^{19}cm^{-3}), demonstrating that Nb ions substituted Sn and donated free electrons to the system. According to the theoretical and experimental analysis, it is concluded that the Nb ions should act as an effective donor in SnSe that improved the carrier concentrations.

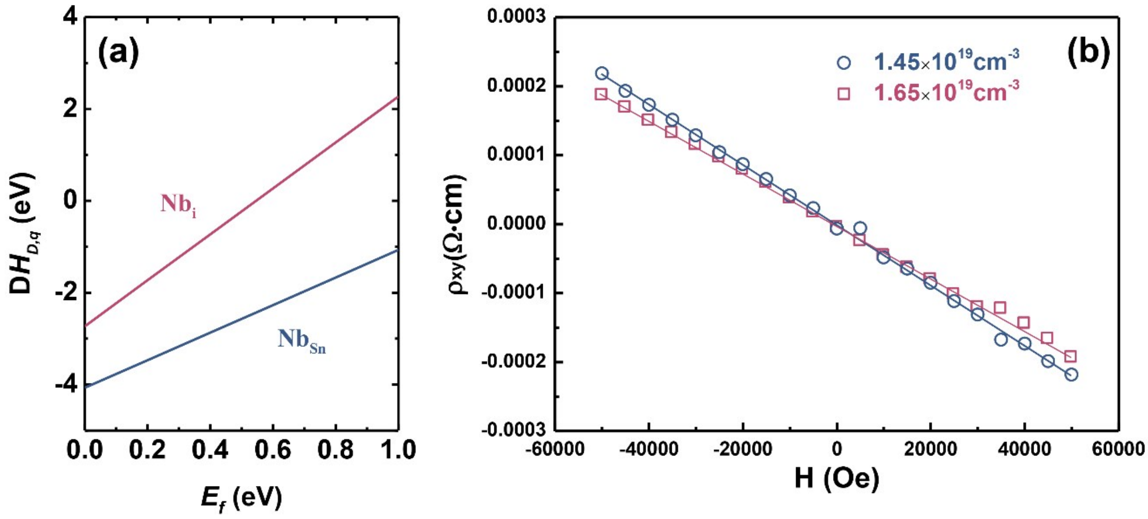

Figure S6. (a) Defect formation energy ($\Delta H_{D,q}$) as a function of the Fermi energy (E_F) for formation energy of substitutional Nb_{Sn} and Nb_i; (b) Hall resistance as a function of magnetic field for the sample $SnSe_{0.95}$+0.5%$NbCl_5$ and $SnSe_{0.95}$+2.5%Cl.

3. Vickers hardness

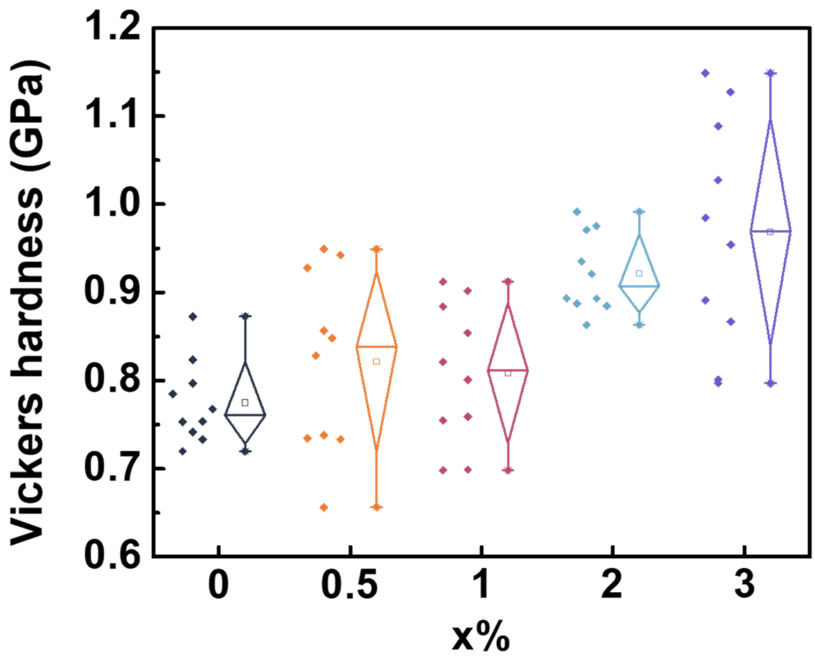

Figure S7. The Vickers hardness of $SnSe_{0.95} + x\%NbCl_5$ (x = 0, 0.5, 1, 2, and 3).

4. Differential thermal analysis and spectral scanning energy spectrum

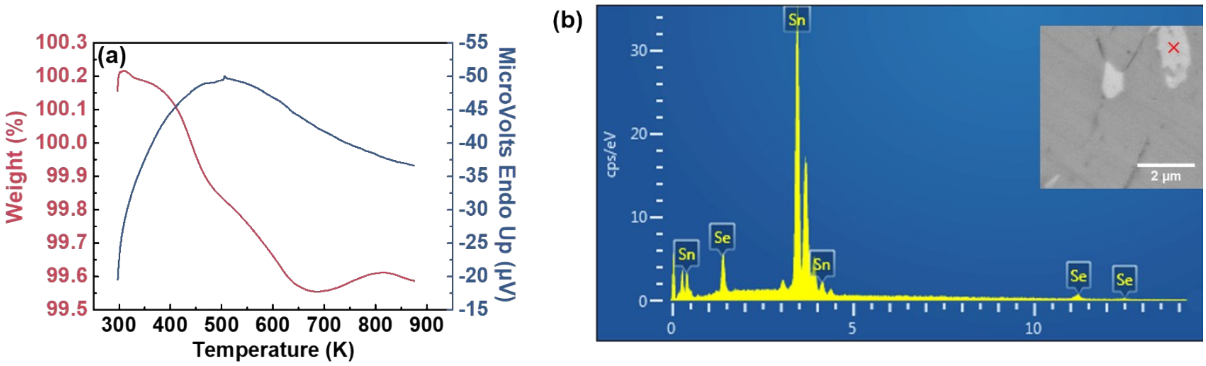

Figure S8. (a) Temperature dependence of the differential thermal analysis of sample $SnSe_{0.95}$+1%$NbCl_5$; (b) Spectral scanning energy spectrum of the sample $SnSe_{0.95}$+1%$NbCl_5$.

References

1. S. Wang, X. Tan, G. Tan, X. She, W. Liu, H. Li, H. Liu and X. Tang, *J Mater Chem*, 2012, **22**.