Supporting Information

Ni and Se Co-doping Increases the Power Factor and Thermoelectric Performance of CoSbS

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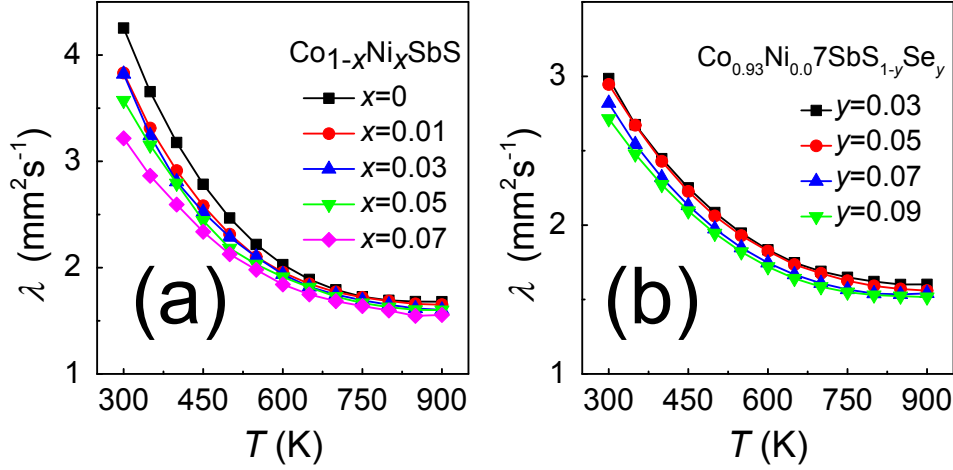
Figure S1 Temperature dependence of thermal diffusivity for (a) $Co_{1-x}Ni_xSbS$, (b) $Co_{0.93}Ni_{0.07}SbS_{1-x}Se_x$ compounds.

Table S1 Estimated bandgap of $Co_{1-x}Ni_xSbS$ ($x = 0 \sim 0.07$).

Sample	CoSbS	$Co_{0.99}Ni_{0.01}SbS$	$Co_{0.97}Ni_{0.03}SbS$	$Co_{0.95}Ni_{0.05}SbS$	$Co_{0.93}Ni_{0.07}SbS$
E_g (eV)	0.69	0.55	0.31	0.29	0.28

The lattice thermal conductivity of alloyed $Co_{0.93}Ni_{0.07}SbS_{1-y}Se_y$ (κ_L) and of pure CoSbS (κ_L^P) compounds can be expressed as:

$$\frac{\kappa_L}{\kappa_L^P} = \frac{\tan^{-1} u}{u} \tag{1}$$

$$u^2 = \frac{\pi^2 \theta_D \Omega}{h v^2} \kappa_L^P \Gamma \tag{2}$$

where u, θ_D, Ω, h, v, Γ are the disorder scaling parameter, Debye temperature, average atomic volume, Planck constant, average sound velocity and scaling parameter, respectively. Γ can be calculated by the model of Abeles and Slack as $\Gamma = \Gamma_M + \Gamma_S$.

$$\Gamma_M = \frac{\sum_{i=1}^{n} c_i \left(\frac{\bar{M}_i}{\bar{\bar{M}}} \right)^2 f_i^1 f_i^2 \left(\frac{M_i^1 - M_i^2}{\bar{M}_i} \right)^2}{\sum_{i=1}^{n} c_i} \tag{3}$$

$$\Gamma_S = \frac{\sum_{i=1}^{n} c_i \left(\frac{\bar{M}_i}{\bar{\bar{M}}} \right)^2 f_i^1 f_i^2 \varepsilon_i \left(\frac{r_i^1 - r_i^2}{\bar{r}_i} \right)^2}{\sum_{i=1}^{n} c_i} \tag{4}$$

where n is the number of different crystallographic sublattice types in the lattice and c_i are the relative degeneracies of the respective sites. In pure CoSbS, $n = 3$, $c_1 = c_2 = c_i = 1$, $\bar{\bar{M}}$ is the average atomic mass, $\bar{M}_i$ and $\bar{r}_i$ are the average atomic mass and radius on the i-th sublattice, respectively. f_i^k is the fractional occupation of the k-th atom on the i-th sublattice. The atomic mass and radius are M_i^k and r_i^k, respectively. The relations discussed above can be expressed as:

$$\bar{M}_i = \sum_k f_i^k M_i^k \tag{5}$$

$$\bar{r}_i = \sum_k f_i^k r_i^k \tag{6}$$

$$\bar{\bar{M}} = \frac{\sum_{i=1}^n c_i \bar{M}_i}{\sum_{i=1}^n c_i} \tag{7}$$

The calculation results are shown in Table 2.

Figure S3 displays the photoemission spectra of Co 2P, Sb 3d and S 2P core states for CoSbS, $Co_{0.93}Ni_{0.07}S$, $CoSbS_{0.95}Se_{0.05}$ and $Co_{0.93}Ni_{0.07}SbS_{0.93}Se_{0.07}$ compounds. Figure S3(a) shows the photoemission spectrum of Co 2P core state, including Co $2P_{1/2}$ and $2P_{3/2}$. The binding energies of Co $2P_{1/2}$ and $2P_{3/2}$ for CoSbS compound are 794.19 eV and 779.02 eV respectively and the intensity of satellite peaks of Co $2P_{1/2}$ and $2P_{3/2}$ at 797.37 eV and 781.93 eV are very weak which is different from that of Co^{2+}. The Co 2P region has well separated spin-orbit components ($\Delta=15.17$ eV) and the shape of the peaks is symmetrical indicating that the valence of Co is +3 rather than +2 in CoSbS compound [1]. Figure S3(b) is the photoemission spectrum of Sb 3d core state, including Sb $3d_{3/2}$ and $3d_{5/2}$. The binding energies of Sb $3d_{3/2}$ and $3d_{5/2}$ for CoSbS compound are 538.23 eV and 528.89 eV respectively. The Sb 3d spin-orbit components are well separated ($\Delta=9.34$ eV) and the shape of the peaks is approximately symmetric, indicating the valence of Sb is -1 in CoSbS compound. The binding energy for the satellite peaks of Sb $3d_{3/2}$ and $3d_{5/2}$ are at 539.66 eV and 530.31 eV respectively. Figure S3(c) displays the photoemission spectrum of S 2P core state, including S $2P_{1/2}$ and $2P_{3/2}$ with binding energies of 164.21 eV and 163.06 eV, respectively. The S 2P region has well separated spin-orbit components ($\Delta=1.15$ eV) which is the typical characteristic of S^{2-} corroborating that the valence of S is -2 in CoSbS compound. Additionally, it can be seen that after Ni doping, the binding energies of Co $2P_{1/2}$ and $2P_{3/2}$, Sb $3d_{3/2}$ and $3d_{5/2}$, and S $2P_{1/2}$ and $2P_{3/2}$ shift to lower binding energies. For $Co_{0.93}Ni_{0.07}SbS$ compound, the binding energies of Co $2P_{1/2}$ and $2P_{3/2}$ are 793.51 eV and 778.52 eV, the binding energies of Sb $3d_{3/2}$ and $3d_{5/2}$ are 537.8 eV and 528.45 eV, the binding energies of S $2P_{1/2}$ and $2P_{3/2}$ are 163.79 eV and 162.64 eV, respectively. It can be speculated that Ni doping enhances the hybridization between Co, Sb and S, thus increase the electron cloud overlap, leading to a reduced Co2P, Sb 3d and S 2P binding energy. In addition, after Se doping, the binding energies of Co $2P_{1/2}$ and $2P_{3/2}$, Sb $3d_{3/2}$ and $3d_{5/2}$, and S $2P_{1/2}$ and $2P_{3/2}$ are also reduced. Referring to the smaller electronegativity of Se (2.55) compared to that

of S (2.58), doping Se on the S site can increase the covalency of the chemical bond and increase the electron cloud overlap around Co, Sb, S and Se atoms, leading to reduced binding energy of Co2P, Sb 3d and S 2P. For $CoSbS_{0.95}Se_{0.03}$ compound, the binding energies of Co $2P_{1/2}$ and $2P_{3/2}$ are 793.82 eV and 778.83 eV, the binding energies of Sb $3d_{3/2}$ and $3d_{5/2}$ are 538.13 eV and 528.78 eV, the binding energies of S $2P_{1/2}$ and $2P_{3/2}$ are 163.71 eV and 162.56 eV, respectively. For Ni, Se co-doped $Co_{0.93}Ni_{0.07}SbS_{0.93}Se_{0.07}$ compound, the binding energies of Co $2P_{1/2}$ and $2P_{3/2}$ are 793.5 eV and 778.51 eV, the binding energies of Sb $3d_{3/2}$ and $3d_{5/2}$ are 537.8 eV and 528.45 eV, the binding energies of S $2P_{1/2}$ and $2P_{3/2}$ are 163.56 eV and 162.41 eV, respectively. Moreover, the increased electron cloud overlap can enhance the DOS both of the valence and conduction band which is beneficial to the electronic transport properties of the compounds. Therefore, both Ni and Se doping in the system increase the dominant electron concentration and the density state effective mass.
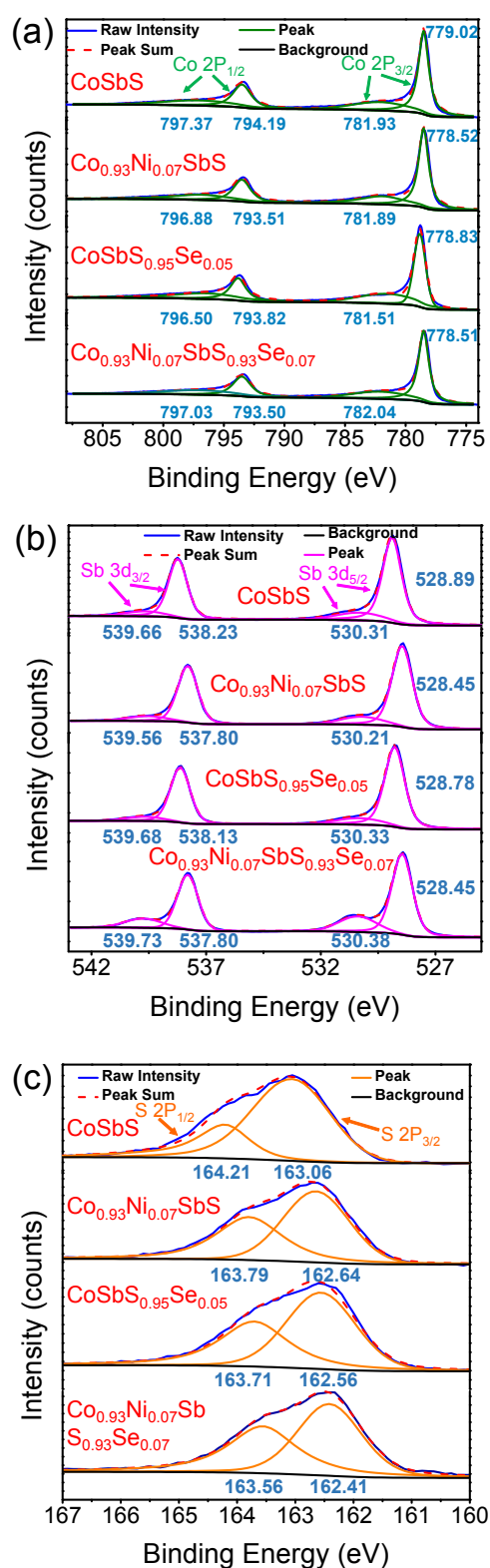
Figure S2 XPS: (a) Co, (b) Sb, and (c) S for CoSbS, $Co_{0.93}Ni_{0.07}S$, $CoSbS_{0.95}Se_{0.05}$ and $Co_{0.93}Ni_{0.07}SbS_{0.93}Se_{0.07}$ compounds.

[1] D. C. Frost, C. A. McDowell, I. S. Woolsey, *Mol. Phys.* **1974,** 27, 1473.