Supporting Information

1. The electronic and phonon transport coefficients

The electronic and phonon transport coefficients in the figure-of-merit can be obtained from the corresponding Boltzmann theory.

(1) Based on the energy band structure, the electronic transport coefficients (the electrical conductivity σ, the Seebeck coefficient S, and the electronic thermal conductivity κ_e) are evaluated by using the Boltzmann transport theory within the rigid-band picture (Phys. Rev. **132**, 2461) and the relaxation time approximation (Solid State Physics, Cornell University, 1975):

$$\sigma(\mu,T)=\frac{1}{N_{\mathbf{k}}V}\sum_{n\mathbf{k}}-e^2v_{n\mathbf{k}}^2\tau_{n\mathbf{k}}(\mu,T)\frac{\partial f_{FD}(\varepsilon_{n\mathbf{k}},\mu,T)}{\partial\varepsilon}, \quad (1)$$

$$S(\mu,T)=-\frac{1}{eT}\frac{\sum_{n\mathbf{k}}(\varepsilon_{n\mathbf{k}}-\mu)v_{n\mathbf{k}}^2\tau_{n\mathbf{k}}(\mu,T)\frac{\partial f_{FD}(\varepsilon_{n\mathbf{k}},\mu,T)}{\partial\varepsilon}}{\sum_{n\mathbf{k}}v_{n\mathbf{k}}^2\tau_{n\mathbf{k}}(\mu,T)\frac{\partial f_{FD}(\varepsilon_{n\mathbf{k}},\mu,T)}{\partial\varepsilon}}, \quad (2)$$

$$\kappa_e(\mu,T)=\frac{1}{N_{\mathbf{k}}V}\sum_{n,\mathbf{k}}-\frac{(\varepsilon_{n\mathbf{k}}-\mu)^2}{T}v_{n\mathbf{k}}^2\tau_{n\mathbf{k}}(\mu,T)\frac{\partial f_{FD}(\varepsilon_{n\mathbf{k}},\mu,T)}{\partial\varepsilon}-TS^2(\mu,T)\sigma(\mu,T), \quad (3)$$

where μ is the chemical potential (corresponds to the carrier concentration), T is absolute temperature, $N_{\mathbf{k}}$ is the total number of **k**-points, V is the volume of the unit cell, e is the electron charge, $v_{n\mathbf{k}}$ and $\varepsilon_{n\mathbf{k}}$ are the group velocity and eigenvalue with band index n at state **k**, f_{FD} is the Fermi-Dirac distribution function. The electron relaxation time $\tau_{nk}(\mu,T)$ is accurately predicted by considering the electron-phonon coupling.

(2) The lattice thermal conductivity (κ_p) is calculated by using the phonon Boltzmann theory, where the required harmonic and anharmonic interatomic force constants can be obtained from density functional calculations combined with the finite displacement method:

$$\kappa_p(\mu,T)=\frac{k_B}{VN_{\mathbf{q}}}\sum_{\nu\mathbf{q}}\left(\frac{\hbar\omega_{\nu\mathbf{q}}}{k_BT}\right)^2 v_{\nu\mathbf{q}}^2\tau_{\nu\mathbf{q},tot}(\mu,T)\,f_{BE}(\omega_{\nu\mathbf{q}},T)\left[\,f_{BE}(\omega_{\nu\mathbf{q}},T)+1\right] \qquad (4)$$

where k_B is the Boltzmann constant, $N_{\mathbf{q}}$ is the total number of **q**-points, $\hbar$ is the reduced Planck constant, $v_{\nu\mathbf{q}}$ and $\omega_{\nu\mathbf{q}}$ are the group velocity and frequency with polarization *v* and vibrational state **q**, f_{BE} is the Bose-Einstein distribution function. The phonon relaxation time $\tau_{\nu\mathbf{q},tot}(\mu,T)$ is determined by considering both phonon-phonon scattering and electron-phonon coupling.

2. Convergence test for the *k*- and *q*-grids

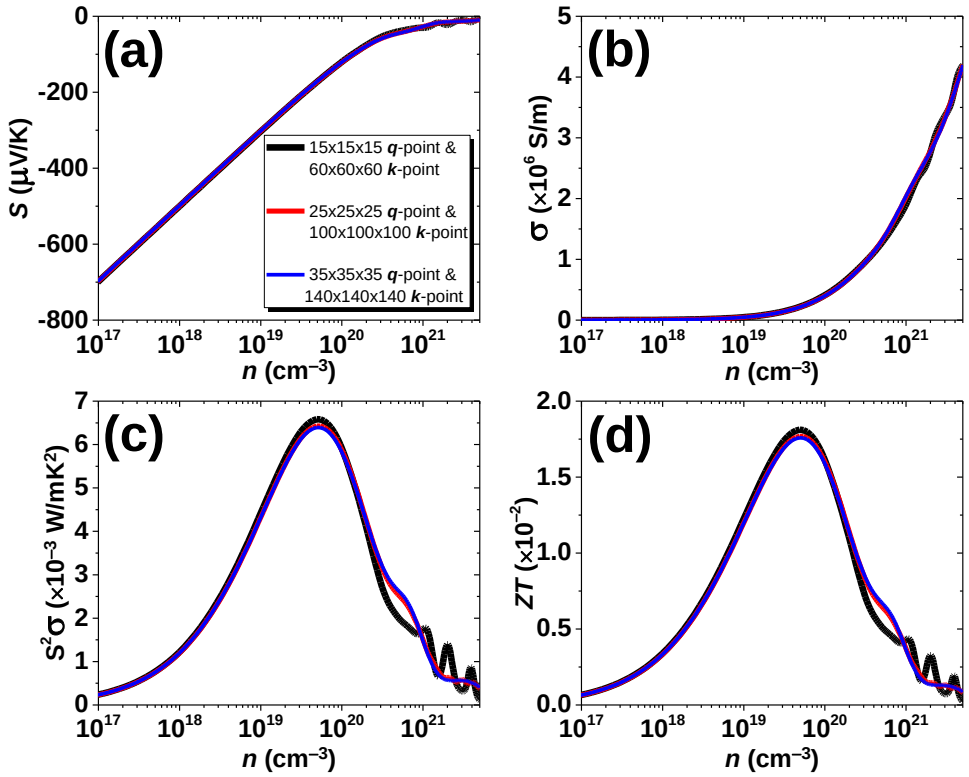

Figure S1. The room temperature (a) Seebeck coefficient *S*, (b) electrical conductivity σ, (c) power factor $S^2\sigma$, and (d) *ZT* value of SiGe compound, calculated with the ***k***-grids of 60×60×60, 100×100×100 and 140×140×140, combined with the ***q***-grids of 15×15×15, 25×25×25 and 35×35×35, respectively.

3. Effects of band gap correction on the electronic transport coefficients

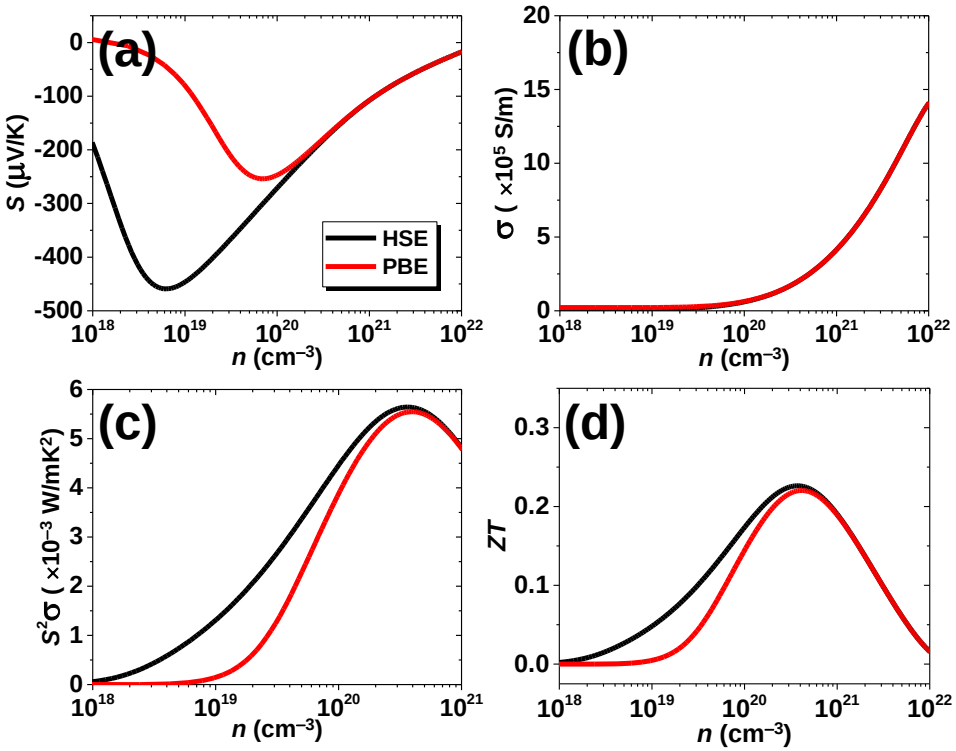

Figure S2. (a) The Seebeck coefficient *S*, (b) the electrical conductivity σ, (c) the power factor $S^2\sigma$, and (d) the *ZT* value of SiGe compound, plotted as a function of carrier concentration at 1200 K. Results with PBE and HSE calculated band gaps are both shown for comparison.

4. The effects of spin-orbital coupling (SOC) on the band structure

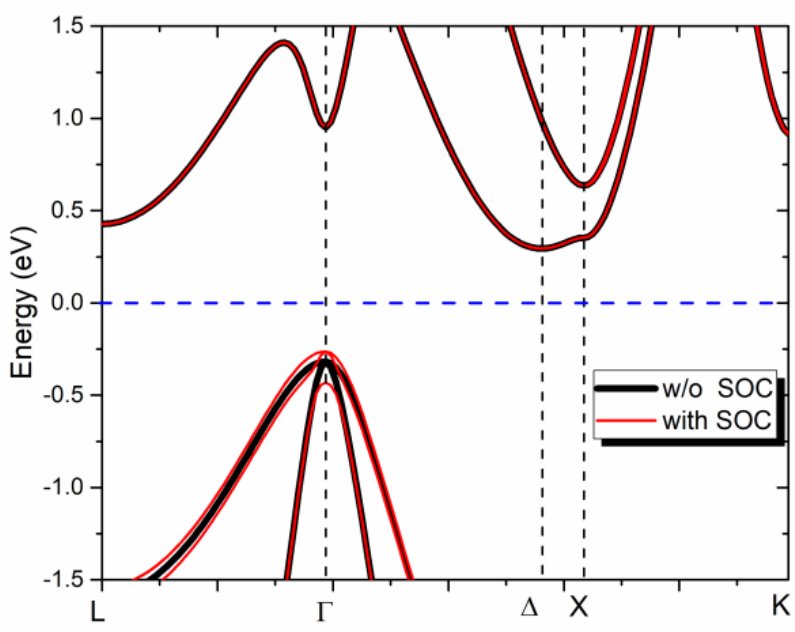

Figure S3 The band structure of SiGe compound calculated with and without SOC.

We see from Figure S3 that SOC leads to moderate changes to the top valence bands while the conduction bands remain the same. This is in good agreement with the conclusion from Ma *et al.* (Phys. Rev. B **97**, 045201) that "*In Si and GaAs, the spin-orbit coupling effect significantly affects the hole mobilities but has no effect on electrons*".

5. Effects of electron-phonon coupling on the lattice thermal conductivity

Table S1. The lattice thermal conductivity (in unit of W/mK) of SiGe compound calculated at a series temperature by including the effect of electron-phonon coupling. The numbers in the parenthesis indicate the corresponding carrier concentration (in unit of cm^{-3}), and the percentage of decrease in the lattice thermal conductivity as compared with that only considering intrinsic phonon scattering (second column).

300 K	106.3	105.5 (1.0×10^{18}, 1%)	102.8 (1.0×10^{19}, 3%)	94.6 (1.0×10^{20}, 11%)	57.6 (1.0×10^{21}, 46%)
600 K	60.6	58.2 (1.7×10^{19}, 4%)	55.9 (5.2×10^{19}, 8%)	51.3 (1.7×10^{20}, 15%)	34.3 (1.1×10^{21}, 43%)
900 K	43.4	39.8 (5.9×10^{19}, 8%)	37.9 (1.2×10^{20}, 13%)	34.7 (2.7×10^{20}, 20%)	24.7 (1.2×10^{21}, 43%)
1200 K	33.9	29.6 (1.2×10^{20}, 13%)	28.1 (2.2×10^{20}, 18%)	25.8 (4.0×10^{20}, 24%)	19.1 (1.4×10^{21}, 43%)