Supporting Information

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Atomic Level Defect Structure Engineering for Unusually High Average Thermoelectric Figure of Merit in n-Type PbSe Rivalling PbTe

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4. References
1. Details in the Theoretical Calculations

**Single parabolic band (SPB) model**\(^2\). Because PbQ (Q=Se and Te) shows single band nature at the conduction band, SPB model was used to calculate the effective mass of electron \((m_0)\) and Lorenz number \((L)\).\(^1\) Assuming SPB model, the Seebeck coefficient \((S)\), the \(n\)th order Fermi integral \((F_n(\eta))\), and the \(m_0\) were computed using the equations S1-S4:

\[
S = \pm \frac{k_B}{e} \frac{(5/2 + r)F_{3/2+r}(\eta)}{(3/2 + r)F_{1/2+r}(\eta)} - \eta \quad (R1)
\]

\[
F_n(\eta) = \int_0^\infty \frac{\chi^n}{1 + e^{\chi - \eta}} d\chi \quad (R2)
\]

\[
r_H = \frac{3}{2} \frac{(3/2 + 2r)F_{1/2}(\eta)F_{2r+1/2}(\eta)}{(3/2 + r)^2 F_{r+1/2}(\eta)} \quad (R3)
\]

\[
m_0 = \frac{\hbar^2}{2k_B T} \left[ \frac{n \cdot r_H}{4\pi F_{1/2}(\eta)} \right]^{2/3} \quad (R4)
\]

where \(\eta\) is the reduced Fermi energy, \(e\) is the charge of an electron, \(r_H\) is the Hall factor, \(\hbar\) is the Planck constant, \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, and \(r\) is the scattering parameter. The \(r\) is set at \(-1/2, 1/2, 3/2, and 0\) when dominant charge scattering mechanism is acoustic phonon, optical phonon, ionized impurity, and neutral impurity scattering, respectively.

The results of temperature-dependent Hall carrier mobility \((\mu_H)\) with respect to temperature in Figure 6a in the main text indicate that the samples with \(x = 0 – 0.025\) show the vacancy scattering mechanism and those with \(x = 0.05 – 0.125\) follow lattice scattering mechanism. In SPB model, the former and latter correspond to the scattering mechanism dominated by acoustic phonon \((r = -1/2)\) and ionized impurity \((r = 3/2)\), respectively. We calculated Pisarenko relation assuming the aforementioned scattering mechanisms in Figure S6. The gray and red lines are given based on acoustic phonon and ionized impurity scattering mechanisms, respectively, with \(m_0\) of
0.30\textit{m}e at 300 K. The experimental \textit{S} values at the given \textit{n}_H of the Pb\textsubscript{1+x}Se\textsubscript{0.8}Te\textsubscript{0.2} (\textit{x} = 0 – 0.125) samples significantly deviate from the ionized impurity scattering mechanism model and moves toward acoustic phonon scattering mechanism model with the introduction of excess Pb (green arrow in Figure S6), which agrees with the findings in Figure 6a.

According to the previous report\cite{3}, charge is scattered at in-grain regions and grain boundaries according to acoustic phonon and ionized impurity scattering mechanisms, respectively. The experimental Seebeck coefficients of pristine PbSe (black square)\cite{1} and our control sample Pb\textsubscript{1.075}Se\textsubscript{0.8}Te\textsubscript{0.2} prepared by traditional melt-synthesis followed by SPS process (purple circle) fall well on the gray line. In sharp contrast, the title ball milled Pb\textsubscript{1.075}Se\textsubscript{0.8}Te\textsubscript{0.2} sample shows their Seebeck coefficients lying far above the gray line and rather moving toward the red line (purple arrow in Figure S6). Namely, grain boundary affects charge transport and thus enhances the Seebeck coefficient due to ionized impurity scattering.

Because thermal conductivity (\textit{\kappa}) is contributed by electronic \textit{\kappa}_e and lattice \textit{\kappa}_\text{lat} thermal conductivity, the subtraction of \textit{\kappa}_{ele} from \textit{\kappa} is calculated by Wiedeman-Franz relation: \textit{\kappa}_\text{lat} = \textit{\kappa} – \textit{\kappa}_{ele} (\textit{\kappa}_{ele} = L \sigma T)\cite{4} where \sigma and \textit{L} is electrical conductivity and Lorenz number, respectively. \textit{L} is calculated using the equation\cite{5} (S5), combined with equations (S1) and (S3).

\[
L = \left(\frac{k_B}{e}\right)^2 \left[ \frac{(r + \frac{7}{2})F_{r+5/2}(\eta)}{(r + \frac{5}{2})F_{r+1/2}(\eta)} - \frac{(r + \frac{5}{2})F_{r+3/2}(\eta)}{(r + \frac{3}{2})F_{r+1/2}(\eta)} \right]
\]

(S5)

where \textit{r} is the scattering factor (\textit{r} = 1/2).

**Density Functional Theory (DFT) calculations.** Theoretical calculations at the DFT
level were conducted using a Cambridge Sequential Total Energy Package (CASTEP) and the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) formulation. A plane wave cutoff energy of 700 eV was used in all DFT calculations. The k-point of the crystal structure was set at 4 × 4 × 4. The self-consistent field (SCF) tolerance was used at 2.0 × 10⁻⁶ eV per atom. A preliminary 2 × 2 × 2 PbSe supercell containing 64 atoms was used to simulate our system. The isovalent Group 16 congener Te was allocated to the crystallographic Se site. All the atoms in the supercell were optimized until the geometric structure reached the forces on every atom less than 0.05 eV Å⁻¹, their total energy difference less than 2 × 10⁻⁵ eV, the maximum ionic placement less than 0.002 Å, and the maximum stress less than 0.1 GPa.

The expression for the formation energy (ΔHₜₚ) of defect (d) in the charge state (q) is defined by the equation (S6),

\[ \Delta H_{d,q}(E_{\text{F}}, \mu) = E_{d,q} - E_{p} - \Sigma n_{\alpha}\mu_{\alpha} + q(E_{\text{F}} + E_{\text{V}} + \varepsilon) \]  

(S6)

where \( E_{d,q} \) and \( E_{p} \) are the total energies of the supercell with the defects obtain from CASTEP in the \( q \) and a perfect host supercell, respectively. \( n_{\alpha} \) is the number of exchanged atoms (\( \alpha \)) in defect supercell system, and \( \mu_{\alpha} \) is the corresponding chemical potential of \( \alpha \). \( E_{\text{F}} \) is the Fermi level, and \( E_{\text{V}} \) corresponds to the valence band maximum, which was corrected by \( \varepsilon \). The formation energy of the defects is a function of the \( E_{\text{F}} \) and \( \mu_{\alpha} \) of reactants.

In order to give the relationship between \( \Delta H_{d,q}(E_{\text{F}}, \mu) \) and \( E_{\text{F}} \), the boundary conditions of \( \mu_{\alpha} \) need to be given. Based on the thermodynamic limits on the
achievable values of the chemical potentials,\textsuperscript{[7b]} the $\mu_\alpha$ can be obtained in Pb-rich and Pb-poor conditions by the method described in previous work.\textsuperscript{[7b]} In Pb-rich condition, the $\mu_{\text{Pb}} = 0$ eV, $\mu_{\text{Se}} = \Delta E_{\text{PbSe}} = -1.08$ eV and $\mu_{\text{Te}} = \Delta E_{\text{PbTe}} = -0.88$ eV. In Pb-poor condition, $\mu_{\text{Pb}} = E_{\text{PbSe}} = -1.08$ eV, $\mu_{\text{Se}} = 0$ eV and $\mu_{\text{Te}} = 0$ eV. Based on the above results, we can obtain the relationship between the $\Delta H_{\text{d,q}}(E_F, \mu)$ and the $E_F$ in Pb-rich and Pb-poor conditions.

The formation energies of PbQ ($\Delta E_{\text{PbQ}}$, Q = Se, Te) were calculated by the following relation:

$$\Delta E_{\text{PbQ}} = E_{\text{PbQ}} - n_{\text{Pb}}E_{\text{Pb}} - n_QE_{\text{Q}}$$

(S7)

where $E_{\text{PbQ}}$, $E_{\text{Pb}}$ and $E_{\text{Q}}$ are the total energies of the PbQ supercell, Pb atom and Q atom obtain from CASTEP, respectively. $n_{\text{Pb}}$ and $n_Q$ are the number of Pb and Q in the PbQ supercell, respectively.
2. Supporting Table

Table S1. Density of the Pb$_{1+x}$Se$_{0.8}$Te$_{0.2}$ samples after spark plasma sintering (SPS) process ($x = 0 - 0.075$).

| Samples             | Density (g cm$^{-3}$) | Relative density (%) |
|---------------------|-----------------------|----------------------|
| PbSe$_{0.8}$Te$_{0.2}$ | 7.85                  | 95.73                |
| Pb$_{1.025}$Se$_{0.8}$Te$_{0.2}$ | 7.88                  | 96.10                |
| Pb$_{1.05}$Se$_{0.8}$Te$_{0.2}$ | 7.87                  | 96.00                |
| Pb$_{1.075}$Se$_{0.8}$Te$_{0.2}$ | 7.90                  | 96.34                |
| Pb$_{1.1}$Se$_{0.8}$Te$_{0.2}$   | 7.92                  | 96.59                |
| Pb$_{1.125}$Se$_{0.8}$Te$_{0.2}$ | 7.92                  | 96.59                |

Table S2. Quantitative elemental analysis by STEM-EDS taken at the matrix and nanostructure embedded in the Pb$_{1.075}$Se$_{0.8}$Te$_{0.2}$ sample. A relative molar ratio for Pb, Se, and Te are given. Although STEM-EDS does not provide the exact value, it is enough to reveal Pb-rich regions.

| Region                | Pb at.% | Se at.% | Te at.% |
|-----------------------|---------|---------|---------|
| Matrix 1              | 49.22   | 39.56   | 11.22   |
| Matrix 2              | 49.59   | 39.34   | 11.07   |
| Nanostructure 1       | 51.06   | 40.05   | 8.89    |
| Nanostructure 2       | 51.25   | 39.67   | 9.08    |
| Nanostructure 3       | 51.16   | 39.71   | 9.13    |
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**Figure S7.** The electronic thermal conductivity ($\kappa_{el}$) of the Pb$_{1-x}$Se$_{0.8}$Te$_{0.2}$ samples ($x = 0 - 0.125$) with respect to temperature.
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