Supplementary Information

Dense dislocations enable high-performance PbSe thermoelectric at low-medium temperatures

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Supplementary Methods

Lorenz number calculation. The Lorenz number \( L \) is used to evaluate the electronic thermal conductivity \( \kappa_{\text{ele}} \) with a Wiedemann-Franz law of \( \kappa_{\text{ele}} = L \sigma T \), where the \( \sigma \) is the electrical conductivity, \( T \) denotes working temperature. The Lorenz number can be obtained by fitting the Seebeck coefficient to the reduced chemical potential with following equations:

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

(S1)

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

(S2)

where the \( F_n(\eta) \) is the \( n \)-th order Fermi integral:

\[
F_n(\eta) = \int_0^\infty \frac{x^n}{1 + e^{x-\eta}} dx
\]  

(S3)

\[
\eta = \frac{E_F}{k_B T}
\]  

(S4)

where \( k_B \) is the Boltzmann constant, \( e \) is the electron charge and \( E_F \) denotes the Fermi level, \( r \) is the scattering factor, and the acoustic phonon scattering has been assumed as the main carrier scattering mechanism with \( r=-1/2 \).

Heat capacity calculation. The heat capacity in this work was theoretically evaluated by Debye model. The Debye model considers the individual contributions of phonons and effects of thermal expansion of lattice. The temperature-dependent total heat capacity \( C_{\text{p, tot}} \) can be obtained with following relationships:

\[
C_{\text{p, tot}} = C_{\text{p, ph}}(T) + C_{\text{p, D}}(T)
\]  

(S5)

where \( C_{\text{p, ph}} \) and \( C_{\text{p, D}} \) denote heat capacity originated from phonon and lattice dilation, respectively. The phonon heat capacity \( C_{\text{p, ph}} \) can be calculated by:

\[
C_{\text{p, ph}}(T/\Theta_D) = 9R \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx
\]  

(S6)

where \( \Theta_D \) is Debye temperature, \( R \) is molar gas constant, \( x = h\omega/k_BT \), in which \( h \) and
denote reduced Planck constant and phonon vibration frequency, respectively.

The effects of lattice dilation on heat capacity \( C_{p, D} \) can be obtained from:

\[
C_{p, D}(T) = C_{\text{ele}, D}(T) + C_{\text{ph}, D}(T) = \frac{9BT\alpha^2}{10^9 \rho}
\]  

(S7)

where \( B \) is the isothermal bulk modulus, \( \alpha \) is the linear coefficient of thermal expansion, and \( \rho \) is sample density. Notably, the electron heat capacity is not taken into account due to its negligible effects on lattice dilation compared with phonon.

**Callaway model to predict lattice thermal conductivity.** Callaway model shows the ratio of the conductivities of material containing defects to that of pure material:

\[
\frac{\kappa_{\text{lat}}}{\kappa_{\text{lat}, p}} = \frac{\tan^{-1}(u)}{u}
\]

(S8)
in which \( \kappa_{\text{lat}} \) and \( \kappa_{\text{lat}, p} \) are the lattice thermal conductivities of the defected and parent materials, respectively, and \( \kappa_{\text{lat}, p} = 1.68 \text{ W m}^{-1} \text{ K}^{-1} \) in this work. \( u \) is defined as:

\[
u = \left( \frac{\pi^2 \Theta_D \Omega}{h v_a^2 \kappa_{\text{lat}, p}} \right)^{1/2}
\]

(S9)

where \( \Omega \) and \( h \) are the average atom volume and Planck constant, respectively. The Debye temperature (\( \Theta_D \)), average sound velocity (\( v_a \)) and can be written as:

\[
\Theta_D = \frac{h}{k_B} \left( \frac{3}{4\pi\Omega} \right)^{1/3} v_a
\]

(S10)

\[
v_a = \left[ \frac{1}{3} \left( \frac{1}{v_l^2} + \frac{1}{v_s^2} \right)^{-1/3} \right]
\]

(S11)

where \( k_B, v_l \) and \( v_s \) are Boltzmann constant, longitudinal and shear sound velocities, respectively. In this work, there is no change on the sites of Pb after Q (Te or S) substituting Se sites, namely the imperfection scattering parameter \( \Gamma_{\text{Pb}} = 0 \). Thus, the \( \Gamma_{\text{Pb}, 1-x\text{Se}, x\text{Q}} \) is defined as:

\[
\Gamma_{\text{Pb}, 1-x\text{Se}, x\text{Q}} = \frac{1}{2} \left( \frac{M_{(\text{Se}, Q)}}{M} \right)^2 \Gamma_{(\text{Se}, Q)}
\]

(S12)

\[
\frac{M}{M} = \frac{1}{2} (M_{\text{Se}} + M_{\text{Q}})
\]

(S13)
where \( M \) is molar mass. Meanwhile, \( \Gamma \) is a weighted sum of the mass fluctuation (\( \Gamma_M \)) and strain field fluctuation (\( \Gamma_S \)), can be written as\(^3,7\):

\[
\Gamma_{(Se, Q)} = \Gamma_M^{(Se, Q)} + \varepsilon \Gamma_S^{(Se, Q)} \tag{S14}
\]

in which \( \varepsilon \) is a phenomenological adjustable parameter related to the Poisson ratio (\( \nu_p \)) and Grüneisen parameter (\( \gamma \)). Moreover, they can be expressed by\(^8,9\):

\[
\varepsilon = \frac{2}{9} \left[ (G + 6.4\gamma) \frac{1 + \nu_p}{1 - \nu_p} \right]^2 \tag{S15}
\]

\[
\gamma = \frac{3}{2} \left( \frac{1 + \nu_p}{2 - 3\nu_p} \right) \tag{S16}
\]

\[
\nu_p = \frac{1 - 2(\nu'/\nu_p)^2}{2 - 2(\nu'/\nu_p)^2} \tag{S17}
\]

where \( G \) is a ratio between the relative change of bulk modulus and banding length.

And \( \Gamma_M^{(Se, Q)} \) and \( \Gamma_S^{(Se, Q)} \) in equation (S14) can be expended as follows:

\[
\Gamma_M^{(Se, Q)} = x(1 - x) \left( \frac{\Delta M}{M_{(Se, Q)}} \right)^2 \tag{S18}
\]

\[
\Gamma_S^{(Se, Q)} = x(1 - x) \left( \frac{\Delta r}{r_{(Se, Q)}} \right)^2 \tag{S19}
\]

where \( \Delta M, \Delta r \) and \( r \) can be written as\(^7\):

\[
M_{(Se, Q)} = (1 - x)M_{Se} + xM_Q \tag{S20}
\]

\[
\Delta M = M_{Se} - M_Q \tag{S21}
\]

\[
r_{(Se, Q)} = (1 - x)r_{Se} + xr_Q \tag{S22}
\]

\[
\Delta r = r_{Se} - r_Q \tag{S23}
\]

Then we can obtain:

\[
\Gamma_{Pb_{1/3}Se_{1/3}, Q} = \frac{1}{2} x(1 - x) \left( \frac{M_{(Se, Q)}}{M} \right)^2 \left[ \left( \frac{\Delta M}{M_{(Se, Q)}} \right)^2 + \varepsilon \left( \frac{\Delta r}{r_{(Se, Q)}} \right)^2 \right] \tag{S24}
\]
Modified Williamson-Hall method to calculate dislocation density. In consideration of that size and strain broadening are diffraction order independent and independent, respectively, Williamson and Hall suggested that the full width at half-maximum (FWHM) of line profiles can be written as\textsuperscript{10-12}:

\[ \Delta K = 0.9/d + \Delta K^d \] (S25)

where \( \Delta K^d \) is the strain contribution to line broadening and \( d \) is the average grain size or particle size. \( K = 2\sin\theta/\lambda \), \( \Delta K = 2\cos\theta(\Delta\theta)/\lambda \), \( \theta \) and \( \lambda \) are the diffraction angle and the wavelength of X-rays, respectively. When strain is caused by dislocations, \( \Delta K^d \) has the following form\textsuperscript{13-15}:

\[ \Delta K^d = A(N_D^*)^{1/2} + A'(Q^*)^{1/2} \] (S26)

where \( A \) and \( A' \) are parameters determined by the effective outer cutoff radius of dislocations, \( R_e \), and the auxiliary parameters \( R_1 \) and \( R_2 \), respectively. \( N_D^* \) and \( Q^* \) are the formal values of dislocation density and the correlation factors, respectively, they are related to the true values \( N_D \) and \( Q \) as\textsuperscript{13-15}:

\[ N_D^* = N_D(\pi g^2 b^2 \overline{C})/2 \] (S27)
\[ Q^* = Q(\pi g^2 b^2 \overline{C})^2/4 \] (S28)

in which \( b \) is the magnitude of Burgers vector and \( \overline{C} \) is the average dislocation contrast factor for a particular reflection \( g \) and \( g=K \) at the exact Bragg position. The average contrast factor is a linear function of the fourth-order invariant of the \( hkl \) indices of the different reflections\textsuperscript{16}:

\[ \overline{C} = \overline{C}_{h00}(1 - qH^2) \] (S29)

where \( H^2 = (h^2+k^2+l^2)/(h^2+k^2+l^2)^3 \) and \( \overline{C}_{h00} \) is the average dislocation contrast factor corresponding to the \( h00 \) reflection determining by elastic modulus. Thus, equation (S25) will be written as:

\[ \Delta K = 0.9/d + (\pi A^2 b^2/2)^{1/2} N_D^{1/2} \left( K \overline{C}^{1/2} \right) \pm O(K^2 \overline{C}) \] (S30)

where \( O = (\pi A^2 b^2/2)Q^{1/2} \).
Supplementary Figure 1. Thermoelectric transport properties in Pb$_{1.02}$Se$_{1-x}$Te$_x$: (a) Electrical conductivity. (b) Seebeck coefficient. (c) Power factor. (d) Total thermal conductivity. (e) Lattice thermal conductivity. (f) ZT values.
Supplementary Figure 2. Electrical transport properties for \( \text{Pb}_{1.02}\text{Se}_{1-x}\text{Te}_x \): (a) Thermal diffusivity. (b) Heat capacity. (c) Lorenz number. (d) Electronic thermal conductivity.
Supplementary Figure 3. Thermoelectric transport properties in $\text{Pb}_{1.02}\text{Se}_{1-y}\text{S}_y$: (a) Electrical conductivity. (b) Seebeck coefficient. (c) Power factor. (d) Total thermal conductivity. (e) Lattice thermal conductivity. (f) $ZT$ values.
Supplementary Figure 4. Electrical transport properties for Pb$_{1.02}$Se$_{1-y}$S$_y$: (a) Thermal diffusivity. (b) Heat capacity. (c) Lorenz number. (d) Electronic thermal conductivity.
**Supplementary Figure 5.** Phase analysis of $\text{Pb}_{1.02}\text{Se}_{0.72}\text{Te}_{0.20}\text{S}_{0.08}-x\%\text{Cu}$: (a) XRD patterns. (b) Lattice parameter as a function of Cu content.
Supplementary Figure 6. Estimation of dislocation density in Pb_{1.02}Se_{0.72}Te_{0.20}S_{0.08} by MWH method: (a) Plot of $\Delta K \sim K$. (b) Plot of $(\Delta K - 0.9/d)/K^2 \sim H^2$. (c) Plot of $\Delta K \sim \overline{C}^{1/2}$. 
**Supplementary Figure 7.** EDS mapping of Pb (a), Te (b) and Se (c) at edge dislocation in Pb$_{1.02}$Se$_{0.72}$Te$_{0.20}$S$_{0.08}$-0.3%Cu.
Supplementary Figure 8. Thermoelectric properties for \( \text{Pb}_{1.02}\text{Se}_{0.72}\text{Te}_{0.20}\text{S}_{0.08-x}\%\text{Cu} \):

(a) Thermal diffusivity. (b) Heat capacity. (c) Lorenz number. (d) Electronic thermal conductivity.
Supplementary Figure 9. Repeatability of the thermoelectric transport properties in Pb$_{1.02}$Se$_{0.72}$Te$_{0.20}$S$_{0.08}$-0.3%Cu: (a) Electrical conductivity. (b) Seebeck coefficient. (c) Power factor. (d) Electronic thermal conductivity. (e) Lattice thermal conductivity. (f) $ZT$ values.
Supplementary Figure 10. Comparison of $ZT$ values between Pb$_{1.02}$Se$_{0.72}$Te$_{0.20}$S$_{0.08}$-0.3%Cu and $n$-type Bi$_2$Te$_3$-based materials.
**Supplementary Table 1.** Parameters used for the Callaway model.

| Parameters | Description                              | PbSe | PbTe | PbS | Ref.   |
|------------|------------------------------------------|------|------|-----|--------|
| $v_l$      | Longitudinal sound velocity (m s$^{-1}$) | 3200 | 2910 | 3450| 17     |
| $v_s$      | Shear sound velocity (m s$^{-1}$)        | 1750 | 1610 | 1900| 17     |
| $G$        | Ratio between the relative change of     |      |      |     |        |
|            | bulk modulus and banding length          |      |      |     | $3, 18-20$ |
Supplementary Table 2. Values of $\theta$, FWHM, $hkl$ and dislocation density in Pb$_{1.02}$Se$_{0.72}$Te$_{0.20}$S$_{0.08}$-x%Cu. The dislocation density is evaluated with a similar Burgers vector $b$ as observed in TEM results.

| Parameters | Samples | Values |
|------------|---------|--------|
| $\theta$ (°) | $x=0$ | 24.8867 | 28.8543 | 41.2968 | 48.8870 | 59.8946 | 75.3682 |
| | $x=0.3$ | 24.9752 | 28.9422 | 41.3717 | 48.9716 | 60.0236 | 75.4747 |
| (hkl) | $x=0$ | (111) | (200) | (220) | (311) | (400) | (422) |
| | $x=0.3$ | (111) | (200) | (220) | (311) | (400) | (422) |
| FWHM (°) | $x=0$ | 0.4032 | 0.4067 | 0.5923 | 0.6185 | 0.6710 | 0.8718 |
| | $x=0.3$ | 0.3951 | 0.3824 | 0.6074 | 0.6750 | 0.7169 | 1.0359 |
| $N_D$ (m$^2$) | $x=0$ | $\sim 2.3 \times 10^{16}$ | | | | | |
| | $x=0.3$ | $\sim 5.4 \times 10^{16}$ | | | | | |
### Supplementary Table 3. Parameters used for the modified Williamson-Hall model.

| Parameters | Description | Value       | Ref.   |
|------------|-------------|-------------|--------|
| \( \lambda \) | Wavelength of the synchrotron X-ray (Å) | 1.5418      | -      |
| \( A \)   | Parameter determined by the effective outer cut-off radius of dislocations | 2.6  | 21     |
| \( b \)   | Magnitude of Burgers vector (m) | \( 4.15 \times 10^{-10} \) | This work |
| \( C_{100} \) | corresponding to the \( h00 \) reflection determining by elastic modulus | 0.12148 | \(^{11, \, 16}\) |
| \( c_{11} \) | Elastic modulus (GPa) | 123.7 |        |
| \( c_{12} \) | Elastic modulus (GPa) | 19.3 | \(^{22}\) |
| \( c_{44} \) | Elastic modulus (GPa) | 15.9 |        |
| \( O \)   | Non-interpreted higher-order error terms | Non | -      |
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