Supporting Information

High Thermoelectric Performance of Pb and Er co-doped Polycrystalline SnSe via Endogenous Hetero-/Homo- Nanostructure and Band Alignment

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Lorenz number calculation in details:

In general, the total (κ) consists of the electronic thermal conductivity (κ_e) and lattice thermal conductivity (κ_L). The electronic part κ_e is directly proportional to the electrical conductivity σ through the Wiedemann-Franz relation, $\kappa_e = L\sigma T$, where L is Lorentz number and its value is calculated by SPB model. The Lorenz number can be given as: [1, 2]

$$L = \frac{k_B^2}{e^2}\left(\frac{(r+3)F_{r+2}(\eta)}{(r+1)F_r(\eta)} - \left[\frac{(r+2)F_{r+1}(\eta)}{(r+1)F_r(\eta)}\right]^2\right) \quad (1)$$

For the Lorenz number calculation, we should get reduced Fermi energy η firstly. The calculation of η can be derived from the measured Seebeck coefficients by using the following relationship:

$$S = \pm\frac{k_B}{e}\left(\frac{(r+2)F_{r+1}(\eta)}{(r+1)F_r(\eta)} - \eta\right) \quad (2)$$

where $F_n(\eta)$ is the n−th order Fermi integral,

$$F_n(\eta) = \int_0^\infty \frac{\chi^n}{1 + e^{\chi - \eta}} d\chi \quad (3)$$

where e is the electron charge, k_B is the Boltzmann constant, h is the Planck constant, r is the scattering factor. Here, r is 0 since acoustic phonon scattering has been assumed as the main carrier scattering mechanism near room temperature (RT). Lorentz number can be obtained by combining equations (1), (2) and (3).

Table S1. The calculated and measured densities for pure SnSe and $Sn_{0.99-x}Pb_{0.01}Er_xSe$.

Compositions	**Theoretical Density (ρ, g/cm^3)**	**Actual Density (ρ, g/cm^3)**	**Density %**
SnSe	6.18	5.93	95.95
x=0.0025	6.201	5.94	95.95
x=0.0075	6.203	5.95	95.79
x=0.015	6.207	5.97	95.92
x=0.0175	6.209	5.95	96.18

Figure S1. XRD patterns for $Sn_{0.9725}Pb_{0.01}Er_{0.0175}Se$ before and after repetitive thermoelectric measurements.

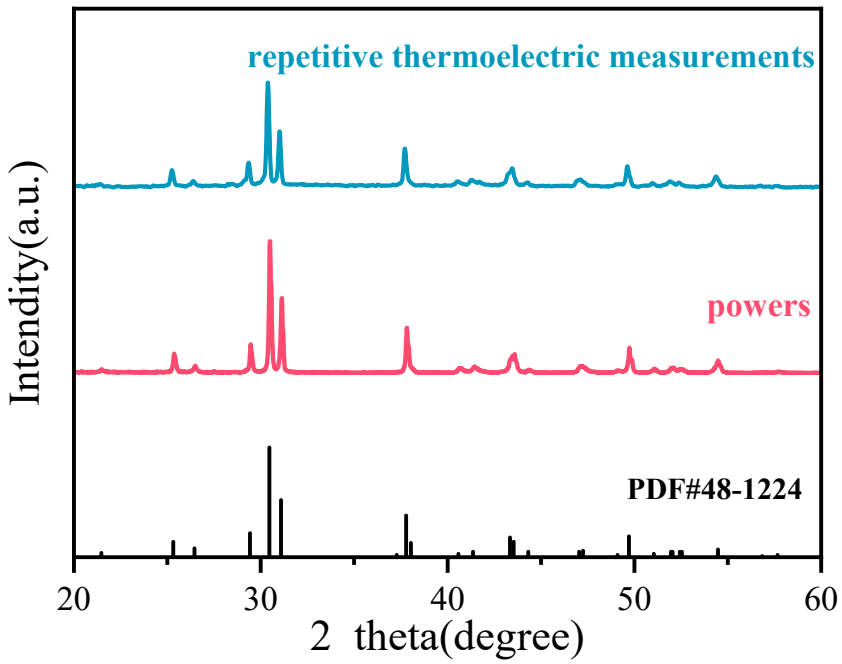

Figure S2. XPS core-level spectra of Sn 3d peak from $Sn_{0.9725}Pb_{0.01}Er_{0.0175}Se$.

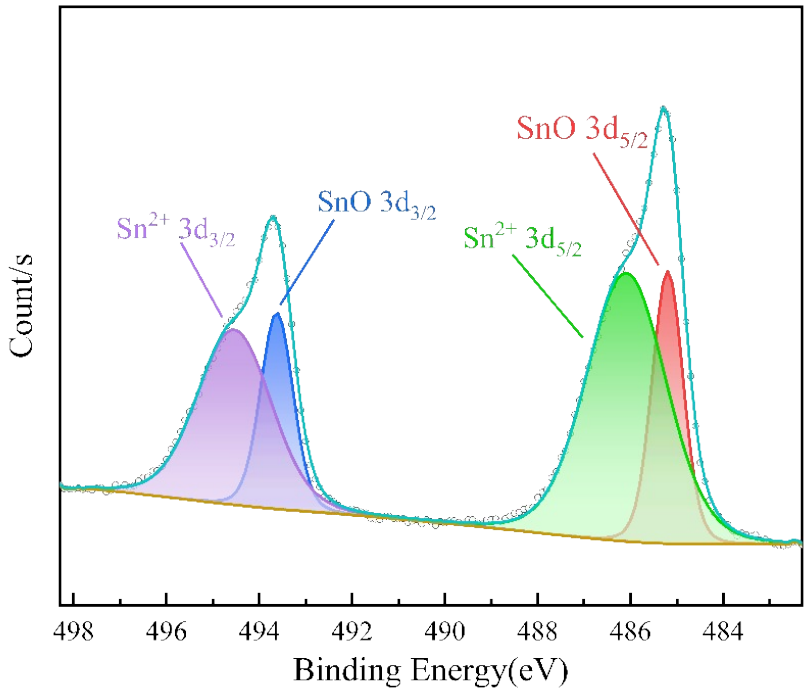

Figure S3. Microstructure characterization. (a) Scanning electron microscope (SEM) images of the $Sn_{0.9725}Pb_{0.01}Er_{0.0175}Se$; (b-e) Elemental mapping of $Sn_{0.9725}Pb_{0.01}Er_{0.0175}Se$ sample taken from the area in (a).

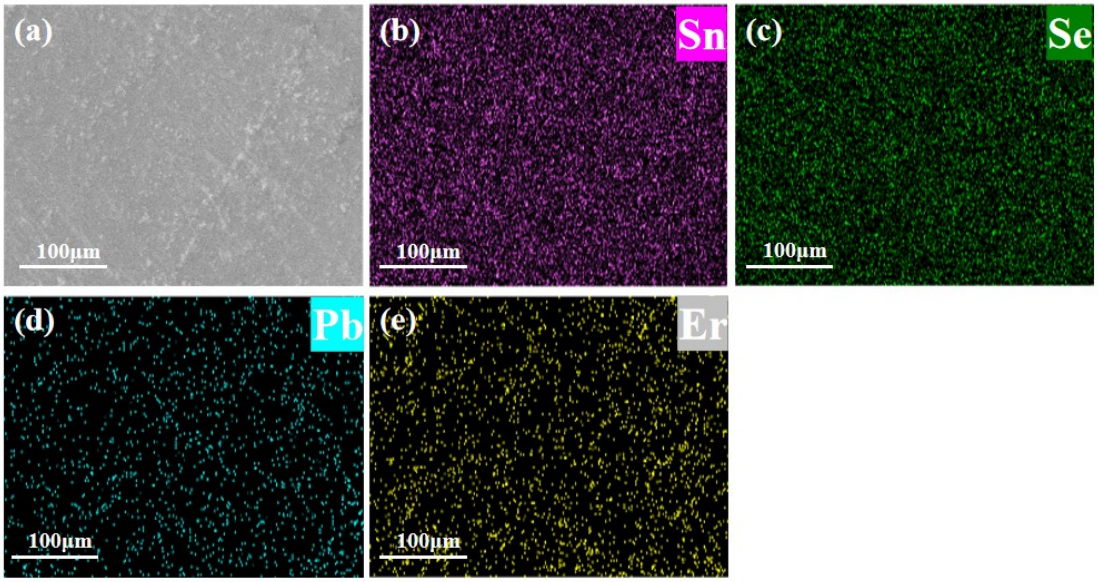

Figure S4. (a) Lorenz number of $Sn_{0.99-x}Pb_{0.01}Er_xSe$ as a function of temperature; (b) Electronic thermal conductivity (κ_e) of $Sn_{0.99-x}Pb_{0.01}Er_xSe$ as a function of temperature.

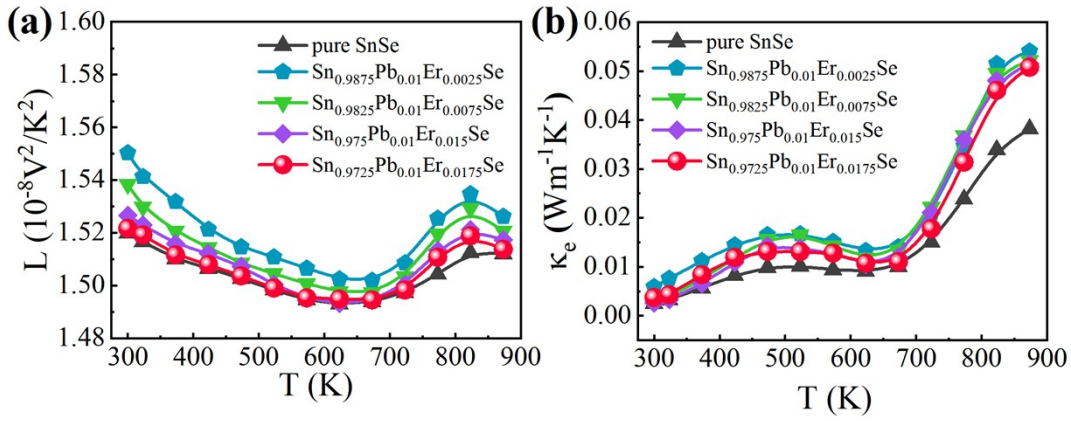

Figure S5. The thermoelectric properties of SnSe along parallel (//) and perpendicular (⊥) to the sintering orientation, (a) power factor (*PF*); (b) thermal conductivity (κ_T); (c) *ZT* value.