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Supporting Information

Realizing High Thermoelectric Performance in Highly Preferentially Oriented SnSe based Nanorods via 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. Rietveld refinement details of the $Sn_{0.96}Ge_{0.04}Se_{0.96}S_{0.04}$.

Atom	Site	x	y	z	Occupancy	FWHM (111)
Sn	4c	-0.3812	0.2500	0.3995	0.48	0.1668
Ge	4c	-0.3812	0.2500	0.3995	0.02	
Se	4c	0.3607	0.2500	0.0153	0.48	
S	4c	0.3607	0.2500	0.0153	0.02	

Table S2. Lattice parameters for $Sn_{1-x}Ge_xSe_{1-x}S_x$ (x=0, 0.02, 0.04, 0.05).

Compositions	**a（Å）**	**b（Å）**	**c（Å）**	**Volume（Å^3）**
SnSe	11.50856	4.15772	4.43934	212.42
x=0.02	11.50585	4.15102	4.43975	212.05
x=0.04	11.49681	4.15403	4.43467	211.79
x=0.05	11.49733	4.15067	4.44046	211.91

Table S3. The calculated and measured densities for pure SnSe and $Sn_{1-x}Ge_xSe_{1-x}S_x$ nanorods.

Compositions	**Theoretical Density (ρ, g/cm^3)**	**Actual Density (ρ, g/cm^3)**	**Density %**
SnSe	6.19	6.03	97.42
x=0.02	6.16	5.89	95.62
x=0.04	6.13	5.86	95.60
x=0.05	6.11	5.78	94.60

Figure S1. SEM images of pristine SnSe synthesized by the same method. Microplates can be clearly observed.

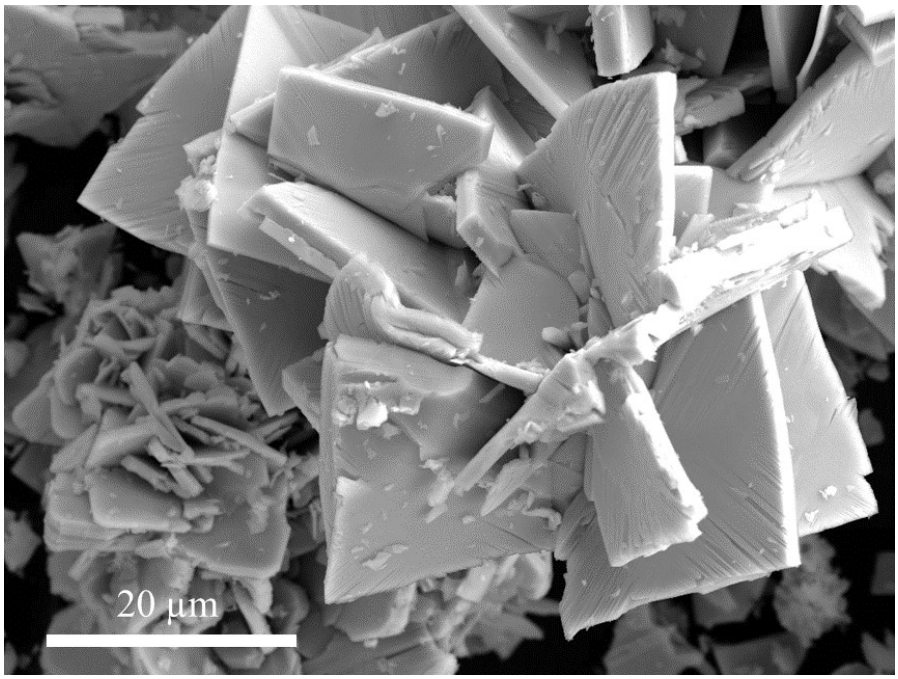


Figure. S2. SEM of $Sn_{0.96}Ge_{0.04}Se_{0.96}S_{0.04}$ nanorods and Elemental mapping.

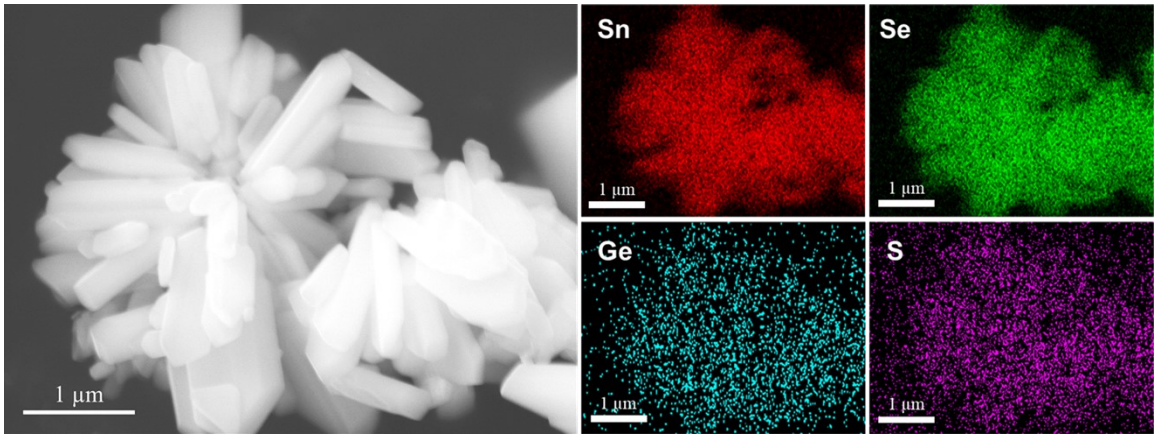


Figure S3. XPS core-level spectra of (a) Sn^{2+} 3d, (b) Se^{2-} 3d peak from $Sn_{0.96}Ge_{0.04}Se_{0.96}S_{0.04}$ nanorods.

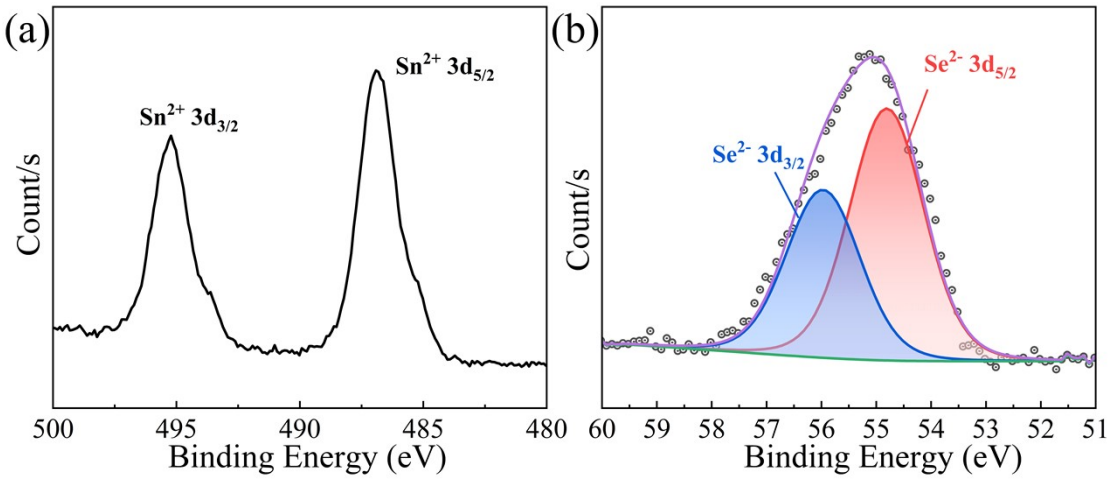


Figure S4. XRD patterns of SnSe and $Sn_{0.96}Ge_{0.04}Se_{0.96}S_{0.04}$ parallel to the pressure direction (//) and perpendicular to the pressure direction (⊥).

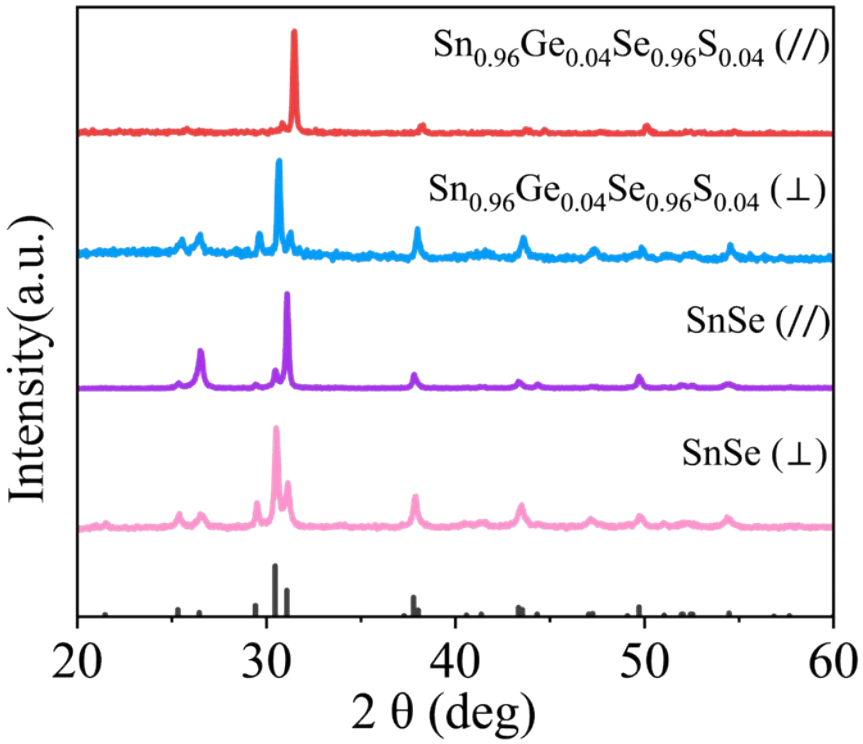


Figure S5. (a) Electronic thermal conductivity (κ_e), (b) Lorenz number for $Sn_{1-x}Ge_xSe_{1-x}S_x$ nanorods as a function of temperature.

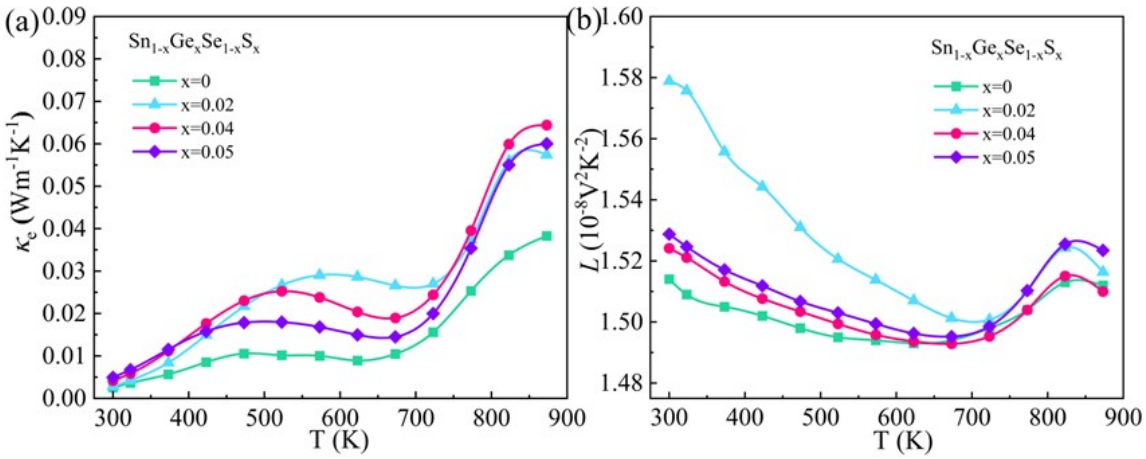


Figure S6. Comparison of Seebeck coefficient of $Sn_{1-x}Ge_xSe_{1-x}S_x$ nanorods with other reported SnSe-based materials.

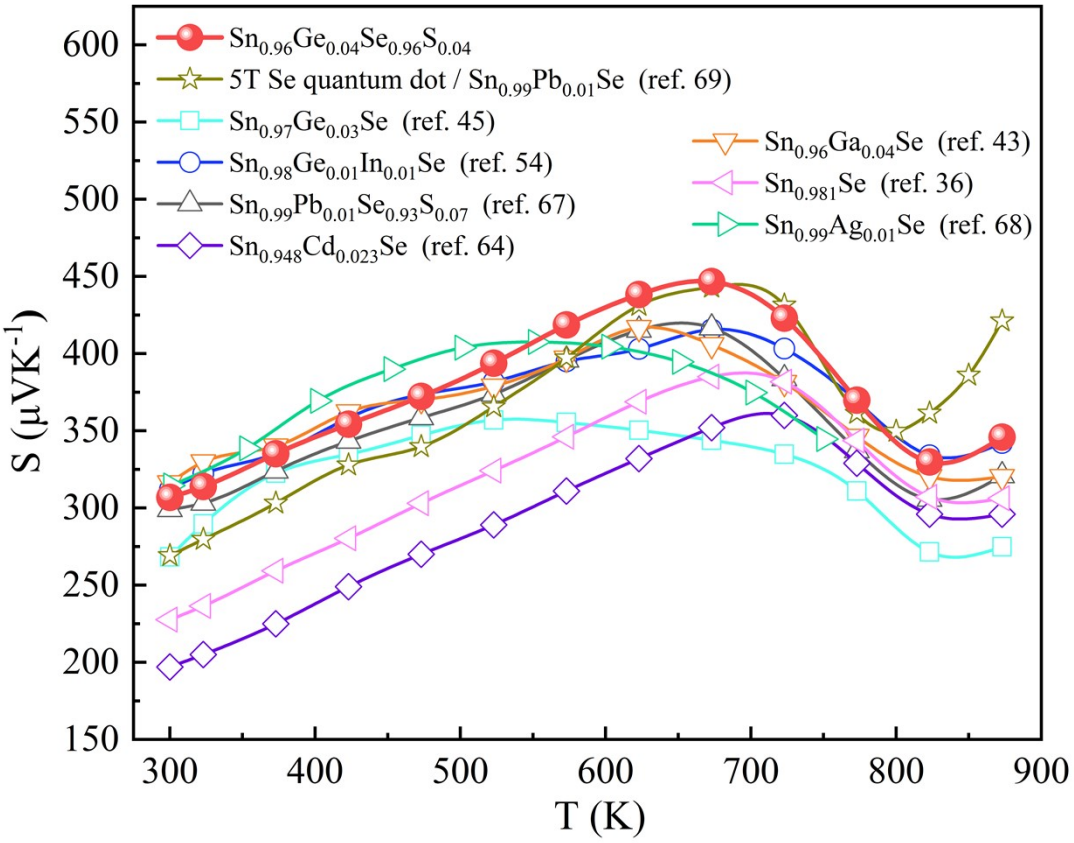


Figure S7. Electronic density of states of $Sn_{24}Se_{24}$, $Sn_{24}Se_{23}S$, $Sn_{23}GeSe_{24}$ and $Sn_{23}GeSe_{23}S$.

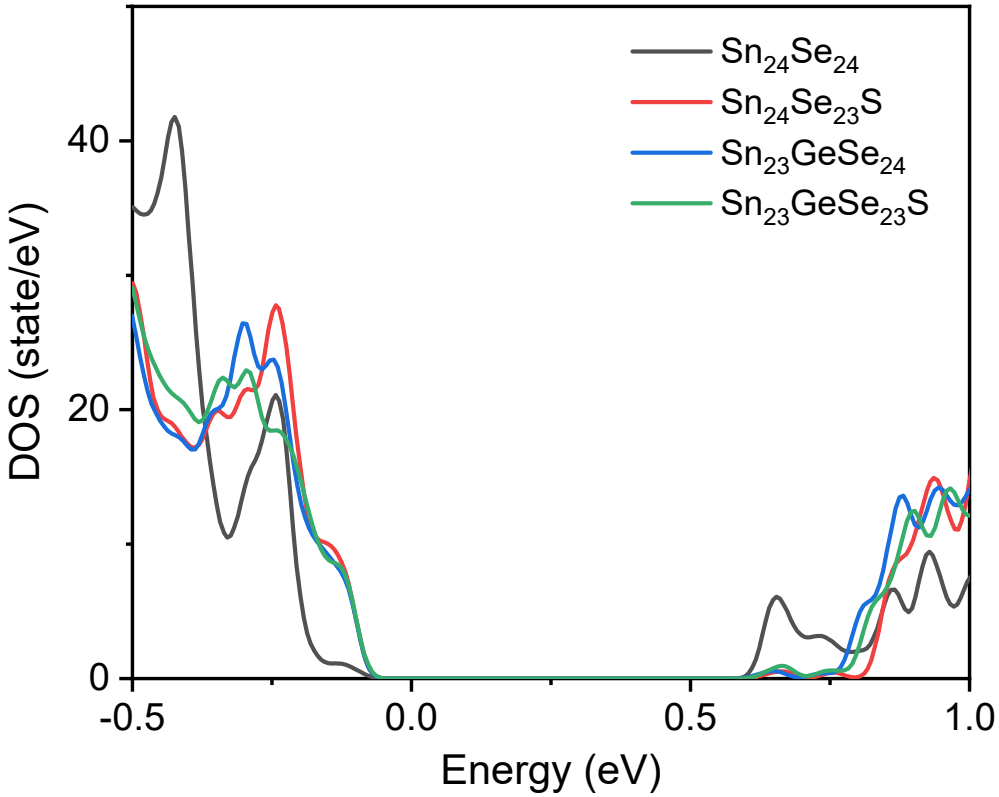


Figure S8. Comparison of *PF* for $Sn_{0.96}Ge_{0.04}Se_{0.96}S_{0.04}$ nanorods with SnSe-based systems.

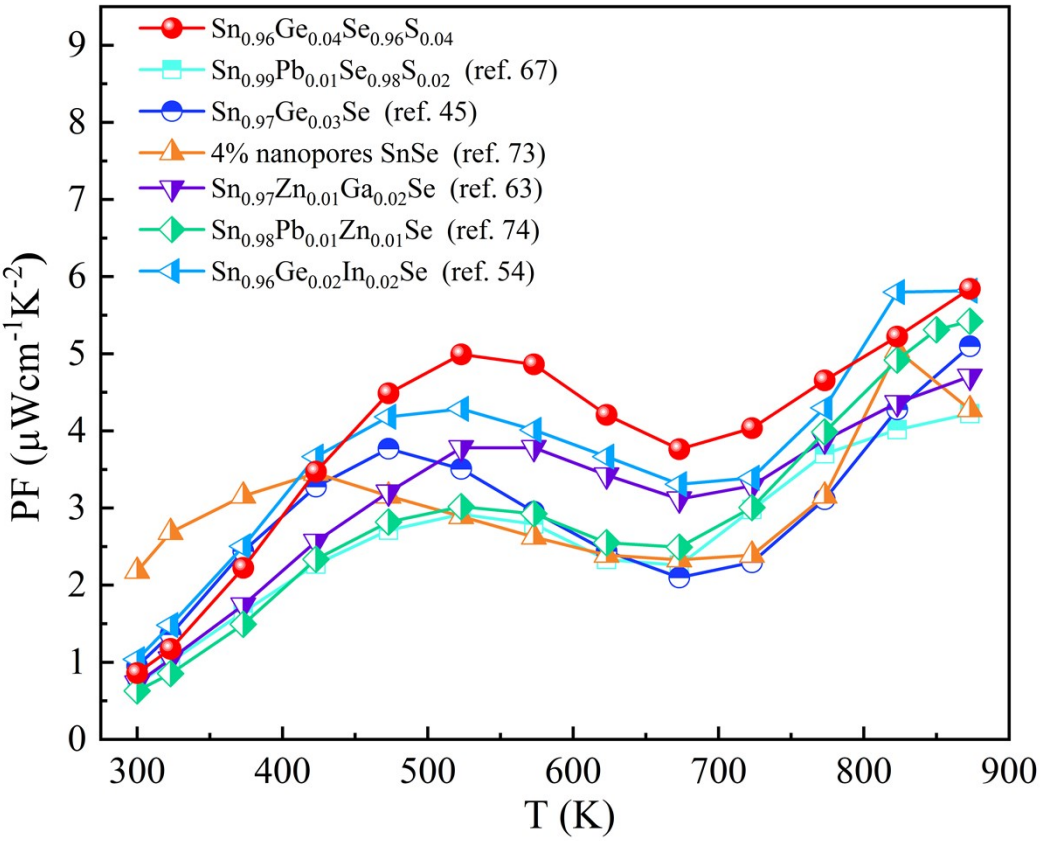


Figure S9. Repeat measurement results of (a) electrical conductivity, (b) Seebeck coefficient, (c) thermal conductivity, (d) *ZT* of $Sn_{0.96}Ge_{0.04}Se_{0.96}S_{0.04}$.

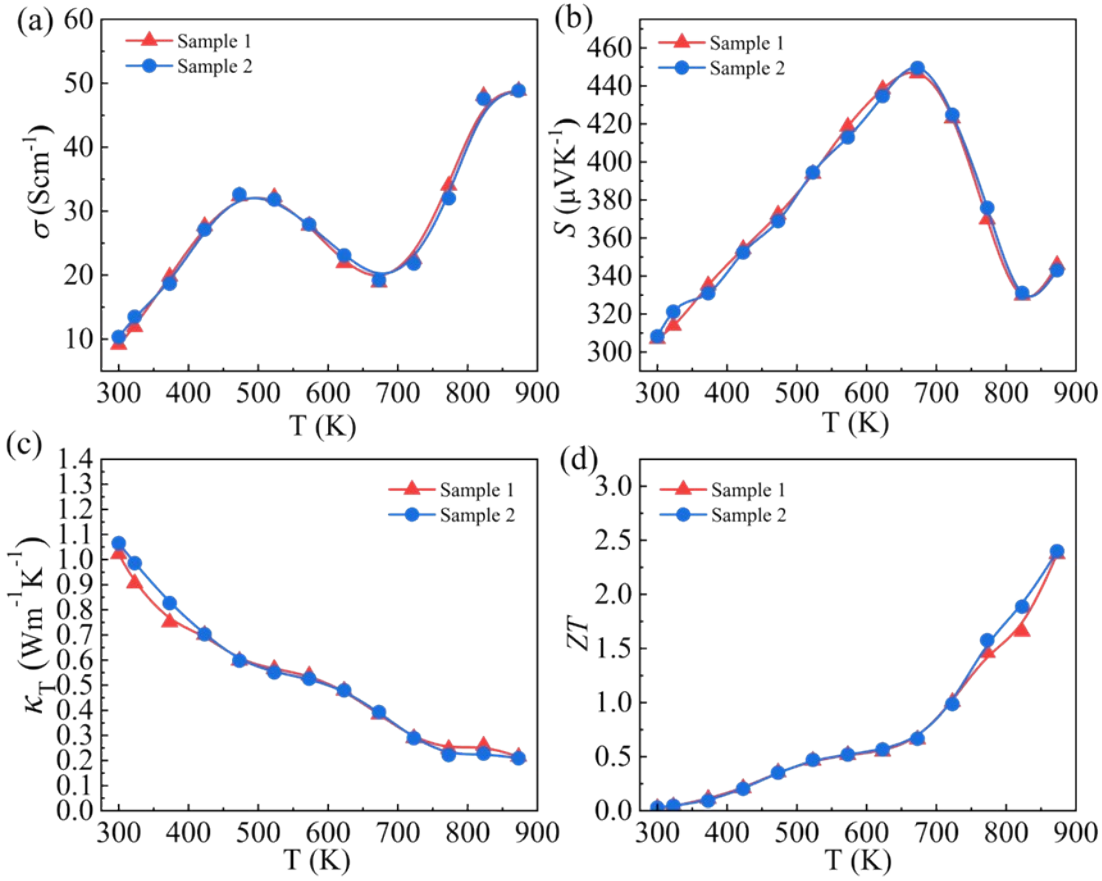


Figure S10. XRD patterns for $Sn_{0.96}Ge_{0.04}Se_{0.96}S_{0.04}$ nanorods before and after repetitive measurements.

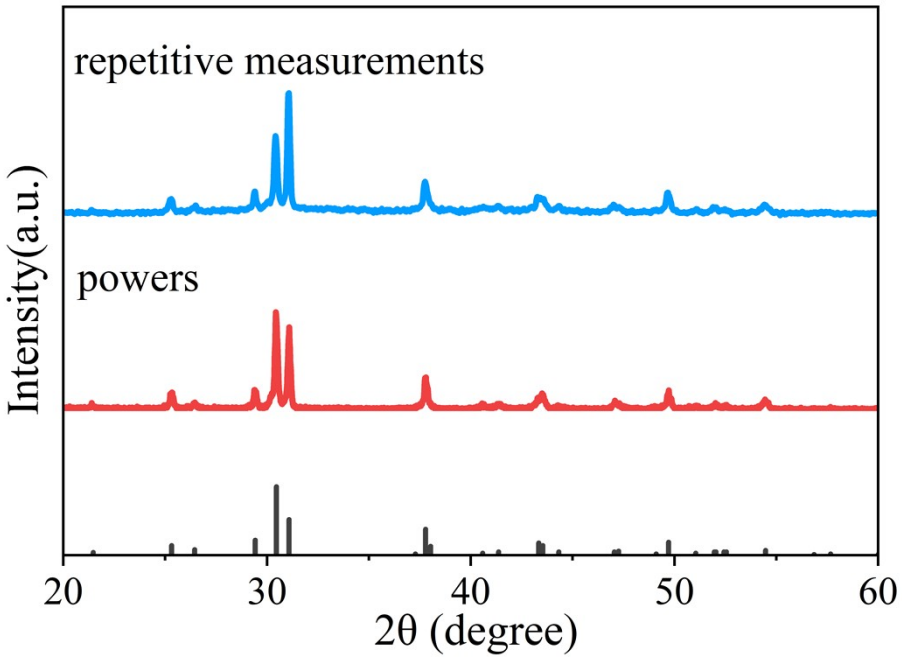


Figure S11. (a) Electrical conductivity (σ), (b) Seebeck coefficient (S), (c) Power factor (PF), (d) Total thermal conductivity (κ_T), (e) Lattice thermal conductivity (κ_L), (f) ZT for $Sn_{0.96}Ge_{0.04}Se_{0.96}S_{0.04}$ nanorods along the pressing direction (//) and perpendicular to the pressing direction (⊥).

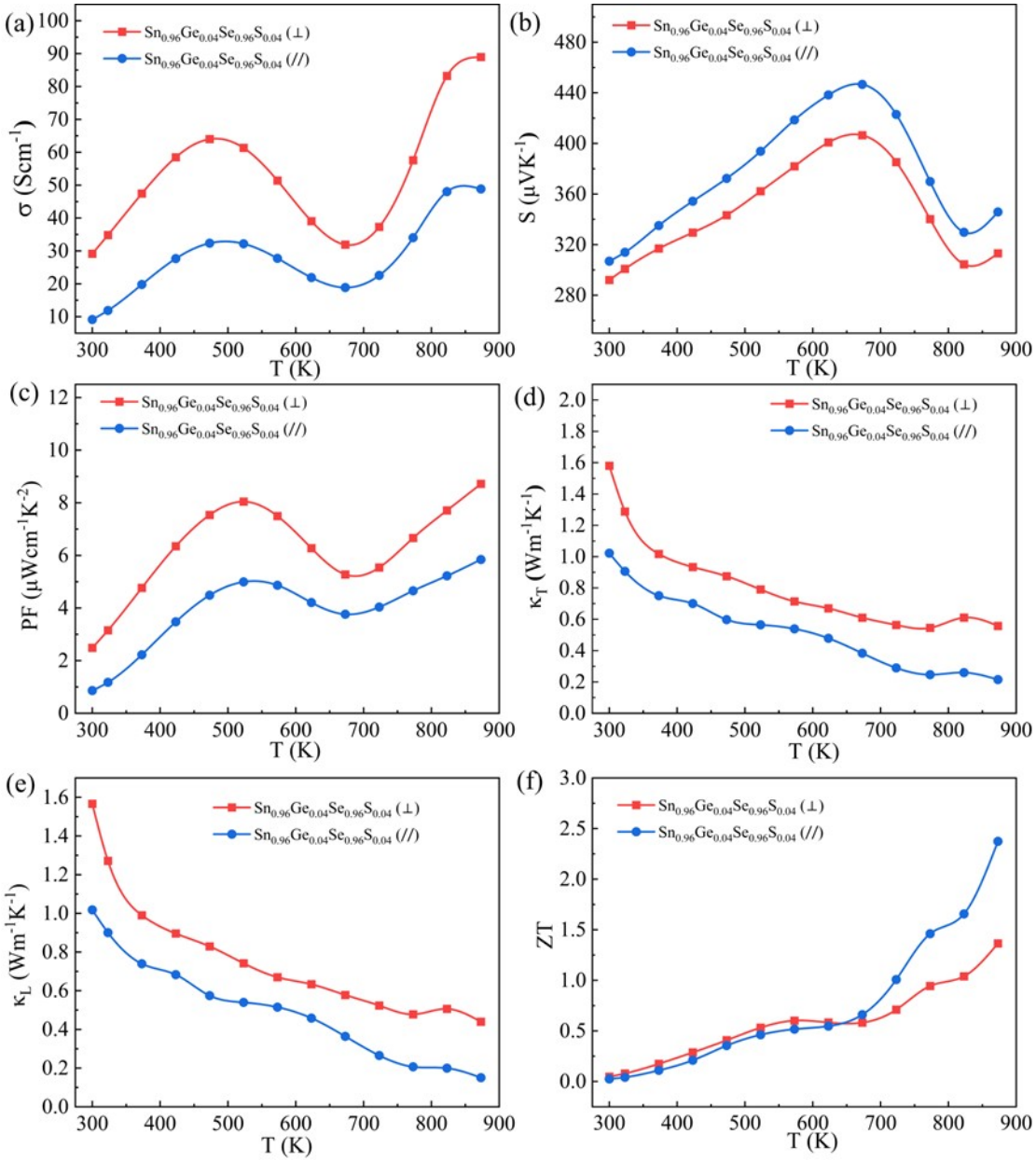
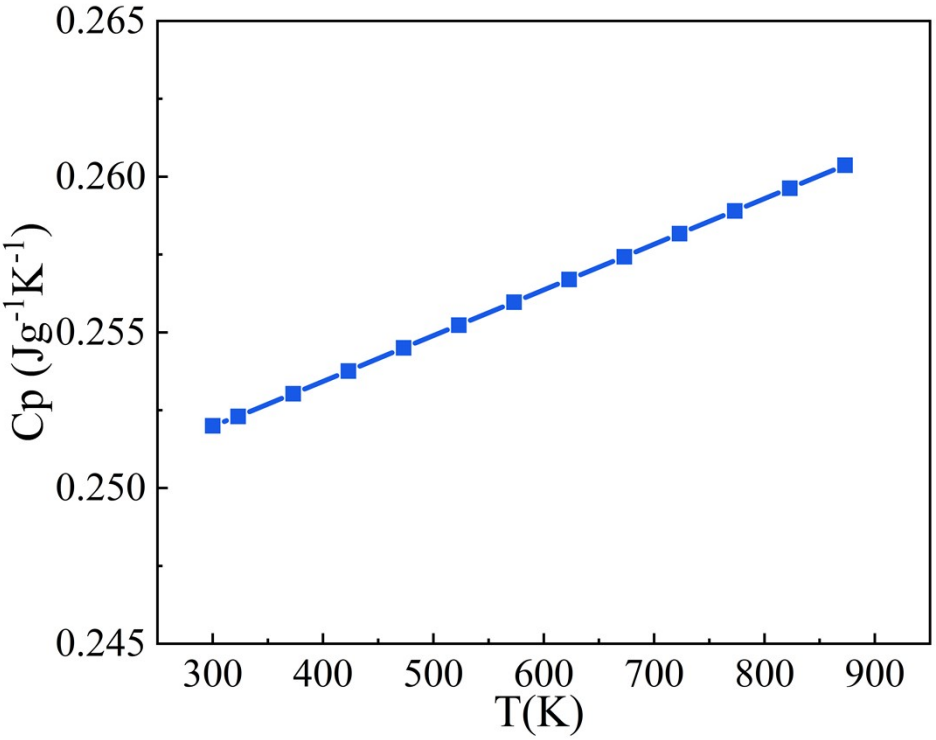


Figure S12. The Cp used for the ZT calculation.[3]



Reference

1. W. G. Zeier, A. LaLonde, Z. M. Gibbs, C. P. Heinrich, M. Panthoefer, G. J. Snyder, W. Tremel. *J. Am. Chem. Soc.* 2012, **134**, 7147-7154

2. A. F. May, E. S. Toberer, A. Saramat, G. J. Snyder. *Phys. Rev. B* 2009, **80**, 125205.

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