

Supporting Information

Two-Dimensional-Like Phonons in Three-Dimensional-Structured Rhombohedral GeSe-Based Compounds with Excellent Thermoelectric Performance

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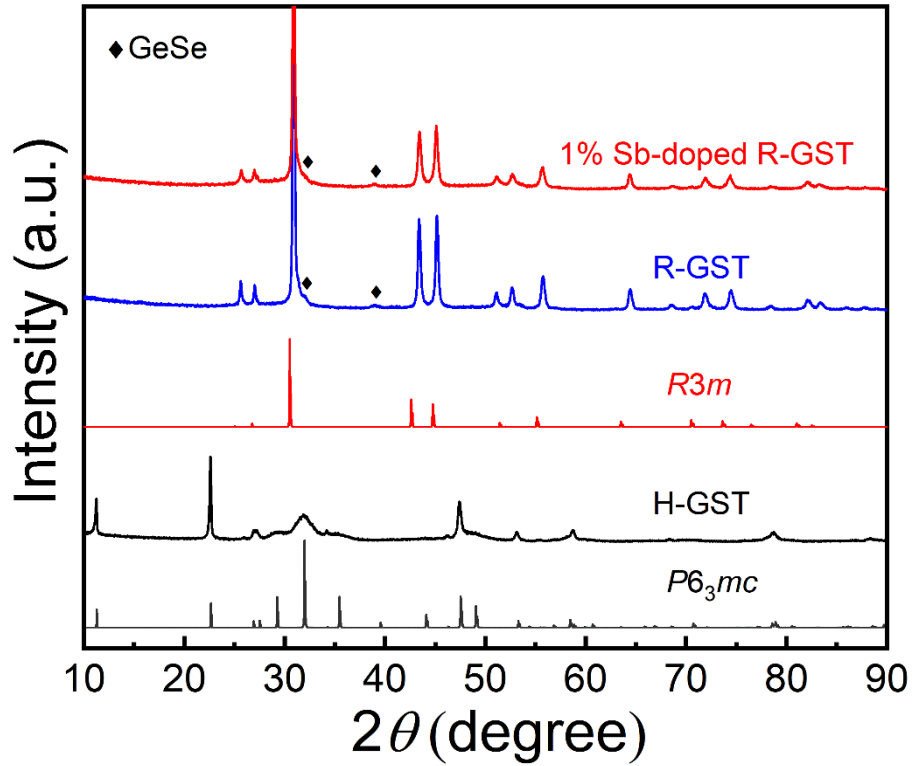


Figure S1. Room temperature powder XRD patterns of H-GST, R-GST and 1% Sb-doped R-GST.

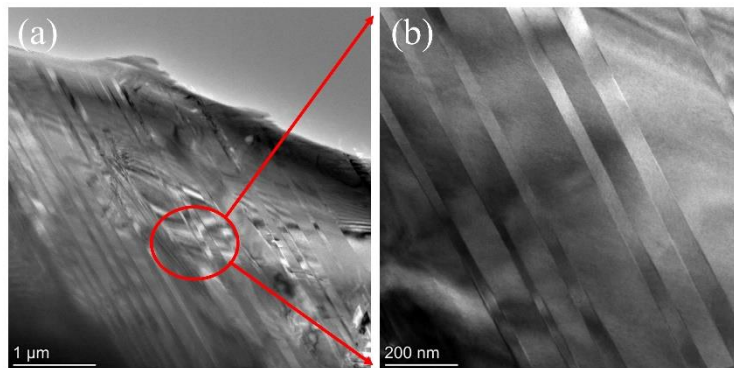


Figure S2. (a) Low-magnificent TEM image and (b) the corresponding high-resolution TEM (HRTEM) image of herringbone-like ferroelectric domains in R-GST.

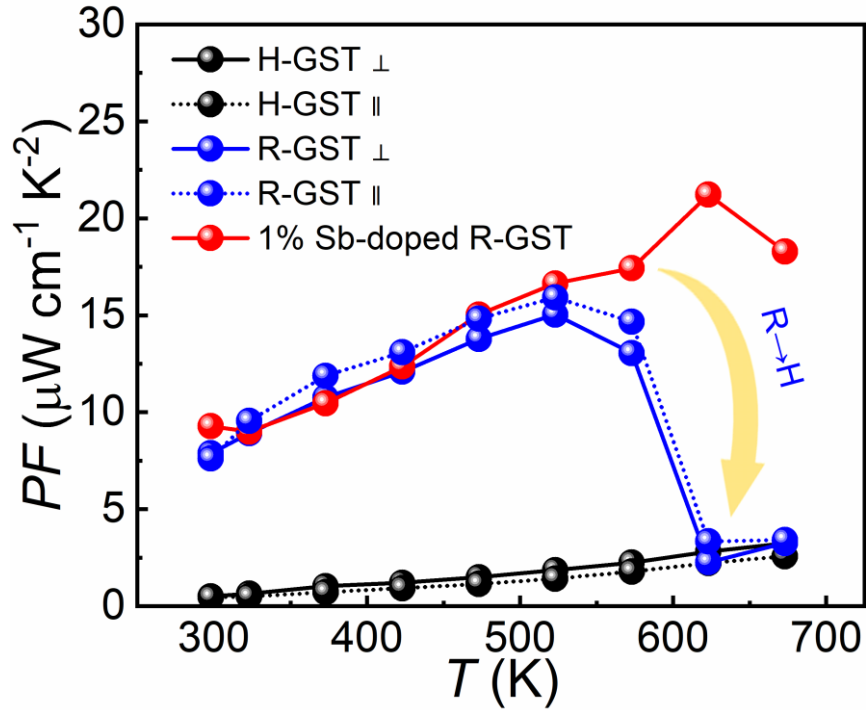


Figure S3. Temperature dependent power factors (PF) of H-GST, R-GST and 1% Sb-doped R-GST.

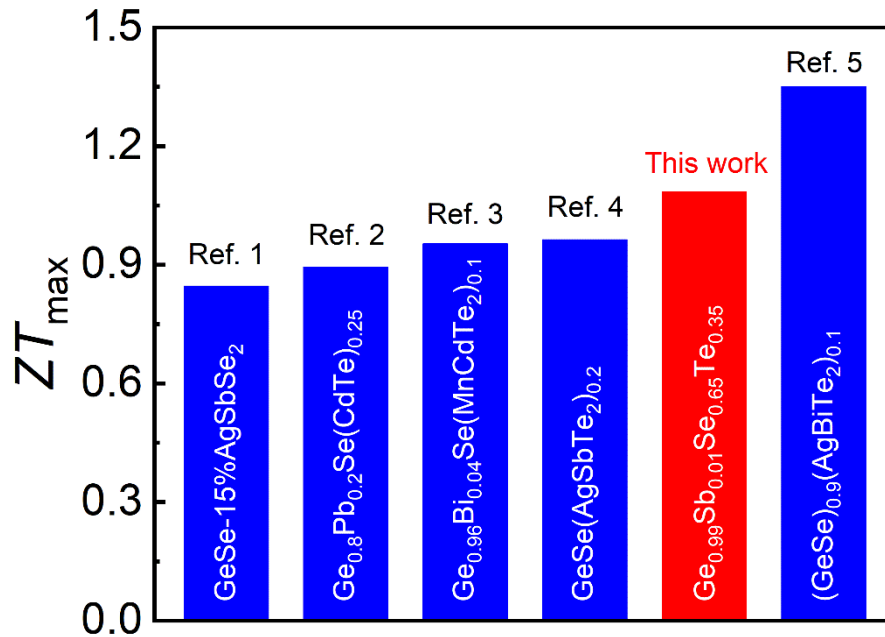


Figure S4. Comparison of maximum ZT of 1% Sb-doped R-GST ($\text{Ge}_{0.99}\text{Sb}_{0.01}\text{Se}_{0.65}\text{Te}_{0.35}$) in this work with that of the other rhombohedral GeSe based thermoelectrics^[1-5].

Table S1. Room temperature densities (ρ) for sintered H-GST, R-GST and 1% Sb-doped R-GST.

Sample	Composition	ρ (g cm ⁻³)
H-GST	GeSe _{0.65} Te _{0.35}	5.4111
R-GST	GeSe _{0.65} Te _{0.35}	5.6956
1%Sb-doped R-GST	Ge _{0.99} Sb _{0.01} Se _{0.65} Te _{0.35}	5.6594

Table S2. Structural parameters of Rietveld refinement for R-GST.

Space group: $R3m$; $a = b = 4.0141$ Å, $c = 10.4107$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

Element	Wyckoff	x	y	z	U_{iso}	Occupancy
Ge	3a	0	0	0.47222	0.023	1.00
Se	3a	0	0	0	0.017	0.65
Te	3a	0	0	0	0.017	0.35

R-factors: R_{wp} :6.44, R_{exp} :3.80

Table S3. The fitting parameters of the low-temperature heat capacity data of R-GST by the Debye–Einstein model.

Parameters	γ (J mol ⁻¹ K ⁻²)	b (J mol ⁻¹ K ⁻²)	A_1	Θ_{E1} (K)	A_2	Θ_{E2} (K)
R-GST	0.01232	9.01×10^{-5}	2.59	53.8	18.85	109.4

Reference:

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- [3] Li, X.; Liang, Z.; Li, J.; Cheng, F.; He, J.; Zhang, C.; Li, J.; Liu, F.; Lyu, T.; Ge, B.; Hu, L. Crystal symmetry enables high thermoelectric performance of rhombohedral GeSe(MnCdTe₂). *Nano Energy* **2022**, *100*, 107434.
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