

Supplementary Information

Copper ion diffusion by solid solution treatment advancing GeTe-based thermoelectrics

Yongqi Chen¹, Meng Li^{1,*}, Xiaodong Wang², Wenyi Chen¹, Siqi Liu¹, Min Zhang¹, Wan-Yu Lyu¹, Nan-Hai Li¹, Han Gao^{3,1,*}, Wei-Di Liu¹, Xiao-Lei Shi¹, and Zhi-Gang Chen^{1,*}

¹ School of Chemistry and Physics, ARC Research Hub in Zero-emission Power Generation for Carbon Neutrality, and Centre for Materials Science, Queensland University of Technology, Brisbane, Queensland 4000, Australia

² Central Analytical Research Facility, Queensland University of Technology, Brisbane, Queensland 4000, Australia

³ School of Physics, Zhengzhou University, Zhengzhou, Henan450001, China

* Corresponding Author:

m93.li@qut.edu.au (ML); hgao@zzu.edu.cn (HG); zhigang.chen@qut.edu.au (ZGC)

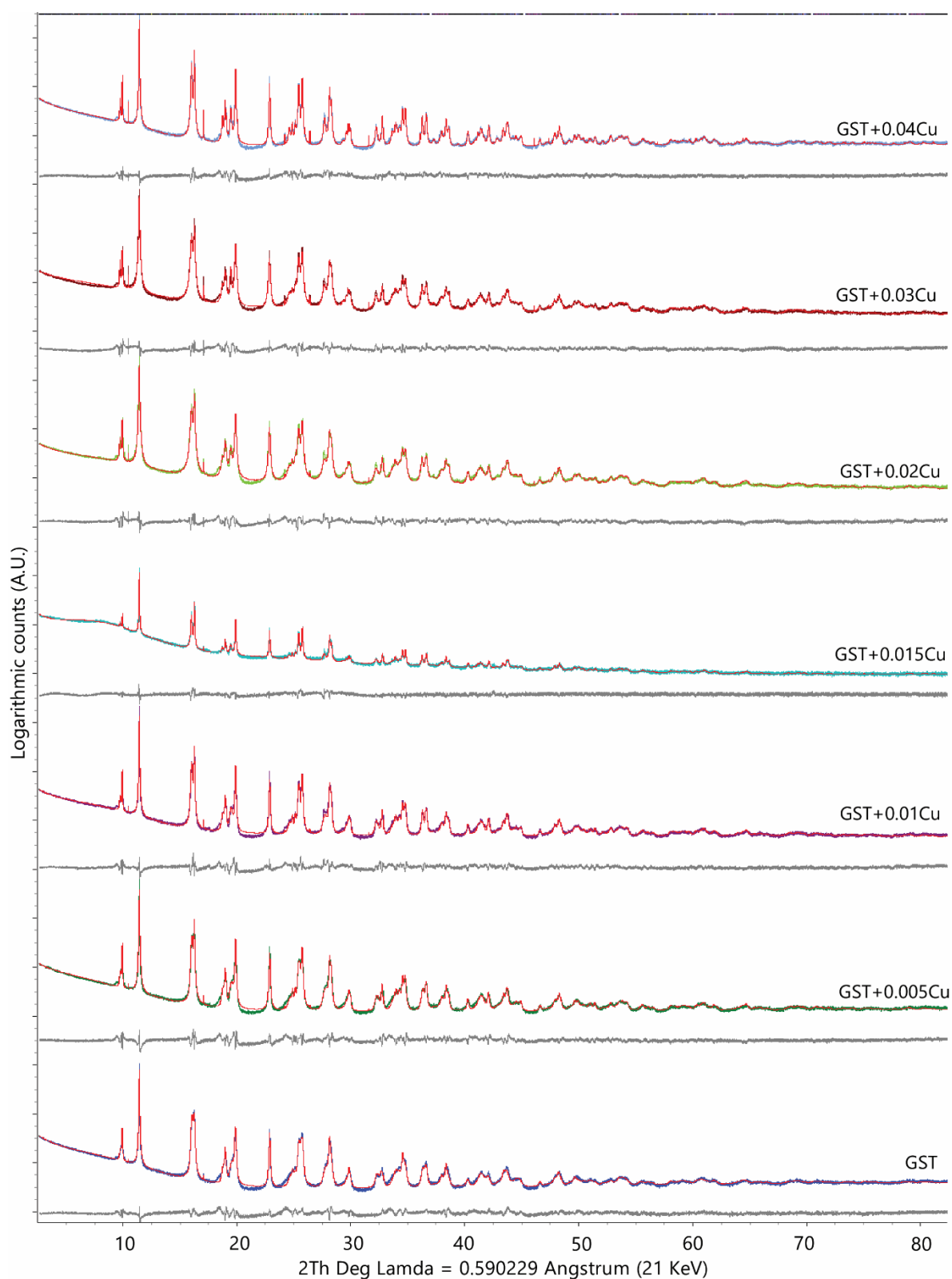
1. Experimental and computational details

Materials characterisation. The fine powder samples are also measured on the Powder Diffraction beamline at Australian Synchrotron¹ in capillaries of 0.3 mm internal diameter. The radiation wavelength is determined to be 0.590229 Å ($E \approx 21$ KeV) by refining the XRD pattern of a NIST SRM 660b LaB₆ standard measured under the same conditions. Phase identification is performed using DIFFRAC.EVA v7.2 software with the ICDD PDF-5+ database. Full pattern Rietveld refinements are conducted in DIFFRAC.TOPAS v7 software. The pair distribution function (PDF)^{2,3} of final powder samples is measured on beamline ID31 of the European Synchrotron Radiation Facility (ESRF) in Rapid Acquisition PDF setup,⁴ using an incident X-ray beam ($\lambda = 0.1646$ Å, $E \approx 75$ KeV) in transmission geometry. NIST SRM 660b (LaB₆) is used for geometry calibration, which is carried out using the pyFAI software,⁵ in which image integration with flat-field, geometry, solid-angle, and polarization corrections are carried out. PDF refinements were conducted in xPDFsuite software.

First-principles calculations. Density-functional theory (DFT) calculations were performed using the all electron projected augmented wave (PAW) method, as implemented in the Vienna Ab initio Simulation Package (VASP).⁶⁻⁹ The generalized gradient approximation (GGA) with the fully relativistic Perdew-Burke-Ernzerhof (PBE) functional is employed to treat the exchange correlations.¹⁰ The recommended pseudopotentials by VASP are used to simulate the ion electron interaction of all constituent elements: Ge ([Ar] 3d¹⁰ 4s² 4p²), Sb ([Kr] 4d¹⁰ 5s² 5p³), Te ([Kr] 4d¹⁰ 5s² 5p⁴), and Cu ([Ar] 3d¹⁰ 4s¹). The valence wave functions were expanded in a plan-wave basis with a cut-off energy of 450 eV. All atoms were allowed to relax in their geometric optimizations until the Hellmann–Feynman force is less than 1×10^{-3} eV·Å⁻¹. The convergence criterion and the Monkhorst-Pack **k**-mesh adopted for ionic relaxation are 1×10^{-7} eV per electron and 0.03 per Å³, respectively. A denser 0.02 Å⁻³ Monkhorst-Pack **k**-mesh was adopted for calculating density-of-state (DOS), and a line-mode **k**-

path based on Brillouin path features indicated by the AFLOW framework was adopted for calculating band structures.¹¹ Spin-orbital coupling (SOC) was considered because Te is a heavy element.

2. Rietveld refinement



Supplementary Fig. 1. Rietveld Refinement of XRD patterns of GST+ x Cu ($x = 0, 0.005, 0.010, 0.015, 0.020, 0.030, 0.040$) series collected in Australian Synchrotron Powder Diffraction Beamline.

Phase identification confirmed the major phase of PDF# 04-002-0577 $\text{Ge}_{0.85}\text{Sb}_{0.1}\text{Te}$ and a minor phase of PDF# 04-016-2396 Ge. There is no detectable metal Cu peak, indicating Cu atoms were diffused into the $\text{Ge}_{0.85}\text{Sb}_{0.1}\text{Te}$ matrix. It also seems that spiking Cu atoms would push Ge atoms out from the system. Since Ge metal was separated from the original $\text{Ge}_{0.85}\text{Sb}_{0.1}\text{Te}$ phase, the “ x ” values in Table S1 can be linked to the weight percentage of the Ge phase in their XRD patterns by setting below equation in the DIFFRAC.TOPAS refinement model:

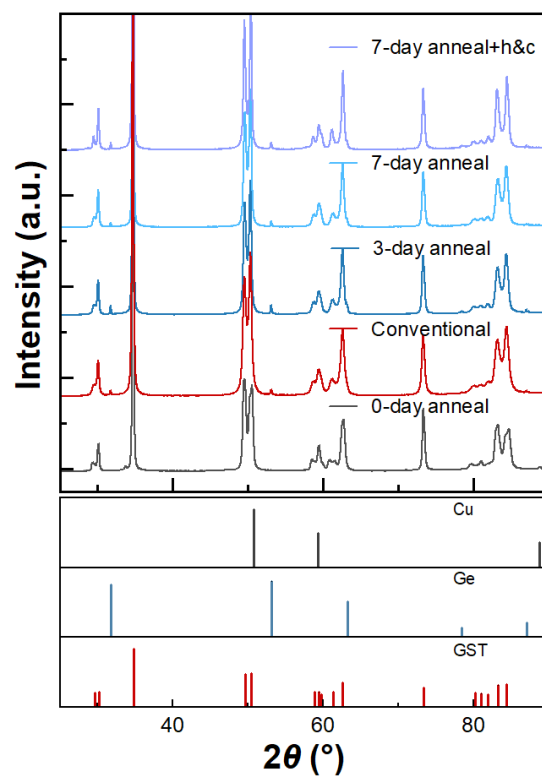
$$\text{occGe} = 0.85 - \text{wt_Ge} * \text{MW}_{\text{GSTC}} / \text{MW}_{\text{Ge}}$$

where “occGe” stands for the occupancy of Ge/Sb/Cu atomic site in the matrix phases; “wt_Ge” the weight percentage of Ge metal phase separated out; “ MW_{GSTC} ” stands for the formula weight of $\text{Ge}_{0.85}\text{Sb}_{0.1}\text{Te}$ (201.52), $\text{Ge}_{0.85}\text{Cu}_{0.01}\text{Sb}_{0.1}\text{Te}$ (202.1555) or $\text{Ge}_{0.85}\text{Cu}_{0.04}\text{Sb}_{0.1}\text{Te}$ (204.062), while “ MW_{Ge} ” is the formula weight of Ge metal (72.64).

Supplementary Table 1. Results of Rietveld refinement of Australian Synchrotron Powder Diffraction for $\text{GST}+x\text{Cu}$ ($x = 0, 0.005, 0.010, 0.015, 0.02, 0.03, 0.040$).

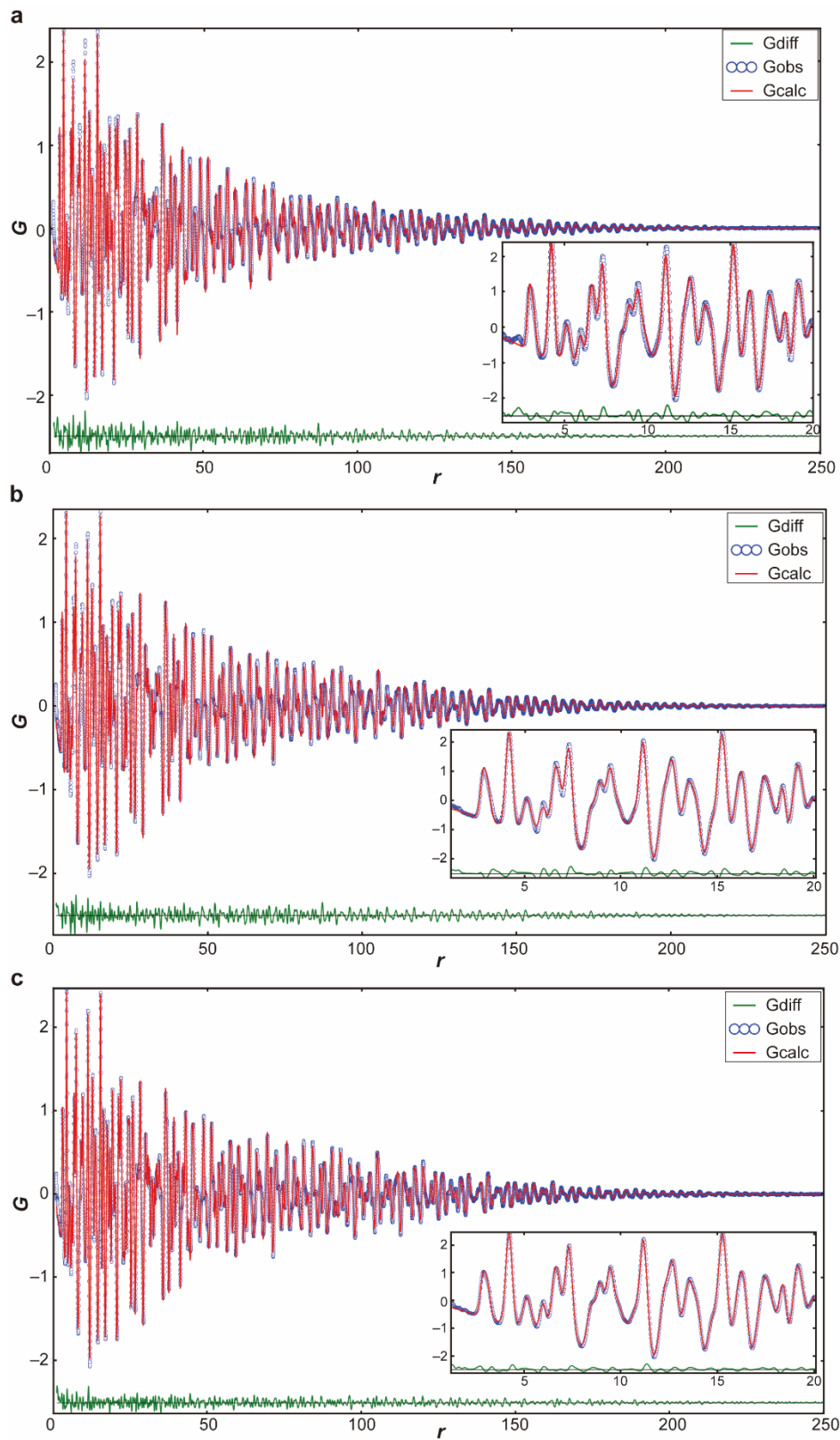
Sample ID	Designed chemical formula	Refined chemical formula*	Lattice Parameter a (Å)	Lattice Parameter c (Å)	GoF	R_{exp}	R_{wp}	R_{p}
GST	$\text{Ge}_{0.85}\text{Sb}_{0.1}\text{Te}$	$\text{Ge}_{0.8466}\text{Sb}_{0.1}\text{Te}$	4.20565(7)	10.4909(4)	5.88	1.58	9.29	6.54
GST+0.005Cu	$\text{Ge}_{0.85}\text{-Cu}_{0.005}\text{Sb}_{0.1}\text{Te}$	$\text{Ge}_{0.8442}\text{Cu}_{0.005}\text{Sb}_{0.1}\text{Te}$	4.20251(4)	10.5032(3)	7.53	1.62	11.69	8.08
GST+0.01Cu	$\text{Ge}_{0.85}\text{-Cu}_{0.01}\text{Sb}_{0.1}\text{Te}$	$\text{Ge}_{0.8436}\text{Cu}_{0.01}\text{Sb}_{0.1}\text{Te}$	4.20106(4)	10.5192(3)	7.36	1.55	11.43	7.84
GST+0.015Cu	$\text{Ge}_{0.85}\text{-Cu}_{0.015}\text{Sb}_{0.1}\text{Te}$	$\text{Ge}_{0.844}\text{Cu}_{0.015}\text{Sb}_{0.1}\text{Te}$	4.19735(8)	10.5456(5)	7.13	1.59	11.05	7.55
GST+0.02Cu	$\text{Ge}_{0.85}\text{-Cu}_{0.02}\text{Sb}_{0.1}\text{Te}$	$\text{Ge}_{0.8397}\text{Cu}_{0.02}\text{Sb}_{0.1}\text{Te}$	4.19994(4)	10.5437(3)	6.93	1.56	10.83	7.03
GST+0.03Cu	$\text{Ge}_{0.85}\text{-Cu}_{0.03}\text{Sb}_{0.1}\text{Te}$	$\text{Ge}_{0.8305}\text{Cu}_{0.03}\text{Sb}_{0.1}\text{Te}$	4.20209(4)	10.5474(2)	6.42	1.60	10.29	6.58
GST+0.04Cu	$\text{Ge}_{0.85}\text{-Cu}_{0.04}\text{Sb}_{0.1}\text{Te}$	$\text{Ge}_{0.8226}\text{Cu}_{0.04}\text{Sb}_{0.1}\text{Te}$	4.19909(3)	10.53451(18)	4.61	1.67	7.70	5.14

3. *Ex-situ* XRD

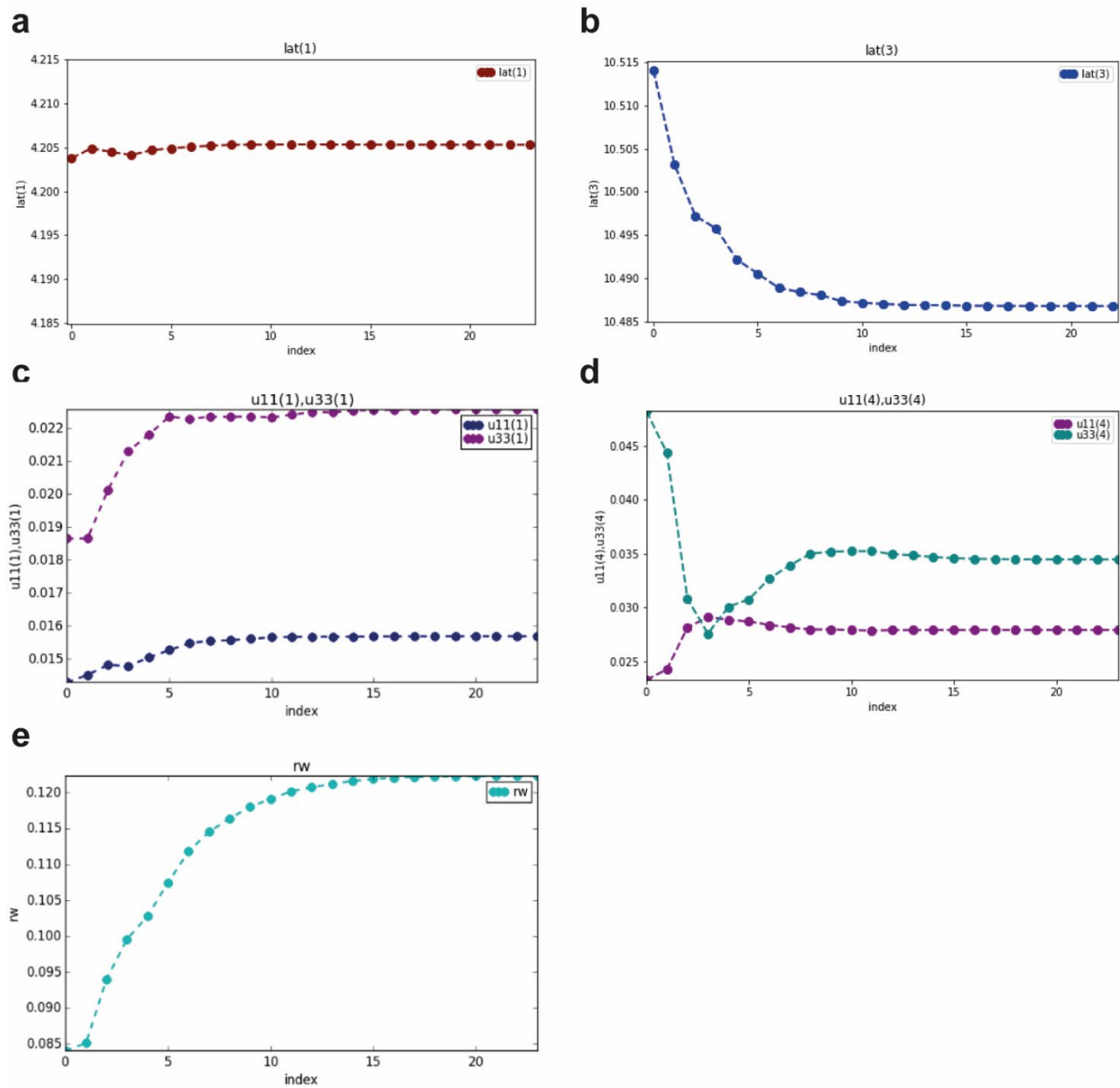


Supplementary Fig. 2. Ex-situ heating of conventional and this work GST+0.04Cu after different heat treatment (Wavelength = 1.78897).

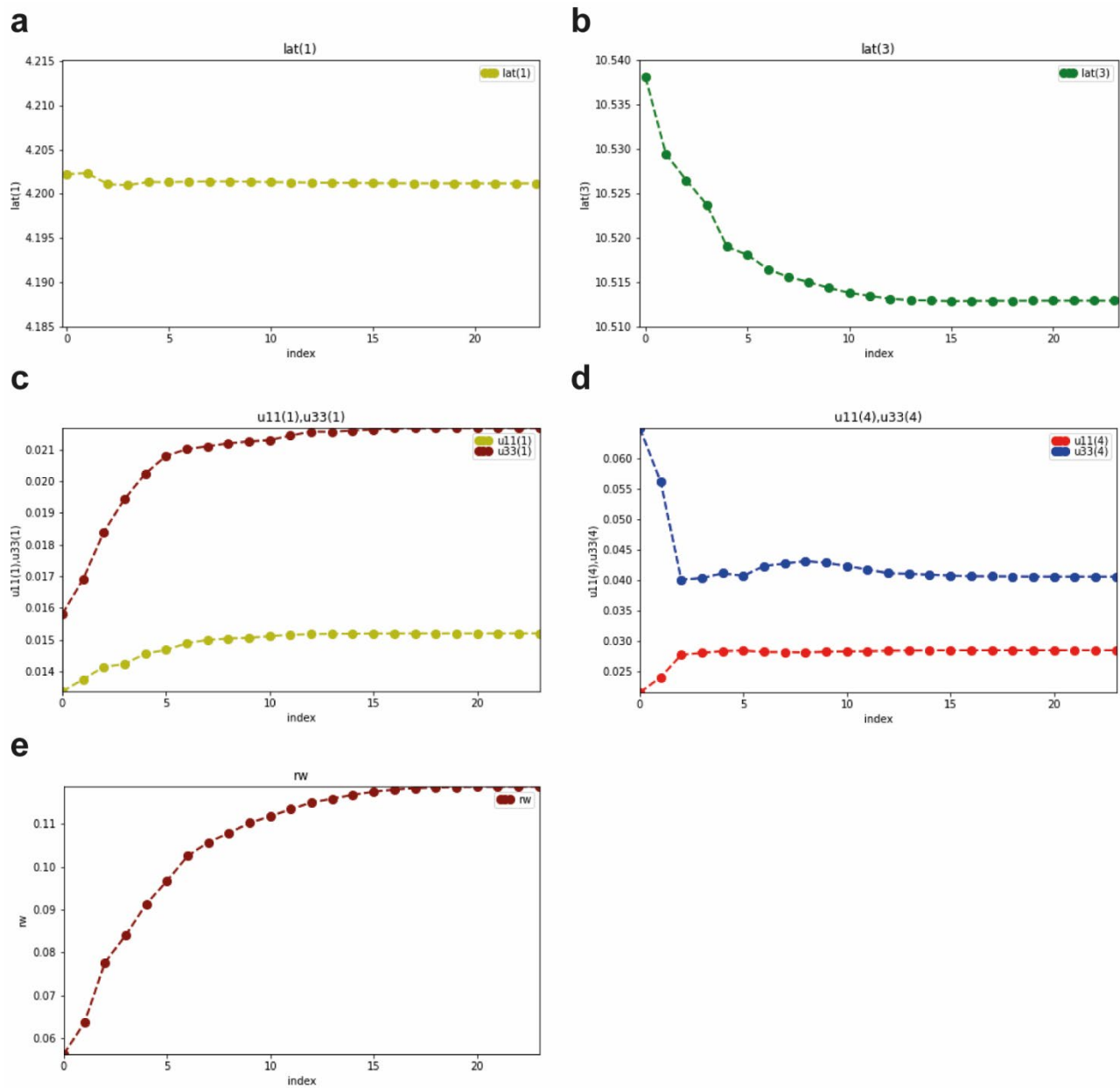
4. Pair Distribution Function Refinement



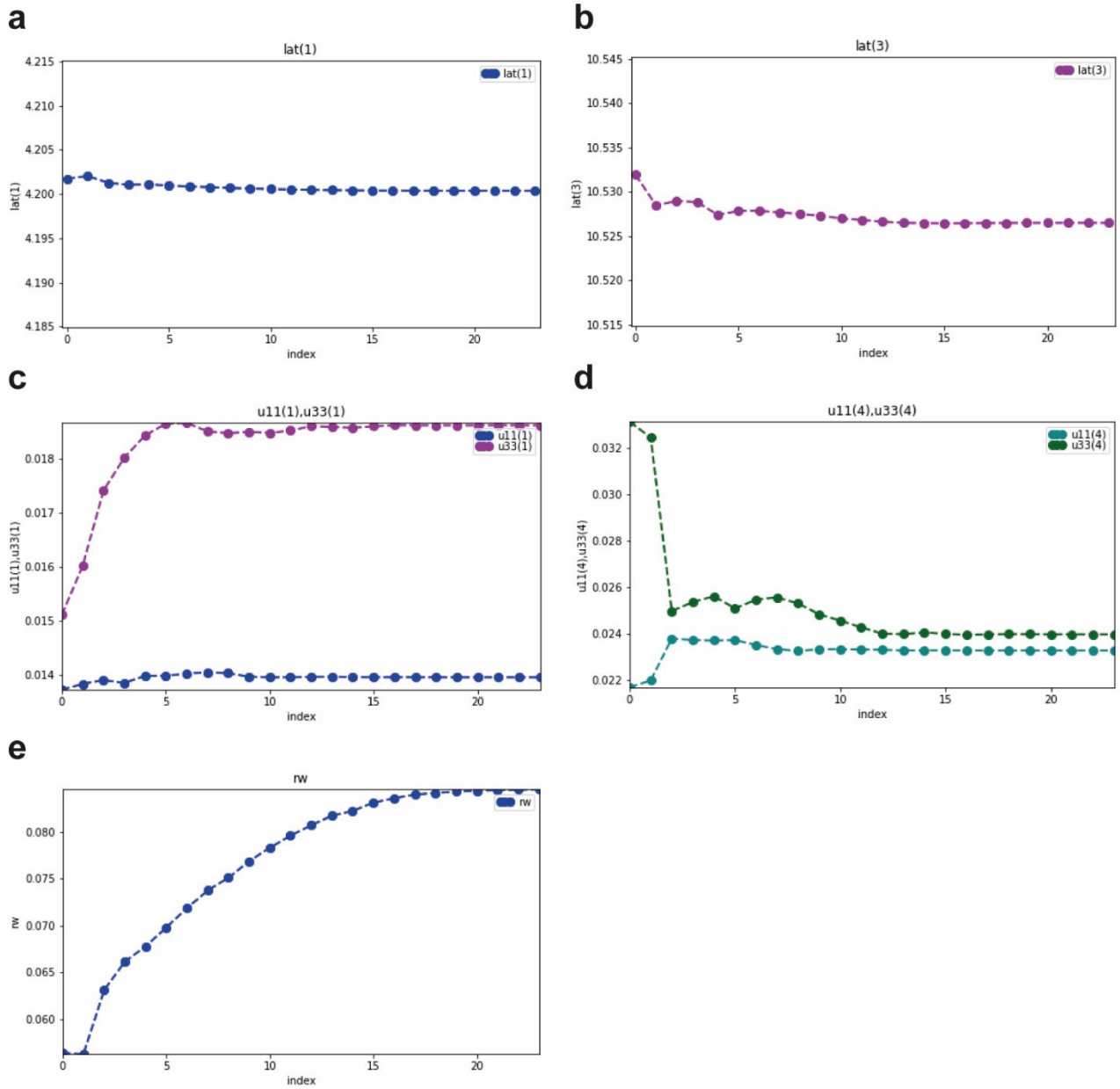
Supplementary Fig. 3. Refinement of pair distribution function for GST+xCu. (a) $x = 0$. (b) $x = 0.010$. (c) $x = 0.040$. Insert shows the zoomed-in view where r ranging from 2 to 24.



Supplementary Fig. 4. The r -series PDF refinement (index 0 to 24 correspond to the r -range (1, 20) Å to (1, 250) Å) dependency of GST. (a) lattice parameter $a = b$. (b) lattice parameter c . (c) ADPS U_{11} and U_{33} of Te site. (d) ADPS U_{11} and U_{33} of Ge/Sb/Cu site. (e) the refined fractional z coordinates of Ge/Sb/Cu site.

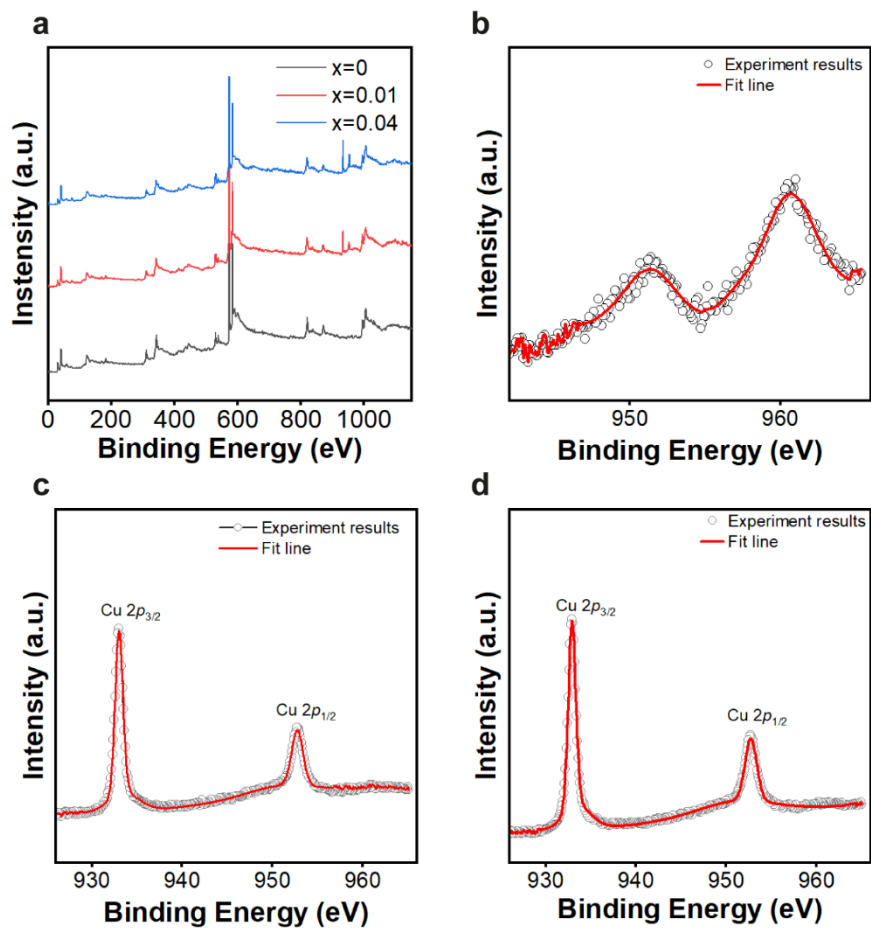


Supplementary Fig. 5. The r -series PDF refinement (index 0 to 24 correspond to the r -range (1, 20) Å to (1, 250) Å) dependency of GST+0.01Cu. (a) lattice parameter $a = b$. (b) lattice parameter c . (c) ADPS U_{11} and U_{33} of Te site. (d) ADPS U_{11} and U_{33} of Ge/Sb/Cu site. (e) the refined fractional z coordinates of Ge/Sb/Cu site.



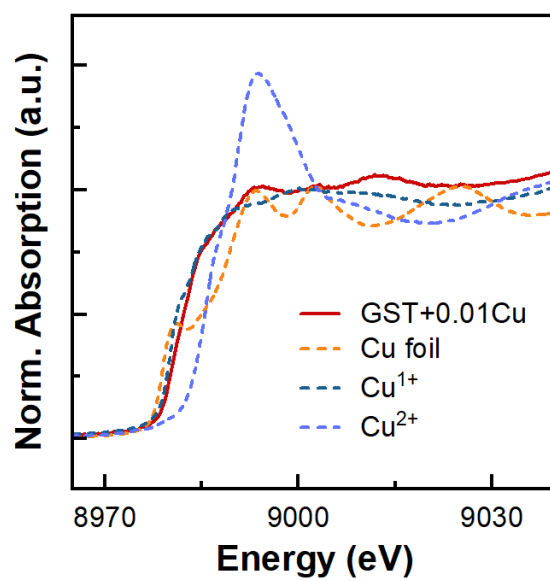
Supplementary Fig. 6. The r -series PDF refinement (index 0 to 24 correspond to the r -range (1, 20) Å to (1, 250) Å) dependency of GST+0.04Cu. (a) lattice parameter $a = b$. (b) lattice parameter c . (c) ADPS U_{11} and U_{33} of Te site. (d) ADPS U_{11} and U_{33} of Ge/Sb/Cu site. (e) the refined fractional z coordinates of Ge/Sb/Cu site.

5. X-ray photoelectron spectroscopy



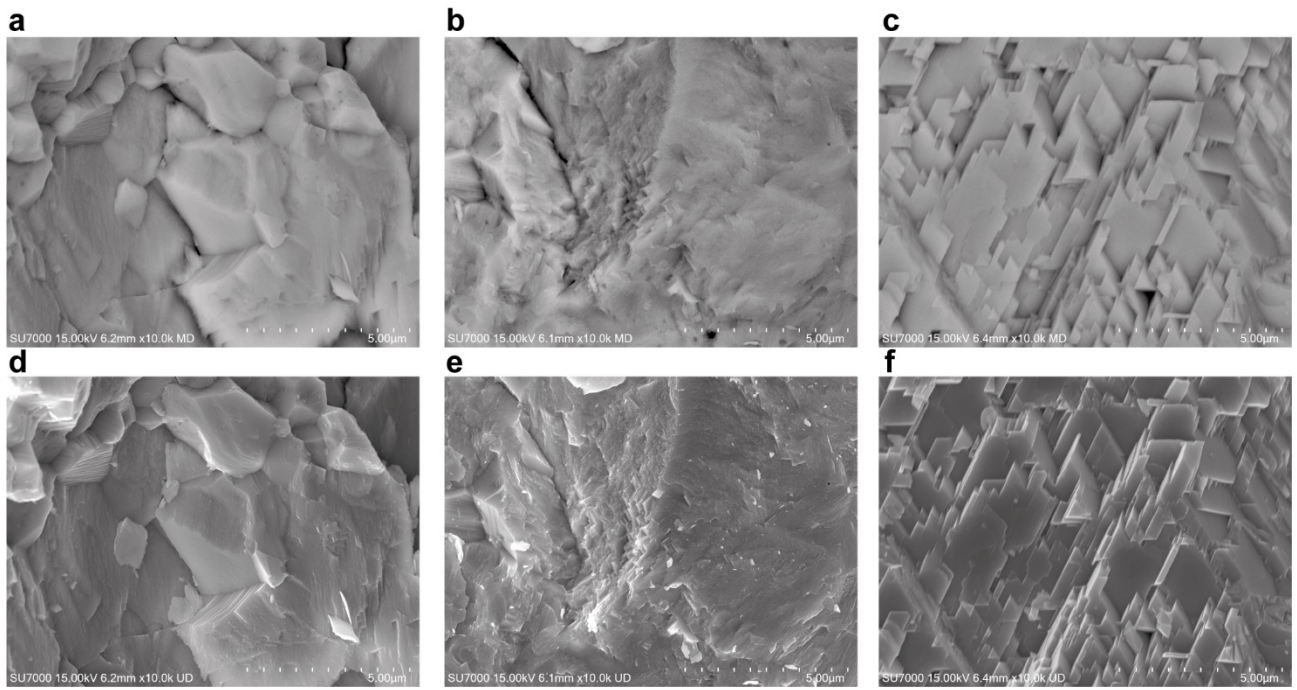
Supplementary Fig. 7. XPS of GST+ x Cu samples. (a) full spectra of the three samples. Cu peak fitting of (b) $x = 0$, (c) $x = 0.010$, (d) $x = 0.040$.

6. X-ray absorption spectroscopy (XAS)

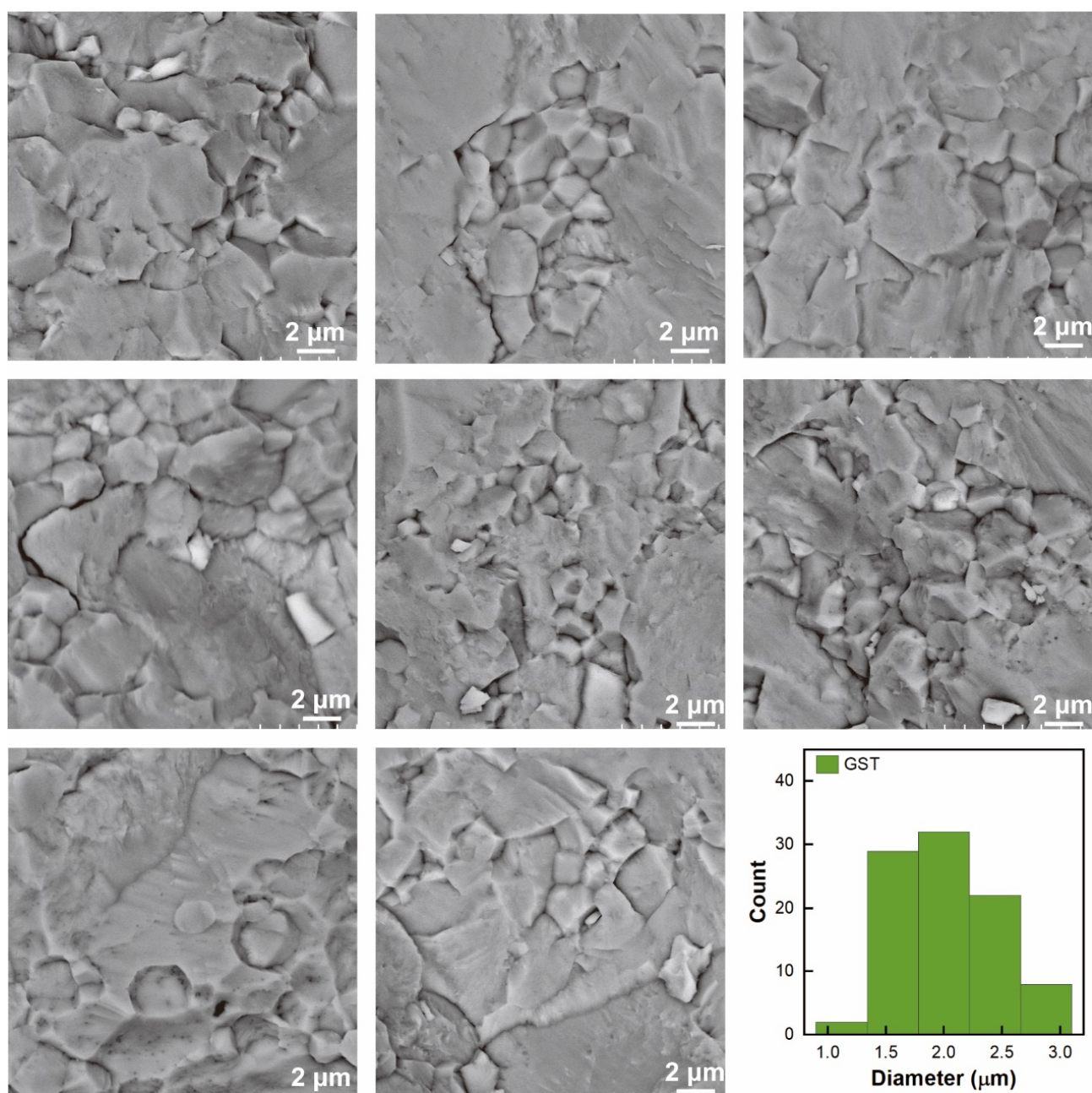


Supplementary Fig. 8. Cu K-edge XANES spectra of GST+0.01Cu and reference samples with different valence state.

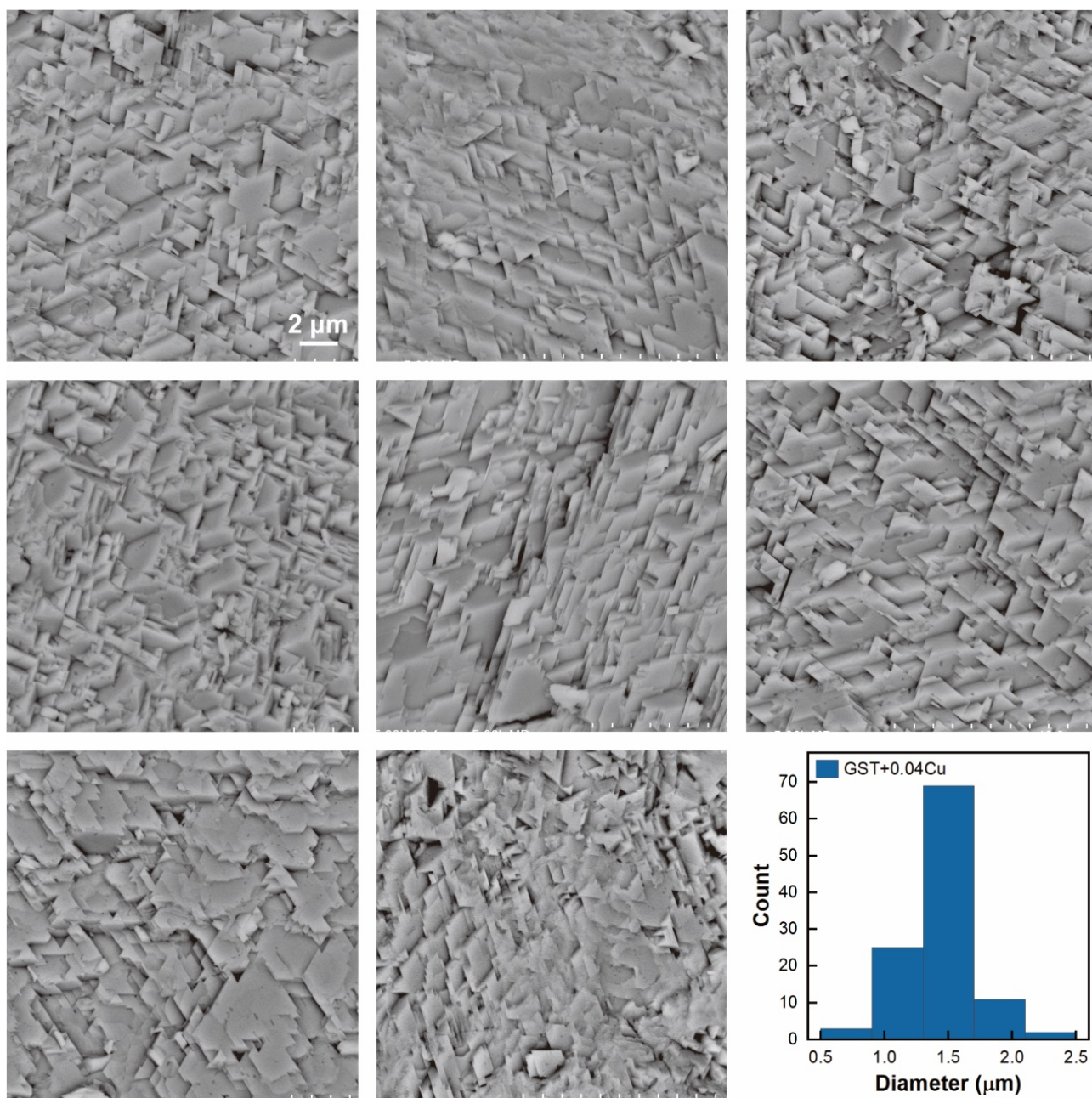
7. Microscopic analysis



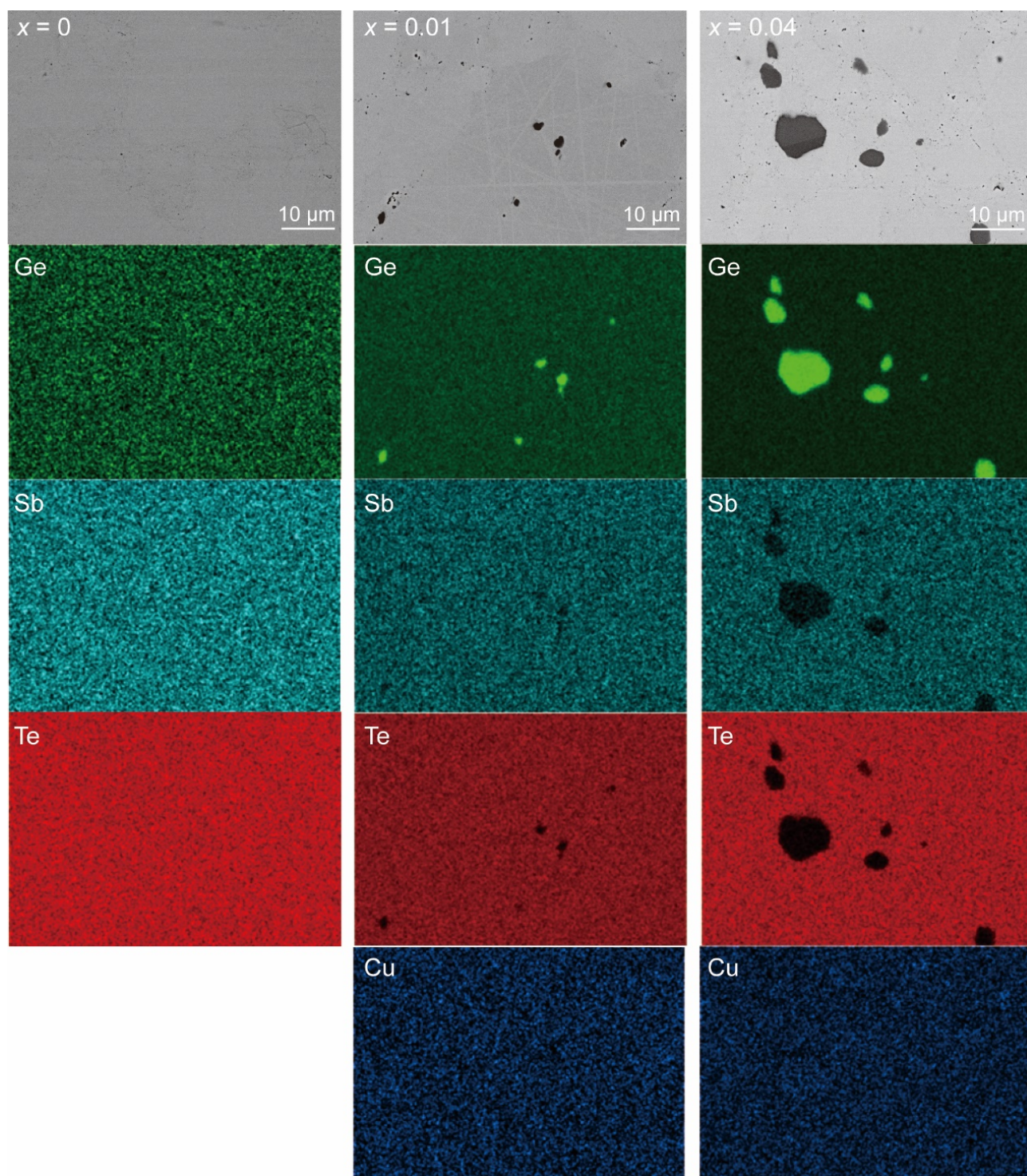
Supplementary Fig. 9. BSE and SE of $\text{GST}+\text{xCu}$ ($x = 0, 0.01, 0.04$). (a–c) BSE of $x = 0, x = 0.01, x = 0.04$. (d–f) SE of $x = 0, x = 0.01, x = 0.04$.



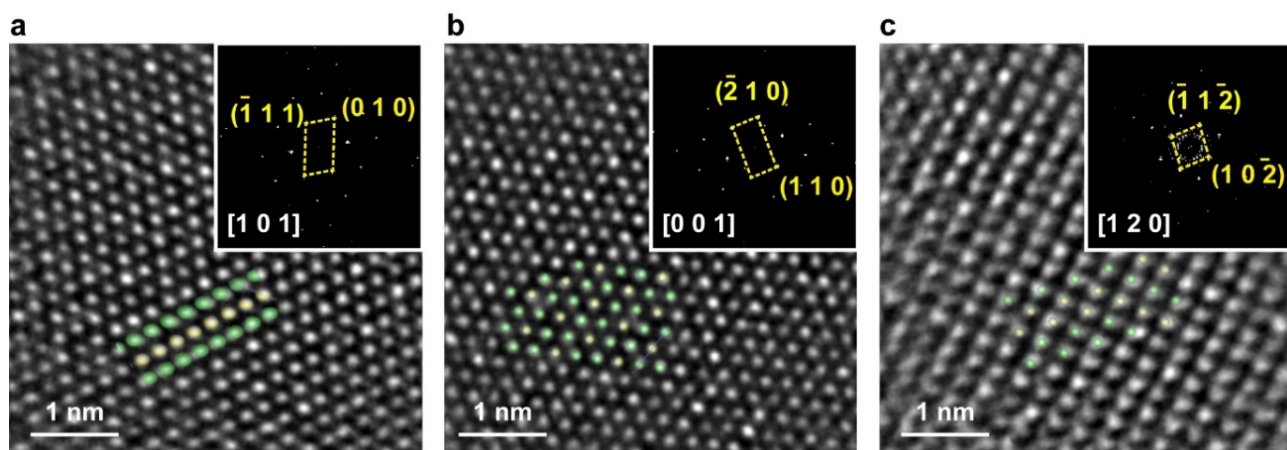
Supplementary Fig. 10. BSE images of pristine GST sample and grain size distribution.



Supplementary Fig. 11. BSE images of GST+0.04Cu and grain size distribution.

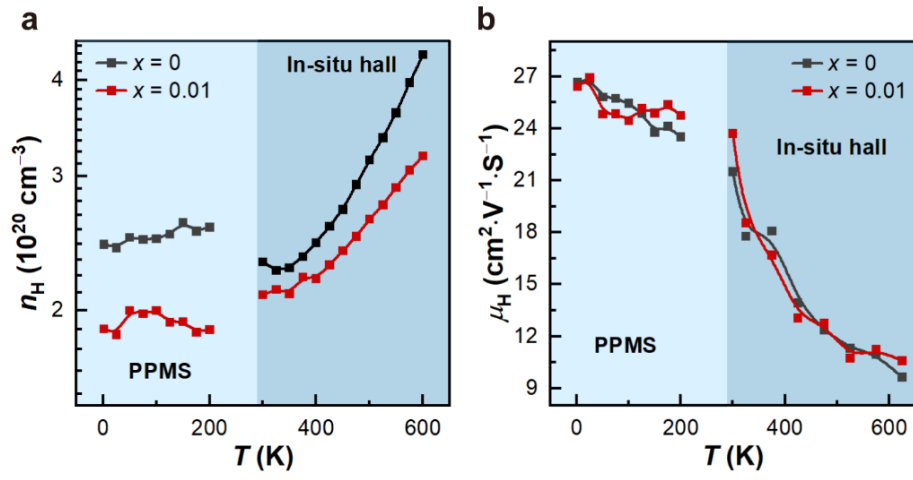


Supplementary Fig. 12. BSE images of polished surfaces and corresponding EDS mapping of GST+xCu ($x = 0, 0.01, \text{ and } 0.04$).



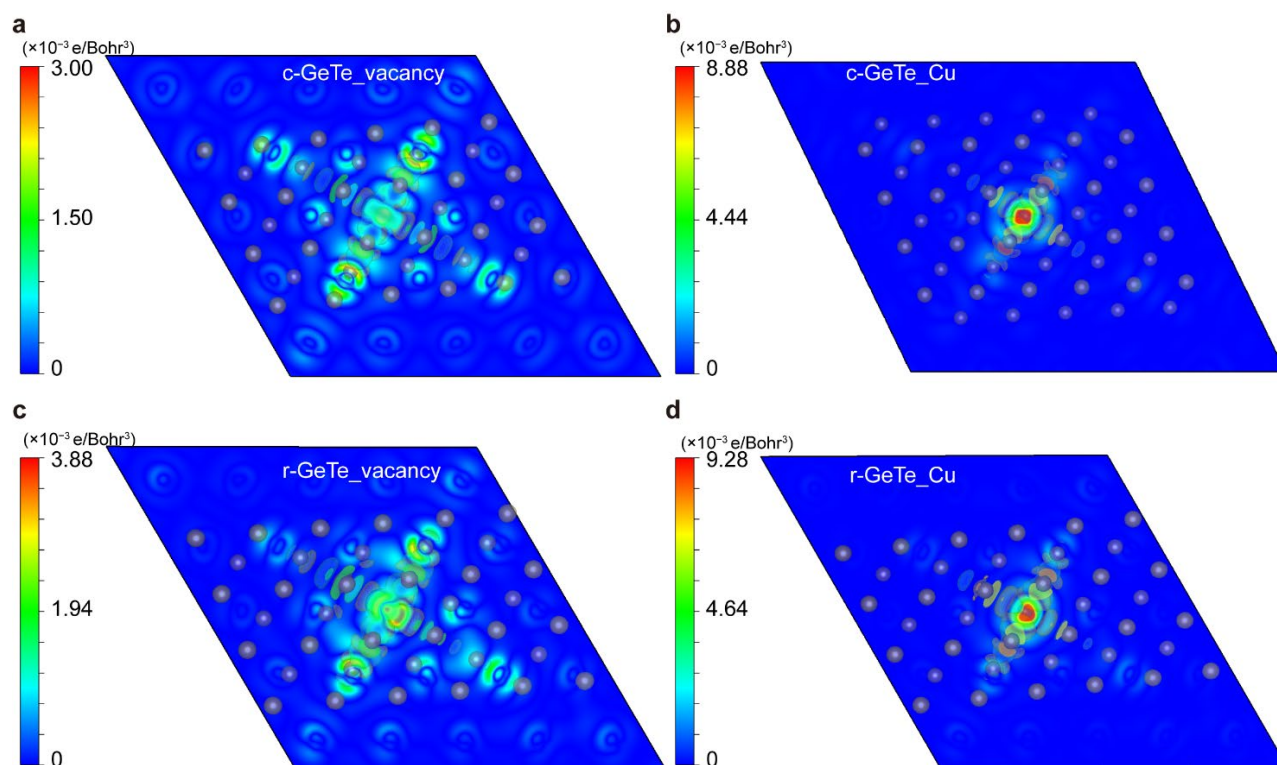
Supplementary Fig. 13. High-resolution TEM images and corresponding FFT of GST+0.01Cu along different zone axes. (a) [101] zone axis. (b) [100] zone axis. (c) [120] zone axis.

8. Carrier concentration and mobility

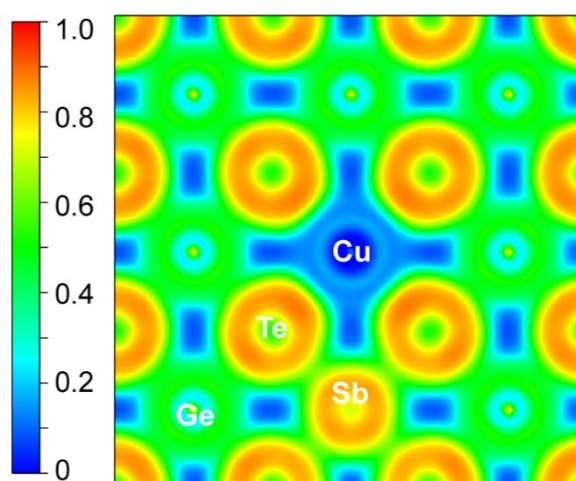


Supplementary Fig. 14. Temperature-dependent carrier transport by PPMS (low temperature) and in-situ hall system (high temperature). (a) Temperature-dependent carrier concentration n_H . (b) Temperature-dependent hall mobility μ_H .

9. Electron localisation and differential charge density

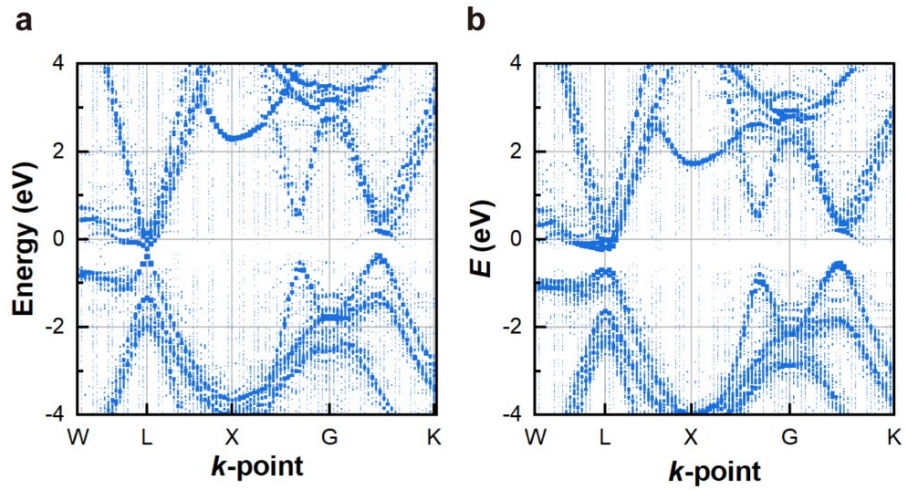


Supplementary Fig. 15. Differential charge density. (a) Vacancy at Ge site for cubic phase. (b) Cu at Ge site for cubic phase. (c) Vacancy at Ge site for rhombohedral phase. (d) Cu at Ge site for rhombohedral phase.

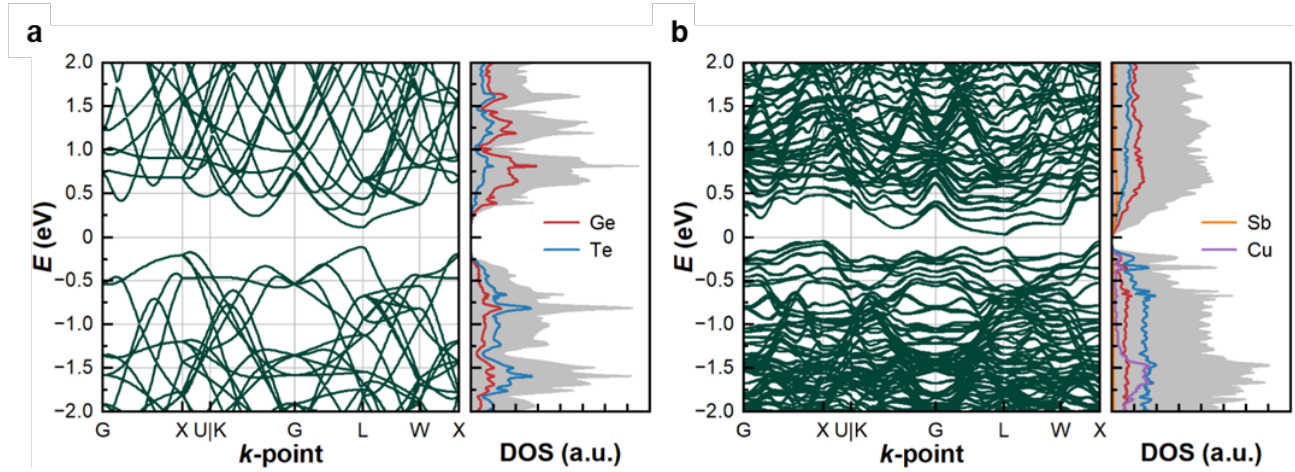


Supplementary Fig. 16. Electron localisation function (ELF) map of GST+Cu.

10. Band structure



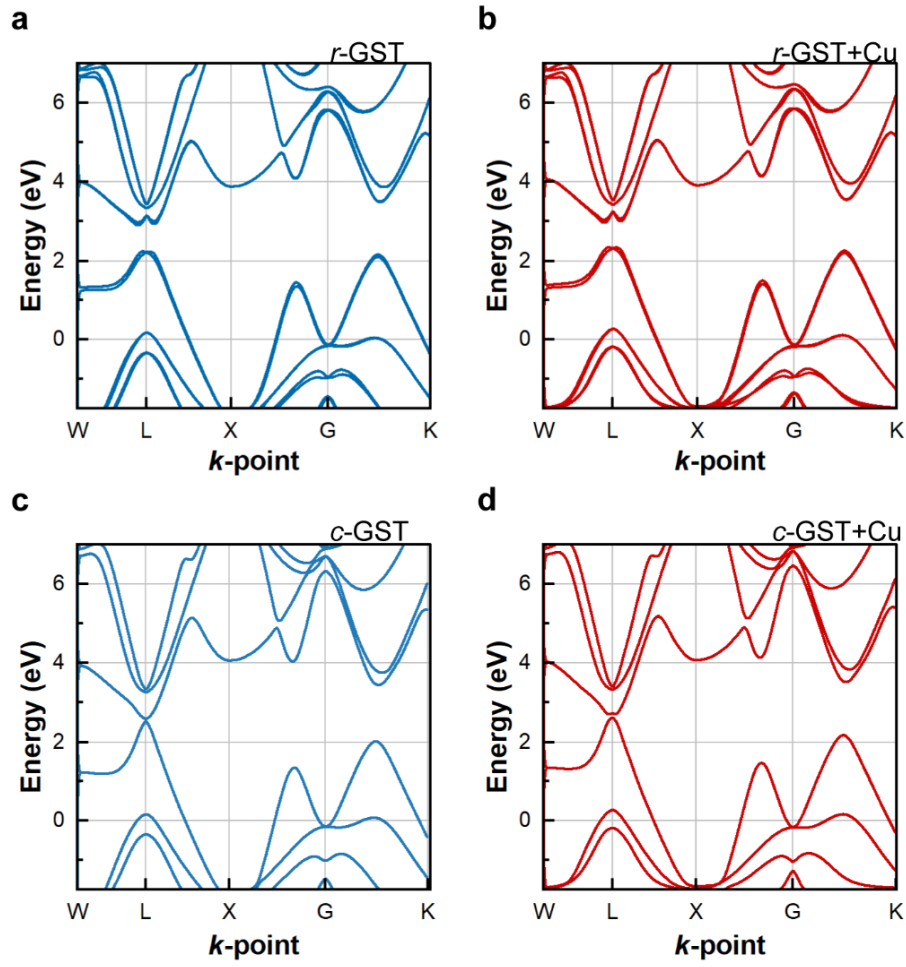
Supplementary Fig. 17. Unfolded band structure. (a) C-Ge₂₃Sb₃Te₂₇. (b) R-Ge₂₃Sb₃Te₂₇.



Supplementary Fig. 18. Folded band structure. (a) C-Ge₂₇Te₂₇. (b) Cu-doped C-Ge₂₃Sb₃Te₂₇.

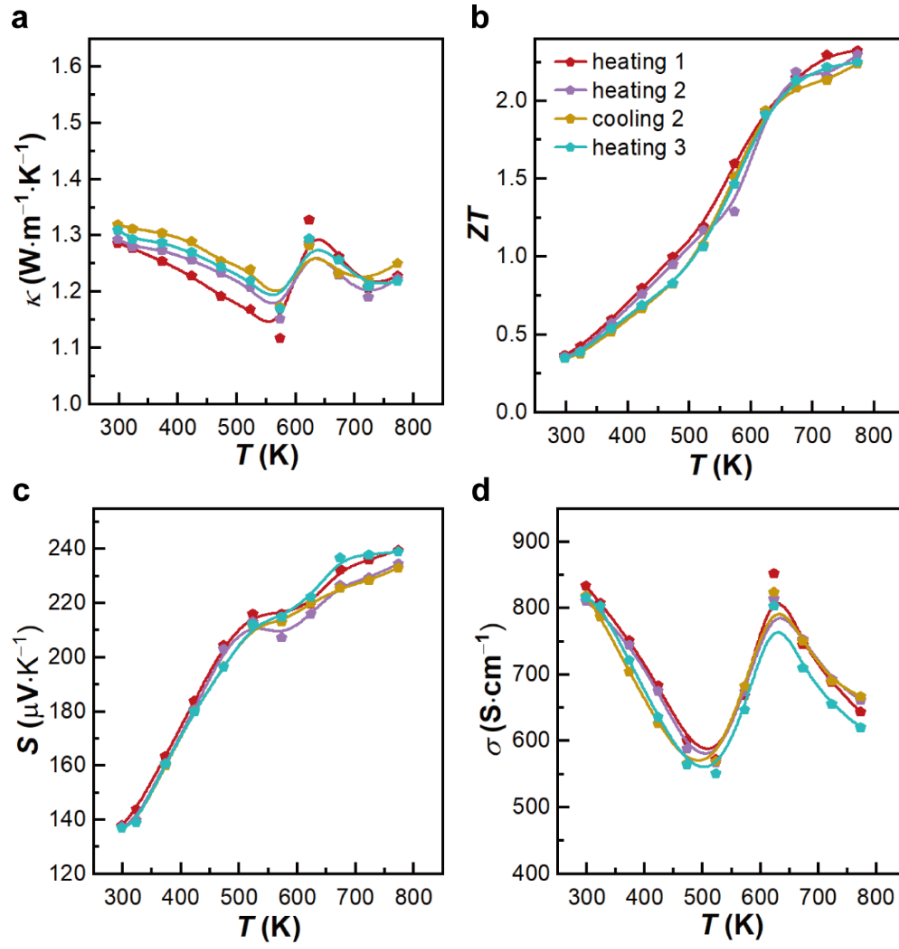
Supplementary Table 2. Relaxed lattice parameters of the simulation.

	$a = b = c$ (Å)	$\alpha = \beta = \gamma$ (°)
C-Ge₂₃Sb₁Te₂₇	4.26037	60
R-Ge₂₃Sb₁Te₂₇	4.25730	59.1989
C-Ge₂₂Sb₃Cu₁Te₂₇	4.23907	60
R-Ge₂₂Sb₃Cu₁Te₂₇	4.26710	58.9484

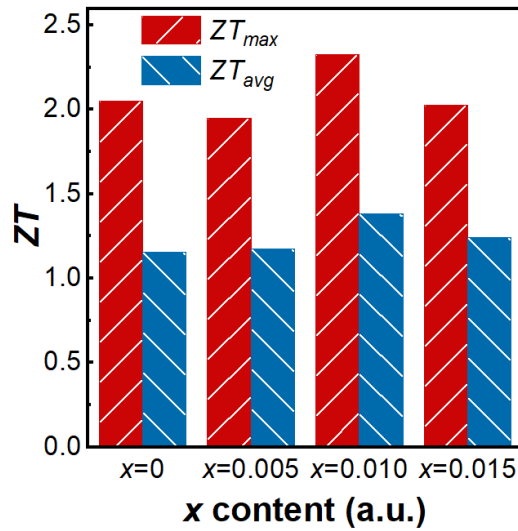


Supplementary Fig. 19. Band structure using green's function. (a) R- Ge₂₃Sb₃Te₂₇, (b) R- Ge₂₃Sb₃Te₂₇ with Cu doping, (c) C- Ge₂₃Sb₃Te₂₇, and (d) C- Ge₂₃Sb₃Te₂₇ with Cu doping.

11. Transport properties



Supplementary Fig. 20. Repeatability test for GST+0.01Cu sample. (a) Thermal conductivity (κ). (b) Figure-of-merit (ZT). (c) Seebeck coefficient (S). (d) Electrical conductivity (σ).



Supplementary Fig. 21. ZT_{max} and ZT_{avg} from 300 to 775 K for GST+ x Cu ($x = 0, 0.005, 0.010, 0.015$).

12. Finite Element Analysis modelling

Finite element simulations of the single-leg device are carried out using ANSYS Workbench platform. Only electrical contact resistances is considered, where the electrical contact resistivity at hot and cold sides is set to $1 \times 10^{-6} \Omega \cdot \text{cm}^2$, referencing the previous studies on the interface of Ni/GeTe. All simulations are iterated until convergence is achieved. The electrical conductivity and Seebeck coefficient are measured using ZEM-3 under helium atmosphere from room temperature to 775 K and fed in FEA simulations as shown in **Supplementary Table 3**.

The aluminium oxide (ceramic) is selected due to its combination of high thermal conductivity and excellent electrical insulation properties. As an electrical insulator, alumina prevents unintended electrical shorts between the p-type and n-type thermoelectric legs, maintaining electrical isolation. Simultaneously, its high thermal conductivity facilitates efficient heat transfer to and from the thermoelectric elements, which is crucial for the thermal performance of device. In terms of high thermal conductivity, it allows heat to transfer efficiently to and from the thermoelectric legs, which is essential for device performance. For the metal contact, nickel alloys are chosen in the simulation because their work function ($\sim 5.0\text{--}5.2$ eV) closely matches that of p-type GeTe ($\sim 4.8\text{--}5.0$ eV).^{12,13} This close alignment reduces or effectively eliminates the Schottky barrier height at the Ni/GeTe interface, enabling efficient hole injection and minimizing contact resistance.¹⁴ We applied a contact resistivity value of $1 \times 10^{-6} \Omega \cdot \text{cm}^2$ for the Ni/GeTe interface, which is consistent with typical values reported for thermoelectric metal–semiconductor contacts and has been shown to provide reliable performance predictions in device simulations.¹⁵

The FEA model comprises five layers; detailed layer information is provided in **Supplementary Table 4**. The interfacial resistivity between Ni and GeTe is $1 \times 10^{-6} \Omega \cdot \text{cm}^2$ from previous study.¹⁵

In terms of geometric optimization, the ANSYS DesignXplorer module was integrated with a Design of Experiments (DOE) approach to identify the optimal leg geometry with respect to power output and thermoelectric conversion efficiency.

The boundary conditions of the simulation:

- The hot side of the device is modelled with an adjustable temperature as heat source.
- The cold side is held at a fixed temperature of 300 K.
- All other surfaces are treated as convective boundaries with forced air cooling to simulate realistic heat loss.
- An electrical potential of 0 V is applied to the bottom electrode (cold side).
- The top electrode (hot side) is assigned a floating potential, allowing the simulation to self-consistently determine the voltage generated by the thermoelectric effect.

The governing equation that be used in the simulation is:

$$\nabla(\kappa \nabla T) + \frac{\mathbf{J}^2}{\sigma} - T \mathbf{J} \cdot \left[\left(\frac{\partial \alpha}{\partial T} \right) \nabla T + (\nabla \alpha)_T \right] = 0$$

$$\nabla \cdot \mathbf{J} = 0$$

$$\mathbf{J} = -\sigma(\nabla V + \alpha \nabla T)$$

$$\mathbf{q} = \alpha T \mathbf{J} - \kappa \nabla T$$

In the above equations, $\mathbf{J}$ and $\mathbf{q}$ represent the electric current density and heat flux density, respectively. S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, T is the absolute temperature (K), and V is the electric potential. All transport properties S , κ , and σ are considered temperature dependent.

Thermoelectric output power and conversion efficiency:

$$P = I \cdot V_{\text{load}}$$

$$\eta = \frac{P}{\dot{Q}_{\text{in}}}$$

where P is output power, and Q_{in} is the heat input at hot side.

To refine the model and simplify calculations, there are some assumptions made.

- The influence of heat radiation is neglected near room temperature.
- Heat convection is included, with an adjustable convection coefficient for air.
- A constant nominal value for electrical resistivity is applied at all interfaces, including the leg/solder interface, with no temperature dependence.
- The heat sinks (if any) are not considered in the computing domain, and its influence is treated as thermal boundary conditions.
- The linear temperature dependence of thermoelectric properties of the leg is considered, while the properties of other materials remain constant.
- The size of the leg and the substrate are shown in **Supplementary Table 5**.

Supplementary Table 3. Thermoelectric properties of materials in the simulation.

Temperature (K)	Thermal Conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	Conductivity (S cm^{-1})	Seebeck coefficient ($\mu\text{V K}^{-1}$)
300	1.29	833.47	137.92
375	1.25	751.16	163.40
475	1.19	601.33	204.4
575	1.12	668.36	215.99
675	1.27	744.91	232.51
775	1.23	643.46	239.54

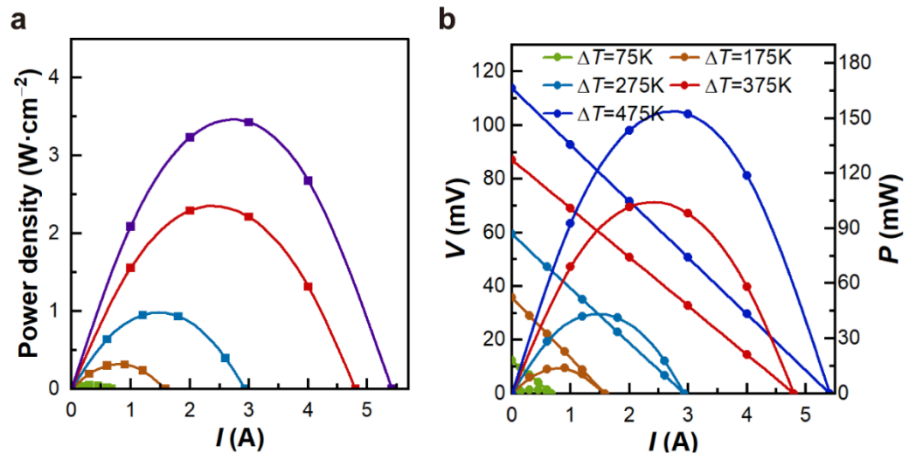
Supplementary Table 4. The layers and dimensions in the FEA model.

Layers	Materials	Dimensions (mm)
Top substrate	Aluminium Oxide (ceramic)	$4 \times 4 \times 0.2$
Top electrode	Ni	$2 \times 2 \times 0.12$

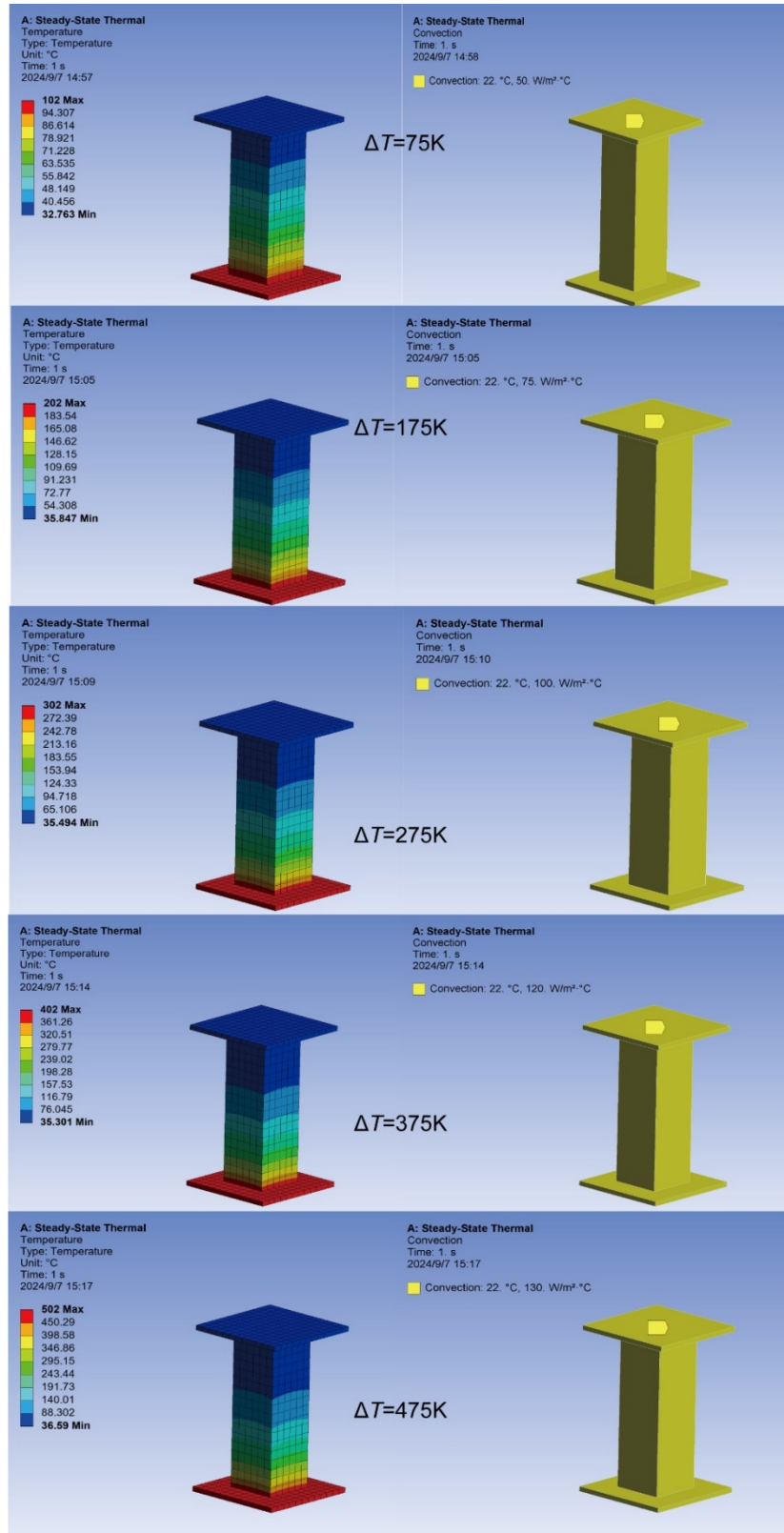
TE leg	p-type GeTe	$6.5 \times 2 \times 2$
Bottom electrode	Ni	$2 \times 2 \times 0.12$
Bottom substrate	Aluminium Oxide (ceramic)	$4 \times 4 \times 0.2$

Supplementary Table 5. The properties of ceramics and solders in the simulation.

Materials	Isotropic Thermal Conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	Isotropic Resistivity ($\Omega \cdot \text{cm}$)
Aluminium Oxide (Ceramic)	35	-
Nickel	91	6.84×10^{-6}

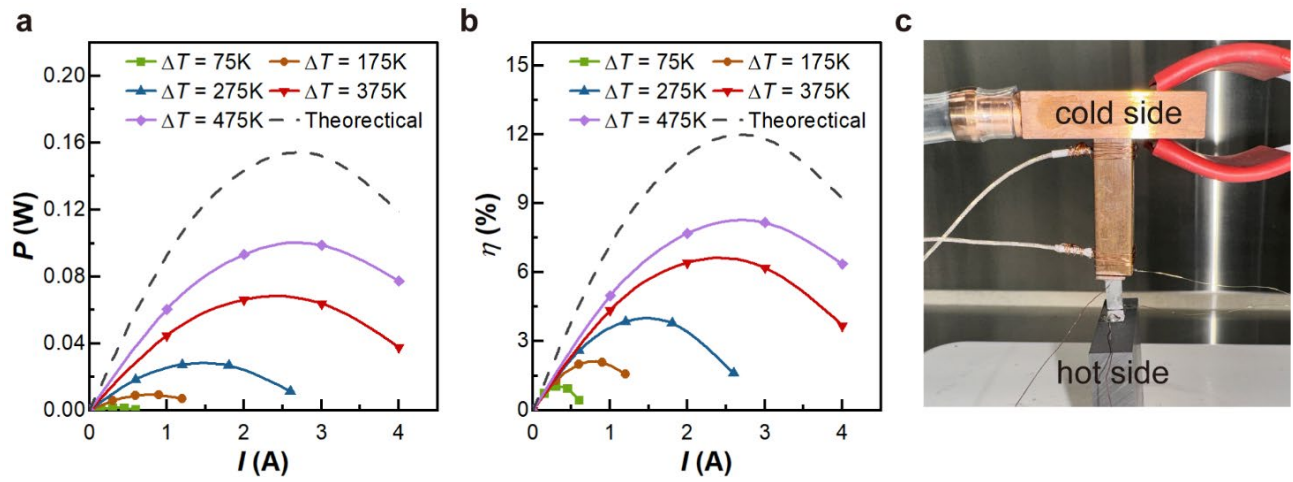


Supplementary Fig. 22. Simulated device performance. (a) Current-dependent power density. (b) Current-dependent open circuit voltage (V) and output power (P) of GST+0.01Cu at $\Delta T = 75 \text{ K}$, 175 K , 275 K , 375 K , and 475 K .



Supplementary Fig. 23. Finite-element analysis (ANSYS) results of temperature distribution of GST+0.01Cu at $\Delta T = 75$ K, 175 K, 275 K, 375 K, and 475 K.

13. Experimental single-leg device



Supplementary Fig. 24. Experimental single-leg device performance of GST+0.01Cu. (a) Current-dependent output power. (b) Current-dependent conversion efficiency. (c) Prototype of single-leg device.

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