

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

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**This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.**

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The manuscript presents a study on the impact of Cu doping on GeTe-based thermoelectric materials, proposing a recently popularized mechanism of "lattice plainification" as a means to enhance thermoelectric performance. The authors utilize advanced synchrotron-based techniques, electron microscopy, and computational approaches to substantiate their findings. The work is commendable in its methodological rigor and provides new insights into the role of Cu in modifying lattice dynamics and defect chemistry. However, several points should be addressed before publication to enhance the clarity and scientific robustness of the manuscript.

Major Comments:

1. To the best of the reviewer's knowledge, the concept of "lattice plainification" means that carrier mobility is effectively boosted by reducing the number of point defect scattering centers (e.g., vacancies). However, in this work, the actual lattice plainification process is not sufficiently evident, because even a minor addition of Cu causes Ge to precipitate as a secondary phase (the total concentration remains around ~0.85 for the whole series, as shown in Table S1). If Ge vacancies were indeed suppressed, one would expect a noticeable change in the carrier concentration, whereas according to the experimental data, it remains almost unchanged. Moreover, the authors do not provide the Hall mobility, using only the weighted mobility, which cannot be employed to discuss increases or decreases in point defect scattering of carriers, since it also includes changes in the effective mass. Therefore, authors have to prove that the proposed lattice plainification mechanism truly occurs, rather than zT enhancement (from 2.0 for GST to 2.3 for GST+0.01Cu) coming from the effect of impurity phases, processing conditions, or changes in the band structure due to the substitution of Ge with Cu.
2. The formation energy depends on the chemical potential of each element, which refers to the growth condition of the material. The different growth conditions will result in different chemical potential, and thus the formation energy will change. Therefore, the formation energy calculations for Ge vacancies and Cu incorporation shown in the introduction are crucial for the study. However, it is unclear under which thermodynamic conditions (Ge-rich or Ge-poor) these calculations were performed. A discussion on how these conditions relate to the experimental synthesis process would strengthen the discussion.
3. Some experimental choices, such as the specific conditions for solid-state reaction (at 875 K for three days to allow Cu diffusion), are not fully justified. Providing the rationale for these choices is necessary. Could alternative processing conditions result in similar or improved outcomes?
4. The authors describe a "phase purification phenomenon" during heating, where Cu initially forms a Cu<sub>1.75</sub>Te phase before dissolving. However, the term "purification" may be misleading, as it does not seem to imply an improvement in compositional homogeneity or phase purity in the final product. The authors should clarify what exactly is being purified in this process.
5. The XRD analysis shows a secondary Ge phase in undoped samples, but no secondary phases in Cu-doped samples at low temperatures (Fig. 2a). This appears inconsistent with the discussion in the text. The authors should provide an explanation or comment on whether Ge is fully dissolved in the Cu-doped samples or remains in undetectable quantities.
6. The Rietveld refinement results are well-presented, but it would be beneficial to include refinement R-factors and goodness-of-fit (GoF) values in a supplementary table. This would further validate the quality of the structural models.
7. The authors claim that Cu substitutes Ge sites rather than occupying interstitial positions. While XPS and XANES data support this conclusion, an additional comparison of R-factors from Rietveld refinements for models with Cu as an interstitial vs. substitutional species would provide stronger evidence.

8. The study discusses an increase in weighted mobility upon Cu doping, but does not present Hall mobility. Since the suppression of Ge vacancies should directly enhance the latter, showing its trend with Cu concentration would provide more direct experimental evidence of lattice plainification.

#### Minor Comments:

1. The introduction could briefly discuss the challenges in controlling Ge vacancies in GeTe and how previous studies have attempted to address this.
2. Figure 3c should include a scale bar for better visualization.
3. The materials and methods section would benefit from more details. For example, authors could mention the magnetic field in which the Hall coefficient measurements were conducted, which model was used for analyzing the raw thermal diffusivity data, whether the measurements in the ZEM were performed only during heating or also during cooling, etc.

#### Reviewer #2

##### (Remarks to the Author)

The manuscript entitled "Copper diffusion rendering lattice plainification for high-performance GeTe-based thermoelectrics" has a potential to publish. However, some comments and questions are to be addressed before publish it.

1. I feel the abstract is not specific, in particular the novelty of the present study as summarized in figures and text.
2. Authors should summarize the high performance of GeTe and its compound alloys (not only consider the low ZT's of GeTe works than the present study) in the literature and revised in the manuscript.
3. The TE properties (sigma and kappa) are drastically changed at the ferroelectric transition temperature. Here, Authors should add more discussion about it.
4. How was the temperature dependance of carrier concentration with the Cu diffused GeTe alloys.
5. Authors has chosen the (Ge<sub>0.85</sub>Sb<sub>0.1</sub>)Te, then doped with Cu. How Cu atoms are filled only in Ge sites? What is the role of Sb in the present work? Why did the authors did not choose pure GeTe?
6. Since the present ZT is promising, It is better to make prototype TEG device using the present alloy, and compare the performance with the simulated single leg device.

#### Reviewer #3

##### (Remarks to the Author)

The present study reported a new synthesis route, a solid-state reaction, which doped the trace amount of Cu element in GeTe-based thermoelectric materials via ion diffusion. Using this technique, the ZT of 2.3 at 775 K and an average ZT (ZT<sub>avg</sub>) of 1.4 at 300–775 K reported in the Cu-doped Ge<sub>0.85</sub>Sb<sub>0.10</sub>Te. Though this study emphasizes the new way to improve the figure-of-merit of GeTe-based thermoelectric materials, there is a lack of experimental/supporting evidence.

The questions are:

1. Ion diffusion is the most favourable thermodynamic mechanism, especially in thermal environments, which degrade the materials' performance and output. Could the authors authenticate their results and claim by experimental evidence?
2. The authors reported the predicted power density is 3.43 W·cm<sup>-2</sup> for a single-leg device under a temperature difference of 475 K and presented the V-I characteristics curve. Could they explain how the experiments/predictions are performed?
3. The transport properties plotted in the graph reveal the ups and downs in two or more places. Is there any other possibility of thermal stability issues on these materials? More studies on thermal stability by DSC or any other suitable thermal analysis are suggested.
4. Microscopic analysis showed most of the morphology aligned with layered structure. Hence, is it possible to make directionality properties? Experimental evidences are needed here.
5. Since a significant difference is reported between the high and average ZT values, measuring the thermoelectric properties measurements on heating and cooling cycles is better.

Hence, I suggest this manuscript needs a major revision before publication.

#### Reviewer #4

##### (Remarks to the Author)

##### Comments to authors

(work summary) This work enhances the thermoelectric properties of GeSbTe by utilizing a non-eutectic structure. It proposes a Cu-induced lattice plainification method, where Cu annihilates Ge vacancies, to enhance the thermoelectric

performance of GeTe-based materials. The authors suggest a traditional processing pathway similar to formation of solid solution state. Previously, the eutectic reaction led to the separation of GeSbTe and CuTe. However, in the newly proposed process, GeSbTe and Cu powders undergo heat treatment at 875 K for three days, enabling the formation of a solid solution. As a result, mobility increases while total thermal conductivity decreases. Consequently, the ZT value appears to be enhanced. Additionally, the authors theoretically estimate the single-leg power density.

(recommendation) I recommend it as publishable. Since this work addresses the importance of microstructure, which was not well understood before, it provides new insights into the role of a solid-solution phase in overcoming the low composite ZT. This process, here referred to as 'lattice plainification,' aligns with conventional homogenization or solid-solution treatment.

(comment overview) However, to further advance the understanding of thermoelectric materials, the following aspects should be addressed. For instance, the state of Cu and the role of Sb require further clarification. Additionally, the theoretical analysis should be presented more explicitly and supported with stronger evidence. Furthermore, I believe that "lattice plainification" is essentially a form of solid solution formation. Therefore, I strongly recommend using traditional terminology consistently throughout the manuscript.

Additionally, the structural stability of the "lattice plainified" phase should be compared to that of the eutectic structure, as the former is likely to be metastable or unstable. A discussion on this aspect would help clarify its long-term stability and potential phase transformations.

Comments.

1) The lattice plainification observed in Cu-doped GeSbTe appears to correspond to the formation of a solid solution rather than a phase-decomposed alloy. I believe that the Cu-doped system is metastable compared to the GeSbTe-CuTe eutectic system: stable at higher temperature, metastable or unstable at room temperature. This raises the question of whether heat treatment could induce phase separation or if increasing the Cu content would trigger this effect. Does a small amount of Cu play a crucial role in stabilizing the solid solution rather than merely facilitating homogenization?

A. The terminology related to precipitation should be revised throughout the manuscript, as it appears to be used incorrectly. In alloy terminology, eutectic reactions and precipitation are distinct processes. Precipitation occurs when a supersaturated solid solution undergoes cooling, leading to the formation of secondary phases. In contrast, a eutectic reaction is a transformation in which a liquid phase solidifies into two distinct solid phases simultaneously at a specific composition and temperature. For instance, in Figure 1(c), the left side panel represents a two-phase system rather than a precipitation process. Precipitation can occur on the right side panel after cooling, when the supersaturated solid solution undergoes phase separation.

i. "Lattice plainification" appears to be a recently introduced term. Instead, I suggest replacing it with "solution treatment," which aligns with established terminology.

Figure 1 Regarding solution treatment and precipitates within grains.

(<https://www.researchgate.net/publication/372675170/figure/fig3/AS:11431281177404390@1690466920745/Solution-heat-treatment-process-scheme.jpg>)

Figure 2 Eutectic structure example

(<https://i.ytimg.com/vi/HreL8-uJBgg/maxresdefault.jpg>)

B. Please compare the results of the GeSbTe-Cu process proposed by the authors with the previous process, particularly regarding the CuTe phase. In the new process, the CuTe phase disappears, whereas it remains in the previous one—this difference should be explicitly discussed using the authors' results (similar compositions used). Currently, the Cu content is small, so it seems plausible that Cu could still dissolve in the GeSbTe matrix using the previous method. However, the results presented in the manuscript indicate that, without following the proposed process, Cu tends to form a CuTe phase. This discrepancy should be further analyzed to clarify the underlying mechanisms.

C. The stability of the solid solution should be evaluated across the working temperature range. In conventional alloys, after heat treatment, the alloy is typically used at room temperature. Even if the solid solution state is metastable, it can maintain its structure due to the high activation barrier at low temperatures. However, thermoelectric materials operate under thermal cycling conditions, which could induce phase transformations. This raises concerns that the solid solution state may undergo particle precipitation within grains or lead to particle formation at grain boundaries.

D. The abstract mentions "high-entropy," but there are no corresponding results or discussions in the article. Please verify the occurrence of the word "entropy" in the manuscript. It appears only once in the abstract and is absent from the main text. If entropy is a key concept, relevant discussions should be included; otherwise, it should be removed from the abstract for consistency.

2) The number of Sb atoms is greater than that of Cu atoms, yet the discussion primarily focuses on Cu-induced defect plainification. This suggests that the authors should compare three different systems: GeTe, GeSbTe, GeSbTe-CuTe, and GeSbTe:Cu (doped).

A. In Figure 4, the band structures are provided for GeTe and GeTe:Cu, whereas the material system under study is GeSbTe. As a result, these band structures may not be fully representative. What is the role of Sb in Cu substitutional doping? Cu is the fourth element in the system, and its impact should be evaluated in the presence of Sb. Additionally, the band structure calculations are based on a 3×3×3 supercell, which may introduce artifacts. Different supercell sizes can lead to variations in the computed band structure. Moreover, the Cu doping in the calculation is ordered due to the periodic boundary condition. However, in reality, it should be disordered. As a result, the supercell band structure may not provide an accurate estimation of the host material's effective mass. In this case, the Green's function method might be a more suitable approach.

B. In Figure 1b, the negative formation energy suggests that GeTe is thermodynamically unstable, leading to the formation of

a secondary phase. I understand that the formation energies are calculated with respect to the Cu elemental phase. However, when considering the Ge-Te-Cu phase diagram, intermetallic Ge-Te-Cu compounds exist. To accurately assess defect formation energies, the correct and reliable reference phases should be considered.

C. Meanwhile, comparing Cu at the Ge site with Cu interstitial-Ge vacancy pairs, the latter appears to be more stable based on the computed formation energies. This implies that Cu is likely to become off-centered over time. Furthermore, an off-centered structure suggests that Cu at the Ge site is in a saddle point configuration or inherently unstable.

3) Phase transformation around 300°C: At this temperature, significant atomic diffusion is expected to occur. After phase transformation, Cu migration should be considered, as diffusion effects may relocate Cu to grain boundaries or interstitial sites

4) Cu state:

A. In Equation (2), the sign of the chemical potential summation should be negative to be consistent with standard conventions.

B. Given its small atomic size, Cu may become off-centered. Is this observed in the structural analysis? It is also related to Figure 1b and my comment of 2C.

C. Is there an interaction between Cu and Sb, similar to the Ag-Sb interaction in LAST (Pb-Ag-Sb-Te)? This should be discussed.

D. Figure 4c. Charge density change alone cannot provide sufficient insight. In this point of view, interstitial Cu is also less affecting structure. It is better to examine the charge density changes by Ge-vacancy or by Cu at Ge site.

5) Power performance from FEM calculations

A. SM Figure 15. The power output is given by  $P=IV$ , meaning that a good voltage (V) fit should lead to an accurate power fit. However, why do the data points (dots) and fitted lines not match? Please clarify this discrepancy.

B. The single-leg performance is estimated based on numerical calculations for the given structures. However, these results remain theoretical. Experimental measurements are needed to validate the findings.

C. The manuscript lacks a detailed description of the parameters required for reproducibility. Please specify calculation settings in the SM, including solder, electrode layer, diffusion barrier, leg dimensions, boundary conditions, and heat loss mechanisms such as convection or radiation. Providing transparent data will enhance reproducibility.

6) In SM,

A. On page 2 of the SM, the phrase "band structure of the orthorhombic phase" should be revised to "band structure of the rhombohedral phase" if applicable. Please verify and correct accordingly.

B. Explicitly state "includes spin-orbit interaction" rather than implying it indirectly.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In my opinion, the authors have adequately addressed all the comments raised by the reviewers. I thank them for their efforts and the work they have done.

Reviewer #2

(Remarks to the Author)

Authors are addressed all comments well, and now the revised manuscript has more clarity than earlier.

Manuscript can be accepted, if all reviewers agree about their comments.

Minor comments:

In Fig 1(d), authors are summarized their data with literature and cited them author names. I think, references numbers should also provided for readers flexibility.

Reviewer #3

(Remarks to the Author)

The authors have answered and incorporated the raised queries in the manuscript. Hence, I recommend the revised manuscript for the publication.

Reviewer #4

(Remarks to the Author)

Thank you for the detailed reply to my previous comments.

However, before publication, I kindly request the authors to revise the following technical points to ensure clarity, correctness, and reproducibility:

Main Manuscript:

Line 76: The statement "Pb doping raises the chemical potential..." is incorrect. It should read "Pb doping decreases the chemical potential...".

Line 262: Correct "von der Pauw method" to "van der Pauw method".

Line 342: The phrase "maximum output power density reaches 3.43 W/cm<sup>2</sup> with ~12%" should be revised to explicitly state that this is a theoretical, predicted, or calculated value. Without this clarification, experimentalists may misinterpret it as an empirical result. Additionally, the efficiency "~12%" is too imprecise—please provide at least one more significant digit (e.g., 12.3% or 11.6%).

Supporting Information (SI):

Page 2 – First-principles Calculations: When using the VASP code, please explicitly state the type of pseudopotentials (POTCAR files) employed. This is crucial for thermoelectric materials, which often have large lattice constants and are sensitive to the choice of pseudopotentials. Also include the relaxed lattice parameters used for the simulation.

Page 23 – FEA Analysis: Please include detailed information about the material properties used in the FEA simulation, such as Seebeck coefficient, electrical and thermal conductivity. Additionally, clarify the interfacial/contact electrical and thermal resistances applied in the model. In particular, the thermal conductivity of the ceramic substrate should be explicitly stated.

Clarification Regarding Contact Resistivity (Reviewer 3 – Comment 2):

In the reply to Reviewer #3 (Comment 2), it is stated that:

"The electrical contact resistivity at hot and cold sides is set to 15  $\mu\Omega\cdot\text{cm}$ , referencing the properties of solder material (tin-lead/60–40) from ANSYS materials database."

This is physically incorrect.

- Contact resistivity (also called specific contact resistance) must have the unit of  $\Omega\cdot\text{m}^2$ , not  $\Omega\cdot\text{m}$  or  $\Omega\cdot\text{cm}$ .
- It is a property of an interface, not a bulk material, and thus cannot be derived from the bulk resistivity of Pb-Sn solder. Rather it requires a combination to define a specific interface.
- Therefore, referencing a value from the bulk material database as contact resistivity is conceptually flawed and must be corrected.

I strongly and kindly request that the authors provide:

- A clear, transparent, and physically valid justification or reference for the chosen value of electrical contact resistivity.
- All related calculation settings used in the FEA simulation (e.g., interfacial resistances, boundary conditions, layer structure) must be explicitly described in either the main text or SI to ensure reproducibility and scientific validity.

Version 2:

Reviewer comments:

Reviewer #4

(Remarks to the Author)

The authors have addressed all the issues raised. I am pleased to recommend this manuscript for publication.

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## Response to reviewers

### Reviewer #1 (Remarks to the Author):

**General comment:** The manuscript presents a study on the impact of Cu doping on GeTe-based thermoelectric materials, proposing a recently popularized mechanism of "lattice plainification" as a means to enhance thermoelectric performance. The authors utilize advanced synchrotron-based techniques, electron microscopy, and computational approaches to substantiate their findings. The work is commendable in its methodological rigor and provides new insights into the role of Cu in modifying lattice dynamics and defect chemistry. However, several points should be addressed before publication to enhance the clarity and scientific robustness of the manuscript.

**Author reply:** Thank you for your rigorous and constructive comments. We have included our point-to-point response in the following and highlight the related amendments in our revised manuscript.

### Major Comments:

**Comment 1.** To the best of the reviewer's knowledge, the concept of "lattice plainification" means that carrier mobility is effectively boosted by reducing the number of point defect scattering centers (e.g., vacancies). However, in this work, the actual lattice plainification process is not sufficiently evident, because even a minor addition of Cu causes Ge to precipitate as a secondary phase (the total concentration remains around ~0.85 for the whole series, as shown in Table S1). If Ge vacancies were indeed suppressed, one would expect a noticeable change in the carrier concentration, whereas according to the experimental data, it remains almost unchanged. Moreover, the authors do not provide the Hall mobility, using only the weighted mobility, which cannot be employed to discuss increases or decreases in point defect scattering of carriers, since it also includes changes in the effective mass. Therefore, authors have to prove that the proposed lattice plainification mechanism truly occurs, rather than  $zT$  enhancement (from 2.0 for GST to 2.3 for GST+0.01Cu) coming from the effect of impurity phases, processing conditions, or changes in the band structure due to the substitution of Ge with Cu.

**Author Reply:** We agree that "lattice plainification" does not consistently or accurately reflect the phenomenon and mechanism observed in our study. After reviewing the relevant literature and careful consideration, we decided to remove this terminology throughout the manuscript. Instead, we now describe the observed phenomenon as "targeted doping" in which Cu ions substitute the host Ge ions only. The underlying mechanism is now described as vacancy suppression, which accounts for the optimized carrier concentration and the preserved carrier mobility.

Indeed, as you mentioned, the minor Cu addition precipitates Ge as secondary phase, the overall Ge content remains  $\sim 0.85$  for the across the whole series samples. This suggests that Cu mainly occupies Ge sites without significantly changing the total stoichiometry. The excessive vacancies are further suppressed due to the counter doping of Sb, which effectively reduces the carrier concentration from  $\sim 10^{21}$  to approximately  $2 \times 10^{20} \text{ cm}^{-3}$  in  $\text{Ge}_{0.85}\text{Sb}_{0.1}\text{Te}$  (GST). While Cu doping does not drastically change the carrier concentration, it likely promotes a more ordered crystal structure by occupying Ge vacancies, indicated by the preferred intensification of diffraction peaks and the more crystalized grains under SEM, which we previously described as “lattice plainification”. This effect is beneficial for electronic transport by reducing local structural disorder and depopulating lattice defects.

In terms of the Hall measurements, the magnetic field strength in typical Hall measurement systems is relatively low, which affects the accuracy of carrier concentration measurement in degenerated semiconductors with a high mobility. To warrant the precise measurement, we used the Physical Property Measurement System (PPMS) to measure the carrier concentration from 4 K to near ambient using an alternating magnetic field of up to 8 T, and also used the homemade instrument to measure the carrier concentration from room temperature to 600 K under alternating magnetic field of up to 1.4 T. As can be seen in **Fig. R1**, the results indicate that after our solid reaction, the Cu ions should be successfully doped in the system to slightly decrease the carrier concentration and maintain the carrier mobility (cf. **Fig. R3**).

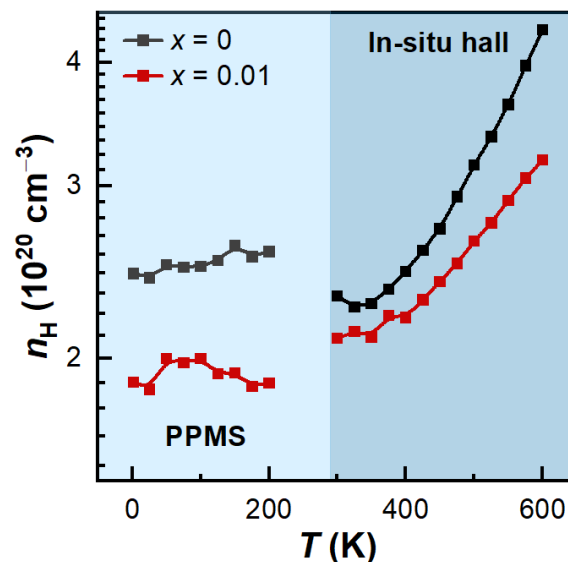


**Fig. R1 (Supplementary Fig. 14a).** Temperature-dependent Hall concentration measured by PPMS and a homemade in-situ heating instrument.

**Comment 2.** The formation energy depends on the chemical potential of each element, which refers to

the growth condition of the material. The different growth conditions will result in different chemical potential, and thus the formation energy will change. Therefore, the formation energy calculations for Ge vacancies and Cu incorporation shown in the introduction are crucial for the study. However, it is unclear under which thermodynamic conditions (Ge-rich or Ge-poor) these calculations were performed. A discussion on how these conditions relate to the experimental synthesis process would strengthen the discussion.

**Author reply:** We agree that the formation energy is dependent on the chemical potentials of elements, which reflect the thermodynamic growth conditions in the actual synthesis of samples. In our previous manuscript, the formation energy calculations are carried out under Ge-rich conditions. To clarify and be rigorous, we have calculated the formation energy of Ge vacancy under Ge-poor conditions, and the results are plotted in **Fig. R2**.

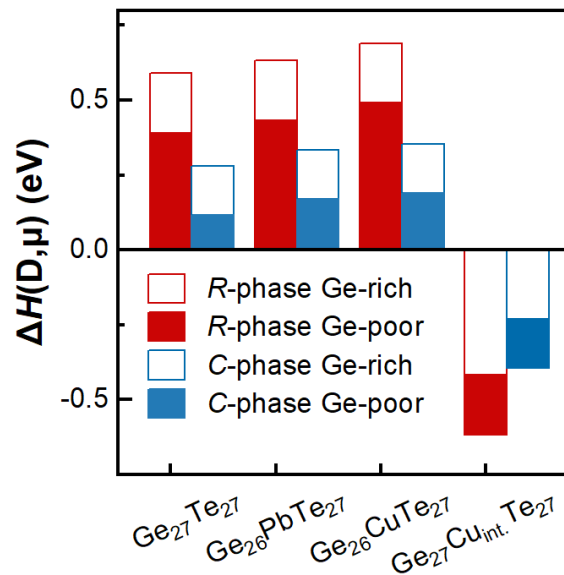


**Fig. R2 (Manuscript Fig. 1b).** Point defect formation energy of a Ge vacancy in a Ge<sub>27</sub>Te<sub>27</sub> supercell doped with various elements in both Ge-rich and Ge-poor conditions.

The results show that the formation energy under Ge-rich condition is higher than under the Ge-poor conditions, while the overall trend of the formation energy remains consistent with Ge-rich conditions. This is mainly because the term of the chemical potential of Ge in Ge-poor condition is of the similar values for the four different cases, so the existence of Ge-poor condition decreases the point defect formation energy by the similar magnitude. This also suggests that the Ge chemical potential is reduced in Ge-poor limit, making the formation of Ge vacancies much easier. Therefore, Cu substitution elevates the average chemical potential of Ge to increase the formation energy of Ge vacancies, making their formation more difficult.

**Comment 3.** Some experimental choices, such as the specific conditions for solid-state reaction (at 875 K for three days to allow Cu diffusion), are not fully justified. Providing the rationale for these choices is necessary. Could alternative processing conditions result in similar or improved outcomes?

**Author reply:** In terms of the temperature profile for the sample synthesis, the solid-state reaction temperature is selected based on the melting points of the constituent elements: Germanium (1211 K), Tellurium (722.5 K), and Antimony (903.6 K). To ensure thorough reaction and homogenisation, the reaction temperature was set to 1225 K, which is just above the highest melting point among the elements. The sample was heated from room temperature to 1225 K at a heating rate of 2 K/min and soaked at that temperature for 12 hours to allow full reaction and the formation of a uniform matrix. An annealing process is employed after Cu addition. This heat treatment process was set as 875 K, the highest working temperature of GeTe-based thermoelectric materials, to make sure the samples were thermally stable.

During the development of fabrication process, various conditions were systematically explored, such as pre-soaking and quenching treatments. For instance, we pre-soaked the samples at near the melting point of Te or Sb (725–925 K) to ensure the homogeneity and uniformity, followed by quenching and subsequent annealing. However, we found that pre-soaking and annealing produced similar effects on the crystal structure and thermoelectric properties. Ultimately, the pre-soaking step was removed, as it doesn't apparently change the microstructure or improve performance. Quenching was also evaluated for its role in suppressing unwanted secondary phase formation. For comparison, we also fabricated samples without ice water quenching and observed no significant change.

Annealing time is another critical parameter. Prior studies, such as the work by Xu et al.,<sup>1</sup> have shown that longer annealing durations benefit both electrical and thermal transport, with optimal performance observed for samples annealed up to 7 days. In our study, rather than varying the annealing time, we kept this parameter constant in order to investigate the effects of Cu addition on the thermoelectric properties and structural characteristics.

The above contents have been incorporated in our revised Supporting Information.

**Comment 4.** The authors describe a "phase purification phenomenon" during heating, where Cu initially forms a  $\text{Cu}_{1.75}\text{Te}$  phase before dissolving. However, the term "purification" may be misleading, as it does not seem to imply an improvement in compositional homogeneity or phase purity in the final product. The authors should clarify what exactly is being purified in this process.

**Author reply:** Our original idea of “phase purification” is to emphasise that our synthesis process is different to the conventional process. In traditional synthesis routes, the  $\text{Cu}_{2-x}\text{Te}$  phase may dissolve at elevated temperatures, then re-precipitates as a secondary phase during cooling. In contrast, during our synthesis,  $\text{Cu}_{2-x}\text{Te}$  forms only as a transient intermediate phase upon heating and dissolves completely into the matrix. This dissolved component then diffuses uniformly, and no re-precipitation occurs upon cooling. Such a process eliminates the potential  $\text{Cu}_{2-x}\text{Te}$  impurity phases, and further promotes a more homogeneous composition stick to the initial recipe through a distinct thermodynamic process. For the sake of clarity, we removed the terminology of “phase purification” in our revised manuscript and used more appropriate descriptions as have been highlighted.

**Comment 5.** The XRD analysis shows a secondary Ge phase in undoped samples, but no secondary phases in Cu-doped samples at low temperatures (Fig. 2a). This appears inconsistent with the discussion in the text. The authors should provide an explanation or comment on whether Ge is fully dissolved in the Cu-doped samples or remains in undetectable quantities.

**Author reply:** We are sorry for the confusion in the original figure and description. In the *in-situ* XRD results (**Manuscript Fig. 2a**), a Ge reflection peak can also be detected in the Cu-doped sample at low temperature and after cooling. The undoped sample is the matrix of the Cu-doped sample. In this work, the *in-situ* XRD experiment is designed to simulate the actual Cu diffusion process by mimicking the same temperature profile in synthesis, under an inert atmosphere. XRD spectrum is recorded every 50 K from room temperature to 875 K. To make it clearer, the Ge peak in the doped sample has been explicitly labelled in our revised manuscript.

**Comment 6.** The Rietveld refinement results are well-presented, but it would be beneficial to include refinement R-factors and goodness-of-fit (GoF) values in a supplementary table. This would further validate the quality of the structural models.

**Author reply:** We have updated the goodness-of-fit (GoF), expected R-factor ( $R_{\text{exp}}$ ), weighted R-factor ( $R_{\text{wp}}$ ), and profile R-factor ( $R_{\text{p}}$ ) of the Rietveld-refinement in **Table R1**. The GoF indicates how well the model fits the data relative to the expected statistical noise, the  $R_{\text{exp}}$  represents the theoretically achievable fit based on counting statistics,  $R_{\text{wp}}$  means the weighted mismatch between experimental data and calculated profiles, and the  $R_{\text{p}}$  measures the unweighted mismatch. Typically, the GoF below 2 and close to 1 is considered acceptable, while the  $R_{\text{wp}}$  is desired to below 10%. However, since our refinement is based on synchrotron powder diffraction, both the  $R_{\text{wp}}$  and the GoF are higher compared

to the lab-scale XRD. This is due to the use of transmission mode, the much more intensive background signal from lime quartz capillaries, and the higher sensitivity and resolution of synchrotron radiations, adding considerable mismatch during the Rietveld refinement.

**Table R1 (Supplementary Table 1).** Results of Rietveld refinement of Australian Synchrotron Powder Diffraction for GST+ $x$ 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  | $R_{\text{exp}}$ | $R_{\text{wp}}$ | $R_p$ |
|-------------|--------------------------------------------------------------|---------------------------------------------------------------|---------------------------|---------------------------|------|------------------|-----------------|-------|
| GST         | Ge <sub>0.85</sub> Sb <sub>0.1</sub> Te                      | Ge <sub>0.8466</sub> Sb <sub>0.1</sub> Te                     | 4.20565(7)                | 10.4909(4)                | 5.88 | 1.58             | 9.29            | 6.54  |
| GST+0.005Cu | Ge <sub>0.85</sub> -Cu <sub>0.005</sub> Sb <sub>0.1</sub> Te | Ge <sub>0.8442</sub> Cu <sub>0.005</sub> Sb <sub>0.1</sub> Te | 4.20251(4)                | 10.5032(3)                | 7.53 | 1.62             | 11.69           | 8.08  |
| GST+0.01Cu  | Ge <sub>0.85</sub> -Cu <sub>0.01</sub> Sb <sub>0.1</sub> Te  | Ge <sub>0.8436</sub> Cu <sub>0.01</sub> Sb <sub>0.1</sub> Te  | 4.20106(4)                | 10.5192(3)                | 7.36 | 1.55             | 11.43           | 7.84  |
| GST+0.015Cu | Ge <sub>0.85</sub> -Cu <sub>0.015</sub> Sb <sub>0.1</sub> Te | Ge <sub>0.844</sub> Cu <sub>0.015</sub> Sb <sub>0.1</sub> Te  | 4.19735(8)                | 10.5456(5)                | 7.13 | 1.59             | 11.05           | 7.55  |
| GST+0.02Cu  | Ge <sub>0.85</sub> -Cu <sub>0.02</sub> Sb <sub>0.1</sub> Te  | Ge <sub>0.8397</sub> Cu <sub>0.02</sub> Sb <sub>0.1</sub> Te  | 4.19994(4)                | 10.5437(3)                | 6.93 | 1.56             | 10.83           | 7.03  |
| GST+0.03Cu  | Ge <sub>0.85</sub> -Cu <sub>0.03</sub> Sb <sub>0.1</sub> Te  | Ge <sub>0.8305</sub> Cu <sub>0.03</sub> Sb <sub>0.1</sub> Te  | 4.20209(4)                | 10.5474(2)                | 6.42 | 1.60             | 10.29           | 6.58  |
| GST+0.04Cu  | Ge <sub>0.85</sub> -Cu <sub>0.04</sub> Sb <sub>0.1</sub> Te) | Ge <sub>0.8226</sub> Cu <sub>0.04</sub> Sb <sub>0.1</sub> Te  | 4.19909(3)                | 10.53451(18)              | 4.61 | 1.67             | 7.70            | 5.14  |

As can be seen in the above table, GoF ranges from 4.61 to 8.08,  $R_{\text{exp}}$  from 1.55 to 1.67,  $R_{\text{wp}}$  from 7.70 to 11.69, and  $R_p$  from 5.14 to 8.08 across all the Cu-doped Ge<sub>0.85</sub>Sb<sub>0.1</sub>Te samples. The satisfactory R - factors and GoF values also confirm the reliability of our structural models.

**Comment 7.** The authors claim that Cu substitutes Ge sites rather than occupying interstitial positions. While XPS and XANES data support this conclusion, an additional comparison of R-factors from Rietveld refinements for models with Cu as an interstitial vs. substitutional species would provide stronger evidence.

**Author reply:** In our work, we only modelled Cu as a substitutional species on the Ge sites, because powder XRD inherently probes only long-range and periodic lattice positions. The corresponding R-factors are shown in the response to your last comment. In contrast, interstitial Cu lacks the regular, therefore cannot be reliably refined in a Rietveld analysis.

Since you pointed out that we should compare the Rietveld refinement for Cu interstitial, we tried to add that to the model with a tiny occupancy. Please note that even the tiny occupancy could result in the periodic image. The R-factors of the Rietveld refinement of the model with interstitial Cu are higher

than the substitutional Cu. For example, the  $R_{wp}$  ranges from 15.3 to 19.2, indicating a larger mismatch between experimental data and the calculated profile. The reverse Monte Carlo (RMC) simulation can reflect such dynamic disorder to some extent, but this is out of the scope of the Rietveld refinement and beyond our current capability, which we may try in future.

Therefore, XPS and XANES are used to confirm the coordination environment and oxidation state of Cu in our work, as these technologies support the substitutional - site assignment, while an interstitial - Cu model would neither converge to a meaningful fit nor yield trustworthy R-factor comparisons.

**Comment 8.** The study discusses an increase in weighted mobility upon Cu doping, but does not present Hall mobility. Since the suppression of Ge vacancies should directly enhance the latter, showing its trend with Cu concentration would provide more direct experimental evidence of lattice plainification.

**Author reply:** As you pointed out, our initial study does not include Hall mobility measurements. In the revised manuscript, we used PPMS and a homemade Hall instrument to measure the temperature-dependent carrier mobility, and the results are shown in **Fig. R3**.

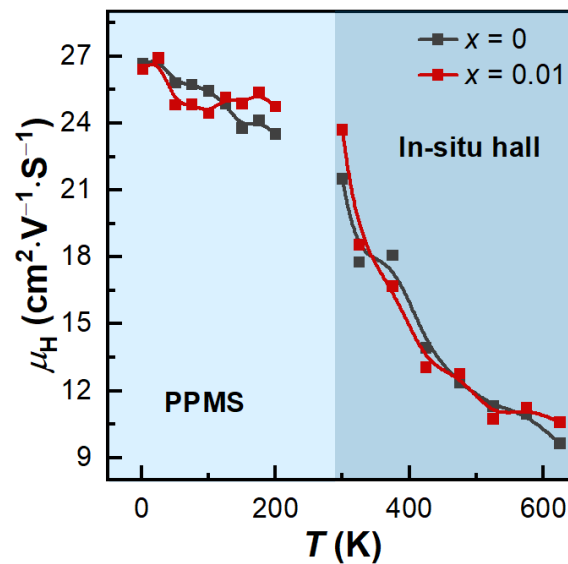


**Fig. R3 (Supplementary Fig. 14b).** Temperature-dependent Hall mobility of the sample GST+xCu ( $x = 0$  and  $0.01$ ).

Unlike the intriguing view that vacancy suppression enhances the carrier mobility, our measurements show no significant difference in hall mobility between GST and GST+0.01Cu. This can be attributed to two competing effects, the diffusion of Cu into matrix fills some Ge vacancies, potentially increasing

mobility by depopulating the point defects; in contrast, substituting the host Ge ions by Ge ions tends to strengthen the point defect scattering to reduce mobility. The interplay between vacancy filling and atomic substitution likely results in the observed negligible change in overall Hall mobility. Moreover, as suggested by XRD and SEM characterizations, the addition of Cu also modifies the microstructures, which may further influence electronic transport. These combined factors could result in the negligible net change in carrier mobility.

#### Minor Comments:

**Comment 9.** The introduction could briefly discuss the challenges in controlling Ge vacancies in GeTe and how previous studies have attempted to address this.

**Author reply:** In our revised manuscript, the introduction has been updated to include an overview of intrinsic defect chemistry in GeTe and previous attempts to address the challenges. We also discuss the challenges in the control of Ge vacancies in GeTe, and how other people tried to control that as show in the below paragraph.

“As one of the most eminent mid-temperature thermoelectric systems, GeTe favours an inherent  $ZT$  of  $\sim 0.9$  due to large band asymmetry and dynamic lattice anharmonicity, which naturally secure both a large  $S^2\sigma$  and a low  $\kappa_l$ .<sup>2-4</sup> As illustrated in **Fig. 1a**, pristine GeTe undergoes a reversible phase transformation from rhombohedral (R-) to cubic (C-) phase at  $650\pm 50$  K, which can be seen as a ferroelectric transition deriving from the Peierls distortion and displacement of Ge and Te sublattices driven by long-range polarizations.<sup>5,6</sup> However, the structural instability also facilitates the formation of intrinsic Ge vacancies, which act as acceptor dopants and result in excessive hole concentration ( $n_h \sim 10^{21} \text{ cm}^{-3}$ ) beyond its optimal range and a degradation on the  $ZT$ .<sup>7-9</sup> This behaviour originates from the intrinsically low formation energy of Ge vacancy, making GeTe thermodynamically prone to cation-deficient, off-stoichiometric compositions and Ge precipitation. Even the high vacancies beneficial for phonon scattering, they impose challenge in balancing thermal and electric transport properties. To overcome this, increasing the formation energy through chemical doping is an effective strategy to shift the defect formation equilibrium. Isovalent or aliovalent doping of  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ , or  $\text{Sb}^{3+}$  has proven effectively suppress Ge vacancy formation and compensate the hole concentration.<sup>10-12</sup> Pb doping raises the average chemical potential ( $\mu$ ) at cation sites, making Ge vacancies formation less favourable, while counter doping induces donor-like effects to optimize  $n_h$ .”

**Comment 10.** Figure 3c should include a scale bar for better visualization.

**Author reply:** We have added the scale bar for the EDS mapping based on your suggestion, as shown in Fig. R4.

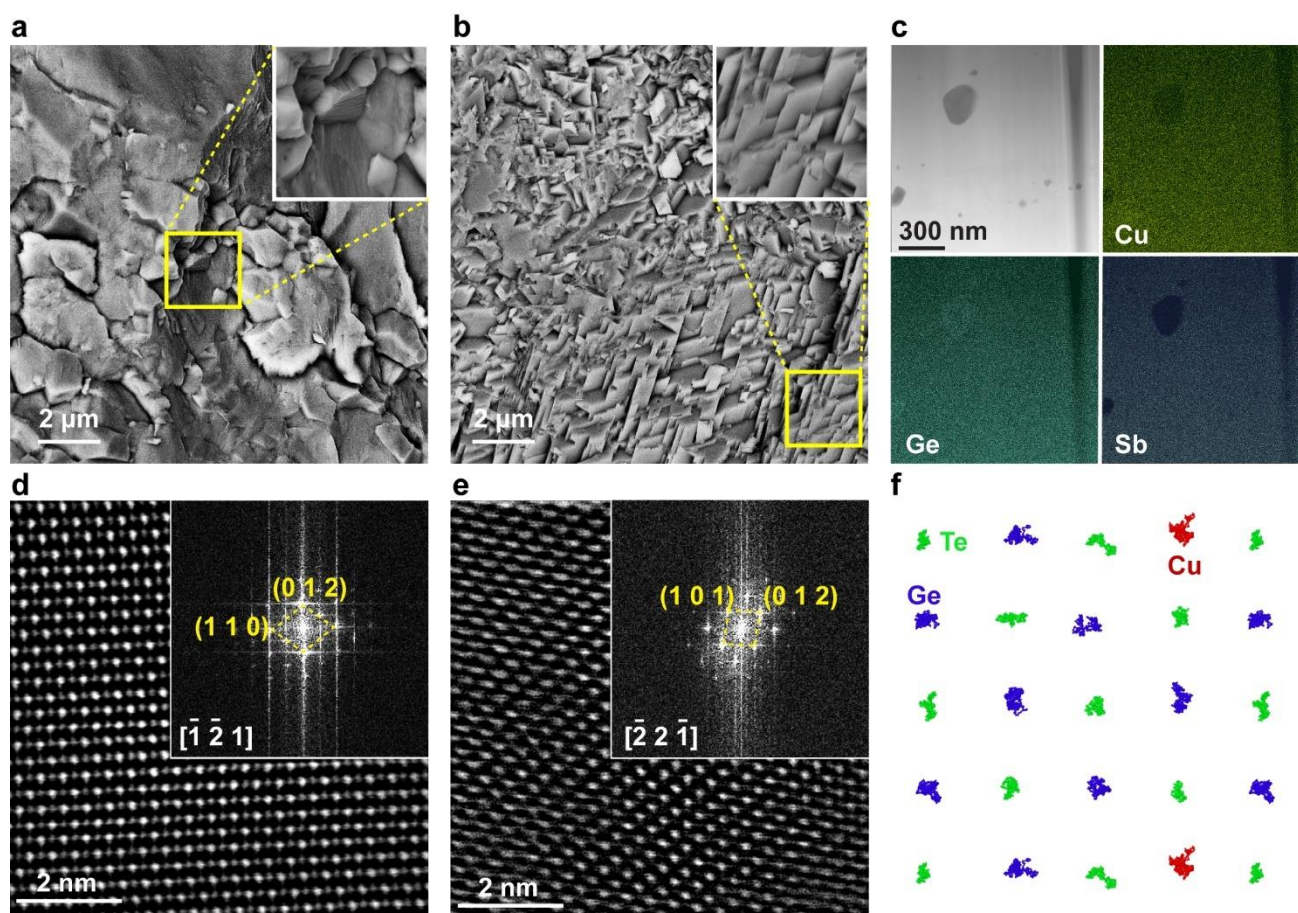


**Fig. R4 (Manuscript Fig. 3). Microstructures analysis.** (a–b) SEM-BSE images of Ge<sub>0.85</sub>Sb<sub>0.10</sub>Te (GST) and GST+0.04 fractographies, respectively. The insets enlarge the labelled area. (c) TEM-EDS mapping of GST. (d–e) STEM-dark field images of GST+0.01Cu in  $[\bar{1}21]$  and  $[2\bar{2}1]$  zone axes. The insets show the corresponding FFT patterns. (f) MD simulated atomic trajectories in the (100) plane of Ge<sub>31</sub>Cu<sub>1</sub>Te<sub>32</sub> at 975 K for 3000 ps.

**Comment 11.** The materials and methods section would benefit from more details. For example, authors could mention the magnetic field in which the Hall coefficient measurements were conducted, which model was used for analysing the raw thermal diffusivity data, whether the measurements in the ZEM were performed only during heating or also during cooling, etc.

**Author reply:** According to your suggestion, we have added more detailed descriptions to the Methods section, including the sample size and measurement environment as below:

“The electrical conductivity ( $\sigma$ ) and Seebeck coefficient ( $S$ ) are measured simultaneously using a commercial system (ZEM-3, ULVAC) with rectangular bar-shaped samples in the size of  $\sim 1.5 \times 1.5 \times 6$  mm<sup>3</sup>. The thermal conductivity ( $\kappa$ ) is calculated by using  $\kappa = D\rho C_p$ , where  $D$  is the thermal diffusivity measured by a Laser Flash thermal analyzer (LFA 467, NETZSCH) under argon atmosphere,  $C_p$  is the specific heat capacity referred to the previously reported data for GST, and  $\rho$  is density. Tests on the reproducibility and repeatability are performed. Specifically, we prepared two independent samples and for each sample we performed measurement in heating-cooling loops. We further used Physical Property Measurement System (PPMS) and homemade equipment to measure temperature-dependent carrier concentration ( $n$ ) and mobility ( $\mu$ ). The Hall coefficient ( $R_H$ ) is obtained by the van der Pauw method, then we calculated  $n$  and  $\mu$  by  $n = 1/(eR_H)$  and  $\mu = \sigma R_H$ , where  $e$  is the elementary charge.”

## **Reviewer #2 (Remarks to the Author):**

**General comment:** The manuscript entitled "Copper diffusion rendering lattice plainification for high-performance GeTe-based thermoelectrics" has a potential to publish. However, some comments and questions are to be addressed before publish it.

**Author reply:** Thank you for your constructive and your supporting feedback.

**Comment 1.** I feel the abstract is not specific, in particular the novelty of the present study as summarized in figures and text.

**Author reply:** We have rewritten the abstract to highlight on the novelty of this work, as following:

“Coinage metals Cu and Ag are widely reckoned as effective dopants in thermoelectric materials due to their ability to optimise carrier concentration while preserving high carrier mobility, attributed to their inherent dynamic features. Traditionally, Cu/Ag ions are introduced through eutectic reactions, which inevitably result in interstitial doping. Here, we develop an innovative solid solution doping strategy that enables targeted doping, whereby Cu ions exclusively occupy host lattice sites rather than interstitial sites. By combining first-principles calculations with in-situ experiments, we demonstrate that this targeted doping approach relies on ion diffusion and induces lattice renormalisation, effectively reducing lattice defects and suppressing hole concentration. Consequently, the 1 at.% Cu doped  $\text{Ge}_{0.85}\text{Sb}_{0.10}\text{Te}$  sample exhibits an exceptional figure-of-merit of 2.3 at 775 K along with a desirable average value of 1.4 scoping 300 to 775 K. The power density of the corresponding single-leg thermoelectric module is  $2.23 \text{ W}\cdot\text{cm}^{-2}$  under a temperature difference of 475 K. This work not only explains the kinetics behind dynamic doping behaviours, but also provide an original method to achieve high-quality functional materials with less lattice defects and a high carrier mobility.”

**Comment 2.** Authors should summarize the high performance of GeTe and its compound alloys (not only consider the low ZT's of GeTe works than the present study) in the literature and revised in the manuscript.

**Author reply:** Following your suggestions, we compared only GeTe-based materials doped or alloyed with Cu. In our revised manuscript, we included those higher-performance Cu-containing alloy in the comparison, as can be seen in **Fig. R5**.

We also included relevant statement in the introduction part, such as:

“Jin et al. alloyed GeTe with 20% CuSbSe<sub>2</sub>, which optimises carrier concentration and triggers numerous point defects that effectively scatter phonons, resulting in a remarkable ZT value of ~2.6.<sup>13</sup>”

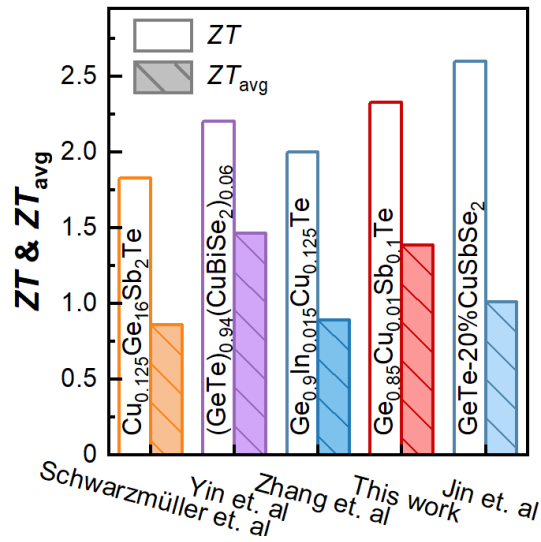


**Fig. R5 (Manuscript Fig. 1d).** Comparison of ZT and ZT<sub>avg</sub> between literature and this work.

**Comment 3.** The TE properties (sigma and kappa) are drastically changed at the ferroelectric transition temperature. Here, Authors should add more discussion about it.

**Author reply:** Following your suggestions, we have added more descriptions on the TE properties that change at the Curie temperature in the revised manuscript, as:

“As  $x$  increases, the  $\sigma$  first increases to 852 S·cm<sup>-1</sup> at 625 K when  $x = 0.010$ , then decreases due to the influence of carrier mobility at higher doping concentrations. Increasing temperature leads to a phase transformation from an amorphous rhombohedral structure to a symmetric cubic structure, resulting in significant changes in electronic transport. Approaching to the Curie temperature of such a ferroelectric transition is accompanied with softening of lattice vibration modes, which enhances acoustic phonon scattering charge carriers and then degrade the  $\sigma$ .<sup>14</sup> Due to symmetrisation, the energy offset from light band to heavy band decreases, leading to band convergence and populated density of states (DOS) near the Fermi level, which further increases the  $\sigma$ .”

**Comment 4.** How was the temperature dependence of carrier concentration with the Cu diffused GeTe alloys.

**Author reply:** As shown in **Fig. R1**, the Hall carrier density  $n_H$  remains almost unchanged in both samples at low temperature. As the temperature increases,  $n_H$  rises sharply, reflecting thermally activated carrier generation. It is observed that the GST+0.01Cu sample maintains a generally lower carrier concentration than the undoped samples.

**Comment 5.** Authors has chosen the  $(\text{Ge}_{0.85}\text{Sb}_{0.1})\text{Te}$ , then doped with Cu. How Cu atoms are filled only in Ge sites? What is the role of Sb in the present work? Why did the authors did not choose pure GeTe?

**Author reply:** The  $\text{Ge}_{0.85}\text{Sb}_{0.1}\text{Te}$  can also be written as  $\text{Sb}_2\text{Te}_3(\text{GeTe})_{17}$  (GST-17), which can be seen as a pseudo-binary alloy of GeTe and  $\text{Sb}_2\text{Te}_3$ . The metastable cubic GST usually exhibits a NaCl rock salt structure, with Te occupying the anion sublattice and Ge/Sb/vacancies randomly occupying the cation sublattice.<sup>15</sup> At ambient temperature,  $\text{Sb}_2\text{Te}_3(\text{GeTe})_n$  is a stable layered structure, comprising  $\text{Sb}_2\text{Te}_3$  slabs extended by GeTe layers, separated by van der Waals gaps.<sup>16</sup> These gaps correspond to ordered cation vacancies, with Te atoms surrounding the distorted octahedral voids at the outermost. Upon heating, the structure transforms into a cubic structure, wherein Ge, Sb, and vacancies randomly occupy at cation sublattice, and Te occupies at anion site.

In our work, Cu incorporation was achieved through a two-step synthesis process: we first synthesised GST matrix and subsequently doped Cu via solid-state reactions after quenching. This approach was intentionally designed to suppress the formation of secondary  $\text{Cu}_2\text{Te}$  phases and to promote controlled substitution of Cu into the cation sub-lattice. Cu in our work is preferentially occupying Ge sites rather than the Sb sites. In XANES analysis indicates that Cu in our samples is predominantly in the +2 state. The ionic radius and electronegativity of  $\text{Cu}^{2+}$  are closer to  $\text{Ge}^{2+}$  than  $\text{Sb}^{3+}$ , potentially making Ge sites energetically favourable for such doping. In addition, while the Ge and Sb are randomly occupied the cation sites, prior studies show that Sb atoms preferentially occupy cation sites adjacent to the van der Waals gaps.<sup>17</sup> This spatial preference occupation limits Cu substitution at Sb sites due to bonding incompatibility. Instead, Cu tends to occupy Ge sites, which are more structurally accessible, vacancy-rich, and thermodynamically favourable.

In our preliminary investigation, we tried to dope Cu in pristine GeTe, and observed Ge precipitation, which is consistent with literatures. The structural instability, coupled with the intrinsically high hole carrier concentration arising from native Ge vacancies, limits the thermoelectric performance of pure

GeTe. Incorporating  $\text{Sb}^{3+}$  into GeTe effectively reduces the carrier concentration to obtain a high power factor.  $\text{Sb}^{3+}$  acts as an electron donor, reduces rhombohedral distortion, and improves band degeneracy, thereby enhancing the Seebeck coefficient.<sup>18,19</sup> Additionally, Sb alloying introduces planar and point defects (including van der Waals gaps and stacking faults), which strongly scatters phonons to reduce lattice thermal conductivity. These effects collectively lead to an improved thermoelectric performance and higher  $ZT$  values.

**Comment 6.** Since the present  $ZT$  is promising, it is better to make prototype TEG device using the present alloy, and compare the performance with the simulated single leg device.

**Author reply:** We first simulate single-leg thermoelectric module based on the experimentally measured electrical and thermal properties of  $\text{Ge}_{0.85}\text{Sb}_{0.1}\text{Te}+0.01\text{Cu}$ . The performance of the single-leg device ( $2 \times 2 \times 6.5$  mm) is simulated by finite element analysis (FEA) using the ANSYS software with parameters from experiments and ANSYS built-in materials datasets, to predict voltage, power output, and conversion efficiency. The results can indicate the maximum conversion efficiency is approximately 12.3% under a temperature difference  $\Delta T = 475$  K.

To further verify the results, we assembled a single-leg module using same material, and measured the power output under various temperature differences. As shown in **Fig. R6**, the measured performance closely follows the theoretical trends. The maximum efficiency is approximately 8%. The discrepancy between the experimental and theoretical results is mainly attributed to contact resistance and heat loss due to thermal radiation.

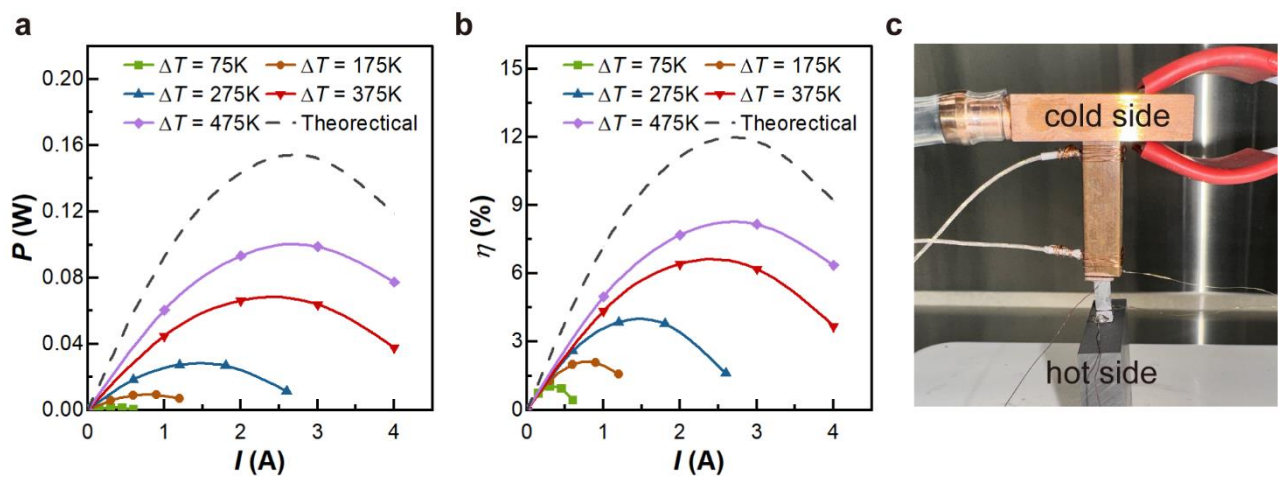


**Fig. R6 (Supplementary Fig. 24). Evaluation of device performance.** (a) Current ( $I$ )-dependent power output ( $P$ ). (b) Current-dependent conversion efficiency ( $\eta$ ). (c) Photo of experimental set-up.

### Reviewer #3 (Remarks to the Author):

**General comments:** The present study reported a new synthesis route, a solid-state reaction, which doped the trace amount of Cu element in GeTe-based thermoelectric materials via ion diffusion. Using this technique, the  $ZT$  of 2.3 at 775 K and an average  $ZT$  ( $ZT_{\text{avg}}$ ) of 1.4 at 300–775 K reported in the Cu-doped  $\text{Ge}_{0.85}\text{Sb}_{0.10}\text{Te}$ . Though this study emphasizes the new way to improve the figure-of-merit of GeTe-based thermoelectric materials, there is a lack of experimental/supporting evidence. Hence, I suggest this manuscript needs a major revision before publication.

**Author reply:** Thank you for your constructive and your supporting feedback. We have followed your comments to make corresponding revisions and responses.

**Comment 1.** Ion diffusion is the most favourable thermodynamic mechanism, especially in thermal environments, which degrade the materials' performance and output. Could the authors authenticate their results and claim by experimental evidence?

**Author reply:** In our study, the term “diffusion” refers to the thermally activated process by which Cu atoms randomly diffuse into the GST matrix during the high temperature soaking. This process allows Cu uniformly distributed in matrix and substitute or occupy Ge sites, rather than undergoing directional migration driven by thermal gradient and occupy the interstitial sites. Theoretically, we used molecular dynamics to predict the vibrational trajectories of atoms at finite temperature. The oscillation amplitude of Cu is slightly larger than that of Ge and Te, suggesting a quasi-coherent vibrational behaviour among the constituent atoms. At the 875 K, the Cu atoms do not show liquid-like behaviour, as they are held back by the more stable Ge and Te sublattices. This means the vibration of Cu is a little stronger than GeTe, but still move in coordinated way with Ge and Te atoms.

To further access the thermal stability, XRD analysis is conducted to the samples with even higher Cu composition ( $\text{GST}+0.04\text{Cu}$ ) for different annealing time (0, 3, 7 and 7 days of annealing and 3 days heating and cooling). As shown in **Fig. R7**, there is no significant Cu agglomeration can be detected, suggesting that Cu is stable in the sample undergoing heat treatment. According to **Fig. R7**, Cu signal is detected in the 0-day annealing sample, while there is no Ge signal detected. By increasing annealing time, the Cu signal disappeared, and the Ge signal can be observed. Moreover, in the 7-day annealing with heating and cooling samples, there is no Cu or Cu compounds can be detected, and the main peaks remains consistent with the samples with shorter annealing time. This implies that the crystal structures and thermoelectric performance (fc. **Fig. R10**) of samples remains stable after heat treatment.

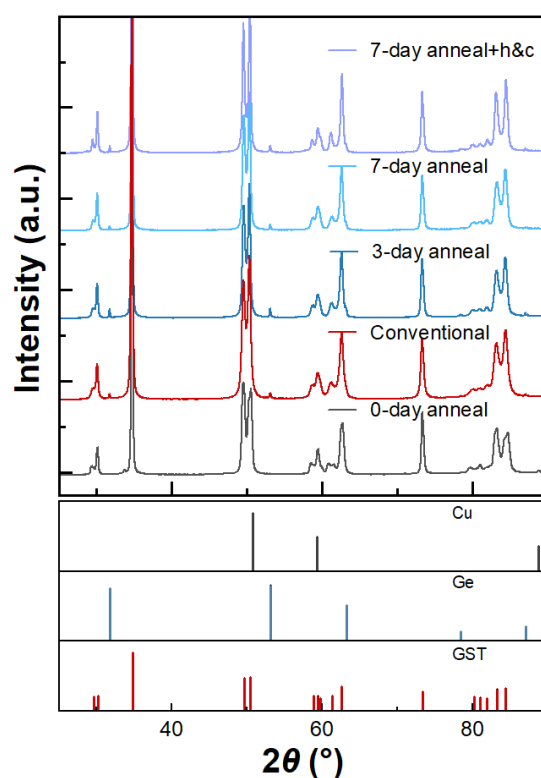


**Fig. R7 (Supplementary Fig. 2).** *Ex-situ* XRD analysis of the samples prepared by conventional and this work's methods.

**Comment 2.** The authors reported the predicted power density is  $3.43 \text{ W} \cdot \text{cm}^{-2}$  for a single-leg device under a temperature difference of 475 K and presented the  $V$ - $I$  characteristics curve. Could they explain how the experiments/predictions are performed?

**Author reply:** The  $V$ - $I$  characterises curve and the predicted power density presented in our work are obtained through theoretical modelling based on experimentally measured material properties.

Finite element simulations of the single-leg device are carried out using ANSYS Workbench platform. Both thermal and electrical contact resistances are considered, where the electrical contact resistivity at hot and cold sides is set to  $15 \mu\Omega \cdot \text{cm}$ , referencing the properties of solder material (tin-lead/60-40) from ANSYS materials database. The thermal contact resistivity at both sides is set to  $2.86 \text{ cm} \cdot \text{K/W}$ , corresponding to ceramic interfaces. All simulations are iterated until the convergence is achieved. The electrical conductivity and Seebeck coefficient are measured using ZEM-3 under helium atmosphere from room temperature to 773 K and fed in FEA simulations.

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 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,  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity,  $T$  is absolute temperature in kelvin, and  $V$  is the electric potential. All transport properties  $S$ ,  $\kappa$ , and  $\sigma$  are considered temperature-dependent.

Thermoelectric output power and conversion efficiency:

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

$$\eta = \frac{P}{Q_{\text{in}}}$$

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

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

- The influence of heat radiation is neglected near room temperature.
- Heat convection is included, with a fixed convection coefficient of  $15 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$  for air.
- A constant nominal value for both electrical and thermal contact resistance 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 nonlinear temperature dependence of thermoelectric properties of the leg is considered, while the properties of other materials remain constant.

**Comment 3.** The transport properties plotted in the graph reveal the ups and downs in two or more places. Is there any other possibility of thermal stability issues on these materials? More studies on thermal stability by DSC or any other suitable thermal analysis are suggested.

**Author reply:** The inflection points in the plot of transport properties are primarily due to the phase transition from rhombohedral to cubic phase that is commonly seen in GeTe system. Repeatability test is conducted by us during the revision for the GST+0.01Cu sample. The transport properties have been measured over heating and cooling cycles. The measurement uncertainties of  $ZT$  value lie within the equipment errors propagation.

We also performed a DSC analysis to further investigate the thermal stability of the materials. As can be seen in **Fig. R8**, pristine GST undergoes a phase transition at around 465 K, and the phase transition temperature decreases to around 435 K for GST+0.04Cu. Moreover, the DSC curves remain relatively stable to higher temperatures, indicating that the Cu-doped samples are thermally stable.

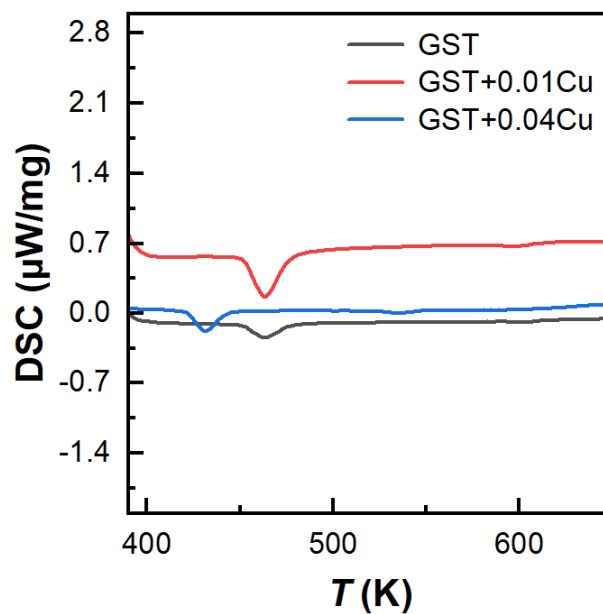


**Fig. R8.** Differential Scanning Calorimetry (DSC) analysis of GST+ $x$ Cu ( $x = 0, 0.01, 0.04$ ).

**Comment 4.** Microscopic analysis showed most of the morphology aligned with layered structure. Hence, is it possible to make directionality properties? Experimental evidences are needed here.

**Author reply:** To investigate the possibility of direction-dependent transport properties, we measured the thermoelectric properties along different directions. According to the results shown in **Fig. R9**, the

Seebeck coefficient, electrical conductivity, thermal conductivity, and the calculated  $ZT$  can be seen as identical along the direction perpendicular or parallel to the uniaxial pressure during SPS.

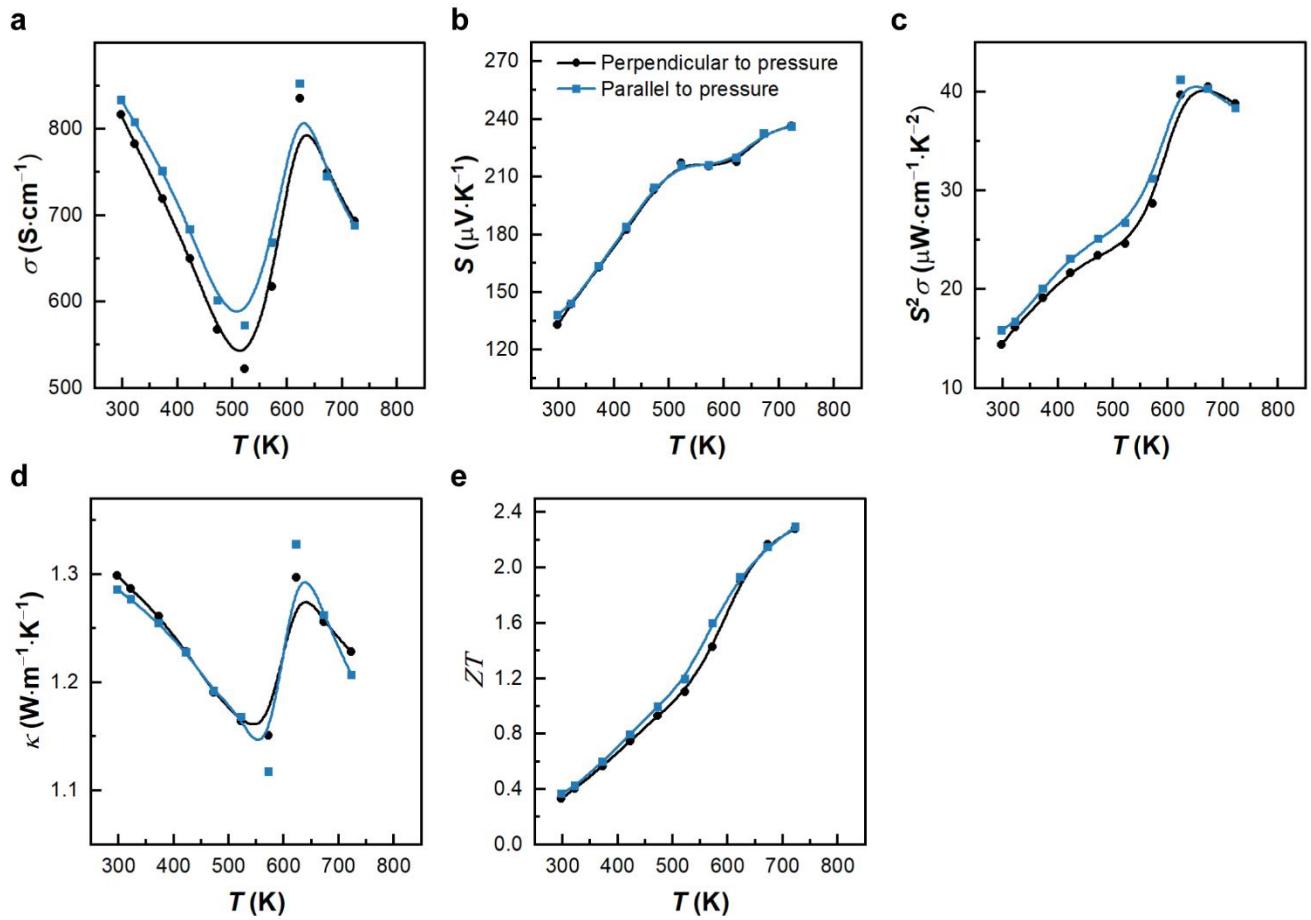


**Fig. R9.** Temperature-dependent thermoelectric performance along different direction.

**Comment 5.** Since a significant difference is reported between the high and average  $ZT$  values, measuring the thermoelectric properties measurements on heating and cooling cycles is better.

**Author reply:** We conducted thermoelectric properties measurement on heating and cooling cycles based on your suggestion, and the results are presented in **Fig. R10**. The number after heating/cooling indicates the processed cycle, for example, heating 1 indicates the first heating of the sample, heating 2 and cooling 2 indicate the second heating cooling subsequently. The results verify the stability of the samples synthesized in this work.

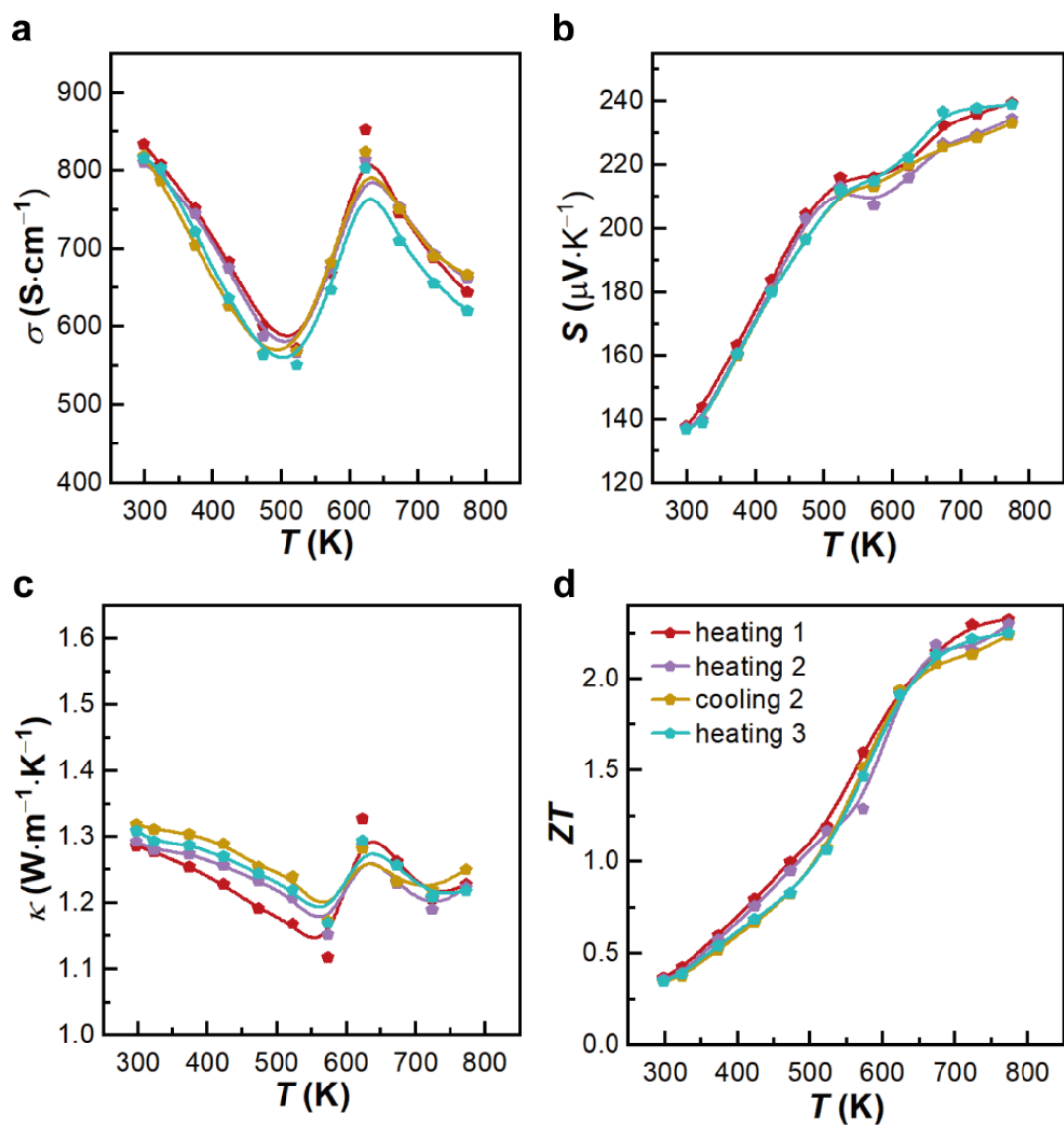


**Fig. R10 (Supplementary Fig. 20). Repeatability test for GST+0.01Cu sample.** (a) Electrical conductivity ( $\sigma$ ). (b) Seebeck coefficient ( $S$ ). (c) Thermal conductivity ( $\kappa$ ). (d) Figure-of-merit ( $ZT$ ).

## Reviewer #4 (Remarks to the Author):

### General comments:

(work summary) This work enhances the thermoelectric properties of GeSbTe by utilizing a non-eutectic structure. It proposes a Cu-induced lattice plainification method, where Cu annihilates Ge vacancies, to enhance the thermoelectric performance of GeTe-based materials. The authors suggest a traditional processing pathway similar to formation of solid solution state. Previously, the eutectic reaction led to the separation of GeSbTe and CuTe. However, in the newly proposed process, GeSbTe and Cu powders undergo heat treatment at 875 K for three days, enabling the formation of a solid solution. As a result, mobility increases while total thermal conductivity decreases. Consequently, the  $ZT$  value appears to be enhanced. Additionally, the authors theoretically estimate the single-leg power density.

(recommendation) I recommend it as publishable. Since this work addresses the importance of microstructure, which was not well understood before, it provides new insights into the role of a solid-solution phase in overcoming the low composite  $ZT$ . This process, here referred to as 'lattice plainification,' aligns with conventional homogenization or solid-solution treatment.

(comment overview) However, to further advance the understanding of thermoelectric materials, the following aspects should be addressed. For instance, the state of Cu and the role of Sb require further clarification. Additionally, the theoretical analysis should be presented more explicitly and supported with stronger evidence. Furthermore, I believe that "lattice plainification" is essentially a form of solid solution formation. Therefore, I strongly recommend using traditional terminology consistently throughout the manuscript.

Additionally, the structural stability of the "lattice plainificated" phase should be compared to that of the eutectic structure, as the former is likely to be metastable or unstable. A discussion on this aspect would help clarify its long-term stability and potential phase transformations.

**Author reply:** Thank you for your valuable feedback and for recognizing the significance of our work. In this revision, the state of Cu and the role of Sb have been further clarified. Moreover, we realised the term “lattice plainification” cannot reflect our observation correctly and might be misleading, and have revised throughout the manuscript. Our point-to-point responses to your detailed comments are included in the following.

**Comment 1.** The lattice plainification observed in Cu-doped GeSbTe appears to correspond to the formation of a solid solution rather than a phase-decomposed alloy. I believe that the Cu-doped system is metastable compared to the GeSbTe-CuTe eutectic system: stable at higher temperature, metastable or unstable at room temperature. This raises the question of whether heat treatment could induce phase separation or if increasing the Cu content would trigger this effect. Does a small amount of Cu play a crucial role in stabilizing the solid solution rather than merely facilitating homogenization?

- A. The terminology related to precipitation should be revised throughout the manuscript, as it appears to be used incorrectly. In alloy terminology, eutectic reactions and precipitation are distinct processes. Precipitation occurs when a supersaturated solid solution undergoes cooling, leading to the formation of secondary phases. In contrast, a eutectic reaction is a transformation in which a liquid phase solidifies into two distinct solid phases simultaneously at a specific composition and temperature. For instance, in Figure 1(c), the left side panel represents a two-phase system rather than a precipitation process. Precipitation can occur on the right side panel after cooling, when the supersaturated solid solution undergoes phase separation. i. "Lattice plainification" appears to be a recently introduced term. Instead, I suggest replacing it with "solution treatment," which aligns with established terminology.

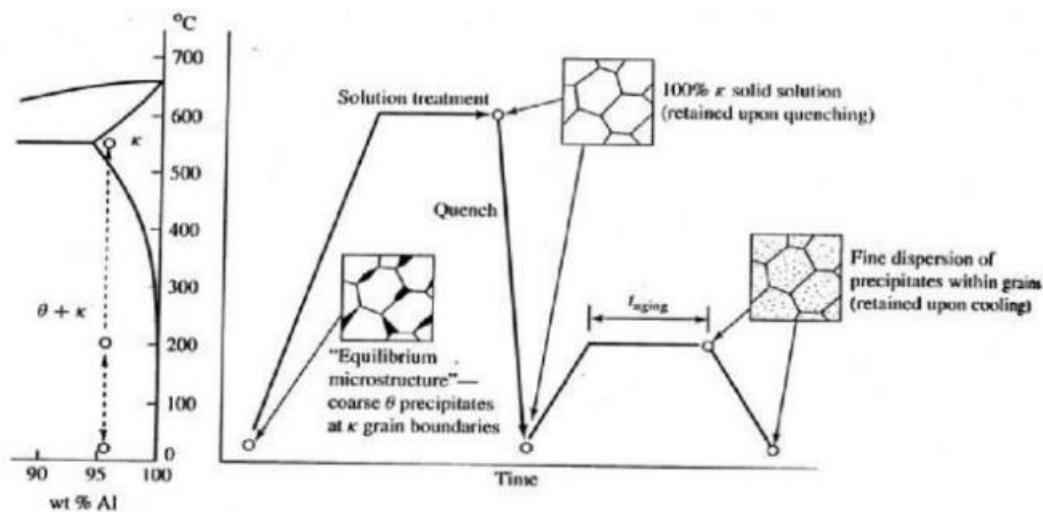


Figure 1 Regarding solution treatment and precipitates within grains. (<https://www.researchgate.net/publication/372675170/figure/fig3/AS:11431281177404390@1690466920745/Solution-heat-treatment-process-scheme.jpg>).

## Lamellar Eutectic Structure

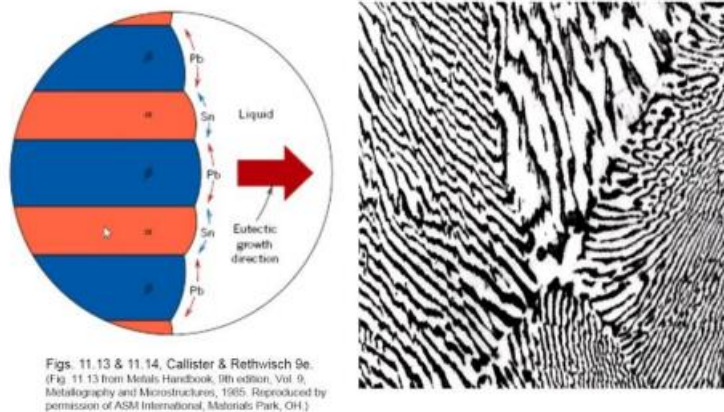


Figure 2 Eutectic structure example (<https://i.ytimg.com/vi/HreL8-uJBgg/maxresdefault.jpg>).

- B. Please compare the results of the GeSbTe-Cu process proposed by the authors with the previous process, particularly regarding the CuTe phase. In the new process, the CuTe phase disappears, whereas it remains in the previous one—this difference should be explicitly discussed using the authors' results (similar compositions used). Currently, the Cu content is small, so it seems plausible that Cu could still dissolve in the GeSbTe matrix using the previous method. However, the results presented in the manuscript indicate that, without following the proposed process, Cu tends to form a CuTe phase. This discrepancy should be further analyzed to clarify the underlying mechanisms.
- C. The stability of the solid solution should be evaluated across the working temperature range. In conventional alloys, after heat treatment, the alloy is typically used at room temperature. Even if the solid solution state is metastable, it can maintain its structure due to the high activation barrier at low temperatures. However, thermoelectric materials operate under thermal cycling conditions, which could induce phase transformations. This raises concerns that the solid solution state may undergo particle precipitation within grains or lead to particle formation at grain boundaries.
- D. The abstract mentions "high-entropy," but there are no corresponding results or discussions in the article. Please verify the occurrence of the word "entropy" in the manuscript. It appears only once in the abstract and is absent from the main text. If entropy is a key concept, relevant discussions should be included; otherwise, it should be removed from the abstract for consistency.

**Author reply:** Referring to your comments:

**To comment A:** We agree that the terminology should be revised throughout the manuscript. After reviewing relevant literature, we confirm that the secondary phase Ge in our system forms due to the eutectic reaction rather than precipitation. Based on **Fig. R11**, when the content of Te is < 50.5 at.%, the actual congruent melting reaction follows  $\text{Liq.} \rightarrow \text{Liq.} + \text{Ge (s)} \rightarrow \text{Ge (s)} + \text{c-GeTe (s)}$ . This suggests Ge phase forms from the liquid phase upon solidification, which is a characteristic of eutectic reaction rather than a solid-state precipitation process.

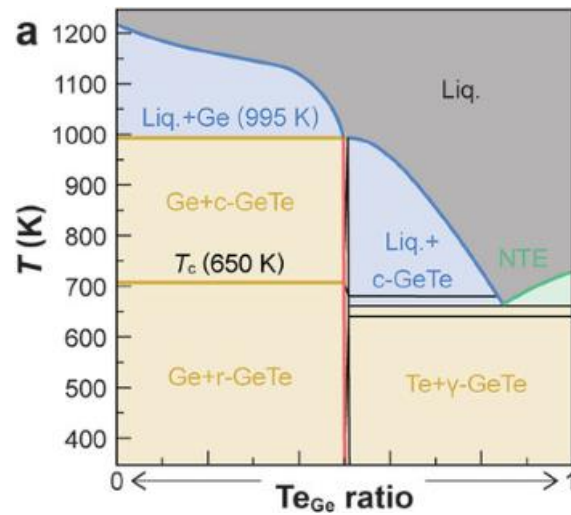


**Fig. R11.** Phase diagram of binary Ge-Te system.<sup>2</sup>

Regarding to “lattice plainification”, we have reconsidered our choice of terminology based on your suggestion. “Lattice plainification” it is a relatively new concept in this field first introduced by Liu et al., which refers to manipulating intrinsic defects and facilitating the carrier transport by incorporating a proper number of extrinsic atoms, leading to achieve the higher thermoelectric performance with plainer lattice.<sup>20</sup> You suggested that “solution treatment” may be a more appropriate term, as solution treatment is a well-established heat treatment method that is used to dissolve solute atoms into a metallic lattice and leading to changes in material properties and microstructure, by creating a solid solution phase through controlling heating and cooling. “Lattice plainification” in our work describes the phenomenon that resulted by the Cu doping, rather than a material treatment method. However, “lattice plainification” induces the improvement of carrier concentration, which is literately not match our observation. In this regard, we replaced the “lattice plainification” by “solid-state reaction” as a treatment process and “vacancy suppression” as a result for better clarification.

**To comment B:** In terms of your concern about the formation of the  $\text{Cu}_2\text{Te}$  phase in conventional synthesis, in conventional one-step synthesis, all constituent elements are stoichiometrically weighed, sealed in a quartz tube, and subjected to direct melting at 950–1000 °C for 12 hours, followed by quenching and annealing. In this process, *in-situ* XRD analysis reveals the formation of a copper

telluride phase at room temperature, which undergoes a phase transition upon heating and subsequently dissolves into the matrix above 580 °C. However, upon cooling,  $\text{Cu}_{2-x}\text{Te}$  tends to re-precipitate, indicating a reversible but persistent secondary phase formation. In contrast, our synthesis approach adopts a two-step strategy. First, the GST matrix is synthesized following the same high temperature melting and quenching procedure as the conventional method. After quenching, the appropriate amount of Cu is introduced into the matrix by thorough mechanical mixing using a mortar and pestle. The homogenized powder is then sealed in a quartz tube and subjected to annealing at 775 K for three days. This delayed Cu incorporation significantly alters the reaction pathway. Unlike the conventional process, we do not observe any copper telluride signal at room temperature. Instead, a weak Cu-rich phase appears around 650 K, disappears at ~800 K, and does not reappear after cooling, indicating that Cu is fully dissolved into the matrix and likely substitutes Ge sites. Moreover, Cu doping leads to increased Ge precipitation, as evidenced by the stronger Ge peak after cooling and confirmed by EDS analysis. The reason could be Cu tends to form  $\text{Cu}_{2-x}\text{Te}$  rather than filling or substituting cationic sites due to its formation energy being close to zero in conventional synthesis.<sup>21</sup> However, in our method, Te atoms are already bonded with cationic atoms (Ge/Sb), which increases the formation energy of  $\text{Cu}_2\text{Te}$ , making its formation thermodynamically unfavourable.

To further confirm that weak signal is not caused by the tiny amount of Cu, we fabricate GST+0.04Cu through the conventional melting-quenching-annealing process., XRD analysis is conducted to clarify the existence of  $\text{Cu}_2\text{Te}$  minority phase (see **Fig. R7**). A minor Cu-rich phase can be detected through pattern matching, supporting its existence.

**To comment C:** We understand the concern about the stability of the solid solution under the thermal cycling conditions. To address this concern, we conducted heating and cooling cycling test on our samples and measured their transport properties, and the results are shown in **Fig. R10**. The results indicated that the thermoelectric performance remains stable after loops of heating and cooling.

To further investigate the thermal stability, we performed ex-situ XRD analysis on the samples after annealing for 3 days, 7 days and 10 days (7 days annealing + 2 heating and cooling cycles for 3 days). As shown in **Fig. R7**, a weak Cu peak appears at around  $88^\circ$  for the 0-day annealed sample, which is because Cu is only mechanically mixed with the GST matrix at this stage. With increasing annealing time, the Cu peak disappears while Ge peaks emerge, and no significant peak shifts are detected. This suggests that Cu either substitutes for Ge or occupies Ge-related vacancies, without altering the overall crystal structure. No Cu or Cu-rich signals are detected in the sample prepared by the conventional method, which contrasts with the findings reported by Schwarzmüller et al.<sup>22</sup>

**To comment D:** The “high entropy” is the conventional strategy that thermoelectric researchers usually use to increase the figure-of-merit. For the sake of clarification, we have revised the abstract.

**Comment 2.** The number of Sb atoms is greater than that of Cu atoms, yet the discussion primarily focuses on Cu-induced defect plainification. This suggests that the authors should compare three different systems: GeTe, GeSbTe, GeSbTe-CuTe, and GeSbTe:Cu (doped).

- A. In Figure 4, the band structures are provided for GeTe and GeTe:Cu, whereas the material system under study is GeSbTe. As a result, these band structures may not be fully representative. What is the role of Sb in Cu substitutional doping? Cu is the fourth element in the system, and its impact should be evaluated in the presence of Sb. Additionally, the band structure calculations are based on a  $3\times3\times3$  supercell, which may introduce artifacts. Different supercell sizes can lead to variations in the computed band structure. Moreover, the Cu doping in the calculation is ordered due to the periodic boundary condition. However, in reality, it should be disordered. As a result, the supercell band structure may not provide an accurate estimation of the host material's effective mass. In this case, the Green's function method might be a more suitable approach.
- B. In Figure 1b, the negative formation energy suggests that GeTe is thermodynamically unstable, leading to the formation of a secondary phase. I understand that the formation energies are calculated with respect to the Cu elemental phase. However, when considering the Ge-Te-Cu phase diagram, intermetallic Ge-Te-Cu compounds exist. To accurately assess defect formation energies, the correct and reliable reference phases should be considered.
- C. Meanwhile, comparing Cu at the Ge site with Cu interstitial-Ge vacancy pairs, the latter appears to be more stable based on the computed formation energies. This implies that Cu is likely to become off-centered over time. Furthermore, an off-centered structure suggests that Cu at the Ge site is in a saddle point configuration or inherently unstable.

**Author reply:** Referring to your comments:

**To comment A:** Firstly, we find that the band structure in **Fig. 4** and the corresponding descriptions is mistakenly writing as Cu-doped GeTe. In fact, the band structure calculations are performed based on the Cu-doped C-Ge<sub>26</sub>Sb<sub>1</sub>Te<sub>27</sub>. We apologise for any confusion in the labelling and have corrected the figure annotations. To clarify it, we replace the band structure figures in **Fig. 4** in the manuscript by unfolded band structure for both cubic and rhombohedral phase for GST+Cu (Ge<sub>22</sub>Sb<sub>3</sub>Cu<sub>1</sub>Te<sub>27</sub>) in **Fig. R12**, and the GST for both phases are plotted in **Fig. R13**.

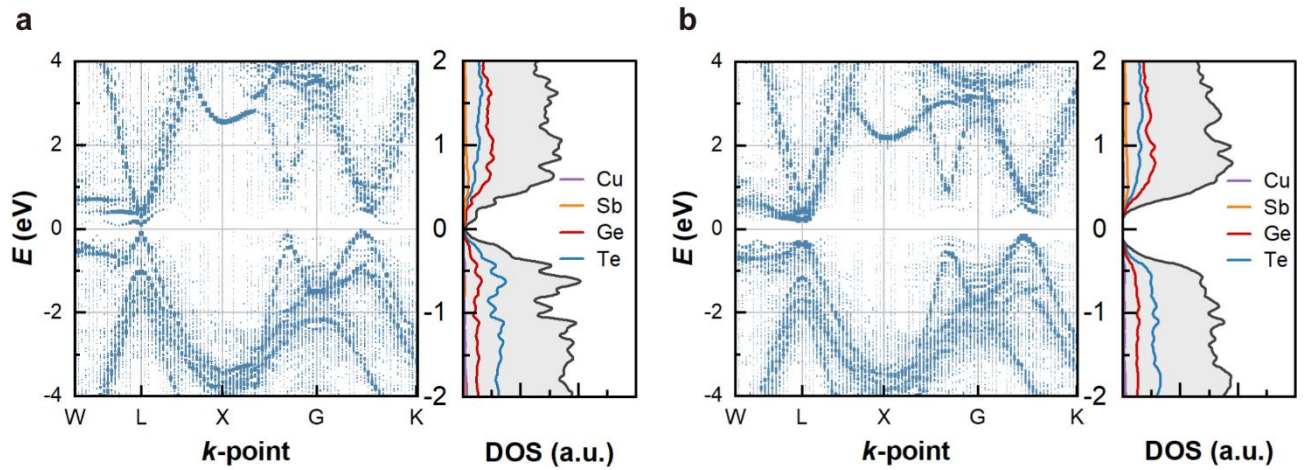


**Fig. R12 (manuscript Fig. 4g & h). Unfolded band structure of both cubic and rhombohedral phase for GST+Cu ( $\text{Ge}_{22}\text{Sb}_3\text{Cu}_1\text{Te}_{27}$ ). (a) C-GST+Cu. (b) R-GST+Cu.**

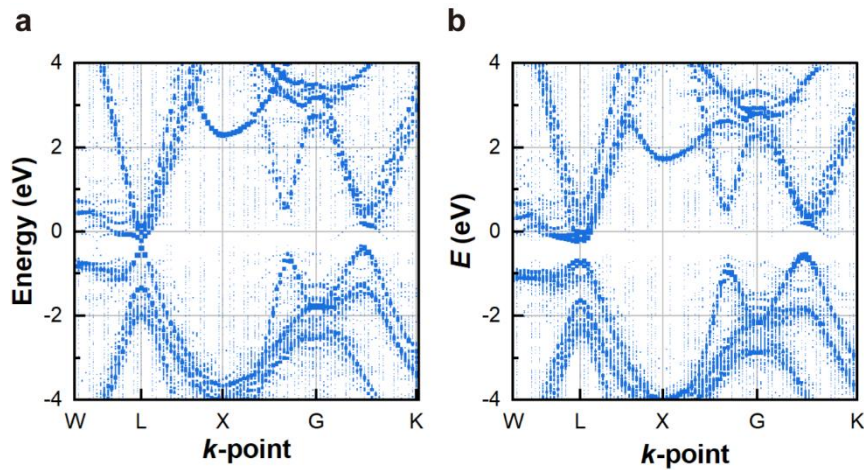


**Fig. R13 (Supplementary Fig. 17). Unfolded band structure. (a) C-GST, and (b) R-GST.**

We agree that the use of a  $3 \times 3 \times 3$  supercell may introduce artifacts due to the periodic arrangement of dopants and limited Brillouin zone sampling. In this revision, we conduct calculations on the unfolded band structures. The unfolded band structure allows us to recover the spectral weight in the primitive Brillouin zone and offers a more direct comparison with the electronic structure of the pristine host material.<sup>23</sup> This approach reduces the influence of artificial band folding and better represents the dispersion relations and effective mass characteristics, especially in the presence of disorder introduced by doping. The unfolded band structure confirms the qualitative trends observed previously, especially the band convergence, offering a clearer interpretation of Cu-induced band perturbation.

Moreover, we consider the suggestion regarding the limitations of ordered doping models in supercell-based DFT calculations due to periodic boundary conditions. To better capture the disordered nature of Cu doping and/or Sb alloying, we perform additional calculations using the Green's function method

in the spirit of the coherent potential approximation (CPA). This approach effectively simulates random substitutional disorder and provides complementary insights into the electronic structure of the system. As can be seen in **Fig. R14**, when the Fermi level is set at  $E = 0$  eV, Cu doping in both the cubic and rhombohedral phases results in a slight upward shift of the valence band maxima (VBM1, VBM2, and VBM3), indicating enhanced electrical conductivity. This band shift suggests that Cu incorporation facilitates improved carrier transport by increasing the carrier concentration and mobility. In addition, band convergence can be observed after doping. Band convergence is associated with an enhancement in the Seebeck coefficient in most cases, due to the increased DOS near the Fermi level. However, in this study, the impact on the Seebeck coefficient appears negligible, attributed to the trade-off between the Seebeck coefficient and electrical conductivity with the carrier transport.

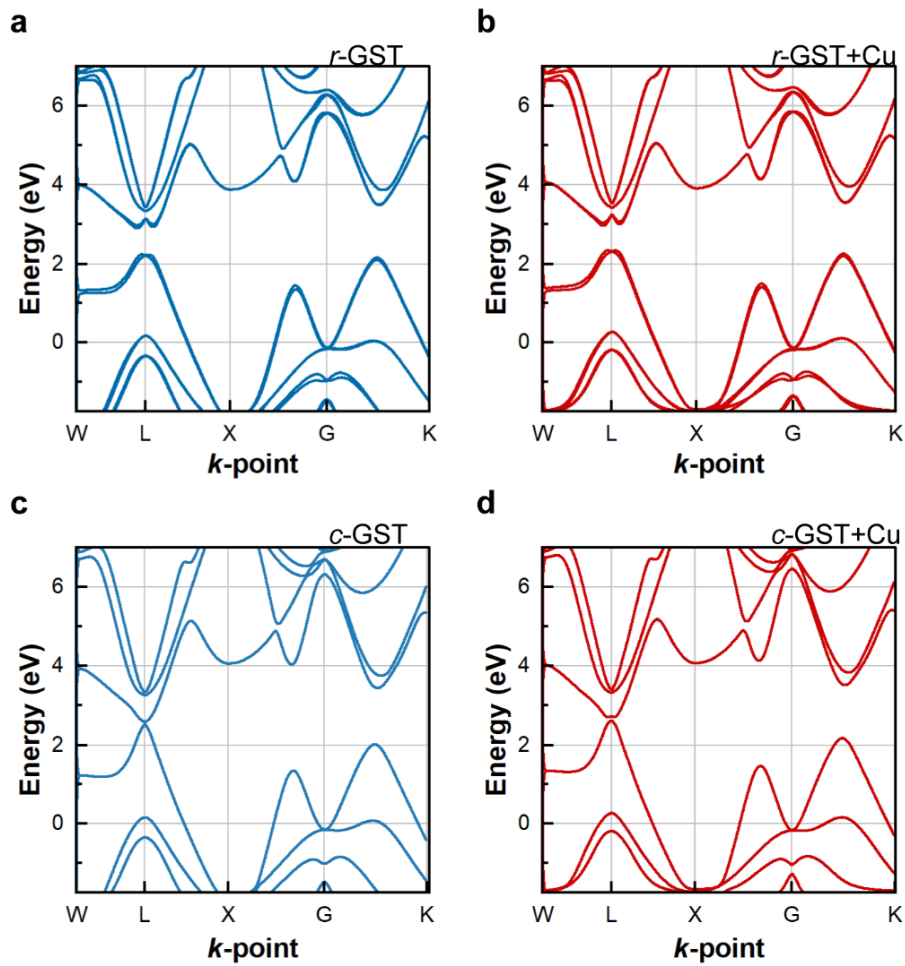


**Fig. R14 (Supplementary Fig. 19). Band structure using green's function.** (a) R-GST, (b) R-GST with Cu doping, (c) C-GST, and (d) C-GST with Cu doping.

**To Comment B:** The formation energy of vacancy is directly related to the chemical potential of the atom that is removed from the system. In our study, the relevant chemical potential is Ge since we only calculate the formation energy of Ge vacancy. For example, the Eqn. 2 in the manuscript describes,

one Ge atom is removed is simplified to “ $-\mu_{\text{Ge}}$ ”. The chemical potential of Ge under different phases and conditions, including  $R3m$  and  $Fm\bar{3}m$  under Ge-rich and Ge-poor environments. As shown in **Fig. R1**, Cu substitution can increase the formation energy of Ge vacancies, and cubic phase has relatively lower formation energy than rhombohedral phase.

**To Comment C:** The formation energy of point defects provides useful information for stability identification, but it is not always sufficient to explain the structural or phase stability. To ensure the accuracy of the calculation, we re-calculate the total energy of Cu at the Ge site and with Cu interstitial–Ge vacancy pairs; The lower energy of Cu at the Ge site appears to be energetically more favourable. Furthermore, the observation that Cu becomes off-centred does not necessarily indicate structural instability. It is well known that even Ge atoms in crystalline GeTe exhibit off-centring, a phenomenon termed “*emphanisis*”, which arises from the anharmonic lattice vibrations rather than a true instability.<sup>2</sup> The idea that Cu at the Ge site may represent a saddle point configuration is one possible explanation for *emphanisis*-like behaviour. To theoretically investigate this, we performed displacement-dependent energy calculations for both Ge and Cu in the  $3\times 3\times 3$  c-Ge<sub>27</sub>Te<sub>27</sub> supercell. In both cases, atoms are displaced along  $[1\ 1\ 1]$  direction, and the energy difference is tracked as a function of displacement.

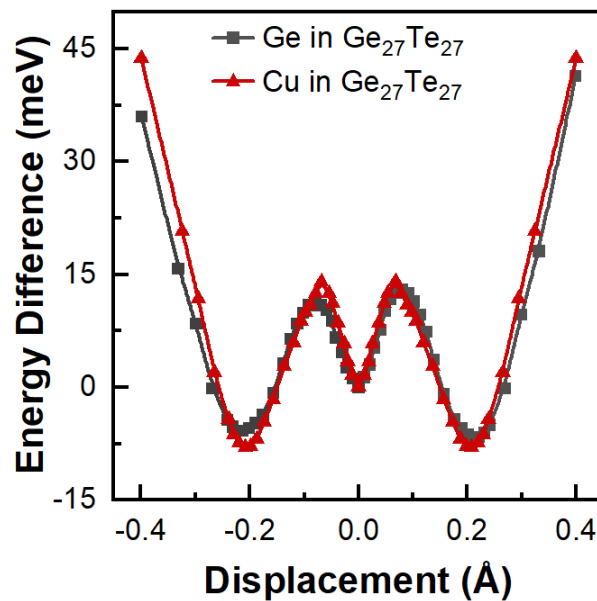


**Fig. R15.** Energy difference when Cu and Ge displace along  $[1\ 1\ 1]$  direction.

As shown in **Fig. R15**, we found that the centre-symmetric position does not correspond to the lowest energy but a local maximum or saddle point. Interestingly, the energy difference between the centred and off-centred configurations for Cu in GeTe is smaller than Ge, suggesting a shallower energy point and thus a suppression of the *emphanisis* effect in Cu-substituted systems. Although we are currently unable to perform high-temperature PDF measurements due to limited beamline availability, our room-

temperature PDF data indicate that the off-centre displacement of Cu is comparable with the undoped sample. It is also worth noting that traditional X-ray diffraction (XRD) techniques are not sufficient to explain emphasisis as they mainly used to investigate average over long-range order and insensitive to dynamic off-centring.

**Comment 3.** Phase transformation around 300°C: At this temperature, significant atomic diffusion is expected to occur. After phase transformation, Cu migration should be considered, as diffusion effects may relocate Cu to grain boundaries or interstitial sites.

Author reply: To investigate the occurrence of atomic diffusion such as Cu migration at around phase transformation temperature, we plot out the *in-situ* heating XRD pattern from 300 to 400°C in **Fig. R16**. It is important to note that XRD primarily detects atoms in periodic lattice positions. However, interstitial Cu does not occupy regular lattice sites periodically, which means cannot be verified by XRD measurements.

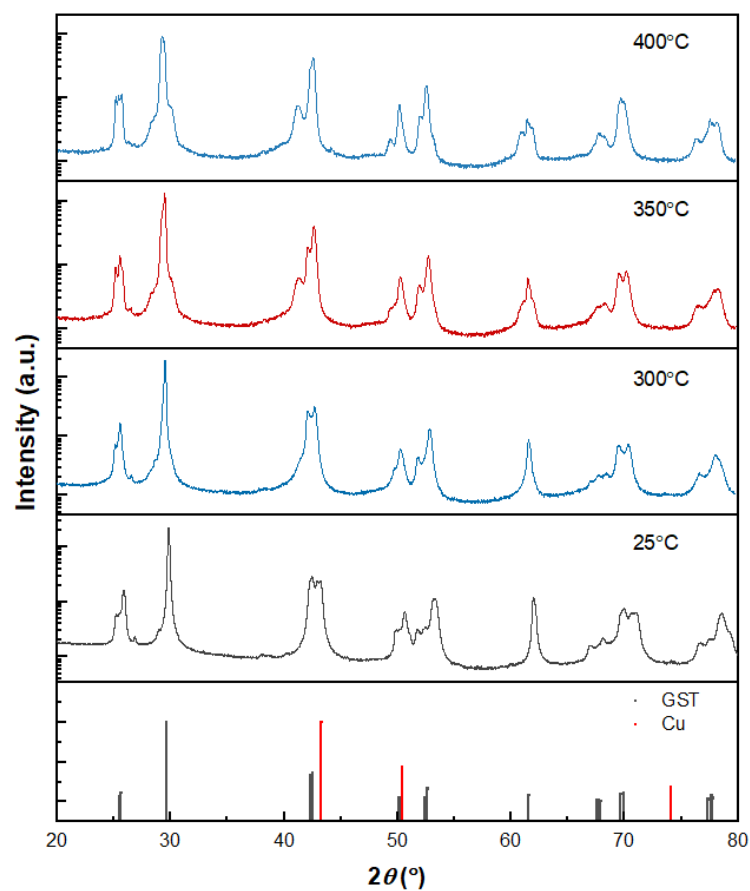


**Fig. R16.** XRD scanning at room temperature, 300°C, 350°C and 400°C.

To investigate the Cu aggregation at grain boundaries, a separate pure Cu phase in the XRD patterns is expected to appear. In our *in-situ* XRD measurements after heating to 300 °C, no Cu diffraction peak can be observed, suggesting that no significant Cu aggregation occurs at the grain boundaries. We also acknowledge that the doping level might be below the detection limit of laboratory XRD, or that any pure Cu phase could be overlapping with the main phase peaks. Trying best to exclude this possibility, we synthesised additional samples with higher Cu doping concentrations and conducted ex-situ XRD measurements under various heat treatment conditions (different annealing durations and heating cycles). The results further support the conclusion that significant Cu segregation is not present under the studied conditions.

**Comment 4.** Cu state:

- A. In Equation (2), the sign of the chemical potential summation should be negative to be consistent with standard conventions.
- B. Given its small atomic size, Cu may become off-centered. Is this observed in the structural analysis? It is also related to Figure 1b and my comment of 2C.
- C. Is there an interaction between Cu and Sb, similar to the Ag-Sb interaction in LAST (Pb-Ag-Sb-Te)? This should be discussed.
- D. Figure 4c. Charge density change alone cannot provide sufficient insight. In this point of view, interstitial Cu is also less affecting structure. It is better to examine the charge density changes by Ge-vacancy or by Cu at Ge site.

**Author reply: To comment A:** We have corrected the Equation (2) in the revised manuscript as:

$$\Delta H(D, \mu) = E_d - E_h - \sum n_i \mu_i + E_c$$

**To comment B:** We would like to clarify that the ionic radius of Cu<sup>2+</sup> is comparable to that of Ge<sup>2+</sup>, suggesting that Cu substitution at the Ge site is unlikely to introduce significant local strain or deteriorate the electrical properties. It is also worth noting that Ge atoms in this are inherently off-centred due to strong anharmonic lattice dynamics and mixed ferroelectric states, a phenomenon often referred to as “*emphanisis*”.<sup>2,24</sup> Regarding structural analysis, off-centring is not easily detectable by conventional X-ray diffraction (XRD) due to its averaged nature over long-range order. However, pair distribution function (PDF) analysis is sensitive to local structural distortions. In our room temperature PDF results, we do not observe significant off-centring compared with the pristine sample, suggesting that Cu substitution is less likely to cause extra deviation from the centre. As we discussed in the

response of your comment 2C, the observed off-centring of Ge atoms in GeTe-based structures arises from intrinsic anharmonic vibrations and does not imply a thermodynamic instability.<sup>24</sup>

**To comment C:** We explored the possibility of Cu–Sb interaction using electron localization function (ELF) calculations based on a face-centred cubic (FCC) supercell to make the comparison between GST and LAST valid. In this analysis, we specifically placed a Cu–Sb atomic pair to probe potential bonding characteristics. A higher plane-wave cutoff energy of 650 eV was employed, and DFT+U corrections were not applied to maintain consistency with the parameters used in our main calculations.

In the LAST ( $\text{AgPb}_m\text{SbTe}_{2+m}$ ) system, Ag and Sb atoms exhibit a strong enthalpic driving force to form ordered substructures such as  $\text{AgSbTe}_2$  nanoclusters within the  $\text{PbTe}$  matrix. These Ag–Sb substructures lead to resonant states near the valence and conduction bands, thereby enhancing the thermoelectric performance by increasing the DOS near the Fermi level and facilitating energy filtering effects.<sup>25</sup> This behaviour is not surprising given that  $\text{Ag}^+$  and  $\text{Sb}^{3+}$  tend to avoid random dispersion due to Coulombic instability, resulting in a lowering of crystallographic symmetry and long-range ordering.<sup>26</sup>

To investigate the interaction between Cu-Sb and Ag-Sb, electron localisation function (ELF) is conducted and shown in **Fig. R17**.

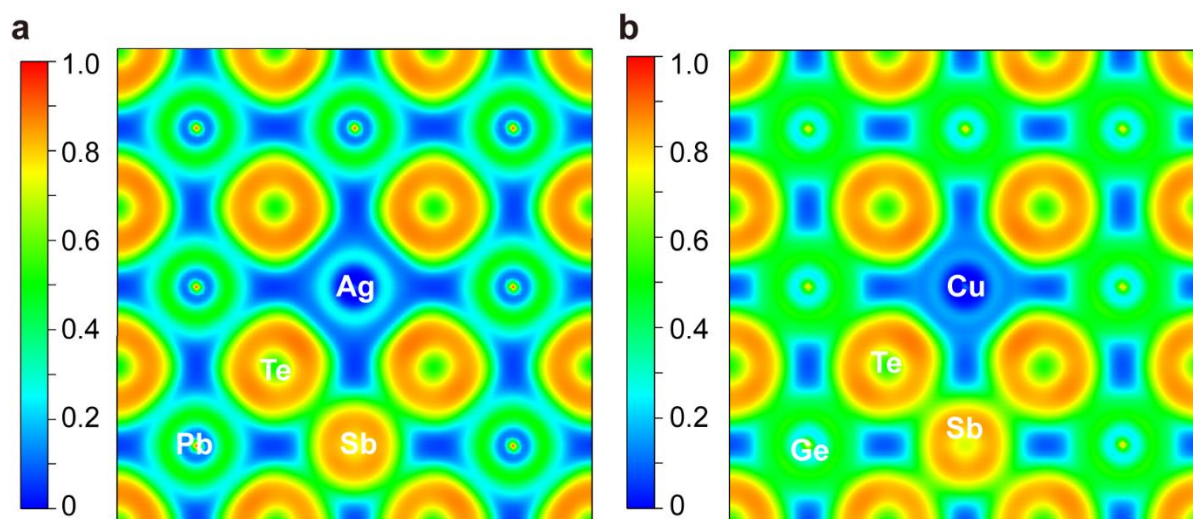


**Fig. R17 (Supplementary Fig. 16). Electron localisation function (ELF) map. (a) LAST system. (b) GST+Cu.**

However, in both systems, the ELF analysis results show no distinct bonding features or charge localisation between Cu and Sb, indicating a much weaker interaction that is unlikely to contribute

similarly to the electronic or thermoelectric properties. These results and a more detailed discussion have been included in the Supporting Information.

**To comment D:** We calculated differential charge density of Ge-vacancy and Cu at Ge site, and for both rhombohedral and cubic GeTe. As we can see in the **Fig. R18**, in both phases, the Ge-vacancy results in weak and diffuse charge distribution, indicating minimal localisation and weak bonding. In contrast, the Cu substitution leads to a strong and localised charge around the Cu atom, suggesting the Cu atom forms stronger bonds with neighbouring atoms. It is worth to note that the Ge-vacancy in rhombohedral phase induces slightly more intense and asymmetric charge redistribution compared to the cubic counterpart, reflecting the enhanced sensitivity of the lower-symmetry structure to local distortions. In addition, the Cu substitution in rhombohedral phase exhibits the highest charge localization among all configurations, indicating strong hybridization between Cu and surrounding Te atoms.

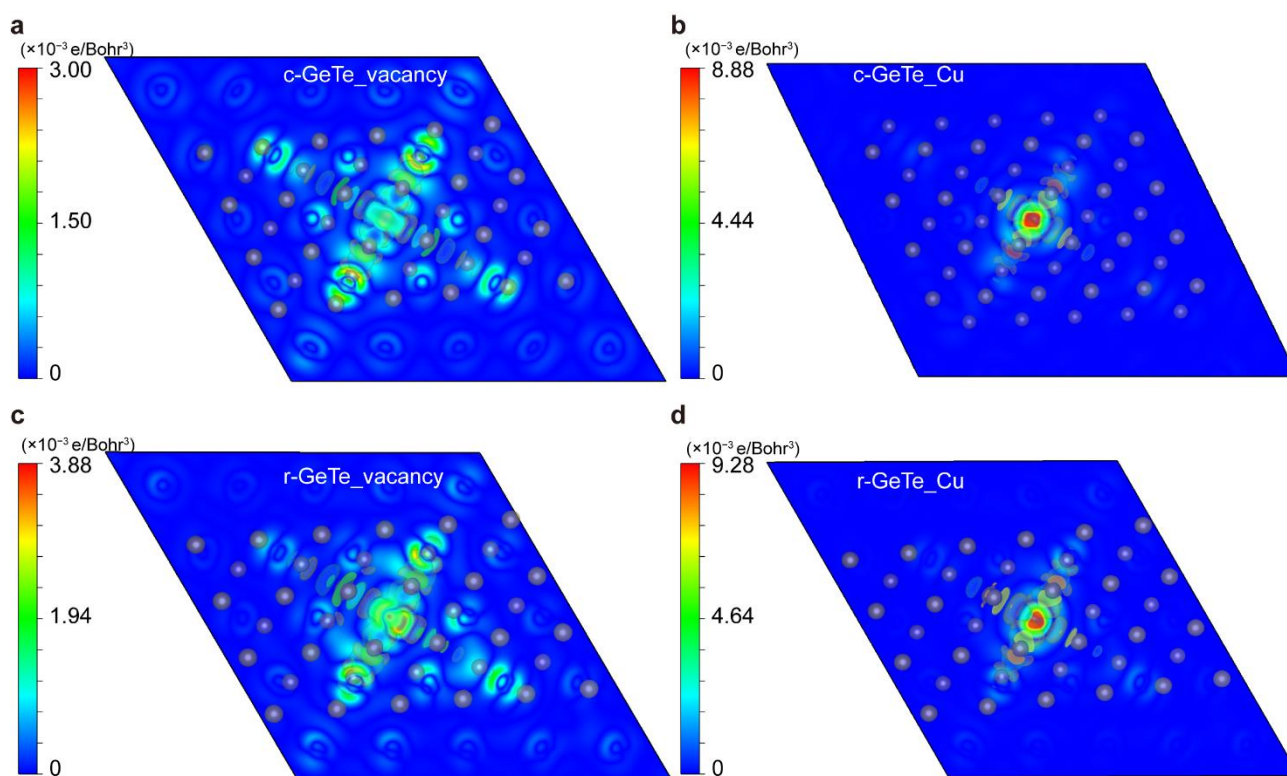


**Fig. R18 (Supplementary Fig. 15). Differential charge density.** (a) Vacancy at Ge site for cubic phase, (b) Cu at Ge site for cubic phase, (c) vacancy at Ge site for rhombohedral phase, and (d) Cu at Ge site for rhombohedral phase.

**Comment 5.** Power performance from FEM calculations

- A. SM Figure 15. The power output is given by  $P=IV$ , meaning that a good voltage (V) fit should lead to an accurate power fit. However, why do the data points (dots) and fitted lines not match? Please clarify this discrepancy.
- B. The single-leg performance is estimated based on numerical calculations for the given structures. However, these results remain theoretical. Experimental measurements are needed to validate the findings.
- C. The manuscript lacks a detailed description of the parameters required for reproducibility. Please specify calculation settings in the SM, including solder, electrode layer, diffusion barrier, leg dimensions, boundary conditions, and heat loss mechanisms such as convection or radiation. Providing transparent data will enhance reproducibility.

**Author reply: To comment A:** This is mainly due to the plotting mistake, that we used “B-spline” line style for the plots. We have included the corrected plots using “Spline” line style in our revised manuscript.

**To comment B:** We fabricated a single-leg device based on your suggestion, and the performance are shown in the **Fig. R6**. As can be seen, the measured performance closely follows the theoretical trends. The maximum efficiency is approximately 8% under a temperature difference of 475 K. The discrepancy between the experimental and theoretical curves maybe attributed to contact resistance and heat loss due to thermal radiation.

**To comment C:** Our simulation was conducted based on the following assumptions and **Table R2**:

- Heat radiation is neglected.
- Heat convection is included, with a fixed convection coefficient of  $15 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$  for air.
- A constant nominal value for both electrical and thermal contact resistance is applied at all interfaces, including the leg/solder interface, with no temperature dependence.
- Heat sinks are not explicitly modelled; their effect is incorporated through thermal boundary conditions.
- Nonlinear temperature dependence of thermoelectric properties is fully considered, based on experimental measurements.
- Electrodes are composed of 60/40 lead-tin solder, and the ceramic substrate material is  $\text{Al}_2\text{O}_3$ . The corresponding electrical and thermal properties are sourced from the ANSYS material library.
- The size of the leg and the subtract are shown in in Table. R2.

**Table R2 (Supplementary Table 2).** The dimensions of the TE leg and ceramics.

|          | LENGTH (MM) | WIDTH (MM) | HEIGHT (MM) |
|----------|-------------|------------|-------------|
| TE LEGS  | 2           | 2          | 6.5         |
| CERAMICS | 4           | 4          | 0.2         |

**Comment 6.** In SM,

- A. On page 2 of the SM, the phrase "band structure of the orthorhombic phase" should be revised to "band structure of the rhombohedral phase" if applicable. Please verify and correct accordingly.
- B. Explicitly state "includes spin-orbit interaction" rather than implying it indirectly.

**Author reply: To comment A:** We have revised the phrase based on your suggestion and updated to our newest supplementary material.

**To comment B:** We have updated the methodology of DFT calculations as:

“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). The generalized gradient approximation (GGA) with the fully relativistic Perdew-Burke-Ernzerhof (PBE) functional was employed to treat the exchange correlations. 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  $1 \times 10^{-3}$  eV·Å<sup>-1</sup>. The convergence criterion and the Monkhorst-Pack **k**-mesh adopted for ionic relaxation are  $1 \times 10^{-7}$  eV per electron and 0.03 per Å<sup>3</sup>, respectively. A denser 0.02 Å<sup>-3</sup> 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. Spin-orbital coupling (SOC) was considered because Te is a heavy element.”

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**Reviewer #1 (Remarks to the Author):**

In my opinion, the authors have adequately addressed all the comments raised by the reviewers. I thank them for their efforts and the work they have done.

**Author Reply:** We sincerely thank you for the rigorous review and recommendations.

## Reviewer #2 (Remarks to the Author):

Authors are addressed all comments well, and now the revised manuscript has more clarity than earlier.

Manuscript can be accepted, if all reviewers agree about their comments.

**Author Reply:** We appreciate your kind comments and positive feedback.

## Minor comments:

In Fig 1(d), authors are summarized their data with literature and cited them author names. I think, references numbers should also provided for readers flexibility.

**Author Reply:** As per your suggested, we have provided the reference numbers in the updated **Fig. 1d** for readability, as shown in **Fig. R1**.

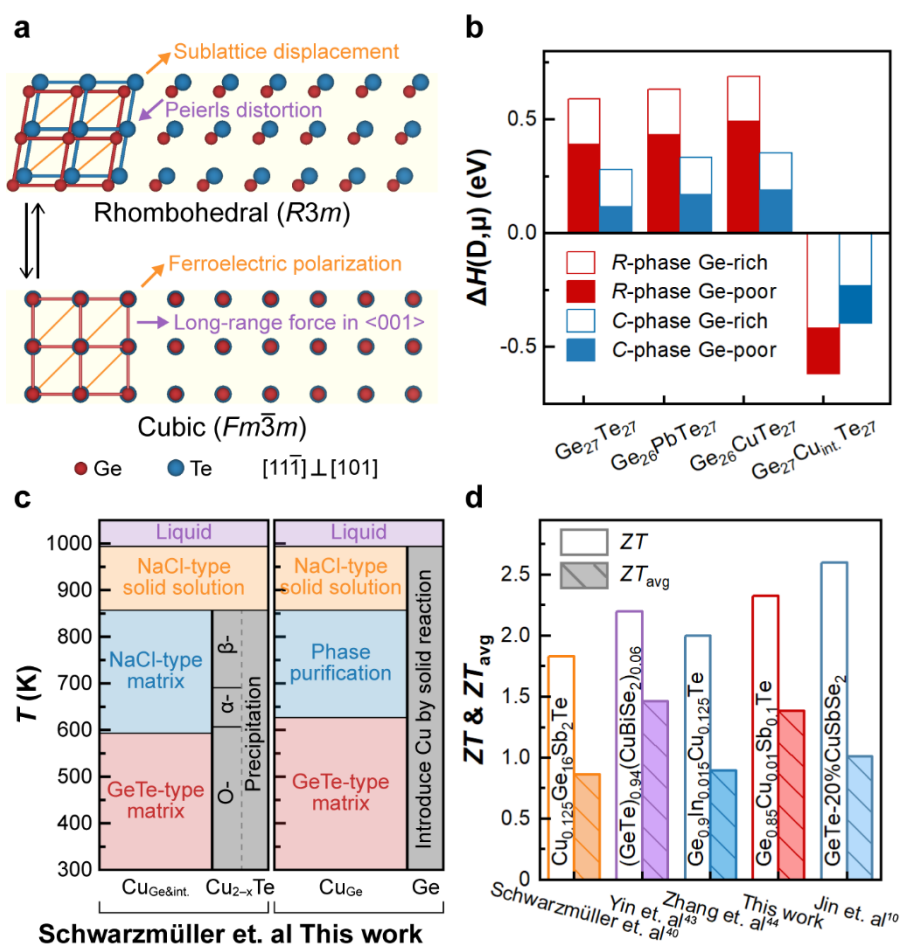


**Fig. R1. Scope and background.** (a) Schematic diagram of the reversible phase transformation between rhombohedral (R-) and cubic (C-) GeTe. (b) Point defect

formation energy of a Ge vacancy in a  $\text{Ge}_{27}\text{Te}_{27}$  supercell doped with various elements in both Ge-rich and Ge-poor conditions. (c) Comparison of the proposed temperature-dependent phase evolution between Ref. 40 and this work, where O-,  $\alpha$ -, and  $\beta$ - indicate orthorhombic, hexagonal, and cubic structure. (d) Comparison of  $ZT$  and average  $ZT_{\text{avg}}$  between literature and this work.

**Reviewer #3 (Remarks to the Author):**

The authors have answered and incorporated the raised queries in the manuscript. Hence, I recommend the revised manuscript for the publication.

**Author Reply:** We sincerely thank you for the rigorous review and recommendations.

#### **Reviewer #4 (Remarks to the Author):**

Thank you for the detailed reply to my previous comments.

However, before publication, I kindly request the authors to revise the following technical points to ensure clarity, correctness, and reproducibility:

**Author Reply:** We are grateful for your rigorous review and constructive comments. We have addressed your comments and the responses are in the following.

#### **Main Manuscript:**

Line 76: The statement "Pb doping raises the chemical potential..." is incorrect. It should read "Pb doping decreases the chemical potential..."

Line 262: Correct "von der Pauw method" to "van der Pauw method".

Line 342: The phrase "maximum output power density reaches 3.43 W/cm<sup>2</sup> with ~12%" should be revised to explicitly state that this is a theoretical, predicted, or calculated value. Without this clarification, experimentalists may misinterpret it as an empirical result. Additionally, the efficiency “~12%” is too imprecise—please provide at least one more significant digit (e.g., 12.3% or 11.6%).

#### **Author Reply:**

Line 76: We have modified the related statement, so it is now consistent with the previously corrected equation of point defect formation energy.

*“Pb doping decrease the average chemical potential ( $\mu$ ) at cation sites, making Ge vacancies formation less favourable, while counter doping induces donor-like effects to optimize  $n_h$ ”*

Line 262: We have corrected the typo.

*“we used van der Pauw method to measure...”*

Line 342: We have made the following updates for clarification.

*“Accordingly, the predicted maximum output power density reaches 3.43 W/cm<sup>2</sup> with 11.82% conversion efficiency ( $\eta$ ).”*

*“When  $\Delta T = 475K$ , the  $P_{max}$  reaches  $\sim 100\text{ mW}$ , the maximum power output approaches  $2.23\text{ W}\cdot\text{cm}^{-2}$  with  $\eta_{max}$  achieves 8.17% for the experimental results.”*

### **Supporting Information (SI):**

Page 2 – First-principles Calculations: When using the VASP code, please explicitly state the type of pseudopotentials (POTCAR files) employed. This is crucial for thermoelectric materials, which often have large lattice constants and are sensitive to the choice of pseudopotentials. Also include the relaxed lattice parameters used for the simulation.

Page 23 – FEA Analysis: Please include detailed information about the material properties used in the FEA simulation, such as Seebeck coefficient, electrical and thermal conductivity. Additionally, clarify the interfacial/contact electrical and thermal resistances applied in the model. In particular, the thermal conductivity of the ceramic substrate should be explicitly stated.

Clarification Regarding Contact Resistivity (Reviewer 3 – Comment 2):

In the reply to Reviewer #3 (Comment 2), it is stated that:

“The electrical contact resistivity at hot and cold sides is set to  $15\text{ }\mu\Omega\cdot\text{cm}$ , referencing the properties of solder material (tin-lead/60–40) from ANSYS materials database.”

This is physically incorrect.

- Contact resistivity (also called specific contact resistance) must have the unit of  $\Omega\cdot\text{m}^2$ , not  $\Omega\cdot\text{m}$  or  $\Omega\cdot\text{cm}$ .
- It is a property of an interface, not a bulk material, and thus cannot be derived from the bulk resistivity of Pb-Sn solder. Rather it requires a combination to define a specific interface.
- Therefore, referencing a value from the bulk material database as contact resistivity is conceptually flawed and must be corrected.

I strongly and kindly request that the authors provide:

- A clear, transparent, and physically valid justification or reference for the chosen value of electrical contact resistivity.
- All related calculation settings used in the FEA simulation (e.g., interfacial resistances, boundary conditions, layer structure) must be explicitly described in either the main text or SI to ensure reproducibility and scientific validity.

#### Author reply:

We admire your rigorous comments and agree that all details should be provided to ensure the reproducibility and scientific validity. In this revised Supporting information, we have made following clarifications:

In terms of the first-principles calculations, the pseudopotentials that we employed are: Ge ([Ar] 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>2</sup>), Sb ([Kr] 4d<sup>10</sup> 5s<sup>2</sup> 5p<sup>3</sup>), Te ([Kr] 4d<sup>10</sup> 5s<sup>2</sup> 5p<sup>4</sup>), and Cu ([Ar] 3d<sup>10</sup>4s<sup>1</sup>). The lattice parameters after ionic relaxation can be referred to **Table R1**.

**Table R1 (Supplementary Table 2).** Relaxed lattice parameters referenced to a primitive unit cell.

|                                                                     | $a = b = c$ (Å) | $\alpha = \beta = \gamma$ (°) |
|---------------------------------------------------------------------|-----------------|-------------------------------|
| <b>C-Ge<sub>23</sub>Sb<sub>3</sub>Te<sub>27</sub></b>               |                 | 60                            |
| <b>R-Ge<sub>23</sub>Sb<sub>3</sub>Te<sub>27</sub></b>               | 4.25730         | 59.1989                       |
| <b>C-Ge<sub>22</sub>Sb<sub>3</sub>Cu<sub>1</sub>Te<sub>27</sub></b> | 4.23907         | 60                            |
| <b>R-Ge<sub>22</sub>Sb<sub>3</sub>Cu<sub>1</sub>Te<sub>27</sub></b> | 4.26710         | 58.9484                       |

According to the FEA simulation, we have corrected and clarified the contact resistance in revised Supporting Information. For the material properties used in our simulations, experimental data are adopted, as summarised in **Table R2**. Additionally, the properties of other constituent materials in the module, such as ceramics and solder, are provided in **Table R3**.

**Table R2 (Supplementary Table 3).** The thermoelectric properties of materials in the simulation.

| Temperature (K) | Thermal Conductivity (W m <sup>-1</sup> K <sup>-1</sup> ) | Conductivity (S cm <sup>-1</sup> ) | Seebeck coefficient (μV K <sup>-1</sup> ) |
|-----------------|-----------------------------------------------------------|------------------------------------|-------------------------------------------|
| 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 |

**Table R3 (Supplementary Table 5).** The physical properties of constituent materials of the simulated thermoelectric module.

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

Regarding aluminium oxide (ceramic), it 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 device's thermal performance. 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).<sup>1,2</sup> This close alignment reduces or effectively eliminates the Schottky barrier height at the Ni/GeTe interface, enabling efficient hole injection and minimizing contact resistance.<sup>3</sup> 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.<sup>4</sup>

Constructed thermoelectric module in FEA simulation consists of five layers; detailed layer information is provided in **Table R4**. The contact resistivity between Ni and GeTe is  $1 \times 10^{-6} \Omega \cdot \text{cm}^2$ , from previous study.<sup>4</sup>

**Table R4 (Supplementary Table 4).** The layers and dimensions in the FEA model.

| Layers        | Materials                 | Dimensions (mm)         |
|---------------|---------------------------|-------------------------|
| Top substrate | Aluminium Oxide (ceramic) | $4 \times 4 \times 0.2$ |

|                         |                           |                          |
|-------------------------|---------------------------|--------------------------|
| <b>Top electrode</b>    | Ni                        | $2 \times 2 \times 0.12$ |
| <b>TE leg</b>           | p-type GeTe               | $6.5 \times 2 \times 2$  |
| <b>Bottom electrode</b> | Ni                        | $2 \times 2 \times 0.12$ |
| <b>Bottom substrate</b> | Aluminium Oxide (ceramic) | $4 \times 4 \times 0.2$  |

Regarding boundary conditions:

- 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.

For the electrical boundary conditions:

- 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.

## Reference

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