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Peer Review File

Approaching crystal's limit of thermoelectrics by nano-sintering-aid at grain boundaries

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Grain boundary significantly affects the physical and chemical properties of solid materials. In this manuscript (NCOMMS-24-26924), Lei et al. reported that the introduction of Mg2Cu nano-sintering-aid into Mg3(Bi, Sb)2-based materials helped to enlarge the grain size effectively, which contributed to remarkable thermoelectric performance in polycrystallines that can be comparable to single crystals. An exciting module performance for power generation was achieved as well, as a strong demonstration for further applications. In principle, the topic is interesting with ultrahigh performance, and the experiments are well executed and analyzed, however, I have issues with the interpretation.

1. The motivation for using Mg2Cu for nano-sintering-aid is not so clear, at least it may question how these authors think about this specific Mg2Cu phase.
2. What is the significance of nano Mg2Cu? Is it appropriate to use the micro Mg2Cu or just Mg2Cu ingot?
3. Why excessive nano-sintering-aid Mg2Cu is ineffective for promoting grain size growth? In general, the grain size should not change too much if the addition content is saturated.
4. How does this Mg2Cu thin or thick layer affect the barrier height or carrier transport? Or there is no observable effect??
5. 'The contact resistivity ρc at the n-type/Fe junction is only 4.5 μΩ cm2 (Fig. 4b), significantly lower than the reported ρc in literatures' How about compared to the recent work of Fe foil as the contact layer for n-type Mg3Sb2?
6. The height of the module element does significantly affect the conversion efficiency, so it is recommended to mention this critical point in the context when compared to previous literature results.
7. Some typo: diffuson limit

Reviewer #2 (Remarks to the Author):

Mg3(Bi,Sb)2 material is one of most important n-type thermoelectric materials and a the potential alternative to bismuth telluride. Its performance has been improved rapidly as our understanding of its transport mechanism has increased. Recent studies have shown that the low temperature electrical transport properties of Mg3(Bi,Sb)2 are heavily influenced by the structure and composition of the grain boundary. In this work, the anthers synthesized high quality Mg3(Bi,Sb)2 material through a melting reaction in a sealed Ta tube. The grain boundary density was further reduced by introducing Mg2Cu as the nano-sintering-aid, leading to significantly increased low temperature mobility and enhanced thermoelectric performance. A reduced potential barrier was also observed by fitting the grain sizes dependent mobility and a high conversion efficiency of 7.4% is obtained under temperature difference of 207 K. However, the following comments need to be addressed before publication:

1. The lattice thermal conductivity of sample prepared by ball-milling, which has smaller grain size, is remarkable lower than that of the sample synthesized by melting. Please provide an explanation and discussion for this observation.

2. Mg2Cu is essentially a metal and, given its high electrical conductivity, it should also

possess high thermal conductivity. It is hard for me to expect a metal phase with high thermal conductivity to reduce the lattice thermal conductivity so effectively.

3. The statement “the modified GBs and Mg2Cu nanoprecipitates, directly observed in Fig. 2, play a vital role in suppressing the heat-carrying phonon propagation” requires detailed discussion. The enlarged grain size is the main observation. What other specific modifications to the GBs are believed to suppress phonon propagation in this work?

4. Please discuss the reason for the reduced potential barrier. Based on Fig.3c, the impact of Mg2Cu on the potential barrier appears negligible.

5. Please provide the relative density of the sample, as the pores are observed in Fig. 2b.

6. The material with a potential barrier height of 170 meV should have the composition Mg3Bi1.5Sb0.5, as mentioned in reference 22.

Reviewer #3 (Remarks to the Author):

This work demonstrates outstanding figure of merit (ZT=1.5 at 500K) of Mg3(Bi,Sb)2 based materials. They also fabricated thermoelectric module of Mg3(Bi,Sb)2/(Bi,Sb)Te3 exhibiting high conversion efficiency of 7.4% under dT=2.7K. The performance was achieved by enlarging the average grain size to 23.7 um. A novel process of liquid-phase sintering was provided. Indeed, the presented process is new and obtained performance is high. However, I cannot find a remarkable progress to justify publishing this manuscript in Nature Communications. The effectivity of enlarging grain size was already reported by [Kanno et al., APL 112 (2018) 033903]. The grain size over 30 um with similar high ZT value was reported by [Wood et al., Adv. Mater. 31 (2019) 1902337]. I feel unfair that authors did not refer those relevant papers.
Further, the efficiency of module is approximately similar as previous reports. Only a slight improve might be but can be within error bars. To claim this small improvement, author must show the accuracy of their measurement, which is lack in the manuscript. No details were described about the equipment of evaluating power generation performance of module except that a home-made test system was used. In addition, there is no data about heat current.
The conclusion that Mg2Cu nanoprecipitates can lead to low lattice thermal conductivity is also not clear. The KL was extracted by subtracting the contribution of carriers and bipolar effect from k. But there is no description of how to calculate the contribution of carriers (Ke). Supposing that they were using Wiedemann−Franz law, how they can estimate the effect of grain boundary scattering on Ke? It is sure that thermal transport by carriers were affected by the grain boundary. I think author must measure low temperature thermal conductivity to make this clear.
Because there is no remarkable progress, I cannot recommend this manuscript to be published in Nature Communications but somewhere else focusing on the new process.

We are sincerely grateful to the reviewers for the helpful comments and suggestions. Detailed response to the reviewers' reports and the description of changes are given below.

Reviewer #1 (Remarks to the Author):

Comments: *Grain boundary significantly affects the physical and chemical properties of solid materials. In this manuscript (NCOMMS-24-26924), Lei et al. reported that the introduction of Mg_2Cu nano-sintering-aid into $Mg_3(Bi, Sb)_2$-based materials helped to enlarge the grain size effectively, which contributed to remarkable thermoelectric performance in polycrystallines that can be comparable to single crystals. An exciting module performance for power generation was achieved as well, as a strong demonstration for further applications. In principle, the topic is interesting with ultrahigh performance, and the experiments are well executed and analyzed, however, I have issues with the interpretation.*

Reply: We appreciate the reviewer's overall positive comments.

Comment 1: *The motivation for using Mg_2Cu for nano-sintering-aid is not so clear, at least it may question how these authors think about this specific Mg_2Cu phase.*

Reply: The choice of Mg_2Cu as a nano-sintering aid is underpinned by a nuanced understanding of its material properties, which make it an ideal candidate for liquid-phase sintering. Sintering aids are known to effectively reduce the sintering temperature and control grain size of polycrystalline materials. However, the selection of a sintering aid should meet several requirements. Firstly, it must have a sufficiently low melting point to facilitate low-temperature liquid-phase sintering. Secondly, it should remain stable during the sintering process and not react with the matrix material to avoid altering the matrix's composition and properties. Thirdly, the aid should disperse uniformly within the matrix to ensure consistent sintering across the entire structure. Considering these requirements, we identified magnesium alloys or magnesium-containing intermetallic compounds as promising sintering aids due to their ability to compensates for Mg deficiencies at grain boundaries. After screening, we found Mg_2Cu could be a potential candidate. It possesses a melting point of 843 K, which is ideal for facilitating liquid-phase sintering of our $Mg_3(Sb,Bi)_2$ materials at 893 K. Additionally, Cu has a very low solubility— potentially being completely insoluble— in $Mg_3(Sb,Bi)_2$[1, 2], ensuring that the addition of Mg_2Cu will not significantly alter the matrix's properties.

Therefore, the incorporation of Mg_2Cu into the Mg_3Sb_2-based material was a strategic decision aimed at promoting grain growth through liquid-phase sintering. This approach has successfully enlarged the

grain size of our material, propelling its thermoelectric performance to rival that of single crystals. We have added several sentences in the revised manuscript to clarify our motivation for using Mg_2Cu for nano-sintering-aid.

Comment 2: *What is the significance of nano Mg_2Cu? Is it appropriate to use the micro Mg_2Cu or just Mg_2Cu ingot?*

Reply: Thanks for the good question. The nano-Mg_2Cu was synthesized through a ball milling method at 1500 rpm for 12 hours. This process yielded a fine powder with broad diffraction peaks clearly observed in the XRD patterns. The nano-sized Mg_2Cu is crucial for the subsequent mixing process, where it can be thoroughly and uniformly mixed with the $Mg_3Bi_{1.195}Sb_{0.795}Te_{0.01}$ matrix. This uniform dispersion is essential for the successful implementation of the liquid-phase sintering process, which in turn, promotes more effective grain growth. While we have not yet explored the use of micro-sized Mg_2Cu or bulk Mg_2Cu ingots, it is reasonable to surmise that the large particles may not achieve the same degree of homogeneity within the mixture. It is conceivable that larger Mg_2Cu particles would not facilitate the uniform grain growth observed with the nano-sized Mg_2Cu. We have added several sentences in the revised manuscript to point out the significance of nano Mg_2Cu.

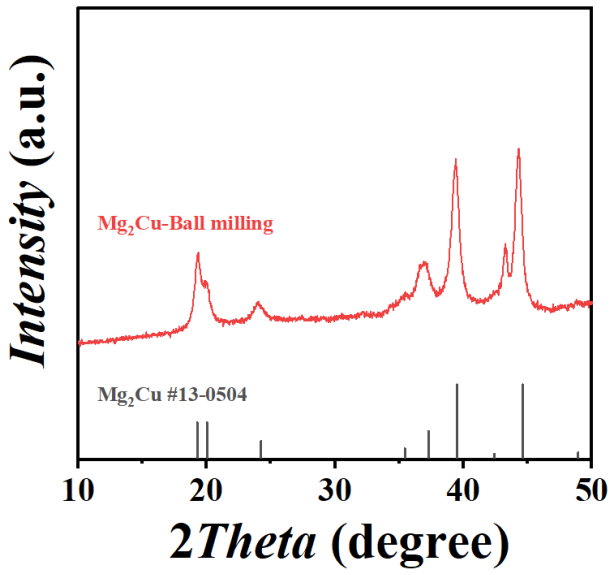

Fig. R1 Room-temperature powder XRD patterns for Mg_2Cu prepared by ball milling.

Comment 3: *Why excessive nano-sintering-aid Mg_2Cu is ineffective for promoting grain size growth? In general, the grain size should not change too much if the addition content is saturated.*

Reply: The appropriate amount of sintering-aid in the sintering process can promote grain growth by enabling particles redistribution, facilitating atomic diffusion, and enhancing Ostwald ripening. However, when an excessive amount of sintering-aid is added, it could accumulate at the grain boundaries, encapsulating the grains and pinning the boundaries, which weakens or even inhibits the recrystallization process—a phenomenon known as the Zener pinning effect[3]. This pinning effect will impede boundary migration and grain growth. In addition, the sintering aid may be extruded during the sintering process, leaving pores behind. An overabundance of sintering aid can increase porosity, which hinders grain-to-grain contact and migration, ultimately detrimental to grain growth. Therefore, controlling the content of sintering aid is crucial for grain growth. For instance, Zawrah et al.[4] found that in the sintering process of SiC, adding 1 vol% CaO improved the average grain size to 10 μm, whereas 3 vol% CaO resulted in a reduced average grain size of 5 μm.

Comment 4: *How does this Mg_2Cu thin or thick layer affect the barrier height or carrier transport? Or there is no observable effect?*

Reply: The experimental data of our samples can be well fitted using a potential barrier height E_b of 130 meV based on a GB dominated transport model. This value is comparable to that (110 meV) of Nb wetted Mg_3Sb_2 samples[5], but lower than the value (170 meV) observed in $Mg_3Bi_{1.5}Sb_{0.5}$ without any GB decoration[6]. It is widely recognized that the barrier height E_b is influenced by a multitude of factors[7], including the density of trapping states at the GBs, the concentration of ionized impurity atoms, and the static dielectric constant, among others. In our study, the introduction of the Mg_2Cu layer at the GBs signifies a modification of local chemical composition, which potentially leads to changes in the concentration of trapping states and ionized impurities, culminating in a reduced barrier height. Previous studies have also demonstrated that wetting the GBs[5, 8, 9] or reducing their misorientation angle[10] can effectively decrease the barrier height. The precise mechanisms of tuning barrier height are topics of substantial interest and will be pursued in future studies.

In response to your comment, we have expanded our discussion in the revised manuscript to elaborate on the potential implications of the Mg_2Cu layer on the barrier height.

Comment 5: '*The contact resistivity ρc at the n-type/Fe junction is only 4.5 μΩ cm^2 (Fig. 4b), significantly lower than the reported ρc in literatures' How about compared to the recent work of Fe foil as the contact layer for n-type Mg_3Sb_2?*

Reply: Our sandwich-structure TE legs, which are composed of an n-type TE material and a contact layer of Fe powder, was fabricated using a one-step sintering technique. The contact resistivity at the n-type/Fe junction, as determined through our measurements, is around 4.5 μΩ cm². This value is significantly lower than the typical values reported in the literature for Fe powder (~20 μΩ cm²)[11, 12, 13], but is slightly higher than the resistivity observed in recent work that employ Fe foil (3.4 μΩ cm²) as the contact layer[14]. The fabricated junction properties are very vulnerable to the sintering condition and the contact material. The sintering temperatures of n-type/Fe powder in the literatures are all above 973 K, which aggravates a significant diffusion of both Mg and Bi elements from the TE material to the interfacial layer. This diffusion is much more intense at higher temperature, leading to the non-dense interfacial layer and thus a higher contact resistivity[14]. However, our sandwich-structure TE legs are sintered at a lower temperature of 893 K, which avoids the volatilization of elements and leads to a lower contact resistivity. In addition, utilization of contact layer Fe foil is another efficient strategy to inhibit the diffusion of Mg and Bi elements from the TE material to the interfacial layer. Overall, a lower contact resistivity between Fe and n-Mg_3Sb_2 is possible by tuning the sintering conditions or just by altering the morphology of the contact material. The related reference has been cited in the revised manuscript

Comment 6: *The height of the module element does significantly affect the conversion efficiency, so it is recommended to mention this critical point in the context when compared to previous literature results.*

Reply: Thanks for the insightful comments and suggestions. A longer leg length will produce a larger effective temperature difference across the TE module due to a smaller proportion of energy dissipation at the interface, which enables a higher conversion efficiency but a lower power output density. Meanwhile, the height of the module element can influence the fabrication process and cost. Longer and thinner modules are more difficult to fabricate with consistent quality. Therefore, optimizing the dimensions of TE legs is essential for achieving a balance between conversion efficiency, power output density, and manufacturing feasibility.

Our TE legs are dimensioned at 1.8 × 1.8 × 5 mm³, with the interfacial layer and TE elements measuring 0.5 mm and 4 mm in height, respectively. These dimensions are roughly in line with the majority of reported leg sizes in the literatures (see Table R1). We believe that with optimization of the TE leg dimensions, the conversion efficiency of our modules could be further improved. We have added several sentences in the revised manuscript to highlight the importance of the height of the module element.

Table R1. Comparison of the structure dimensions of thermoelectric leg among Mg_3Sb_2-based modules[6, 11, 12, 13, 15, 16, 17].

	Ying *et al.*	Liu *et al.*	Jiang *et al.*	Liang *et al.*	Xie *et al.*	Chen *et al.*	Bu *et al.*	This work
Cross-section (mm^2)	4 × 4	2 × 2	1.8 × 1.8	2 × 2	1.5 × 1.5	1.3 × 1.3	1.5 × 1.5	1.8 × 1.8
Height (mm)	7.9	1.75	5.7	4.6	3	3	6	5

Comment 7: *Some typo: diffuson limit.*

Reply: Considering the limitations of phonons, the thermal transports in amorphous or disordered materials are generally quantified in terms of diffusons (rather than diffusions), locons, and propagons[18]. An assessment of the high temperature limit of lattice thermal conductivity is generally termed as 'diffuson limit'. We have thoroughly reviewed the manuscript and made the necessary corrections to ensure clarity and accuracy in our writing.

Reviewer #2 (Remarks to the Author):

Comments: *$Mg_3(Bi,Sb)_2$ material is one of most important n-type thermoelectric materials and a the potential alternative to bismuth telluride. Its performance has been improved rapidly as our understanding of its transport mechanism has increased. Recent studies have shown that the low temperature electrical transport properties of $Mg_3(Bi,Sb)_2$ are heavily influenced by the structure and composition of the grain boundary. In this work, the anthers synthesized high quality $Mg_3(Bi,Sb)_2$ material through a melting reaction in a sealed Ta tube. The grain boundary density was further reduced by introducing Mg_2Cu as the nano-sintering-aid, leading to significantly increased low temperature mobility and enhanced thermoelectric performance. A reduced potential barrier was also observed by fitting the grain sizes dependent mobility and a high conversion efficiency of 7.4% is obtained under temperature difference of 207 K. However, the following comments need to be addressed before publication:*

Reply: We appreciate the reviewer's overall positive comments.

Comment 1: *The lattice thermal conductivity of sample prepared by ball-milling, which has smaller grain size, is remarkable lower than that of the sample synthesized by melting. Please provide an explanation and discussion for this observation.*

Reply: It appears there may have been a misunderstanding in the initial observation. The ball-milled sample, despite having a smaller grain size, actually exhibits a higher lattice thermal conductivity compared to the sample synthesized by melting. This discrepancy can be primarily attributed to the increased oxidation that occurs during the ball-milling process[19]. The higher degree of oxidation in the ball-milled magnesium oxide results in an enhanced lattice thermal conductivity, as MgO has a much higher thermal conductivity (~75 W m^{-1} K^{-1})[20]. Previous studies have also consistently demonstrated a direct correlation between the lattice thermal conductivity of Mg_3Sb_2 and the degree of oxidation[21]. We have added several sentences in the revised manuscript to discuss this observation.

Comment 2: *Mg_2Cu is essentially a metal and, given its high electrical conductivity, it should also possess high thermal conductivity. It is hard for me to expect a metal phase with high thermal conductivity to reduce the lattice thermal conductivity so effectively.*

Reply: Thanks for the good question. Mg_2Cu is indeed an intermetallic compound exhibiting high electrical conductivity and thermal conductivity. Its electrical conductivity is as high as 1×10^7 S m^{-1} (Fig. R2a), and its thermal conductivity is approximately 110 W m^{-1} K^{-1} [22], both of which are significantly higher than the values of our $Mg_{3.2}Bi_{1.195}Sb_{0.795}Te_{0.01}$ samples.

When a high concentration of Mg_2Cu is added into $Mg_{3.2}Bi_{1.195}Sb_{0.795}Te_{0.01}$ and form a network, the lattice thermal conductivity could be potentially increased and adhere to the mixing rule. However, herein, Mg_2Cu is present in a low concentration and at the nanoscale, it can effectively scatter phonons and thereby reduce the overall lattice thermal conductivity. This phenomenon, although counterintuitive, is not without precedent. Actually, the use of high thermal conductivity nanoprecipitates to scatter phonons and reduce lattice thermal conductivity is a well-established concept in the field of TE materials. A lot of studies have demonstrated that the lattice thermal conductivity of composite materials is generally beyond the traditional mixing rule. For example, carbon nanotubes (CNTs), which have a thermal conductivity of 10^2–10^3 W m^{-1} K^{-1} [23], are several orders of magnitude higher than that of Cu_2Se. Yet, when dispersed within Cu_2Se, they effectively scatter phonons and reduce the lattice thermal conductivity of the composite material (Fig. R2b)[24]. Similar phenomenon have been also observed in Bi_2Te_3-SiC[25] and Mg_3Sb_2-graphene composite materials[26].

To elucidate the role of Mg_2Cu more clearly, we conducted low-temperature thermal conductivity measurements and employed the Debye-Callaway model for theoretical analysis (Fig. R3). The experimental data can be better fitted when the contribution of Mg_2Cu nanoprecipitates is considered in

the model. This suggests that Mg_2Cu nanoprecipitates play a substantial role in reducing the overall lattice thermal conductivity, especially at low temperatures.

We have expanded our discussion in the revised manuscript to provide a more comprehensive explanation of how Mg_2Cu nanoprecipitates influence the lattice thermal conductivity.

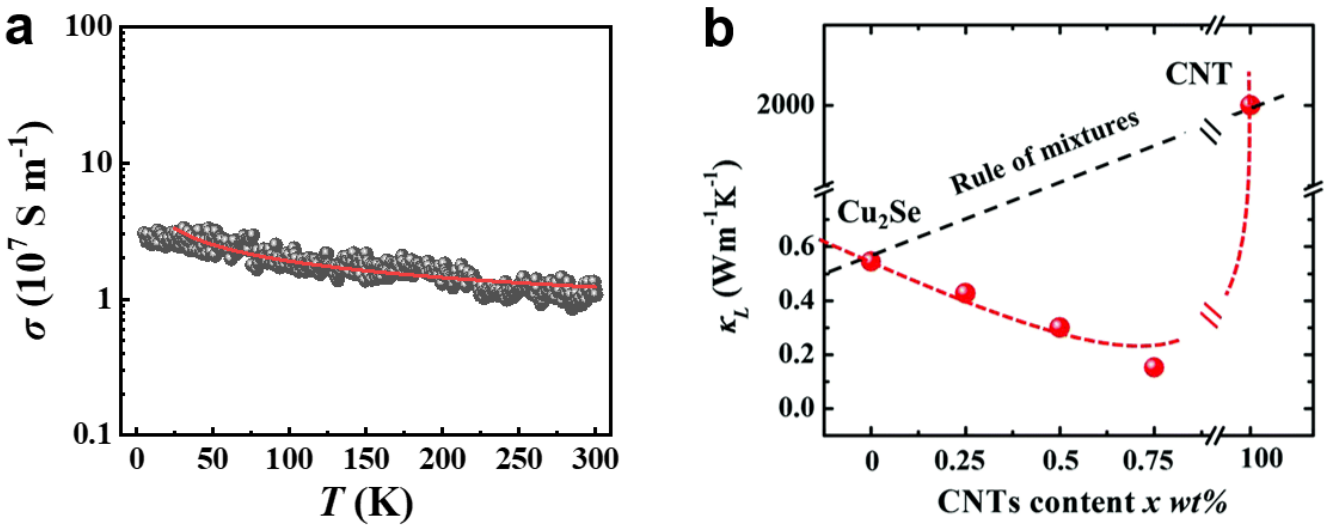

Fig. R2 **a** Temperature dependent electrical conductivity of Mg_2Cu. **b** Lattice thermal conductivity as a function of the CNT content for the Cu_2Se/x wt% CNT (x = 0, 0.25, 0.5, and 0.75) samples[24].

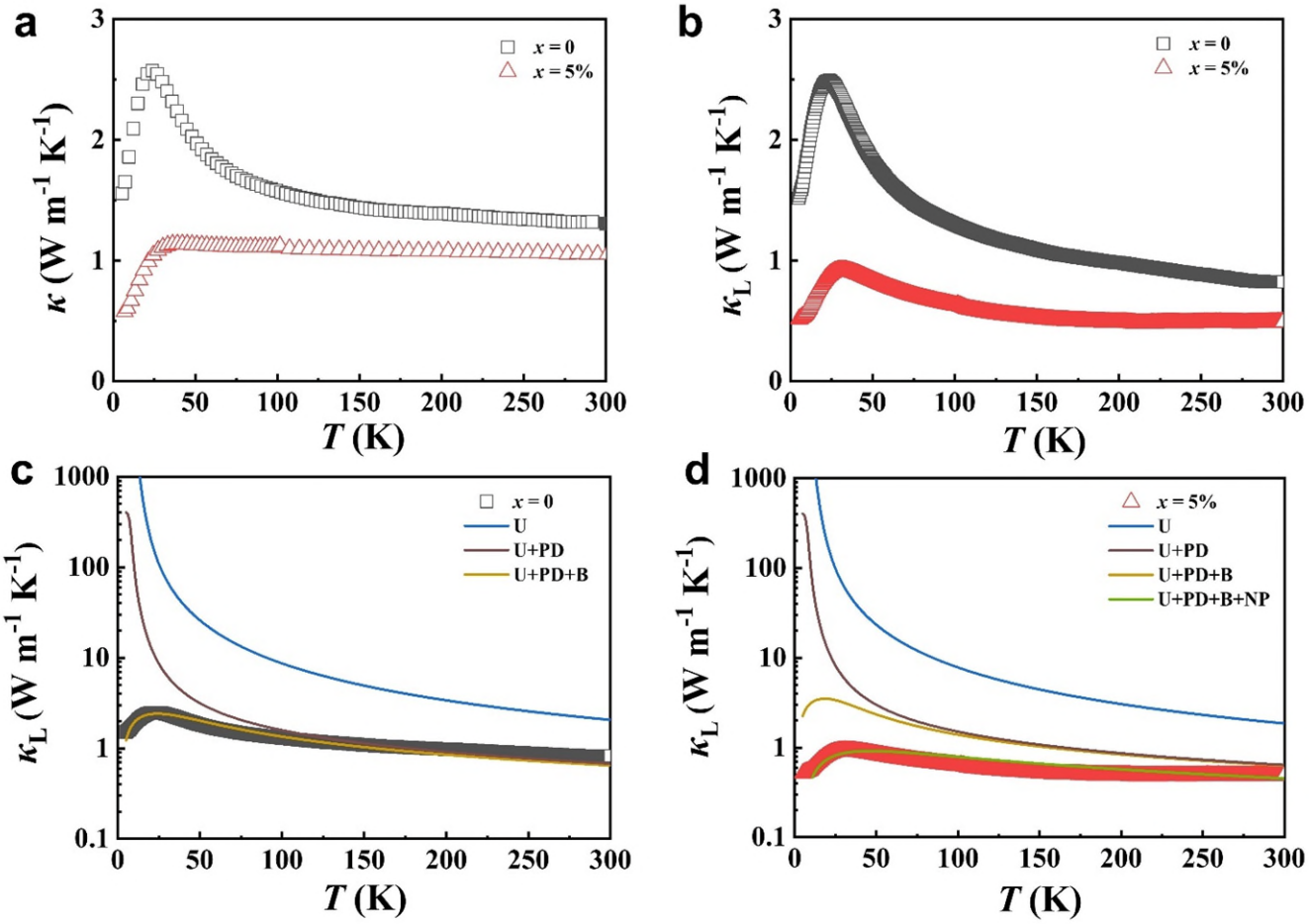

Fig. R3 Temperature dependent **a** thermal conductivity κ, **b** lattice thermal conductivity κ_L. Contributions from various phonon scattering mechanisms to the κ_L of **c** $Mg_{3.2}Bi_{1.195}Sb_{0.795}Te_{0.01}$ (x = 0) and **d** $Mg_{3.2}Bi_{1.195}Sb_{0.795}Te_{0.01}$-5 wt% Mg_2Cu (x = 5%) samples.

Comment 3: *The statement "the modified GBs and Mg_2Cu nanoprecipitates, directly observed in Fig. 2, play a vital role in suppressing the heat-carrying phonon propagation" requires detailed discussion. The enlarged grain size is the main observation. What other specific modifications to the GBs are believed to suppress phonon propagation in this work?*

Reply: We apologize for the unclear explanation of the reduced κ_L by the existence of Mg_2Cu nanoprecipitates. The term "specific modifications" refers to the formation of Mg_2Cu nanoprecipitates during liquid phase sintering. Experimental low temperature κ_L and calculated curves confirm that these nanoprecipitates play a vital role in further suppressing the heat-carrying phonon propagation (Fig. R3). We have corrected the words to dispel misunderstanding in the revised manuscript.

Comment 4: *Please discuss the reason for the reduced potential barrier. Based on Fig.3c, the impact of Mg_2Cu on the potential barrier appears negligible.*

Reply: The experimental data of our samples can be well fitted using a potential barrier height E_b of 130 meV based on a GB dominated transport model. This value is comparable to that (110 meV) of Nb wetted Mg_3Sb_2 samples[5], but lower than the value (170 meV) observed in $Mg_3Bi_{1.5}Sb_{0.5}$ without any GB decoration[6]. It is widely recognized that the barrier height E_b is influenced by a multitude of factors[7], including the density of trapping states at the GBs, the concentration of ionized impurity atoms, and the static dielectric constant, among others. In our study, the introduction of the Mg_2Cu layer at the GBs signifies a modification of local chemical composition, which potentially leads to changes in the concentration of trapping states and ionized impurities, culminating in a reduced barrier height. Previous studies have also demonstrated that wetting the GBs[5, 8, 9] or reducing their misorientation angle[10] can effectively decrease the barrier height. The precise mechanisms of tuning barrier height are topics of substantial interest and will be pursued in future studies.

In Fig. 3c, the referred data also utilize the strategy of modifying the grain boundaries, including the addition of Cu elements to form Mg-Cu wetting phase or excessive Mg to compensate for the Mg-deficient region in the grain boundaries. Therefore, the potential barrier in these studies may exhibit a similar low E_b, akin to our samples. However, when juxtaposed with samples without any GB decoration, the lower E_b in our samples indicates that the addition of Mg_2Cu is indeed effective in mitigating the potential barrier.

Comment 5: *Please provide the relative density of the sample, as the pores are observed in Fig. 2b.*

Reply: During the sintering process, most of the Mg_2Cu sintering aid is squeezed out of the sample, leaving a small amount of nanopores at grain boundaries. Consequently, the density ρ of the Mg_2Cu-containing samples are slightly lower than the matrix. Nonetheless, all the samples remain robust, with relative density exceeding 98%. We have included the specific density data in Table R2 and add them in the Supplementary Information.

Table R2. The density and relative density for $Mg_{3.2}Bi_{1.195}Sb_{0.795}Te_{0.01} - x$ wt% Mg_2Cu samples. Herein, the relative density of all samples is calculated in comparison to $Mg_{3.2}Bi_{1.195}Sb_{0.795}Te_{0.01}$. The actual

relative density might be higher, considering that the density of Mg_2Cu is lower than that of $Mg_{3.2}Bi_{1.195}Sb_{0.795}Te_{0.01}$.

	$x = 0$	$x = 2$	$x = 3$	$x = 5$	$x = 7$	$x = 10$
Density (g cm^3)	5.12	5.12	5.05	5.09	5.06	5.11
Relative density (%)	99.8	99.8	98.4	99.2	98.6	99.6

Comment 6: *The material with a potential barrier height of 170 meV should have the composition $Mg_3Bi_{1.5}Sb_{0.5}$, as mentioned in reference 22.*

Reply: We extend our apologies for the oversight. The material with a potential barrier height of 170 meV should be identified as having the composition $Mg_3Bi_{1.5}Sb_{0.5}$. We have modified our description in the revised manuscript.

Reviewer #3 (Remarks to the Author):

Comments: *This work demonstrates outstanding figure of merit (ZT=1.5 at 500K) of $Mg_3(Bi,Sb)_2$ based materials. They also fabricated thermoelectric module of $Mg_3(Bi,Sb)_2$/$(Bi,Sb)Te_3$ exhibiting high conversion efficiency of 7.4% under dT=2.7K. The performance was achieved by enlarging the average grain size to 23.7 um. A novel process of liquid-phase sintering was provided. Indeed, the presented process is new and obtained performance is high. However, I cannot find a remarkable progress to justify publishing this manuscript in Nature Communications. The effectivity of enlarging grain size was already reported by [Kanno et al., APL 112 (2018) 033903].*

Reply: Thanks for the insightful comments and suggestions. As the reviewer rightly pointed out, many useful methods, such as elevating the sintering temperature[11, 12, 29] and extending annealing times[30], have been reported effective in enlarging grain size for high-performance n-Mg_3Sb_2 materials. However, these methods typically require high temperatures, such as 1123 K in the mentioned work of Kanno *et al.*[29], which makes controlling the content of volatile reactants challenging, potentially leading to deviations from the target composition. The innovation of our work lies in the introduction of a novel liquid-phase sintering method that can significantly enhances grain size without relying on such high temperatures. Our sintering process operates at a temperature of 893 K, which allows for better control over the target composition. Besides, the grain boundaries decorated with nano-sintering aids exhibit a reduced boundary barrier, which in turn further facilitates the transport of charge carriers. Moreover, the nano-sintering-aid is effective in scattering phonons, leading to a reduction in lattice thermal conductivity. The interplay of

these factors culminates in the exceptional TE performance of our materials. We believe this novel approach, combined with the high performance demonstrated by our $Mg_3(Bi, Sb)_2$-based materials, offers substantial value to the field and contributes to the ongoing efforts to improve TE conversion efficiency.

Comment 1: *The grain size over 30 um with similar high ZT value was reported by [Wood et al., Adv. Mater. 31 (2019) 1902337]. I feel unfair that authors did not refer those relevant papers.*

Reply: Wood *et al.* increased the grain size from <1 μm to 10 μm by elevating the sintering temperature from 600 °C to 800 °C, and further grew the grain size from 10 μm to 30 μm by using a Mg-vapor anneal processing step[30]. It should be noted that our method of utilizing sintering aids to enhance grain size is fundamentally different from the approach taken by Wood *et al.* Moreover, the sintering-aids are conducive to reducing the boundary barrier and enhancing phonon scattering, beyond mere grain size adjustment.

The comparison of the figure of merit *zT* of literature and our work is shown in Fig. R4. It is evident that the *zT* values of our samples are notably superior to those reported in the literature within the temperature range of 400 to 600 K. We have added the reported data in Fig. 1b in the revised manuscript.

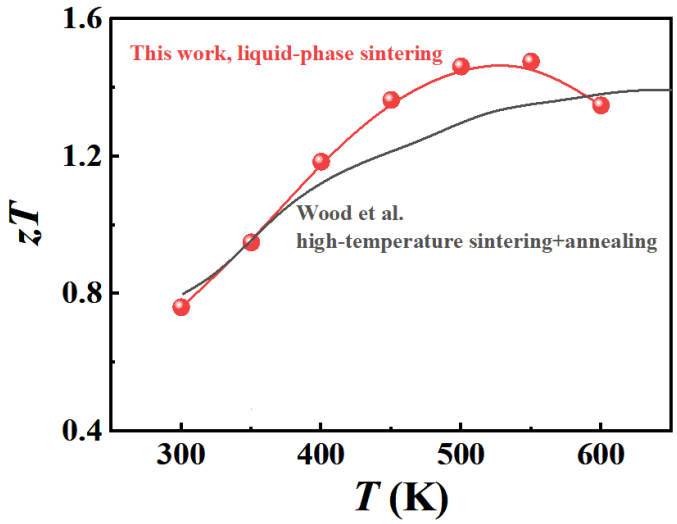

Fig. R4 Temperature dependent figure of merit *zT* for $Mg_{3.2}Bi_{1.195}Sb_{0.795}Te_{0.01}$ – 5 wt% Mg_2Cu in comparison with the reported data of Wood *et al.*[30].

Comment 2: *Further, the efficiency of module is approximately similar as previous reports. Only a slight improve might be but can be within error bars. To claim this small improvement, author must show the*

accuracy of their measurement, which is lack in the manuscript. No details were described about the equipment of evaluating power generation performance of module except that a home-made test system was used. In addition, there is no data about heat current.

Reply: In this work, we fabricate an 8-pair TE module by using the n-type $Mg_{3.2}Bi_{1.195}Sb_{0.795}Te_{0.01}$ – 0.5 wt% Mg_2Cu and p-type $Bi_{0.495}Cu_{0.005}Sb_{1.5}Te_3$ materials to demonstrate the strength for low-temperature waste heat recovery of Mg_2Cu-contained $Mg_3(Bi, Sb)_2$. A high conversion efficiency η of 7.4 % is achieved when the hot-side temperature is 495 K and ΔT is 207 K, surpassing all previously reported power generation modules in the same temperature range. Unlike the high-performance p-type counterparts used in previous studies, the TE performance of the p-type partner in our work is much lower than the n-type partner above 350 K, and the outstanding module performance is mainly contributed by our n-type materials.

As far as we know, using a home-made test system to characterize the modules is a common practice in the field of thermoelectrics due to the specific requirements and control over experimental conditions that are often necessary. Our system, developed at the Shanghai Institute of Ceramics, offers precise temperature regulation, which is crucial for accurate measurement of TE performance, especially under the fluctuating conditions of the hot-side temperature. We have validated the accuracy of our home-made test system by comparing it with a commercial Power Generation Efficiency Characteristics Evaluation System (PEM-2, Advance Riko, Japan). Moreover, repeated measurements of the same module in this home-made test system were in good agreement with a discrepancy of less than 2%. We have also applied for patents for this test system (CN105203940A) and it has been accepted and purchased by many of our peers. Many high-level works have also been published using this system, e.g., Science, 371, 830-834 (2021); Nat Commun. 13, 7738 (2022); Joule 4, 2475-2483, 18 (2020); Energy Environ. Sci., 10, 956-963 (2017); Energy Environ. Sci. 12, 3390-3399 (2019). These validations confirm the reliability of our measurements and the robustness of our system.

Furthermore, to address the absence of detailed equipment description and data about heat current in the manuscript, we have now included a comprehensive description of our home-made test system, highlighting its capabilities and the rationale behind its design and selection. Additionally, we have provided supplementary data that illustrates the heat current measurements, ensuring transparency and reproducibility of our findings.

We believe that these additions to the manuscript will address your concerns and strengthen the presentation of our work.

Comment 3: *The conclusion that Mg_2Cu nanoprecipitates can lead to low lattice thermal conductivity is also not clear. The κ_L was extracted by subtracting the contribution of carriers and bipolar effect from κ. But there is no description of how to calculate the contribution of carriers (κ_e). Supposing that they were using Wiedemann−Franz law, how they can estimate the effect of grain boundary scattering on κ_e? It is sure that thermal transport by carriers were affected by the grain boundary. I think author must measure low temperature thermal conductivity to make this clear.*

Because there is no remarkable progress, I cannot recommend this manuscript to be published in Nature Communications but somewhere else focusing on the new process.

Reply: As the reviewer rightly points out, the carrier transport is much influenced by the grain boundary in some TE materials, such as $Mg_3(Sb, Bi)_2$, resulting in a distinct temperature dependency of electrical conductivity with different grain sizes. It is widely recognized that grain boundary dominates the carrier transport in fined-grain $Mg_3(Sb, Bi)_2$ at low temperature range, which can be alleviated by enlarging the grain size method[5, 7, 8, 11, 12, 21, 29, 31, 32]. To estimate the effect from different scattering mechanisms, based on the two-phase model[31], we calculate the Lorenz number L using the acoustic-phonon scattering (AP) model and the grain boundary scattering (GB) model, respectively. For the acoustic-phonon scattering, L is calculated using

$$L_{AP} = \left(\frac{k_B}{e}\right)^2 \left\{\frac{(\lambda+2)F_{\lambda+1}(\eta)}{\lambda F_{\lambda-1}(\eta)} - \left[\frac{(\lambda+1)F_{\lambda}(\eta)}{\lambda F_{\lambda-1}(\eta)}\right]^2\right\}. \quad (1)$$

For the grain boundary scattering, L is calculated using

$$L_{GB} = \left(\frac{k_B}{e}\right)^2 \left\{\frac{\lambda(\lambda+2)F_{\lambda-1}(\eta)F_{\lambda+1}(\eta)}{\lambda^2 {F_{\lambda-1}}^2(\eta)} - \left[\frac{(\lambda+1)F_{\lambda}(\eta)}{\lambda F_{\lambda-1}(\eta)}\right]^2\right\}, \quad (2)$$

where η is the reduced Fermi-level E_F/k_BT, $F_\lambda(\eta)$ is the Fermi–Dirac integral $F_\lambda(\eta) = \int_0^\infty \frac{x^\lambda dx}{1+e^{x-\eta}}$, λ is a parameter for the conduction mechanism. $\lambda = 1$ in acoustic-phonon scattering model and $\lambda = 3$ in grain boundary scattering model. η can be retrieved by calculating the equation based on the experimental Seebeck coefficient

$$S = \pm\frac{k_B}{e}\left[\frac{(\lambda+1)F_{\lambda}(\eta)}{\lambda F_{\lambda-1}(\eta)} - \eta\right]. \quad (3)$$

As shown in Fig. R5a, taking the $Mg_{3.2}Bi_{1.195}Sb_{0.795}Te_{0.01}$ sample as an example, the calculated L in the two scattering mechanisms is almost the same at low temperatures and slowly diverges with increasing temperature. The largest discrepancy occurs at 600 K and the corresponding value of L is 2.24×10^{-8} W

ΩK^{-2} for GB scattering and 1.94×10^{-8} W ΩK^{-2} for AP scattering. Furtherly, according to the Wiedemann-Franz law ($\kappa_e = L\sigma T$), the contribution of grain boundaries to the carrier thermal conductivity κ_e was calculated, as shown in Fig. R5b. The variance between the influence of the two scattering mechanisms on κ_e only occurs in the high-temperature region. However, the grain boundary scattering is progressively insignificant with increasing temperature. That is, the carriers are virtually unaffected by the scattering of the grain boundaries in the high-temperature region. Likewise, the thermal transport by carriers are scarcely affected by the grain boundary with increasing temperature.

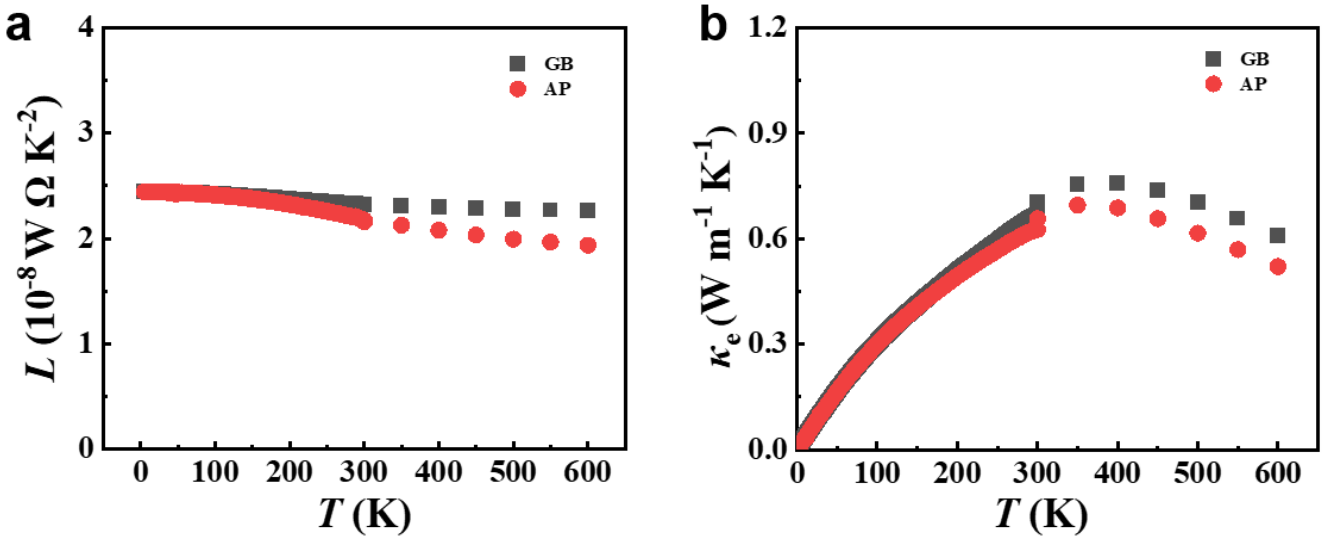

Fig. R5 Temperature dependent **a** Lorenz number L and **b** carrier thermal conductivity for $Mg_{3.2}Bi_{1.195}Sb_{0.795}Te_{0.01}$. GB and AP denote grain boundary scattering and acoustic-phonon scattering, respectively.

To address the reviewer's concern, the κ_L of $x = 0$ and $x = 5\%$ samples below 300 K were measured, being plotted in Fig. R3a. The κ_L is assessed by subtracting the κ_e from the total thermal conductivity and κ_e is obtained by Wiedemann-Franz law. Lorentz number is calculated using an acoustic-phonon scattering based on our experimental Seebeck coefficient data below 300 K (Fig 3f). As shown in Fig. R3b, the κ_L of Mg_2Cu-containing sample is much lower than that of Mg_2Cu-free sample. Furtherly, we use the Debye-Callaway model to separate the different contributions of scattering mechanisms to the reduction in κ_L (Fig. R3c, d). This calculation includes all the possible mechanisms: phonon–phonon Umklapp process (U), point defect scattering (PD), grain boundary scattering (B), and nanoprecipitate scattering (NP). The detailed calculation and fitted parameters are added in the Supplementary Information. The fitted parameter A for U scattering relaxation time is 2.2×10^{-17} s K^{-1}, which is also checked by fitting the

crystalline sample from the previous work[33]. Scattering by point defects arises from both mass and strain differences within the lattice. By calculating the disorder scattering parameters due to mass and strain field fluctuations, the parameter B of PD scattering is 10×10^{-41} s^3, which is consistent with reported works[32, 34]. Grain boundary scattering is determined by the grain size and nanoprecipitate scattering depends on the radius and number density of nanoprecipitates. The values of these parameters can be retrieved by our EBSD and SEM data, which are listed in the Table R3. The experimental data can be better fitted when the contribution of Mg_2Cu nanoprecipitate is considered in the model. This suggests that Mg_2Cu nanoprecipitates play a substantial role in reducing the overall lattice thermal conductivity, especially at low temperatures. We believe these additional data and analyses will make the point mentioned by the reviewer clear. We have expanded our discussion in the revised manuscript to elaborate on the effect of Mg_2Cu nanoprecipitates on the κ_L.

Table R3 Parameters used for the Debye-Callaway model based on the various phonon scattering mechanisms.

Parameters	Values (x = 0)	Values (x = 5%)
Debye temperature (K)	190	190
Average sound velocity v (m s^{-1})	1910	1910
Parameter A (s K^{-1})	2.2×10^{-17}	2.2×10^{-17}
Parameter B (s^3)	10×10^{-41}	10×10^{-41}
Grain size d (um)	7.2	23.7
Γ_M	0.019	0.019
Γ_S	0.037	0.037
Number density of precipitates N_P (m^{-3})	-	1.25×10^{20}
Average radius for precipitates R (nm)	-	80
Mass density of matrix D_M (g cm^{-3})	-	5.12
Mass density of precipitates D_P (g cm^{-3})	-	3.4

References

1. Gorai, P. *et al.* Investigation of n-type doping strategies for Mg_3Sb_2. *J. Mater. Chem. A* **6**, 13806-13815 (2018).
2. Liu, Z. *et al.* Demonstration of ultrahigh thermoelectric efficiency of ~7.3% in Mg_3Sb_2/MgAgSb module for low-temperature energy harvesting. *Joule* **5**, 1196-1208 (2021).
3. Kim, BN. *et al.* Finite element simulation of Zener pinning behavior. *Acta. mater.* **47**, 2293-2301 (1999).
4. Zawrah, MF. *et al.* Liquid-phase sintering of SiC in presence of CaO. *Ceram. Int.* **30**, 721-725 (2004).

5. Luo, T. *et al.* Nb-mediated grain growth and grain-boundary engineering in Mg_3Sb_2-Based thermoelectric materials. *Adv. Funct. Mater.* **31**, 2100258 (2021).
6. Chen, N. *et al.* Improved figure of merit (z) at low temperatures for superior thermoelectric cooling in $Mg_3(Bi,Sb)_2$. *Nat. Commun.* **14**, 4932 (2023).
7. Hu, C. *et al.* Carrier grain boundary scattering in thermoelectric materials. *Energy Environ. Sci.* **15**, 1406-1422 (2022).
8. Li, J-W. *et al.* Wide-temperature-range thermoelectric n-type $Mg_3(Sb,Bi)_2$ with high average and peak *zT* values. *Nat. Commun.* **14**, 7428 (2023).
9. Wang, L. *et al.* Realizing high thermoelectric performance in n-type $Mg_3(Sb, Bi)_2$-based materials via synergetic Mo addition and Sb–Bi ratio refining. *Adv. Energy Mater.* **13**, 2301667 (2023).
10. Wu, R. *et al.* Strong charge carrier scattering at grain boundaries of PbTe caused by the collapse of metavalent bonding. *Nat. Commun.* **14**, 719 (2023).
11. Ying, P. *et al.* A robust thermoelectric module based on $MgAgSb/Mg_3(Sb,Bi)_2$ with a conversion efficiency of 8.5% and a maximum cooling of 72 K. *Energy Environ. Sci.* **15**, 2557-2566 (2022).
12. Liu, Z. *et al.* Maximizing the performance of n-type Mg_3Bi_2 based materials for room-temperature power generation and thermoelectric cooling. *Nat. Commun.* **13**, 1120 (2022).
13. Jiang, M. *et al.* High-efficiency and reliable same-parent thermoelectric modules using Mg_3Sb_2-based compounds. *Nat. Sci. Rev.* **10**, nwad095 (2023).
14. Qu, N. *et al.* Interfacial Design Contributing to High Conversion Efficiency in $Mg_3(Sb, Bi)_2/Bi_2Te_3$ Thermoelectric Module with Superior Stability. *Adv. Energy Mater.* **14**, 2302818 (2024).
15. Liang, Z. *et al.* Enhanced thermoelectric performance of p-type Mg_3Sb_2 for reliable and low-cost all-Mg_3Sb_2-based thermoelectric low-grade heat recovery. *Adv. Funct. Mater.* **33**, 2210016 (2023).
16. Bu, Z. *et al.* A record thermoelectric efficiency in tellurium-free modules for low-grade waste heat recovery. *Nat. Commun.* **13**, 237 (2022).
17. Xie, L. *et al.* Screening strategy for developing thermoelectric interface materials. *Science* **382**, 921-928 (2023).
18. Allen, PB. *et al.* Diffusons, locons and propagons: Character of atomic vibrations in amorphous Si. *Philos. Mag. B* **79**, 1715-1731 (1999).
19. Song, J. *et al.* Bismuth-free Mg_3Sb_2 with enhanced room-temperature thermoelectric and mechanical properties. *J. Materiomics*, (2023).
20. Imada, S. *et al.* Measurements of lattice thermal conductivity of MgO to core-mantle boundary pressures. *Geophys. Res. Lett.* **41**, 4542-4547 (2014).
21. Shi, X. *et al.* Revelation of inherently high mobility enables Mg_3Sb_2 as a sustainable alternative to n-Bi_2Te_3 thermoelectrics. *Adv. Sci.* **6** 1802286 (2019).
22. Sun, Z. *et al.* Fabrication, Structure, and Thermal Properties of Mg–Cu Alloys as High Temperature PCM for Thermal Energy Storage. *Materials* **14**, 4246 (2021).
23. Fujii, M. *et al.* Measuring the Thermal Conductivity of a Single Carbon Nanotube. *Phys. Rev. Lett.* **95**, 065502 (2005).
24. Nunna, R. *et al.* Ultrahigh thermoelectric performance in Cu_2Se-based hybrid materials with highly dispersed molecular CNTs. *Energy Environ. Sci.* **10**, 1928-1935 (2017).
25. Li, J. *et al.* BiSbTe-Based Nanocomposites with High ZT: The Effect of SiC Nanodispersion on Thermoelectric Properties. *Adv. Funct. Mater.* **23**, 4317-4323 (2013).
26. Lin, Y. *et al.* Expression of interfacial Seebeck coefficient through grain boundary engineering with multi-layer graphene nanoplatelets. *Energy Environ. Sci.* **13**, 4114-4121 (2020).
27. Lei, J. *et al.* Enhancement of thermoelectric figure of merit by the insertion of multi-walled carbon nanotubes in $$-MgAgSb. *Appl. Phys. Lett.* **113** 083901 (2018).
28. Wang, T. *et al.* Simultaneous enhancement of thermoelectric and mechanical performance for SnTe by nano SiC compositing. *J. Mater. Chem. C* **8**, 7393-7400 (2020).
29. Kanno, T. *et al.* Enhancement of average thermoelectric figure of merit by increasing the grain-size of $Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}$. *Appl. Phys. Lett.* **112** 033903 (2018).
30. Wood, M. *et al.* Improvement of Low-Temperature zT in a Mg_3Sb_2-Mg_3Bi_2 Solid Solution via Mg-Vapor Annealing. *Adv. Mater* **31** 1902337 (2019).
31. Kuo, JJ. *et al.* Grain boundary dominated charge transport in Mg_3Sb_2-based compounds. *Energy Environ. Sci.* **11**, 429-434 (2018).
32. Lei, J. *et al.* Efficient lanthanide Gd doping promoting the thermoelectric performance of Mg_3Sb_2-based materials. *J. Mater. Chem. A* **9**, 25944-25953 (2021).

33. Pan, Y. *et al.* $Mg_3(Bi,Sb)_2$ single crystals towards high thermoelectric performance. *Energy Environ. Sci.* **13**, 1717-1724 (2020).
34. Chen, S. *et al.* Enhancement of thermoelectric performance in $Mg_3(Sb,Bi)_2$ through engineered lattice strain and controlled carrier scattering. *Chem. Eng. J.* **490**, 151404 (2024).

Summary of the changes

1. The reported data from the literature mentioned by the Reviewer #3 is added in Fig. 1b to compare the figure of merit zT.
2. Three sentences are added in first paragraph of page 5 in the Results to clarify our motivation for using Mg_2Cu for nano-sintering-aid.
3. Two sentences are added in first paragraph of page 5 in the Results to point out the significance of nano Mg_2Cu.
4. A few sentences are added in page 9 to elaborate on the potential implications of the Mg_2Cu layer on the barrier height.
5. The composition is corrected to $Mg_3Bi_{1.5}Sb_{0.5}$ on page 9.
6. The Figure 3 in initial manuscript are divided into Figure 3 and Figure 4 in the revised manuscript on page 11.
7. A few sentences for discussing the κ_e and low temperature κ_L are added on page 12. The specific density data are added in Supplementary Table R1.
8. Two sentences to discuss the enhanced lattice thermal conductivity of ball-milling sample due to the magnesium oxide are added on page 12.
9. The descriptions on contact resistivity are modified on page 14.
10. Several sentences to highlight the importance of the height of the module element are added in TE module fabrication section on page 17.
11. The structure dimensions of thermoelectric legs are corrected in TE module fabrication section on page 18.
12. A comprehensive description of our home-made system for device testing is added in TE module fabrication section on page 18. The measured heat flow data are added in Supplementary Fig. 9.
13. The calculated details about phonon relaxation time calculation are added in the Supplementary Information. The corresponding fitting parameters are listed in Supplementary Table 2.

We sincerely thank the two reviewers again for their careful consideration and very helpful suggestions as well as comments. We believe that we have made clear explanations and proper modifications.

Sincerely yours,

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REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

I went over the revised manuscript and the response letter and found the answers satisfactory.
With these changes, I can recommend the manuscript for publication on Nat Commun.

Reviewer #2 (Remarks to the Author):

I have thoroughly reviewed the reply. The detailed explanation is helpful in understanding the results of this work, and the additional data strengthens their findings. As the revised paper is polished and significantly improved, I am pleased to recommend the publication of the current version.

Reviewer #3 (Remarks to the Author):

I found some progress on the manuscript, but my main concern about the lack of remarkable progress to justify publishing this manuscript in Nature Communications is still unsolved. The main claim of liquid-phase sintering technique itself was established long time ago [for example, G. Gottstein et al., Acta Mater 48, 397 and also ref. 42 and 43 in the manuscript] and the technique was applied to Mg3(Sb,Bi)2 system using Mg-Cu liquid state [Z. Liu et al., Joule 5, 1196 (2021)], which is the same as the present manuscript. Although there might be a progress, I cannot find that this manuscript achieves the criteria for being published in Nature Communications.

Reviewer #1 (Remarks to the Author):

Comments: *I went over the revised manuscript and the response letter and found the answers satisfactory. With these changes, I can recommend the manuscript for publication on Nat Commun.*

Reply: We sincerely thank the reviewer again for the careful consideration and very helpful suggestions as well as comments.

Reviewer #2 (Remarks to the Author):

Comments: *I have thoroughly reviewed the reply. The detailed explanation is helpful in understanding the results of this work, and the additional data strengthens their findings. As the revised paper is polished and significantly improved, I am pleased to recommend the publication of the current version.*

Reply: We sincerely thank the reviewer again for the careful consideration and very helpful suggestions as well as comments.

Reviewer #3 (Remarks to the Author):

Comments: *I found some progress on the manuscript, but my main concern about the lack of remarkable progress to justify publishing this manuscript in Nature Communications is still unsolved.*

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Reply: Thanks for your insightful comments and for recognizing the progress made in our manuscript. We acknowledge that the liquid-phase sintering technique has indeed been a staple in the field of ceramics. However, we would like to emphasize that its application in the realm of thermoelectric materials, particularly for the control of grain size, grain boundary barriers, and sintering temperature, is less common and represents a novel approach in our study. Moreover, we have discovered that the nano-sintering-aid can effectively scatter phonons, thereby reducing the lattice thermal conductivity—a finding that has not been previously reported.

Our focus on the role of sintering aids in the control of grain size, grain boundary barriers, and sintering temperature, as well as phonon scattering is a key distinction from the work of Z. Liu et al., where the primary aim was to enhance the thermoelectric properties of Mg_3Sb_2 through Cu doping, without an in-

depth discussion on the function of the Mg-Cu phase. This divergence in research emphasis underscores the originality and significance of our findings.

We believe that our manuscript meets the criteria for publication in Nature Communications by offering a fresh perspective on the application of liquid-phase sintering in thermoelectric materials and providing new insights into the role of sintering aids in enhancing thermoelectric performance.

We sincerely thank the three reviewers again for their careful consideration and very helpful suggestions as well as comments.

Sincerely yours,
Xun Shi

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