

Plastic processing induced multiscale microstructures for simultaneous thermoelectric and mechanical enhancements in PbTe

Shujing Yang^{1,#}, Shanshan Hu^{1,#}, Ziyang Li^{2,#}, Changyuan Li¹, Long Yang¹, Zhiwei Chen¹, Juan Chen², Jun Luo¹, Wen Li^{1,*} & Yanzhong Pei¹

Thermoelectric technology, facilitating the direct transduction of heat into electricity, represents a highly promising sustainable solution to mitigate energy crisis by harnessing waste heat without emissions. The conversion efficiency is quantified by the dimensionless thermoelectric figure of merit, $zT = S^2 T / \rho(\kappa_E + \kappa_L)$, which depends on the Seebeck coefficient (S), the electrical resistivity (ρ), the absolute temperature (T), as well as the electronic (κ_E) and lattice (κ_L) contributions to the thermal conductivity. Hence, considerable research efforts have been directed toward improving zT to realize higher conversion efficiency.

Thermally, minimizing the κ_L is a universally validated route for zT -enhancement [1]. This can be achieved by engineering microstructure with multi-dimensional (D) defects, such as 0D point defects [2-6], 1D dislocations [7-12] and 2D grain boundaries [13-17], to enable selective phonon scattering across high-, mid- and low-frequency ranges. Electrically, band convergence provides an effective mechanism to decouple the interrelationship between S and r , thereby enabling substantial enhancement of the power factor ($PF = S^2 / r$) in numerous thermoelectric materials [18-26]. Note that both the maximum PF and zT are accessible only within a narrow optimal range of carrier concentration (n) [27]. It underscores n -optimization as a cornerstone alongside the proven strategies above for maximizing thermoelectric performance [28-30].

Conventionally, the pursuit of the highest performance demands intricate and precise chemical tuning via heavy doping and alloying [31, 32]. While proven effective across numerous materials, this paradigm carries an inherent risk: driving materials toward metastable states or phase boundaries [33-35]. This instability may trigger unfavorable phase transformations or detrimental second-phase formation, ultimately degrading performance [36]. Therefore, developing alternative pathways represents a critical imperative for advancing thermoelectric materials.

Beyond thermoelectric performance, mechanical robustness can be equally critical to ensure the structural integrity and long-term reliability of devices [37]. As is well recognized, high-performance inorganic thermoelectric materials are inherently brittle, a consequence of the dominant ionic and/or covalent

bonding in their atomic structures [38,39]. This brittleness renders them susceptible to fracture during leg segmentation and device operation, especially under high thermal stresses or intense mechanical vibrations. These limitations highlight the necessity of exceptional mechanical strength and plastic strain to guarantee structural integrity during manufacturing and operation.

Engineering microstructures with desired defects [40-42] and specific textures [43] has emerged as a viable pathway to optimize mechanical performance. Nevertheless, a key challenge remains: developing a technique capable of simultaneously engineering multiscale microstructures to concurrently advance thermoelectric and mechanical properties, moving beyond the limitations of conventional chemical manipulation alone.

Plastic deformation is a well-established technique for microstructural control, offering a direct route to tailor mechanical properties [44-46]. It has been developed as a universal technique for scalable production of materials with enhanced mechanical properties, extending its applicability from conventional metals [47,48] to functional materials like Bi₂Te₃-based thermoelectrics [49, 50], Ag₂Se [51] and Bi_{0.85}Sb_{0.15} [52]. The underlying mechanism is crystallographic slip mediated by dislocation motion, which enables the possibility of concurrent introduction of vacancies, dislocations, grain refinement, and texture by means of the controlled adjustment of processing parameters. This orchestrated defect ensemble would contribute to the n -optimization via the vacancy [53] and κ_L -reduction by the multiple-defect phonon scattering [54]. Therefore, the plastic deformation offers a promising alternative to the conventional chemical manipulation toward simultaneous advancement of thermoelectric and mechanical properties through integrated microstructure engineering.

Guided by these insights, this work aims to optimize both thermoelectric and mechanical properties of binary PbTe through microstructure engineering using hot extrusion (**Fig. 1a**). The multiple defects of Te vacancies, dislocations and grain refinement are concurrently introduced (**Fig. 1b**), which collectively facilitate broad-frequency phonon scattering and yield a substantial reduction in lattice thermal conductivity (**Fig. 1c**). Simultaneously, the Te vacancy contribute to an

¹Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, Shanghai 201804, China

²National Engineering Research Center of Light Alloy Net Forming and State Key Laboratory of Metal Matrix Composite, Shanghai Jiao Tong University, Shanghai, 200240, China

* Corresponding author (email: liwen@tongji.edu.cn)

increase in electron concentration, enabling a notable enhancement in the power factor (**Fig. 1d**). The synergistic optimization of thermal and electronic performance achieves a superior peak zT of ~ 1.3 at 800 K in n-type binary PbTe, which corresponds to a conversion efficiency of $\sim 7.2\%$ for a single-leg device under a temperature gradient of ~ 500 K. Furthermore, the hot-extruded PbTe with a preferred $[100]$ orientation exhibits substantially improved compressive strength and plastic strain (**Fig. 1e**), originating from the contributions of the multiple defects and crystallographic texturing, respectively. These results robustly demonstrate the efficacy of rational microstructural design via plastic deformation for the simultaneous optimization of thermoelectric and mechanical performance.

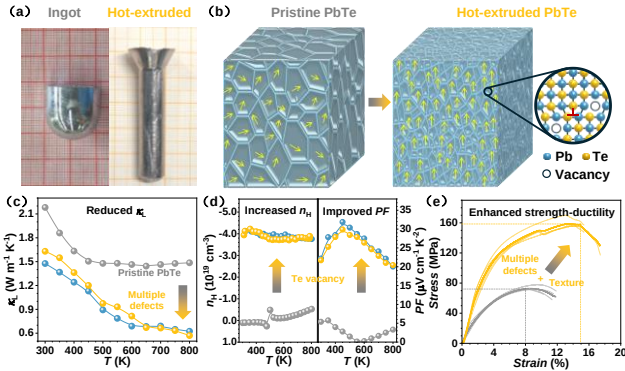


Fig. 1. (a) Photographs of PbTe before and after hot extrusion, (b) Schematic illustrating the microstructure evolution of binary PbTe during hot extrusion, Temperature dependent (c) lattice thermal conductivity, (d) Hall carrier concentration and power factor, (e) Stress-strain curves for pristine PbTe and hot-extruded ones with different preferred orientations.

In this work, hot extrusion, a non-chemical means, is employed to modulate the microstructure of binary PbTe ingot. Detailed procedures for material synthesis, hot extrusion, characterization, and transport property measurements of both materials and devices are provided in the Supplementary Information. PbTe ingots with 20 mm in diameter and ~ 20 mm in height were used as the starting materials (**Fig. 1a**). Schematic of the hot extrusion setup is presented in **Fig. S1**. After hot extrusion, the obtained sample displays a predominantly cylindrical morphology with a diameter of 10 mm. Pellets were sliced from the hot-extruded PbTe along the directions perpendicular and parallel to that of extrusion, for unveiling the influence of plastic deformation on microstructure and resultant properties of binary PbTe.

X-ray diffraction (XRD) patterns for all the samples are shown in **Fig. S2**. All diffraction peaks can be found to well correspond to the cubic PbTe, indicating the single phase. Moreover, distinct preferred crystallographic orientations of (200) and (220) are evident in hot-extruded PbTe sectioned perpendicular and parallel to the extrusion direction, respectively. Quantitative texture analysis, based on XRD results [55], yields orientation factors of $F_{[100]}=0.82$ and $F_{[110]}=0.62$, suggesting a strongly textured microstructure for the hot-extruded PbTe. Furthermore, scanning electron microscopy (SEM) observations and electron back-scattering diffraction (EBSD) analysis are conducted

on pristine and hot-extruded PbTe to elucidate the evolution of microstructure under extrusion processing.

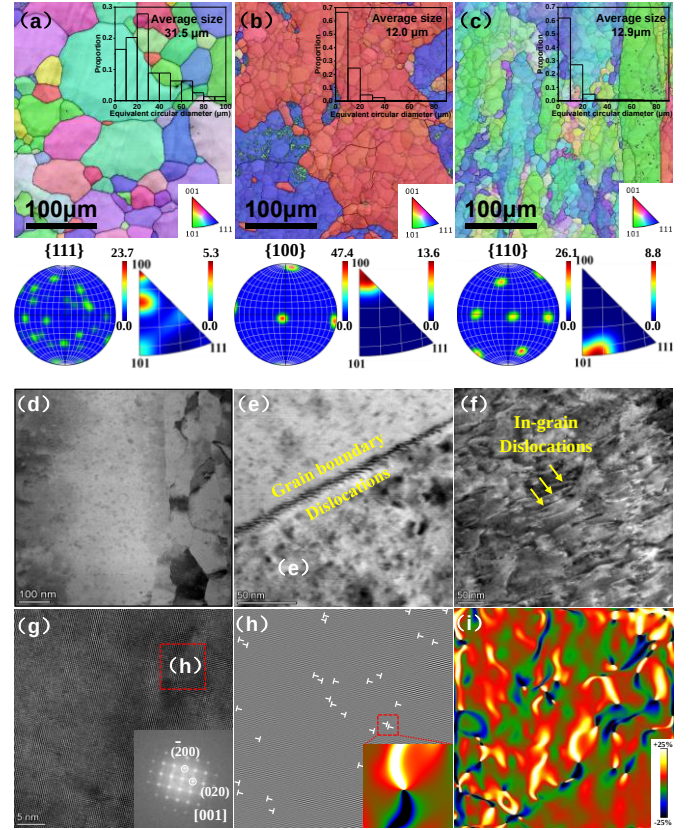


Fig. 2. Electron back-scattering diffraction (EBSD) maps with pole figures and inverse pole figures for (a) pristine PbTe and hot-extruded PbTe sectioned (b) perpendicular and (c) parallel to the extrusion direction. The statistics of the grain size are shown in the inset. (d-f) Low-magnification resolution scanning transmission electron microscopy (STEM) images, (g) high-resolution TEM (HRTEM) image with an inset of corresponding fast Fourier transform (FFT) pattern, (h) HRTEM image showing details on dislocations and (i) the corresponding strain mappings for the hot-extruded PbTe.

As shown in **Fig. S3**, the hot extrusion effectively refines the crystalline grains in binary PbTe, as evidenced by SEM images. Energy dispersive spectrometer (EDS) analysis reveals the homogeneity of elemental distributions, affirming the high purity of hot-extruded PbTe. Moreover, the SEM images of the center and edge of the extruded sample along the radial direction exhibit similar grain refinement, which prove the high uniformity of the microstructure and performance. This grain refinement is further quantitatively supported by EBSD maps, which documents a statistically significant reduction in average grain size from ~ 31 mm to ~ 12 mm (**Fig. 2a-c**). Additionally, the pole figure and inverse pole figures for pristine PbTe (**Fig. 2a**) indicate random crystallographic orientation, whereas the hot-extruded samples exhibit strong preferential alignment along the $[100]$ (**Fig. 2b**) and $[110]$ (**Fig. 2c**) directions in the directions perpendicular and parallel to the extrusion, respectively. These results align closely with the XRD data and further corroborate the development of a pronounced crystallographic texture.

Additionally, the evolution of low-angle grain

boundaries (LAGBs, 2° – 10°) and high-angle grain boundaries (HAGBs, $>10^{\circ}$) before and after hot extrusion was quantitatively analyzed based on the EBSD data (Fig. S4a–c). The increased LAGB fraction after extrusion indicates enhanced dynamic recovery and the formation of abundant subgrain boundaries through dislocation rearrangement. Concurrent dynamic recrystallization further promotes grain refinement and the partial transformation of LAGBs into HAGBs. Moreover, the geometrically necessary dislocations (GND) density of the extruded PbTe is significantly higher than that of the pristine one, clearly demonstrating the successful introduction of a dense dislocation network in PbTe through the hot-extrusion process (Fig. S4d–f). The resulting subgrain boundaries and dislocations provide additional phonon-scattering sources, particularly for low- and medium-frequency phonons, thereby contributing to the reduced lattice thermal conductivity of the extruded samples.

Atomic-scale microstructural analysis was further performed via scanning transmission electron microscopy (STEM), with representative results shown in Fig. 2d–f. Fine grains with a size of ~ 100 nm are observed in Fig. 2d, accompanied by dense dislocations located both at grain boundaries (Fig. 2e) and within the grain interiors (Fig. 2f) for hot-extruded PbTe. The liquid-phase compaction and chemical manipulation have been proven to successfully introduce dislocations in thermoelectric materials, but these dislocations are predominantly confined either to grain boundaries [9] or to grain interiors [11,12,56–58], respectively. It is therefore believed that a higher density of dislocations can be achieved in thermoelectric materials through hot extrusion processing compared to the reported strategies. Therefore, a substantial reduction in lattice thermal conductivity is anticipated, arising from the strong additional phonon scattering at refined grain boundaries and by dense dislocations.

As shown in Fig. 2g, high-resolution TEM images, along with the corresponding fast Fourier transform (FFT) pattern, confirm that the matrix possesses a cubic PbTe phase structure. Moreover, atomic-resolution TEM image reveals a high density of dislocations, accompanied by substantial lattice strain within hot-extruded PbTe (Fig. 2h), as further evidence by the strain field distribution quantified through geometric phase analysis (GPA, Fig. 2i). Given that both transport properties and mechanical behavior are sensitive to microstructural features of defects and texture, the observed structural evolution underscores the necessity of evaluating the resulting thermoelectric and mechanical performance.

The thermoelectric transport properties of pristine and hot-extruded PbTe are measured, with the detailed results shown in Fig. 1c–d and Fig. S5. Pristine PbTe exhibits intrinsic semiconducting behavior, whereas the hot-extruded samples possess a substantially elevated room-temperature Hall carrier concentration (n_H) of $\sim 5 \times 10^{19} \text{ cm}^{-3}$, along with a negative sign (Fig. 1d), indicating n-type conduction. This transition can be reasonably understood by the Te deficiency introduced during the extrusion process, as evidenced by electron paramagnetic resonance (EPR) spectroscopy, which reveals an increased concentration of Te vacancies (Fig.

S5a). The low formation energy for Te vacancy, as theoretically calculated and shown in Fig. 3a, provides a further support for its existence. Fig. S5b displays the temperature dependence of Hall mobility (μ_H), which follows a relationship of $\mu_H \sim T^{2.75}$. This scaling is characteristic of n-type PbTe, where carrier scattering is dominated by acoustic phonons, suggesting that the mechanism of carrier scattering remains unaltered in the hot-extruded PbTe.

Both electrical resistivity (Fig. S5c) and Seebeck coefficient (Fig. S5d) of hot-extruded PbTe are found to increase with increasing temperature, showing degenerate semiconducting behavior resulting from the increased n_H . The negative sign of the Seebeck coefficient further confirms n-type conduction. The increased n_H thereby achieves a significant enhancement in the power factor, reaching $\sim 30 \text{ mW/cm}^2\text{K}$. Temperature dependent total (κ) and lattice (κ_L) thermal conductivities are shown in Fig. S5e and Fig. 1d, respectively. The κ_L is estimated by subtracting the electronic thermal conductivity (κ_E), calculated using the Wiedemann-Franz law ($\kappa_E = L T / \rho$), from the κ , where the Lorenz number L is determined via the single Kane band (SKB) model [59]. Owing to the synergistic effects of Te vacancies, dense dislocations and grain refinement, which collectively enable broad-frequency phonon scattering, the κ_L of the hot-extruded PbTe is significantly reduced to $\sim 0.55 \text{ W/m}^2\text{K}$ at 800 K. Consequently, an exceptional peak zT of ~ 1.3 is impressively achieved in n-type hot-extruded PbTe (Fig. S5f), attributable solely to microstructural control rather than chemical composition manipulation. This unique approach makes binary PbTe comparable to the reported high-performance PbTe via chemical doping (Fig. S6).

Notably, the isotropic nature of thermoelectric transport in hot-extruded PbTe is demonstrated by the consistent electrical and thermal properties observed across samples with varying crystallographic orientations (Fig. S5b–f). This performance is highly reproducible, as validated by the comparable transport data obtained from six independently fabricated samples under identical processing conditions (Fig. 3b and Fig. S7). Moreover, the thermal stability of the hot-extruded samples was assessed through repeated measurements over multiple 300–800 K cycles and an extended 60-hour hold at 800 K, as shown in Fig. S8 and Fig. S9, respectively. The minimal variation in transport properties under these conditions validates their exceptional stability of the introduced defects at high operating temperatures.

The mechanical properties of a material are highly sensitive to its microstructure, yet can exhibit anisotropic behavior even within cubic crystal structures of PbTe. Theoretical prediction of the elastic modulus for cubic PbTe illustrates strong anisotropy in its mechanical properties (Fig. S10) [60]. Hence, compression tests were performed on pristine and hot-extruded PbTe with varying preferred orientations to evaluate the influence of microstructural evolution on the mechanical performance. As shown in Fig. 1e and Fig. S11, the hot-extruded PbTe with a preferred [100] orientation shows the highest compressive strength of 158 MPa, corresponding to a 120% improvement over pristine PbTe (72 MPa). This

significant improvement can be reasonably understood by the incorporation of multiple microstructural defects, including vacancies, dislocations and refined grain boundaries. Fracture morphology in the **Fig. S12** shows obvious plastic deformation-induced transformation. The pristine PbTe shows a flat fracture surface with more cleavage characteristics and a small amount of tearing ridge traces of plastic fracture. In contrast, the extruded sample exhibits significant grain refinement and a highly undulating surface with densely interlaced slip lines and micro-tearing edges, showing more significant plastic fracture characteristics. This microstructural evolution from cleavage to slip-dominated fracture significantly improves the toughness of the material. The hot-extruded [100]-oriented PbTe materials exhibit strong competitiveness in both thermoelectric performance and mechanical properties.

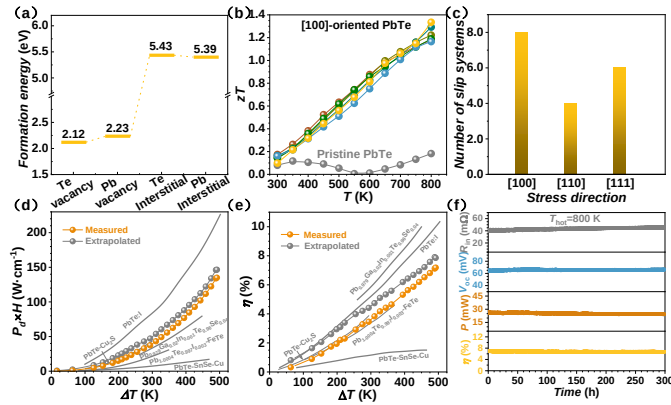


Fig. 3. (a) Calculated formation energy of various defects in PbTe. (b) Temperature dependent zT for pristine and six independently hot-extruded PbTe samples with a [100] preferred orientation. (c) Number of slip system for PbTe along with different stress direction. (d) Specific power density and (e) maximum conversion efficiency versus temperature difference (ΔT) for the hot-extruded PbTe single-leg device with a comparison to the prediction and the literature results [61-64]. (f) Open circuit voltage (V_{oc}), internal resistance (R_{in}), maximum output power (P_{max}) and maximum conversion efficiency (η_{max}) for the device during the long-term measurements at the hot side temperature of 800 K.

Furthermore, a maximum plastic strain of $\sim 15\%$ is impressively achieved in the [100]-oriented PbTe, which represents a 90% enhancement over pristine PbTe and a 2.5-fold increase compared to the [110]-oriented sample. It is well-recognized that enhanced mechanical strength is typically accompanied by a reduction in plastic strain [65]. Although grain refinement to the nanoscale enables concurrent improvements in strength and strain in structural materials [41], achieving such synergy remains a key challenge in thermoelectric materials. Thus, the enhanced plastic strain of the [100]-oriented PbTe here is rationally revealed to arise from its crystallographic texture, which activates a greater number of slip systems compared to the [110]-oriented sample (**Fig. 3c** and **Table S1**). Therefore, the coordinated introduction of multidimensional defects and crystallographic texture enables simultaneous enhancements of compressive strength and plastic strain, respectively. Such a superior mechanical performance the [100]-oriented PbTe is

beneficial for ensuring the structural integrity during material processing and device operation. Compared with previously reported PbTe materials, the PbTe developed in this work exhibits significantly enhanced plasticity and strength (**Fig. S13**). These results offer a viable strategy for synergistic optimization of mechanical strength and plastic strain in thermoelectric materials.

A hot-extruded PbTe single-leg device measuring 1.9 mm $\times$ 1.9 mm $\times$ 18 mm was sliced to evaluate its power output and conversion efficiency, as shown in **Fig. S14**. The corresponding measurements were performed using the setup illustrated in the inset of **Fig. S14a**. The cold-side temperature was stabilized at 300 K via a water-cooling system. **Fig. S14a** presents the output voltage (V) as a function of current (I) under different temperature gradients (ΔT). The open circuit voltage (V_{oc}) and the internal resistance (R_{in}) can be determined from the intercept and the slope, respectively, obtained by linear regression of the V - I curves. As shown in **Fig. S15a-b**, both the measured V_{oc} and R_{in} are found to agree well with the predictions based on the temperature dependent Seebeck coefficient and electrical resistivity, respectively. The observed increases in V_{oc} and R_{in} with increasing temperature are attributed to the corresponding rise in the Seebeck coefficient and electrical resistivity at elevated temperatures.

Current dependent output power (P) and conversion efficiency (η) under different ΔT are shown in **Fig. S14b** and **Fig. S14c**, respectively. A maximum output power (P_{max}) of ~ 27 mW is achieved under a ΔT of ~ 500 K. Thus, a maximum efficiency (η_{max}) of $\sim 7.2\%$ is realized under a ΔT of ~ 500 K. The measurement methodology employed in this work effectively eliminates the influence of interfacial resistance on the P and η [66]. Both measured P_{max} and η_{max} are found to be lower than those extrapolated results (**Fig. S15c** and **Fig. S15d**). This discrepancy would originate from the R_{in} of the single-leg device being smaller than the minimum load resistance (R_{load}) of the measurement system. The extrapolations from the measured results yield achievable P_{max} of 29.3 mW and η_{max} of 7.9%. The maximum extrapolated P_{max} and η_{max} at different ΔT could well follow the predictions.

Fig. 3d and **Fig. 3e** respectively compares the specific power density ($P_d \times H$, where H represents the leg height) and the η_{max} of the hot-extruded binary PbTe with reported results for PbTe-based single-leg devices in the literatures [62-65]. Although the specific power density and η_{max} achieved in this work are below their theoretically attainable values (**Fig. S15**), these still ranks among the highest values reported for PbTe-based materials. The long-term measurements for the single-leg device are conducted at a hot-side temperature of 800 K for 300 hours to illustrate the thermal stability, as shown in **Fig. 3f**. The near-constant values of R_{in} , V_{oc} , P_{max} and η_{max} during long-term measurements confirm the exceptional stability of the single-leg device at an operational temperature below 800 K. These results strongly demonstrate that the hot-extruded PbTe is a highly promising mid-temperature n-type component for the assembly of high-performance thermoelectric modules.

In summary, hot extrusion plastic deformation enables simultaneous introduction of multi-dimension

defects and crystallographic texturing in binary PbTe. The coordinated presence of Te vacancies, dislocations and refine grain boundaries effectively scatters phonons across a broad frequency spectrum, resulting in a significant reduction in lattice thermal conductivity to ~ 0.55 W/m-K. Concurrently, Te vacancies elevate the electron carrier concentration, leading to a substantial enhancement in power factor. This synergistic optimization of thermal and electronic transport properties yields an exceptional peak zT of ~ 1.3 , which corresponds to a durable conversion efficiency of 7.2% in an n-type PbTe single-leg device under a temperature gradient of 500 K. Moreover, the defect- and texture-engineered microstructure enables concurrent improvements by about 100% in both compression strength and plastic strain in the hot-extruded PbTe with a preferred [100] orientation. This work not only establishes hot-extruded PbTe as a robust n-type candidate for thermoelectric generators, but also outlines a microstructural design strategy via plastic processing for the synergistic efficiency enhancement and mechanical properties in thermoelectrics.

- 1 Chen, Z., et al., Manipulation of phonon transport in thermoelectrics. *Advanced Materials*, 2018, 30: 1705617
- 2 Ioffe, A, Ioffe AV Thermal conductivity of solid solutions. *Soviet Physics Solid State*, 1960, 2: 719-728
- 3 Pei, Y., et al., Interstitial point defect scattering contributing to high thermoelectric performance in SnTe. *Advanced Electronic Materials*, 2016, 2: 1600019
- 4 He, R., et al., Improved thermoelectric performance of n-type half-heusler $\text{MCo}_{1-x}\text{Ni}_x\text{Sb}$ ($m=\text{Hf, Zr}$). *Materials Today Physics*, 2017, 1: 24-30
- 5 Fu, L., et al., Large enhancement of thermoelectric properties in n-type PbTe via dual-site point defects. *Energy & Environmental Science*, 2017, 10: 2030-2040
- 6 Qi, J., et al., Dimer rattling mode induced low thermal conductivity in an excellent acoustic conductor. *Nature Communications*, 2020, 11: 5197
- 7 Chen, Z., et al., Lattice dislocations enhancing thermoelectric PbTe in addition to band convergence. *Advanced Materials*, 2017, 29: 1606768
- 8 Nan, P., et al., Revealing the origin of dislocations in $\text{Pb}_{1-x}\text{Sb}_{2x/3}\text{Se}$ ($0 < x \leq 0.07$). *Nanoscale*, 2020, 12: 19165-19169
- 9 Kim, S, et al., Dense dislocation arrays embedded in grain boundaries for high-performance bulk thermoelectrics. *Science*, 2015, 348: 109-114
- 10 Xin, J., et al., Mg vacancy and dislocation strains as strong phonon scatterers in $\text{Mg}_2\text{Si}_{1-x}\text{Sb}_x$ thermoelectric materials. *Nano Energy*, 2017, 34: 428-436
- 11 Wu, Y., et al, Lattice strain advances thermoelectrics. *Joule*, 2019, 3: 1276-1288
- 12 Xiao, Y., et al., Cu-interstitials enable carriers and dislocations for thermoelectric enhancements in n-PbTe_{0.75}Se_{0.25}. *Chem*, 2020, 6: 523-537
- 13 Zhang, Q., et al., Realizing high-performance thermoelectric power generation through grain boundary engineering of skutterudite-based nanocomposites. *Nano Energy*, 2017, 41: 501-510
- 14 Wu, R., et al., Strong charge carrier scattering at grain boundaries of PbTe caused by the collapse of metavalent bonding. *Nature Communications*, 2023, 14: 719
- 15 Poudel, B, et al., High-thermoelectric performance of nanostructured bismuth antimony telluride bulk alloys. *Science*, 2008, 320: 634-638
- 16 Cao, Q., et al., Engineering MgAg alloy segregation at grain boundary for enhanced room-temperature n-type $\text{Mg}_3(\text{Sb,Bi})_2$ -based thermoelectrics. *Science China Materials*, 2026, 69: 2309-2316
- 17 Yang, T., et al., Realizing high thermoelectric performance in copper sulfide via intermediate doping. *Science China Materials*, 2025, 68: 2497-2506
- 18 Pei, Y., et al., Convergence of electronic bands for high performance bulk thermoelectrics. *Nature*, 2011, 473: 66-69
- 19 Liu, W., et al., Convergence of conduction bands as a means of enhancing thermoelectric performance of n-type $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ solid solutions. *Physical Review Letters*, 2012, 108: 166601
- 20 Tang, Y., et al., Convergence of multi-valley bands as the electronic origin of high thermoelectric performance in CoSb_3 skutterudites. *Nature Materials*, 2015, 14: 1223-1228
- 21 Fu, C., et al., High band degeneracy contributes to high thermoelectric performance in p-type half-heusler compounds. *Advanced Energy Materials*, 2014, 4: 1400600
- 22 Fu, C., et al., Realizing high figure of merit in heavy-band p-type half-heusler thermoelectric materials. *Nature Communications*, 2015, 6: 8144
- 23 Zheng, L., et al., Alloying for orbital alignment enables thermoelectric enhancement of EuCd_2Sb_2 . *Journal of Materials Chemistry A*, 2019, 7: 12773-12778
- 24 Imasato, K, et al., Band engineering in Mg_3Sb_2 by alloying with Mg_3Bi_2 for enhanced thermoelectric performance. *Materials Horizons*, 2018, 5: 59-64
- 25 Li, W., et al., Promoting SnTe as eco-friendly solution for p-PbTe thermoelectric via band convergence and interstitial defects. *Advanced Materials*, 2017, 29: 1605887
- 26 Lin, S., et al., Tellurium as a high-performance elemental thermoelectric. *Nature Communications*, 2016, 7: 10287
- 27 Pei, Y., et al., Optimum carrier concentration in n-type PbTe thermoelectrics. *Advanced Energy Materials*, 2014, 4: 1400486
- 28 LaLonde, A, et al., Reevaluation of $\text{PbTe}_{1-x}\text{I}_x$ as high performance n-type thermoelectric material. *Energy & Environmental*

- Science, 2011, 4: 2090-2096
- 29 Luo, Z., et al., Extraordinary role of Zn in enhancing thermoelectric performance of Ga-doped n-type PbTe. *Energy & Environmental Science*, 2022, 15: 368-375
 - 30 Wang, S., et al., A route to high thermoelectric performance of lead chalcogenides: Enhancing carrier mobility. *Science China Materials*, 2025, 68: 780-784
 - 31 Snyder, G. and E. Toberer, Complex thermoelectric materials. 2008, 7: 114
 - 32 Pei, Y., et al., Band engineering of thermoelectric materials. *Advanced Materials*, 2012, 24: 6125-6135
 - 33 Wang, H., et al., The criteria for beneficial disorder in thermoelectric solid solutions. *Advanced Functional Materials*, 2012, 23: 1586-1596
 - 34 Yan, Q. and M. Kanatzidis, High-performance thermoelectrics and challenges for practical devices. *Nature Materials*, 2021, 21: 503-513
 - 35 Wu, Y., et al., Investigation on the decomposition behavior of AgSbTe₂-based chalcogenides. *Science China Materials*, 2025, 68: 912-919
 - 36 Lo, C., et al., Microstructural instability and its effects on thermoelectric properties of SnSe and Na-doped SnSe. *ACS Applied Materials & Interfaces*, 2024, 16: 49442-49453
 - 37 Liu, J., et al., High-performance near-room-temperature n-type Bi₂Te₃-based thermoelectric alloys with superior mechanical properties. *Science China Materials*, 2025, 68: 920-927
 - 38 Fang, T., et al., Complex band structures and lattice dynamics of Bi₂Te₃-based compounds and solid solutions. *Advanced Functional Materials*, 2019, 29: 1900677
 - 39 Hu, X., et al., Power generation from nanostructured PbTe-based thermoelectrics: Comprehensive development from materials to modules. *Energy & Environmental Science*, 2016, 9: 517-529
 - 40 Duan, F., et al., Ultrastrong nanotwinned pure nickel with extremely fine twin thickness. *Science Advances*, 2021, 7: eabg5113
 - 41 Zhou, X., et al., High-pressure strengthening in ultrafine-grained metals. *Nature*, 2020, 579: 67-72
 - 42 Yang, T., et al., Multicomponent intermetallic nanoparticles and superb mechanical behaviors of complex alloys. *Science*, 2018, 362: 933
 - 43 Shen, X., et al., Elastic thermoelectric generators illustrated in constantan. *Interdisciplinary Materials*, 2025, 4: 508-514
 - 44 Hu, J., et al., Tailoring retained austenite and mechanical property improvement in Al-Si-V containing medium Mn steel via direct intercritical rolling. *Materials Science and Engineering: A*, 2022, 855: 143904
 - 45 Wang, L., et al., Tailoring planar slip to achieve pure metal-like ductility in body-centred-cubic multi-principal element alloys. *Nature Materials*, 2023, 22: 950-957
 - Liu, W., et al., Deformation-induced dynamic precipitation of 14h-lpso structure and its effect on dynamic recrystallization in hot-extruded Mg-Y-Zn alloys. *International Journal of Plasticity*, 2023, 164: 103573
 - Du, B., et al., Microstructural characteristics and mechanical properties of the hot extruded Mg-Zn-Y-Nd alloys. *Journal of Materials Science & Technology*, 2021, 60: 44-55
 - Du, B., et al., Effect of extrusion process on the mechanical and in vitro degradation performance of a biomedical Mg-Zn-Y-Nd alloy. *Bioactive Materials*, 2020, 5: 219-227
 - Lu, T., et al., Synergistically enhanced thermoelectric and mechanical performance of Bi₂Te₃ via industrial scalable hot extrusion method for cooling and power generation applications. *Materials Today Physics*, 2023, 32: 101035
 - Chen, S., et al., Regulation of dynamic recrystallization in p-type Bi₂Te₃-based compounds leads to high thermoelectric performance and robust mechanical properties. *Materials Today Physics*, 2024, 46:
 - Gao, Z., et al., Warm metalworking for plastic manufacturing in brittle semiconductors. *Nature Materials*, 2025, 24: 1538-1544
 - Fu, L., et al., Warm metalworking for brittle liquid-nitrogen-temperature thermoelectric materials. *Advanced Energy Materials*, 2025, 15: e03241
 - Li, Y., et al., Grain recovery facilitated low-angle grain boundaries and texture for high-performance BiSbTe alloys. *Materials Today Physics*, 2024, 49: 101591
 - Zhang, Q., et al., Robust Bi₂(Te,Se)₃ thermoelectrics from large shrinkage ratio extrusion drives advanced peltier microcooler and power generator. *Advanced Functional Materials*, 2025, 35: 2500731
 - Parashchuk, T, et al., Ultralow lattice thermal conductivity and improved thermoelectric performance in Cl-doped Bi₂Te_{3-x}Se_x alloys. *ACS Applied Materials & Interfaces*, 2022, 14: 33567-33579
 - Pan, Y., et al., Melt-centrifuged (Bi,Sb)₂Te₃: Engineering microstructure toward high thermoelectric efficiency. *Advanced Materials*, 2018, 30: 1802016
 - Chen, Z., et al., Vacancy-induced dislocations within grains for high-performance PbSe thermoelectrics. *Nature Communications*, 2017, 8: 13828
 - Chen, Z., et al., Lattice dislocations enhancing thermoelectric PbTe in addition to band convergence. *Advanced Materials*, 2017, 29: 1606768
 - Ravich, Y, et al., Semiconducting lead chalcogenides. Place Published: Semiconducting Lead Chalcogenides,1970
 - Dobson, P, Physical properties of crystals – their representation

by tensors and matrices. *Physics Bulletin*, 1985, 36: 506

- 61 Xiao, Y., et al., High-ranged zT value promotes thermoelectric cooling and power generation in n-type PbTe. *Advanced Energy Materials*, 2022, 12: 2200204
- 62 Deng, P., et al., Liquid-like copper chalcogenide modulates electron donors in high-performance n-type PbTe thermoelectrics. *Cell Reports Physical Science*, 2023, 4: 101413
- 63 Chen, S., et al., Thermoelectric and mechanical characterization of the utilization of FeTe as an electrode for iodine-doped PbTe. *Journal of Alloys and Compounds*, 2022, 905: 164267
- 64 He, H., et al., Multicomponent synergistic doping enables high-efficiency n-type PbTe thermoelectric devices. *Small*, 2024, 21: 2408864
- 65 Yoshida, S, et al., Friction stress and hall-petch relationship in cocrni equi-atomic medium entropy alloy processed by severe plastic deformation and subsequent annealing. *Scripta Materialia*, 2017, 134: 33-36
- 66 Zhou, J. et al. Gradient doping enables an extraordinary efficiency in thermoelectric $\text{PbTe}_{1-x}\text{I}_x$. *Advanced Materials*, 2024, 36: 2405299

Acknowledgements This work was financially supported by the National Key Research and Development Program of China (2023YFB3809400), the National Natural Science Foundation of China (Grant No. T2125008, 52532009, 52371234), the Hong Kong, Macao and Taiwan Science and Technology Cooperation Project for Science and Technology Innovation Plan of Shanghai (23520760600), the Innovation Program of Shanghai Municipal Education Commission (2021-01-07-00-07-E00096) and the Fundamental Research Funds for the Central Universities.

Author contributions Yang S and Hu S performed the experiments, analyzed the data. Li Z and Chen J conducted the transmission electron microscopy characterization and analysis. li C and Yang L performed the theoretical calculations. Luo J and Chen Z optimized the design details of the experiment. Li W revised the manuscript. Pei Y supervised the whole project. All authors contributed to the general discussion

Conflict of interest The authors declare that they have no conflict of interest.



Wen Li has been working on the bottleneck problem of low conversion efficiency of current thermoelectric materials, devoted to designing and developing high performance thermoelectric materials. He holds a B.E. and a M.S. degree from Zhengzhou University, a Ph.D. degree from Shizuoka University. He became an assistant researcher in 2013, an associate professor in 2017 and a professor in 2021 at the School of Materials Science and Engineering, Tongji University, Shanghai, China. His interests are focused on flexible thermoelectric materials and new biomedical materials.



Shujing Yang received his bachelor 's degree from Guangxi University. He is currently a graduate student under the guidance of Professor Wen Li of Tongji University. His research focuses on hot extrusion materials.



Shanshan Hu received her MS degree from South China Normal University, China. She is now a PhD candidate at Tongji University under the supervision of Prof. Wen Li. Her research focuses on magnesium-based thermoelectric materials and hot extrusion materials.



Ziyang Li is a PhD student at the School of Materials Science and Engineering, Shanghai Jiao Tong University. His research focuses on the plastic deformation mechanisms of metallic materials, and their application in both structural and functional materials.

塑性加工诱导的多尺度微结构使 PbTe 的热电性能和机械性能同时增强

杨树靖 1, #, 胡珊珊 1, #, 李子言 2, #, 李昌源 1, 杨龙 1, 陈志炜 1, 陈娟 2, 骆军 1, 李文 1, * & 裴艳中 1

微结构工程是一种调控材料功能的通用方法 ,但性能与微结构间的复杂关系使得多性能优化极具挑战。随着热电技术向大规模、可靠应用转变 ,同时提高转换效率和机械性能成为关键。本工作采用热挤压工艺 ,在二元 PbTe 中引入多维缺陷和特定织构。多维缺陷在宽频范围内散射声子 ,显著降低晶格热导率 ;结合 Te 空位提升的电子浓度 ,协同优化了功率因子。同时 , [100]织构使压缩强度和延展性均提高约 100%。与传统依赖复杂成分调控的热电材料不同 ,本研究证明 ,即使在二元 PbTe 中 ,塑性加工也是一种可行策略 ,能提供高重复性的热电与机械性能 ,从而推动热电发展。