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Elastic thermoelectric generators

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Thermoelectric generators, with the unique ability to convert temperature gradients into electricity, have long been acknowledged as a sustainable technique for waste heat recovery. The remarkable advancements in both thermoelectric materials and devices have substantially propelled the practical applications of thermoelectric generators. The capability of generating electricity through the temperature gradient between the human body and the ambient environment highlights the significant potential of flexible thermoelectric devices as self-powered energy sources for wearable electronics. However, this leaves a formidable challenge with respect to the bendability of the high-performance, yet inherently brittle, inorganic thermoelectric materials. The strategies of dislocationization and grain refinement have been reported to effectively enhance the elastic strain, thereby ensuring fully recoverable bendability for inorganic thermoelectric materials [1,2]. This offers a versatile approach for enhancing the elastic bendability of inorganic thermoelectric generators.

High power output and exceptional bendability are the pivotal parameters for a powerful flexible thermoelectric generator. The power output is dominantly determined by the power factor of the materials, which can be effectively improved via band convergence [3] or lattice plainification [4]. Due to the interconnection between atoms via ionic and/or covalent bonds, the inorganic thermoelectric materials are generally accompanied by a characteristic of rigidity that largely restricts their applications in flexible scenarios. To overcome this challenge, adopting thin film substrate designs [5] or sandwich structures [6] has become a major strategy to impart flexibility to these inorganic materials.

Ductile inorganic semiconductors [7,8] enable a high degree of flexibility stemming from their inherent plasticity. However, the irreversible lattice slip due to the plastic deformations may result in the initial functionality irrecoverable and therefore a compromise in performance. Once a material deforms within the elastic region, it ensures that its functionalities can fully recover. The elastic deformability can be effectively enhanced by geometrically reducing the thickness or scientifically increasing the material's elastic strain [9]. Enhancements of elastic strain serve as an intrinsic solution to enable the accommodation of large-curvature elastic bending within the same thickness.

A high yield strength (σ_E) is responsible for a large maximum elastic strain (ε_E), which sensitively depends on the microstructure. Strategies such as refining grains, creating dense dislocations and introducing point

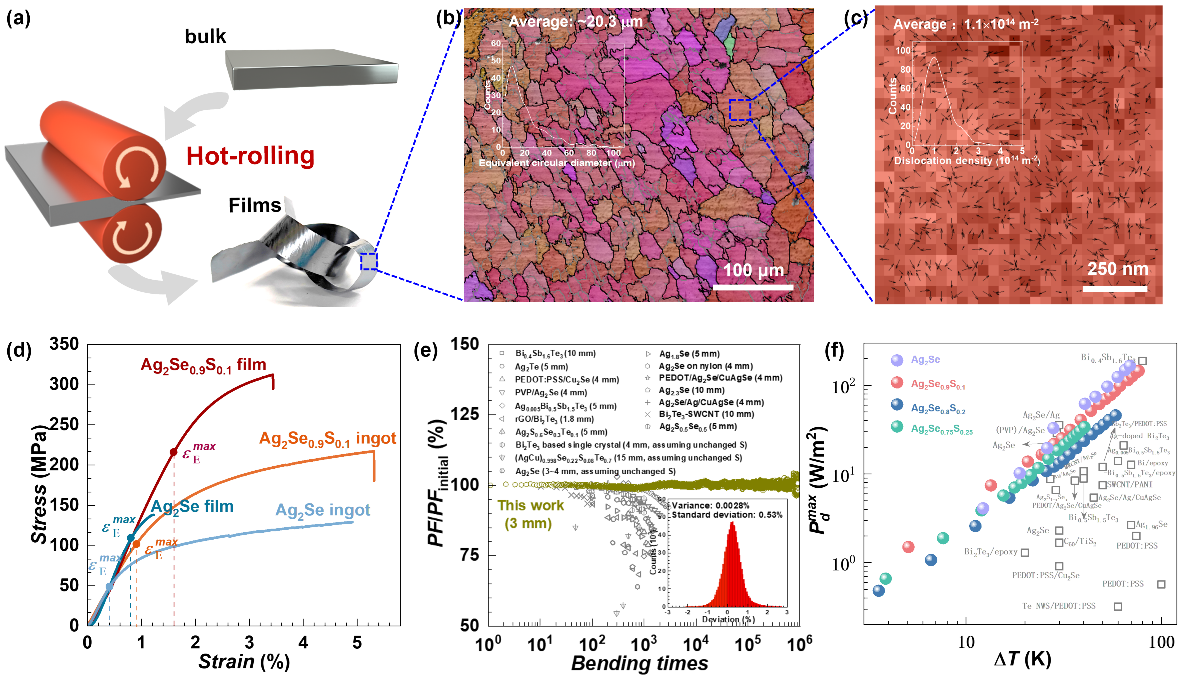

Figure 1 (a) Schematic of hot-rolling process for foils; (b) electron back-scattering diffraction (EBSD) image with a statistical analysis of the grain size in the rolled Ag_2Se film; (c) zoomed-in one showing dense dislocations with a statistical analysis; (d) stress *versus* strain of three-point bending test for the ingot and rolled film of Ag_2Se and $Ag_2Se_{0.9}S_{0.1}$; (e) the unchanged power factor with a statistical analysis in a 36 μm thick Ag_2Se device after 1,000,000 bending cycles at a radius of 3 mm [1]; (f) maximum power densities (P_d^{max}) versus ΔT for six-leg Ag_2Se, $Ag_2Se_{0.9}S_{0.1}$, $Ag_2Se_{0.8}S_{0.2}$, and $Ag_2Se_{0.75}S_{0.25}$ film devices. Reproduced with permission from Ref. [2]. Copyright©2024, American Chemical Society.

defects would significantly improve the σ_E. Both grain refinement and the creation of dislocations creation can technically be realized through plastic deformation, while the introduction of point defects can be achieved by the formation of solid solutions. Although plastic processing has been extensively employed in metals, it remains challenging for the high-performance inorganic thermoelectric materials due to their inherent rigidity.

To address this difficulty, Ding *et al*. [1,2] developed a hot-rolling technique that facilitates the initial softening of materials at appropriate temperatures, enabling plastic processing of inorganic thermoelectric materials (Figure 1a). This method enables not only plastic deformation for the purpose of microstructure engineering but also the thinning of bulk for the fabrication of films. The rigid Ag_2Se becomes deformable upon being heated up to 150°C [1]. The plastic deformation through the hot rolling successfully refined grain-size from millimeters to ~20 μm and achieved dense dislocations (~10^{14} mm^2) in the hot-rolled Ag_2Se (Figure 1b and c). These characteristics contribute to a substantial increase in the σ_E, which in turn results in an enhanced ε_E of 0.8% which is twice that of the unrolled Ag_2Se (Figure 1d). The hot-rolling technique also facilitated controllable fabrication of Ag_2Se films with various thickness via the multi-pass processing. The exceptional elasticity leads the ~36 μm thick film to be capable of undergoing elastic bending at a curvature radius of ~3 mm, remarkably ensuring a full recoverability of its transport properties after being bent 1,000,000 times (Figure 1e). The films fabricated by other techniques often exhibit significant performance degradation, even with the bending times <2000 [10,11]. The deformation beyond the elastic limit can potentially be considered as one of the underlying causes. Further alloying with Ag_2S leads to a much higher

σ_E compared to the Ag_2Se ingot, eventually endowing a ε_E up to ~1.6% in the rolled $Ag_2Se_{0.9}S_{0.1}$ [2] (Figure 1d). This could guarantee a thicker film can be bent at the same curvature radius.

Due to the excellent machinability, the devices were assembled using bolts and nuts. The firm contact between the Au-deposited films and the electrodes results in low interfacial contact resistance. The rolled Ag_2Se and $Ag_2Se_{0.9}S_{0.1}$ films almost inherited the outstanding transport properties of their ingots. These eventually achieved a competitive power density for the elastic Ag_2Se and $Ag_2Se_{0.9}S_{0.1}$ thermoelectric devices (Figure 1f). For practical applications, the comfortability is also a crucial factor for wearable thermoelectric devices. Therefore, it is essential to optimize the method employed for connecting the films and the electrodes. The metallic layers deposited by the magnetron sputtering can metalize the surface for the ohmic contact with electrodes and render the surface weldable [12]. The welding using a thin solder would endow the contact between the films and the electrodes with low interfacial resistance and flexibility.

Despite the fact that plastic processing can bring about remarkable augmentations in elastic strain, the efforts have been solely concentrated on n-type Ag_2Se- [1,2] and Ag_2Te-based [13] thermoelectric materials. This can be ascribed to the necessity for inorganic thermoelectric materials to possess plasticity characteristics at room or low temperatures. The recently discovered Mg_3Bi_2, which exhibits both ductility and high thermoelectric performance, is a promising candidate for elastic generators [14,15]. So far, the ductile thermoelectric materials at room temperature are still limited, the high-temperature plastic processing is required for the majority of conventional ones. Therefore, the development of facilities that can meet the requirements of vacuum and high-temperature conditions is urgently needed. These research findings not only comprehensively demonstrate the considerable promise of elastic thermoelectric generators but also provide a versatile approach for enhancing the elasticity and fabricating inorganic thermoelectric films.

Conflict of interest

The authors declared no conflict of interest.

References

1 Ding W, Shen X, Jin M, *et al.* Robust bendable thermoelectric generators enabled by elasticity strengthening. *Nat Commun* 2024; **15**: 9767.

2 Ding W, Shen X, Li Z, *et al.* Enhancing recoverable bendability in high-performance Ag_2Se-based thermoelectrics through plastic processing. *ACS Energy Lett* 2024; **9**: 5483–5491.

3 Pei Y, Shi X, LaLonde A, *et al.* Convergence of electronic bands for high performance bulk thermoelectrics. *Nature* 2011; **473**: 66–69.

4 Liu D, Wang D, Hong T, *et al.* Lattice plainification advances highly effective SnSe crystalline thermoelectrics. *Science* 2023; **380**: 841–846.

5 Gao J, Miao L, Lai H, *et al.* Thermoelectric flexible silver selenide films: Compositional and length optimization. *iScience* 2020; **23**: 100753.

6 Miao L, Zhu S, Liu C, *et al.* Comfortable wearable thermoelectric generator with high output power. *Nat Commun* 2024; **15**: 8516.

7 Wei TR, Jin M, Wang Y, *et al.* Exceptional plasticity in the bulk single-crystalline van der Waals semiconductor InSe. *Science* 2020; **369**: 542–545.

8 Shi X, Chen H, Hao F, *et al.* Room-temperature ductile inorganic semiconductor. *Nat Mater* 2018; **17**: 421–426.

9 Peng J, Snyder GJ. A figure of merit for flexibility. *Science* 2019; **366**: 690–691.

10 Lu Y, Zhou Y, Wang W, *et al.* Staggered-layer-boosted flexible Bi_2Te_3 films with high thermoelectric performance. *Nat Nanotechnol* 2023; **18**: 1281–1288.

11 Liu Y, Zhang Q, Huang A, *et al.* Fully inkjet-printed Ag_2Se flexible thermoelectric devices for sustainable power generation. *Nat Commun* 2024; **15**: 2141.

12 Yang Q, Yang S, Qiu P, *et al.* Flexible thermoelectrics based on ductile semiconductors. *Science* 2022; **377**: 854–858.

13 Fan Z, Ding W, Shen X, *et al.* Enhancing recoverable bendability of Ag_2Te-based thermoelectrics by elastic strain manipulation. *Adv Elect Mater* 2025; **11**: 2400728.

14 Zhao P, Xue W, Zhang Y, *et al.* Plasticity in single-crystalline Mg_3Bi_2 thermoelectric material. *Nature* 2024; **631**: 777–782.

15 Li A, Wang Y, Li Y, *et al.* High performance magnesium-based plastic semiconductors for flexible thermoelectrics. *Nat Commun* 2024; **15**: 5108.