

Defects enable Bi_2Te_3 crystal to exhibit exceptional plasticity

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Thermoelectric (TE) technology can mutually convert between heat and electricity power, exhibiting its capacity for power regeneration and cooling. However, traditional TE materials are usually brittle, limiting their applications on curved surfaces. Recent research conducted by Deng *et al.* has discovered that bismuth telluride (Bi_2Te_3), a classic room-temperature thermoelectric material, has transformed from brittle semiconductor to plastic semiconductor through various microstructures caused by antisite defects, achieving the highest ZT value of ~ 1.05 at 300 K compared to other reported plastic semiconductors. Herein, we highlight that this work not only obtained a new high-performance plastic thermoelectric material but also provided an effective way to transform traditional brittle materials into plastic materials.

Thermoelectric materials rely on the migration of internal carriers under a temperature gradient field to realize the direct conversion between heat and electricity [1–3]. With its direct conversion characteristics, thermoelectric devices can create a clean, mute, and efficient working environment, showing great application potential in the energy-renewable area [4–6]. With the development of bulk thermoelectric materials in decades, researchers have exploited a series of inorganic thermoelectric systems, including the PbSe-based [7,8], SnS-based [9,10], SnSe-based [11–14], and other TE semiconductors. High ZT values and elevated conversion efficiencies are achieved in these systems. Nevertheless, the aforementioned materials are brittle, and unable to withstand a small deformation strain at room temperature, limiting their applications to deformable electronic devices. Both flexibility and plasticity are criteria for assessing the material's suitability for deformable devices, but unlike flexibility, which refers to the reversible deformation of the material, plasticity specifically denotes the ability of a material to undergo permanent deformation under external force.

Organic TE materials, including organic semiconductor molecules, hybrid organic materials, and organic ionogel-based materials, exhibit excellent deformability due to their weak intermolecular forces and are already applied to the manufacture of versatile devices.[15] Besides, researchers have successfully produced a series of functional plastic inorganic TE materials and devices by integrating room-temperature metal-like plasticity with a tunable bandgap and high carrier mobil-

ity [16]. However, the ZT values of these materials are much lower than those of state-of-the-art brittle TE materials.

Instead of exploring new intrinsic plastic TE material, a new way of thinking is to turn the existing high-performance brittle TE material into plastic TE materials [17]. Bi_2Te_3 , as a classical room-temperature TE material, has shown great thermoelectric performance both in crystalline[18] and polycrystalline[19,20]. Recently, Deng *et al.* discovered a new approach to transform Bi_2Te_3 from brittle to plastic, obtaining excellent thermoelectric performance. Firstly, they obtained the Bi_2Te_3 crystal close to the theoretical chemistry stoichiometry through the temperature gradient method, facilitating the formation of both antisite Bi_{Te} and Te_{Bi} defects [21,22]. Unlike the perfect crystal structure shown in Figure 1A, these defects induce a various range of microstructures in Bi_2Te_3 , leading to a defective crystal structure. Figure 1B shows the composition of these microstructures, including the stacking fault, swapped bilayer, dislocation, ripplcation, and lattice dislocation. The unique interaction between these microstructures under external stress is the reason why Bi_2Te_3 obtains plasticity.

Researchers first confirm the existence of interlayer Bi-Te bonds in the defective Bi_2Te_3 crystal with swapped bilayer. They figured out that these bonds not only can “glue” the adjacent van der Waals layers together suppressing the interlayer cleavage, but also form Te-Bi-Te-Bi rings conducive to inter-layer sliding under stress to maintain overall integrity. When external forces are applied to the defective Bi_2Te_3 crystal, the corresponding cross-layer shear mainly concentrates around the ripplcation and swapped bilayer, causing the microcracks around the swapped bilayer. However, due to the interlayer Bi-Te bonds, the adjacent van der Waals layers are tightly connected with each other, remaining stable under the pressure. Moreover, the ripplcations block the propaga-

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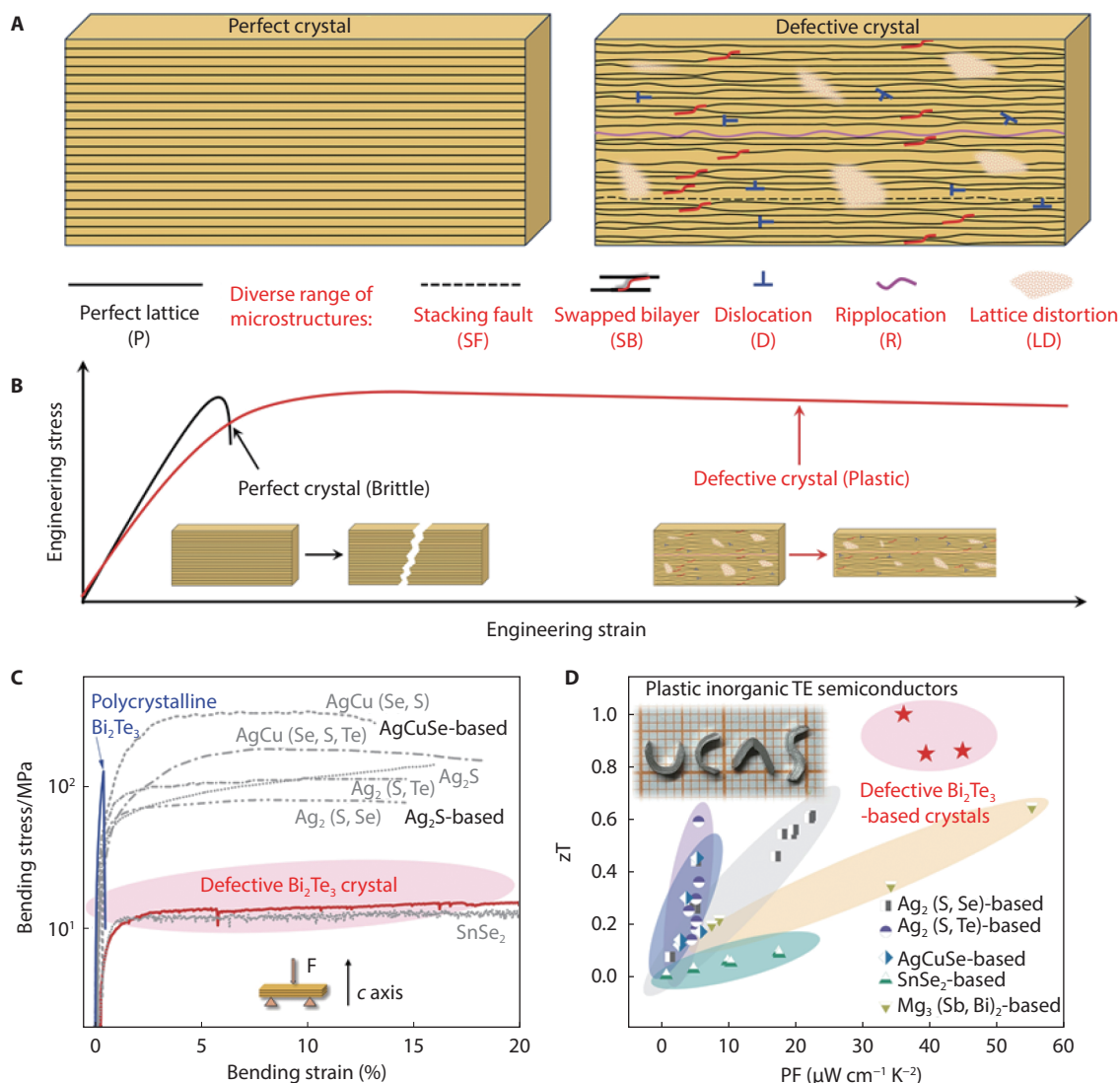


Fig. 1 Defective Bi_2Te_3 -based TE crystals exhibit exceptional plasticity. Schematics of **a** perfect and defective crystals and **b** Their stress-strain curves in engineering contexts. **c** The stress-strain curve was obtained from a three-point bending test conducted on a defective Bi_2Te_3 bulk crystal. For comparative purposes, the data for plastic Ag_2S -based, AgCuSe -based, SnSe_2 -based, and polycrystalline Bi_2Te_3 semiconductors have been included. **d** the room-temperature zT value and power factor for plastic Bi_2Te_3 -based bulk crystals (red stars). Copyright 2024, The American Association for the Advancement of Science.

tion of these microcracks. Thus, the structure of the defective Bi_2Te_3 crystal maintains integrity during the tensile experiment.

The variety of these microstructures is capable of hindering crack propagation by effectively alleviating and distributing the applied stress. Hence, the defective Bi_2Te_3 crystal shows comparable plastic ability to good plastic semiconductors in three point-bending, uniaxial tensile, and compression tests, as shown in Figure 1C. Moreover, the defective Bi_2Te_3 crystal shows excellent TE performance, exceeding the value of other reported plastic TE materials (Figure 1D).

In conclusion, this work illustrates that both antisite Bi_{Te} and Te_{Bi} defects can lead to the formation of high-density and diverse microstructures in Bi_2Te_3 crystals, resulting in the transformation from brittle to plastic behavior. Also, this work introduces a new idea to convert traditional brittle TE materi-

als into plastic ones through defect engineering, holding great guiding significance for follow-up research.

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■ CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

This highlight was written by Baocheng Yuan and revised by Prof. Cheng Chang and Prof. Li-Dong Zhao. All authors have approved the final version of the manuscript.

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