





## MATERIALS SCIENCE

# Bi<sub>2</sub>Te<sub>3</sub>-based applied thermoelectric materials: research advances and new challenges

Jun Pei <sup>†</sup>, Bowen Cai <sup>\*,†</sup>, Hua-Lu Zhuang  and Jing-Feng Li <sup>\*</sup>

Thermoelectric (TE) materials can directly exchange heat and electricity in the solid state. TE devices that do not contain moving parts or produce emissions have been commercialized as electronic coolers and temperature stabilizers, such as refrigerators, wine cellars, portable coolers and temperature controllers for optical communication equipment, infrared sensors and high-powered lasers. TE cooling is suitable for both localized and active cooling and may be the only viable solution to heat management challenges that restrict the development of next-generation communication and computer technologies. In the last few decades, increasing attention has been paid to TE technology because of its ability to harvest and convert waste heat into electricity, leading to the efficient use of energy. Furthermore, miniaturized TE power generators can be used in portable and/or self-powered energy sources [1], including wearable electronics [2] and the Internet of things (IoT) systems [3].

The performance of a TE material is characterized by the dimensionless figure of merit  $ZT = S^2\sigma T/\kappa$ , where  $S$  is the Seebeck coefficient,  $T$  is the absolute temperature,  $\sigma$  is the electrical conductivity and  $\kappa$  is the thermal conductivity.

Semiconductors possess a greater TE effect than metallic materials, which led to the discovery of the first viable TE material, Bi<sub>2</sub>Te<sub>3</sub>. At the end of the last century, TE technology and materials received significant attention because of energy and environmental issues, and great progress has been made in both fundamental research and materials development. As the first TE material discovered ~70 years ago, Bi<sub>2</sub>Te<sub>3</sub>-based materials remain at the forefront of TE

research [4]; so far no TE materials have outperformed Bi<sub>2</sub>Te<sub>3</sub> near room temperature.

Industrially, Bi<sub>2</sub>Te<sub>3</sub>-based TE materials ( $ZT < 1.0$ ) are fabricated by zone melting and unidirectional solidification. The last decade has witnessed the development of Bi<sub>2</sub>Te<sub>3</sub>-based materials with even higher  $ZT$ . Figure 1 summarizes peak  $ZT$  ( $> 1$ ) of Bi<sub>2</sub>Te<sub>3</sub>-based materials along with the years and optimal temperature regions in both  $p$ - and  $n$ -type materials [5,6]. All related references in Fig. 1 are listed in the Supplementary data (Table S1). Two trends were observed:  $p$ -type materials have higher  $ZT$ , while the peak  $ZT$  of  $n$ -type materials was obtained at higher temperatures. Although the same polycrystalline fabrication process was applied to  $n$ -type materials, expected performance enhancement has not been realized as in the  $p$ -type materials [7]. Nanocrystals allowed the peak  $ZT$  to reach up to 1.4 through intense phonon scattering by grain boundaries

and defects [8]. Dispersed nano-SiC partially decoupled  $S$  and  $\sigma$  via an energy-filtering effect, leading to peak  $ZT$  as high as 1.33 at 373 K [9]. In 2015, an exceptional peak  $ZT$  of 1.86 was achieved by introducing dense dislocation arrays based on liquid-phase Te extrusion [10]. The idea of introducing dense dislocations has drawn great interest from researchers, leading to the recent studies devoted to processing innovations [11,12].

The peak  $ZT$  of  $n$ -type materials is often located at 400–470 K, which is higher than room temperature (Fig. 1). Commercial Bi<sub>2</sub>Te<sub>3</sub>-based materials are mainly used for refrigeration and cooling, and the optimal temperature region of  $p$ -type materials is near room temperature, making them more suitable for cooling applications. It is necessary to lower the optimal temperature region of  $n$ -type materials to near room temperature to match  $p$ -type materials and improve the overall performance of Bi<sub>2</sub>Te<sub>3</sub>-based TE devices.

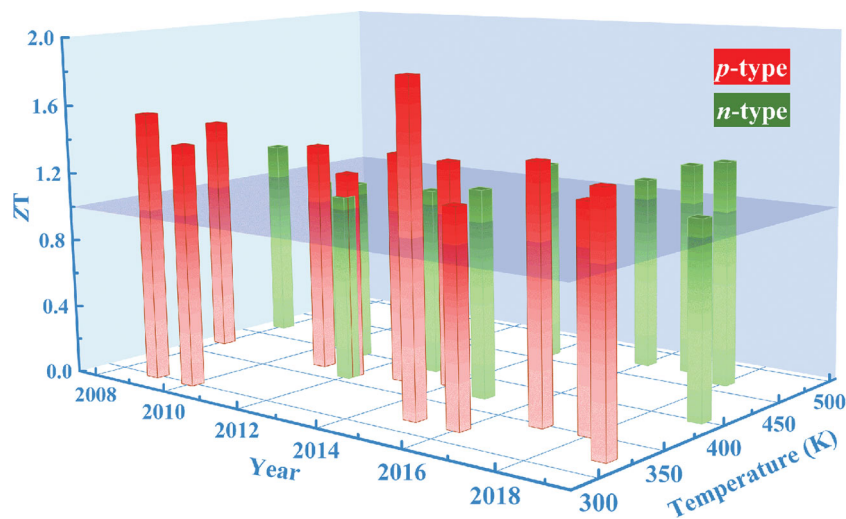
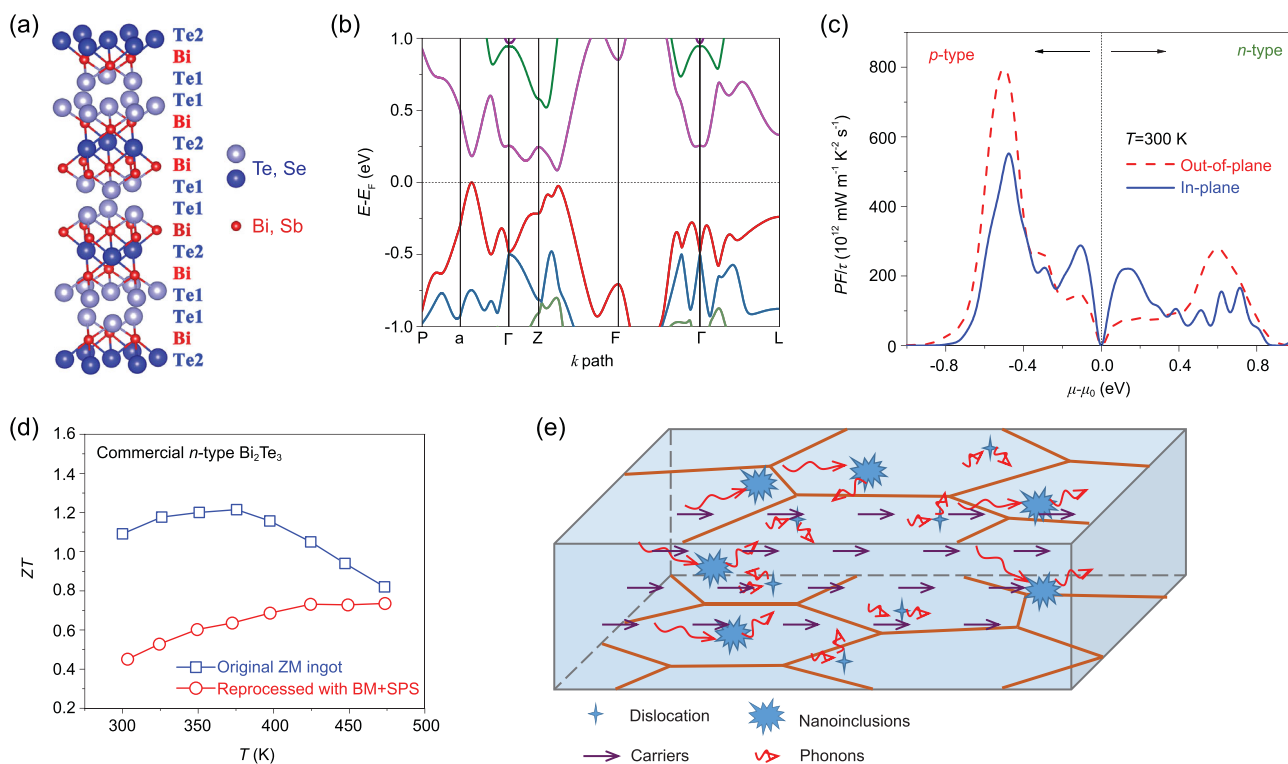


Figure 1. Collections of high peak  $ZT$  ( $> 1$ ) in Bi<sub>2</sub>Te<sub>3</sub>-based materials.



**Figure 2.** Fundamental features and research progress of  $\text{Bi}_2\text{Te}_3$ -based TE materials (a–c) showing the crystal structure, band structure and calculated power factor of  $\text{Bi}_2\text{Te}_3$ , respectively. (d) Comparison of  $ZT$ s of commercial  $n$ -type  $\text{Bi}_2\text{Te}_3$ -based ZM ingots and reprocessed bulks by BM + SPS. (e) Strategy for obtaining high-performance  $n$ -type  $\text{Bi}_2\text{Te}_3$ -based materials.

$\text{Bi}_2\text{Te}_3$  has a rhombohedral structure with a quintuple-layer (QL) structure stacked in the order Te1-Bi-Te2-Bi-Te1 (Fig. 2a). The five atoms are bonded via mixed ionic-covalent bonding, and the interlayers are connected via van der Waals interactions. The calculated band structure of  $\text{Bi}_2\text{Te}_3$  indicated an indirect band gap of 0.08 eV (Fig. 2b). Figure 2c shows the calculated electrical transport properties along the in-plane and out-of-plane directions, respectively.  $\mu - \mu_0$  represents the carrier concentration, and the sign of  $\mu - \mu_0$  indicates the semiconductor type. Calculations indicated that  $p$ -type  $\text{Bi}_2\text{Te}_3$  materials possess higher  $PF/\tau$  ( $\tau$ : relaxation time) than  $n$ -type materials in both the in-plane and out-of-plane directions, because of higher band convergence and smaller band effective mass in valence band maxima. Detailed analysis can be found in the Supplementary data (Fig. S1). In addition,  $PF/\tau$  is insensitive to  $\mu - \mu_0$  along the in-plane direction in  $n$ -type, implying that  $PF$  is insensitive to carrier concentration. Lattice thermal

conductivity is similar in both  $n$ -type and  $p$ -type  $\text{Bi}_2\text{Te}_3$  crystals [13]. The  $PF/\tau$  difference between in-plane and out-of-plane directions for  $n$ -type materials is larger than for  $p$ -type materials, indicating that anisotropy more strongly affects the  $ZT$  in  $n$ -type  $\text{Bi}_2\text{Te}_3$ . This is why  $n$ -type polycrystalline materials always show inferior performance under the same fabrication processes.

Conventional  $\text{Bi}_2\text{Te}_3$ -based ingots fabricated by zone melting (ZM) display preferred crystallographic orientations, leading to strong anisotropic electrical properties. The nanostructures formed by advanced sintering or deformation processes improve the performance of  $p$ -type materials (Fig. 1). Sintered materials usually show a lower electrical conductivity because of randomly oriented refined grains, but they also show reduced thermal conductivity because of enhanced phonon scattering resulting from microstructure refinement. However, as shown in Fig. 2d, the  $ZT$  of  $n$ -type materials decreased over a wide range when ingots fabricated by ZM

were reprocessed into polycrystalline sintered materials using ball-milling (BM) and spark plasma sintering (SPS), as a result of the disappearance of intrinsic anisotropy and the increased carrier concentration originating from the ‘the donor-like effect’. Detailed analysis can be found in the Supplementary data (Fig. S2).

A breakthrough in the performance enhancement of  $n$ -type  $\text{Bi}_2\text{Te}_3$ -based materials requires creation of ideal microstructures with enhanced thermal resistivity and electrical conductivity. Fabricating nanostructured polycrystalline bulk materials appears to be a common method for  $p$ -type  $\text{Bi}_2\text{Te}_3$  materials; however, fabricating polycrystals seems less suitable for  $n$ -type materials. Pan and Li [14] fabricated highly textured  $n$ -type  $\text{Bi}_2(\text{Te}, \text{Se})_3$  alloys with a further optimized composition by a repeated SPS hot-deformation process, which produced excellent carrier transport channels along the in-plane direction. Other works have shown similar results [15]. As shown in Fig. 2e,

combining texturing with nanostructuring provides a balance between TE and mechanical performance in *n*-type Bi<sub>2</sub>Te<sub>3</sub>-based materials. Low/mid-frequency phonons are most likely to be scattered by nanoscale defects, thus significantly reducing the lattice thermal conductivity.

High efficiency TE devices are needed to meet the increasing demand for electronic cooling applications, which is driving current research activities devoted to performance enhancement for the *n*-type materials. Creating textured microstructure in favor of carrier transport, together with optimized nanostructure strengthening phonon scattering, could be an effective strategy. Additionally, the *n*-type base composition could be further tuned to raise the *ZT* values around room temperature, not by increasing the peak temperature.

## SUPPLEMENTARY DATA

Supplementary data are available at [NSR](#) online.

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Jun Pei <sup>†</sup>, Bowen Cai <sup>\*,†</sup>,  
Hua-Lu Zhuang  and Jing-Feng Li <sup>\*</sup>

State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, China

**\*Corresponding authors.** E-mails:

[jingfeng@mail.tsinghua.edu.cn](mailto:jingfeng@mail.tsinghua.edu.cn);

[easoncc@mail.tsinghua.edu.cn](mailto:easoncc@mail.tsinghua.edu.cn)

<sup>†</sup>Equally contributed to this work.

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## EARTH SCIENCES

# Microbes mediated comprehensive carbon sequestration for negative emissions in the ocean

Nianzhi Jiao<sup>1,2,\*</sup>, Jihua Liu<sup>2,3</sup>, Fanglue Jiao<sup>2</sup>, Quanrui Chen <sup>1,2</sup> and Xiaoxue Wang<sup>4</sup>

The crisis of the COVID-19 pandemic is warning of a more profound crisis—climate change. Since the Industrial Revolution, anthropogenic activities, such as the burning of fossil fuels and deforestation, have led to a significant increase in atmospheric CO<sub>2</sub> concentration, exacerbating climate change and causing ecosystem imbalances, abrupt ecosystem successions and serious ecological disasters, which will finally threaten the sustainable development of human society.

What we can do to mitigate climate change is to minimize greenhouse-gas emissions in daily life and economic

practice. The effects of such countermeasures happened to have been tested out by the COVID-19 pandemic event, during which an abrupt drop in CO<sub>2</sub> emissions equivalent to 17% of the total for 2019 was recorded in the first four months of 2020 [1]. Significant improvements in air quality have been observed across countries, such as a 30% reduction in pollution in northeastern USA and the first sighting of the Himalayas from Indian cities for >30 years. However, such a blessing in disguise will not last for long, just as the emission fall during the 2008 financial crisis was followed by an immediate emission increase of 5% in 2009.

There will very likely be a rebound in emissions post COVID-19.

While it is well understood that a feasible way to mitigate climate change at present is to reduce CO<sub>2</sub> emissions to zero, it is unrealistic to achieve this goal in the short term. Under such circumstances, an alternative scheme to remove CO<sub>2</sub> from the atmosphere has become urgently necessary, i.e. negative emission. Many approaches have been proposed in the literature in this regard, among which an emerging area—the marine carbon sink—is particularly promising. In fact, the ocean is the largest carbon reservoir on the planet and did play an important