Materials LAB Perspective

Ferroelectric Engineering Advances Thermoelectric Materials

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Yuting Fan and Gangjian Tan*

State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China
* Corresponding author, E-mail: gtan@whut.edu.cn

Abstract

It is commonly believed that wide band gap ferroelectrics are electrically insulating and can hardly be promising thermoelectric materials. However, things could be different if their gaps are reduced while the ferroelectricity is well reserved. Here we propose that the exploration of narrow band gap semiconductors with ferroelectric characteristic might lead to simultaneous optimization of electrical and thermal transport properties for advanced thermoelectric materials. Narrow gap endows the materials with good dopability, which is a prerequisite for high electrical conductivity. In the meanwhile, ferroelectricity-induced Rashba band splitting and lattice softening would yield large Seebeck coefficient and low thermal conductivity, respectively. Altogether, excellent thermoelectric performance can be expected in the narrow gap ferroelectric semiconductors (NGFS). We also propose the design principles of potential NGFSs.

Key words: Thermoelectrics; Ferroelectricity; Rashba effect; Lattice softening

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Main text

Heat is almost always encountered as a major waste by-product in the use of any form of energy. Recycling the waste heat is therefore of great economic and environmental significance. Thermoelectric materials enable the direct and reversible conversion between heat and electricity, and have gained increasing attention in the past few decades as a possible means of addressing the global issues associated with energy crisis and climate changes.[1–2] However, the practical applications of thermoelectric technology are hindered by their low hitherto conversion efficiency, which is positively related to the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S, σ, T and κ represent Seebeck coefficient, electrical conductivity, working temperature and thermal conductivity, respectively.[3–4] Improving ZT values of a given compound is challenging because of the strong coupling of these transport parameters in solid materials.[5–6]

There has been a long history of thermoelectric research since the discovery of Seebeck effect nearly two centuries ago. However, its progress was very slow in the first century until 1950s when semiconductor technology was established.[7] Later in 1990s, nano-engineering became a hot topic in various research fields and was found effective in boosting thermoelectric performance of existing materials mostly by thermal conductivity reduction (interface scattering against heat-carrying phonons).[8–9] Another breakthrough of thermoelectrics took place in 2000s: enhancement of Seebeck coefficient through electronic band structure modification by resonant scattering of impurity states or convergence of multiple Fermi pockets or both.[10–12] Recently, in addition to liquid-like ions,[13] high-entropy alloys,[14–15] modulation doping[16] and magnetic interactions,[17] exploring new materials with intrinsically low thermal conductivity (large bonding anharmonicity) enriches the strategies towards high thermoelectric performance.[18–19]

Figure 1 illustrates how the above-mentioned strategies effectively increase the maximum ZT ($ZT_{\max}$) of thermoelectric compounds stepwise: taking p-type PbTe as an example. Despite the tremendous progress of thermoelectric research in the past thirty years, there is still a long way to go before thermoelectric technology is brought into commercialization (benchmark ZT of 3).[21] As we know, nanostructuring has its bottleneck in improving ZT, because all solid materials have their theoretically minimum thermal conductivity (amorphous limit).[22] Likewise, the effectiveness of electronic band structure modification is limited by: (i) the species and concentrations of dopants; (ii) the locations of impurity states and their compatibility with Fermi energy. Therefore, it is of great importance to explore new mechanisms that are able to boost ZT values of thermoelectric materials to a higher degree than ever before.

Ferroelectric engineering might be a promising strategy of optimizing the electron and phonon transport properties of thermoelectric materials in a synergistic fashion.[24–25] Owing to their unique spontaneous polarization characteristics, ferroelectric materials exhibit rich physical properties and have great application potential in piezoelectric, pyroelectric, optoelectronic, logic storage and many other fields.[26] Since high-efficiency capacitors, piezoelectric sensing, photoelectric con-

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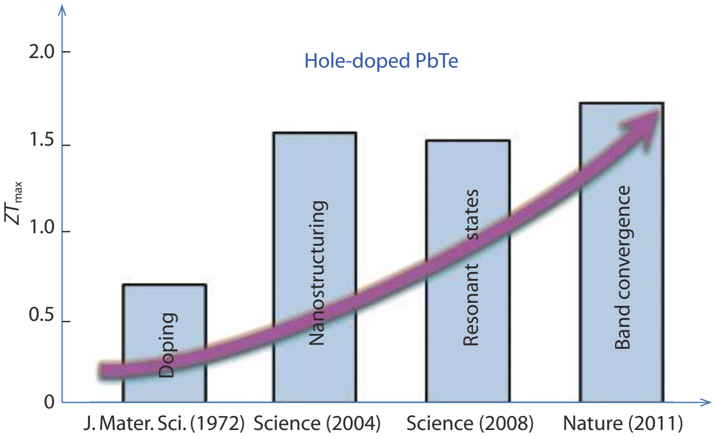

Fig. 1 Strategies that boost the thermoelectric performance of hole-doped PbTe.[20-23]

version, and non-volatile memory require materials with extremely high resistance to reduce leakage current, the vast majority of previously researched and reported ferroelectric materials are insulators or wide band-gap semiconductors (E_g > 1 eV).[27–28] They cannot compete with traditional non-polar narrow band-gap semiconductors from the perspective of thermoelectric performance due to their poor electrical conductivities. However, the distinct spontaneous polarization behavior of ferroelectric materials may lead to the generation of a series of new physical effects such as Rashba band splitting and phonon softening, which will be a new addition to thermoelectric research.[29–30]

As shown in Figure 2, the Rashba effect is an energy band splitting phenomenon driven by spin-orbit coupling and symmetry breaking (such as the non-centrosymmetric structure of the ferroelectric phase). The splitting bands have more number of degenerate valleys than the spin degenerate band, thus yielding higher values of Seebeck coefficient at given carrier concentrations.[31] In the meanwhile, due to the interactions between the dipoles in the ferroelectric crystal, the energy of polar transverse optical phonons at the center of the Brillouin zone gets lower and becomes comparable to that of heat-carrying acoustic phonons.[32] This brings about strong acoustic-optical phonon coupling, and consequently leads to significant scattering of acoustic phonons (suppression of phonon group velocity) and remarkable reduction of thermal conductivity.[33–34] Therefore, extraordinary *ZT* values are expected to be achieved in ferroelectric semiconductors, given that high electrical conductivities are attainable as well.

Of course, it is highly challenging to search conductive ferroelectrics because of the screening effect of free carriers. One of few good examples includes α-GeTe, a narrow gap ferroelectric semiconductor with unexpectedly high Curie temperature (T_C) of ~750 K. This material has a rare combination

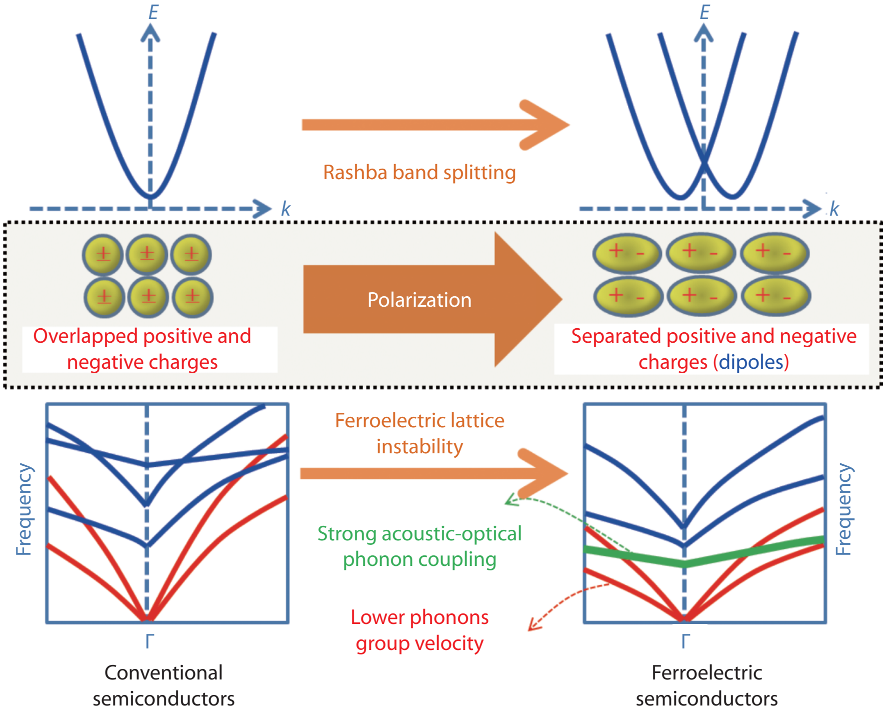

Fig. 2 Ferroelectricity leads to Rashba band splitting and lattice instability (phonons softening).

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of large electrical conductivity, high Seebeck coefficient and low thermal conductivity, contributing to excellent thermoelectric performance with the reported $ZT_{\max}$ exceeding 2.5.[35] We believe that its unusual thermoelectric transport properties are closely related to the inherent and unique ferroelectric characteristic. Another example is BiTeI, which features narrow band gap, robust ferroelectricity and promising thermoelectric performance as well.[36] Besides, BiSb thermoelectric alloys are supposed to be giant ferroelectric Rashba semiconductors in the cryogenic temperature range.[37] In fact, ferroelectric engineering has become a viable way of enhancing ZT values of some state-of-the-art thermoelectric materials. For instance, GeTe alloying in SnTe is found to result in remarkable ferroelectric lattice instability, which should be responsible for the ultralow thermal conductivity of SnTe-GeTe alloys.[38] Sn-doped GeTe, on the other hand, has a strong Rashba effect and yields an ultra-high power factor.[39]

At this stage we can conclude that exploration of new ferroelectric compounds with narrow band gaps (particularly those with reasonably high T_C) like α-GeTe might be an important direction in thermoelectric research in the next few years, Figure 3. It leads to simultaneous optimization of three key physical parameters (S, σ and κ) in a single material, and therefore contributes to remarkably improved ZT values. The narrow gap means good dopability of materials which ensures desirable electrical conduction. Ferroelectricity, on the other hand, introduces Rashba band splitting and lattice softening, which lead to enhancement of Seebeck coefficient and reduction of thermal conductivity, respectively. Nonetheless, it is not an easy task to acquire narrow gap ferroelectric semiconductors (NGFSs), because ferroelectricity and electrical conduction seem to be inherently exclusive. The discovery of NGFSs relies on the close cooperation between experimenters and theorists by use of high-throughput tools.[40–41] Potential candidates could be compounds with narrow band gap and non-centrosymmetric space group. Moreover, future work should focus on understanding of dipoles-carriers interaction mechanism and its influence on charge and phonon transport behavior. This is a complicated system because more number of degrees of freedom is introduced. Last but not the least, the characterization technique of ferroelectricity in the narrow-gap ferroelectric semiconductors is urgently needed. Unlike conventional wide-gap ferroelectric materials, the large population of free carriers in narrow gap ferroelectric semiconductors masks the signals associated with ferroelectricity. How to identify ferroelectricity and determine its strength is a precondition of research on NGFSs.

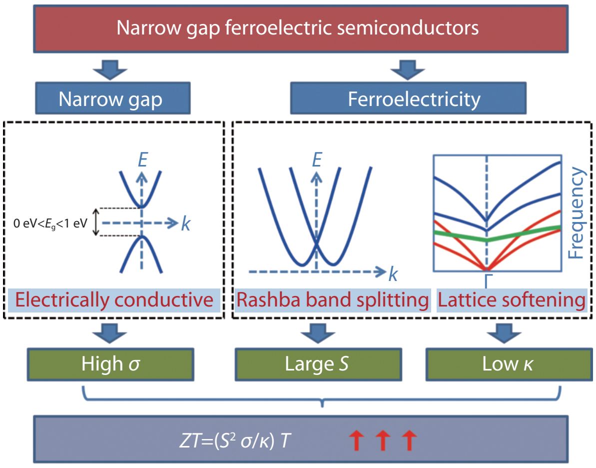

Fig. 3 Simultaneous optimization of three key physical parameters (S, σ and κ) in narrow gap ferroelectric semiconductors and remarkably improved ZT values by ferroelectric engineering.

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Conflict of interest

The authors declare no conflict of interest.

Author contributions

G. T. wrote the manuscript; Y. F. formatted the manuscript; all authors had approved the final version.

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Biographies

Yuting Fan is currently a PhD student working on thermoelectric materials at Wuhan University of Technology (WUT), under the supervision of Prof. Gangjian Tan. She received her Master degree from WUT in 2019. Her research interests focus on design and optimization of advanced GeTe-based thermoelectric materials.

Gangjian Tan is now a full professor of materials science at Wuhan University of Technology (WUT), China. He received his Ph.D. degree from WUT in 2013. Following that, he worked as a postdoctoral research fellow at Northwestern University, Evanston till 2018. He is interested in the understanding of electron, phonon and ionic transport behaviors in solids for energy conversion and storage. He has authored over 80 peer-reviewed publications in international journals with an h-index of 39.