Challenges for Thermoelectric Power Generation: From a Material Perspective

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Abstract

Thermoelectric devices enable the direct conversion of heat flux into electrical energy, which have attracted considerable research interests for energy harvesting to address the challenges of energy sustainability. Owing to the emerging concepts or strategies, the dimensionless thermoelectric figure of merit (*ZT*), dominating the device's conversion efficiency, has been significantly boosted during the last two decades. However, thermoelectric materials remain stagnant for practical applications. In this review, future challenges from a material perspective are discussed and emphasized. It includes fundamental theories, design criteria, material synthesis, and properties measurement. Our review tries to point out these important research directions in the near future, thereby enabling rationally developing thermoelectric science and pushing thermoelectric devices for large-scale applications.

Key words: Thermoelectric materials; future challenges; power generation; material perspective

1 Introduction

Thermoelectric devices, having unique advantages of simple design, no pollutants, reliable operation, no noise, system scalability, can convert heat energy into electrical energy and vice versa.[1,2] Thermoelectric power generation (TEG) has reliably power electricity for spacecraft based on the Radioisotope Thermoelectric Generator (RTG) from the 1950s.[3] In the last two decades, in the context of natural resource depletion, environmental degradation, and global warming, clean and renewable energy conversion technologies have received intensive interest from the scientific community and commercial industry for reducing the use of fossil fuels. More importantly, the majority of the primary energy (more than half) in the United States was rejected by emission to the atmosphere, leading to different types of heat sources. Meanwhile, natural resources, like solar energy and geothermal energy, are also employed as heat sources. Very recently, the topic of organic materials and inorganic-organic hybrid materials for thermal-energy harvesting recently become an active research field,[4–6] which has a high possibility for powering billions of Internet of things (IoT) sensors,[7] and wearable or flexible electronics applications.[8,9] All of these above-mentioned aspects motivate people to reconsider TEG as a feasible energy-harvesting technology. Currently, the most challenging and important task of TEG technology lies in developing promising thermoelectric materials.

Figure 1 shows the timeline of thermoelectric theory devel-opment. Thermoelectric effects include three separate phenomena, namely the Seebeck effect, Peltier effect, and Thomson effect, all of which were discovered over 150 years ago. Until the 1950s, this period is at the early study of thermoelectric theory and most of the thermoelectric studies focused on the pure metal element and alloys.[10] Ioffe established the thermoelectric theory frame structure at 1949 and proposed that material's thermoelectric performance is evaluated by the dimensionless thermoelectric figure of merit (*ZT*), *ZT* = $[S^2\sigma/(\kappa_{lat} + \kappa_{ele})]T$, where *S*, σ, κ_{lat}, κ_{ele}, and *T* are the Seebeck coefficient, electrical conductivity, lattice thermal conductivity, electronic thermal conductivity, and absolute temperature, respectively. Afterward, thermoelectric research interests have shifted to semiconductor areas and some high-performance materials, including Bi_2Te_3,[11] PbTe,[12] $AgSbTe_2$,[13] and SiGe,[14] *etc*., have been identified and designed. However, the peak *ZT*s were invariably around 1 at the initial stage from the 1950s to 1990s due to the intertwined or contradicted characteristics of thermoelectric parameters. Thus, thermoelectric materials have long been inefficient to be cost-effective in broader applications. In 1993, Dresselhaus proposed "Quantum Effect" as the conceptual breakthrough in thermoelectric science,[15] which highlights the manipulation of electron and phonon transport in nanoscale thermoelectrics by controlling the material's dimensionality. This has led to the "renaissance of the thermoelectric field" to date. Followed by this pioneering concept, electronic band structure modifica-
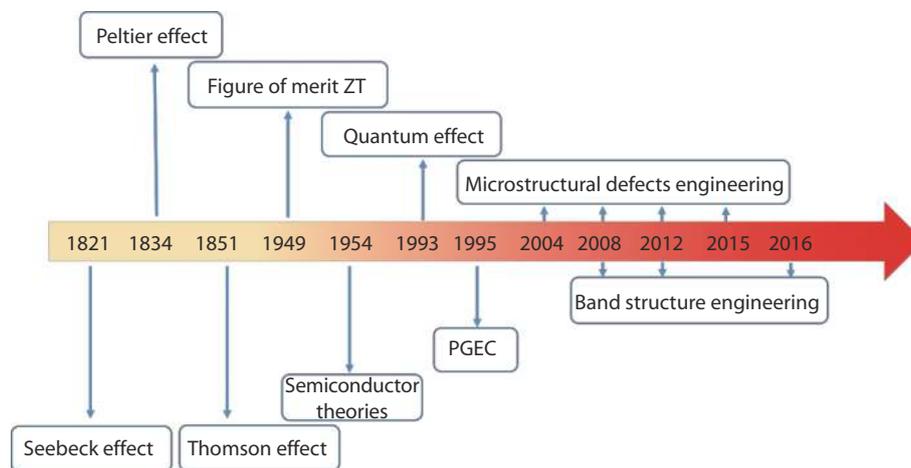
Fig. 1 Timeline of thermoelectric theory development.

tion to increase the power factor ($PF = S^{[2]}\sigma$) and microstructural defect engineering to minimize the κ_{lat} are developed and demonstrated in traditional bulk thermoelectrics,[16–19] which results in remarkable progress in this area. Simultaneously, the "phonon glass electron-crystal" (PGEC) paradigm gives the new direction for designing new thermoelectric materials and some novel materials with unprecedentedly high ZTs are discovered owing to the advanced synthesis methods.[20–36] Interested readers may refer to some critical reviews about fundamental theory,[37–45], quantum effect,[15,46] nanostructured thermoelectric,[15,47,48] synthesis methods,[49,50] inorganic materials[51–66], organic materials,[4,67] inorganic-organic hybrid materials,[7,68] modules and devices,[69,70] thermoelectric applications,[71] and also recent advances.[72–75]

From the 1990s up to now, thermoelectric science is in a booming age that attracts renewed scientific and industrial interests. It seems that the largescale utilization of TEG for energy harvesting is on the way. In reality, the thermoelectric devices' performance, including output power density and conversion efficiency, does not show remarkable advances. Figure 2 summarizes the measured conversion efficiency η of
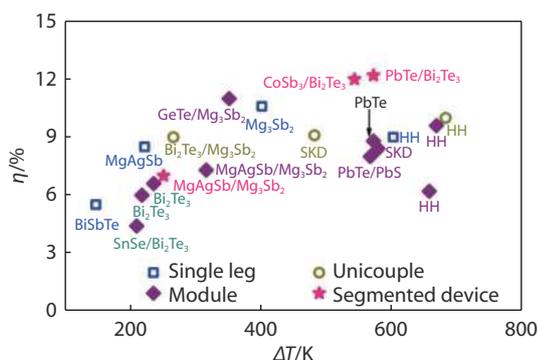
Fig. 2 The measured conversion efficiency η of current state-of-the-art thermoelectric devices as a function of working temperature difference ΔT, including single legs,[76-79] unicouples,[80-82] modules,[36,83-89] and segmented devices.[90-94] Here single leg, unicouple, module, and segmented device mean only n or p-type material, one-pair n and p-type material, two or more elements of n and p-type material, and two or more different n and p-type materials packing in parallel, respectively.

current state-of-the-art thermoelectric devices as a function of working temperature difference ΔT, including single legs,[76–79] unicouples,[80–82] modules,[36,83–89] and segmented devices.[90,91] It should be highlighted that some encouraging results of low-temperature non-Bi$_2$Te$_3$ modules were demonstrated recently[36,92], which provide great promise for harvesting the low-grade waste heat. Obviously, the record value is still around 10% for non-segmented devices while segmented design contributes to higher values up to 12%, but with a huge increase in fabrication time and cost. Therefore, TEG could not compete with other renewable energy conversion technologies and conventional heat engines, which currently still confines to a niche market. From the material's perspective, this indicates that thermoelectric ZT needs to be further largely improved or there is a huge gap between fundamental research and commercial applications.

Since inorganic materials dominate the current research mainstream, in this review we discussed and highlighted scientific challenges that we believe as the most important for the coming years in this area. It consists of six critical aspects, including the role of point defect physics, new theories to decouple the thermoelectric parameters, the multi-criteria of good thermoelectric materials, discoveries of new materials, material synthesis challenges, and reliable and valid measurement. Solving these critical challenges may be helpful to promote the next-step benign development of thermoelectric technology.

1.1 The role of point defect physics

Conventionally, tuning charge carrier concentration by element doping and strengthening point-defect scattering by isoelectronic alloying are utilized to enhance thermoelectric performance.[12] Manipulation of point defects is conventionally targeted for suppressing the κ_{lat}, but its effect on the carrier transport properties has been long neglected. Understanding defect physics is the prerequisite to designing materials with tailored properties through defect engineering. Point defect physics plays a vital role in dopability, intrinsic conductivity, carrier concentration, and carrier mobility of semiconductor materials. This is usually revealed by the calculated defect formation energies by first-principles calculations, shown in the schematic diagram in Figure 3a.[95] Based on this calculation result, we can know the formation energy,

(a)

(b)
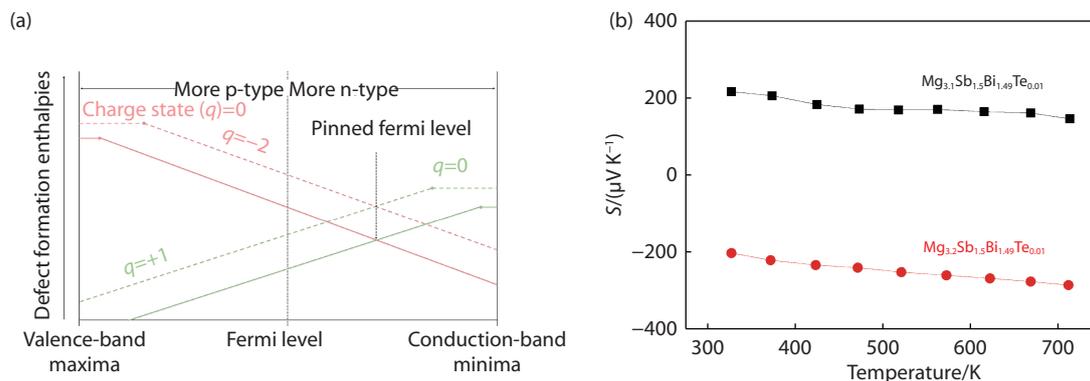
Fig. 3 (a) Schematic diagram of the defect formation energies in the semiconductor by first-principles calculations;[96] (b) the effect of Mg stoichiometry in $Mg_{3+x}Sb_{1.5}Bi_{0.49}Te_{0.01}$ on the measured Seebeck coefficient.[27]

charged state, defect energy level, pinned Fermi level, self-compensation behavior, *etc.* To effectively tune the carrier concentration, dopants need to meet the requirements of having low formation energy, shallow defect level, and no self-compensation "killers".

Although first-principles calculation enables a thorough understanding of defect physics in the pure or doped compound, it is mostly time-consuming for large supercell calculations. Experimentally few characterization techniques, such as spherical aberration-corrected scanning transmission electron microscope and positron annihilation spectroscopy, can be utilized to verify the simulation results. The most challenging issues are how to experimentally overcome the doping bottlenecks and intentionally manipulate the native defects to maximize the performance. One good example is the realization of n-type conduction in Mg_3Sb_2 by adding extra Mg to reduce the Mg vacancies concentration due to the increased defect formation energy, displayed in Figure 3b.[27]

1.2 New theories to boost *ZT*

In 2009, Vining wrote a commentary titled "An inconvenient truth about thermoelectrics" and claimed, "Thermoelectric energy conversion will never be as efficient as steam engines".[97] Fundamental understanding of phonon and electron transport behavior in thermoelectrics has advanced rapidly over the past decade that contributes to achieving high performance in traditional and new materials. However, until now ten years' concentrated efforts still could not overcome this dilemma and researchers failed to demonstrate ultrahigh *ZT* in bulk thermoelectric materials. Optimizing thermoelectric parameters to pursue high *ZT* involves multiple free degrees of freedom, including lattice structure, charge carrier, atomic orbital, and quantum spin.[45] Fundamental obstacles for achieving high *ZT* arise from the fact that basic thermoelectric parameters are mutually interrelated or even contradicted for a single material.[40] Therefore, how to synergistically optimize the thermoelectric properties, including decoupling the intricate relationship or tuning the target parameter without the deterioration of others, has long been a critical challenge for the thermoelectric community.

For electrical transport properties, the electronic band structure decides the level of power factor *PF*. The small bandgap results in high electrical conductivity but this is usually accompanied by the onset of a bipolar effect that reduces the Seebeck coefficient significantly. Small band effect-

ive mass is theoretically beneficial for realizing a high power factor,[98] but as a consequence of the impurity scattering, the reduction of carrier mobility is more pronounced than materials with high effective mass when considering. As known, maintaining the originally high carrier mobility is vital for achieving the good electronic transport properties.[99,100] Moreover, the maximum power factor is achieved by tuning the Fermi level, but sometimes it is impossible to reach this targeted range by doping due to the high defect formation energy, pinned Fermi level, self-compensation behavior, *etc.* Some recently proposed strategies, like band convergence and energy filtering, contribute to some breakthroughs in some systems,[38,101] but they have some shortcomings that can not be neglected.

Band convergence is claimed to be beneficial for enhancing performance in many thermoelectric systems,[38] but its effectiveness relies on the neglection of interband or intervalley scattering on the charge carrier transport, as shown in Figure 4a.[102] In general, more bands or valleys provide a more carrier-scattering possibility and thus decrease carrier mobility. For example, the inter-valley scattering in n-type Si is generally assumed as a strong and non-negligible factor.[103,104] Very recently, theoretical calculations revealed that the strong inter-band scattering in $CaZn_{2-x}Mg_xSb_2$ renders the band convergence ineffective.[105] Indeed, it is impossible to quantify exactly the effect of band convergence (or inter-valley scattering or inter-band scattering) alone in polycrystals. For pure systems, like superlattices or low-dimensional materials, it is conventional to extract the electron-phonon coupling parameters, including the inter-valley scattering or inter-band scattering values, based on the experimental results (scanning tunneling spectroscopy, Raman scattering, intense terahertz measurements) and theoretical calculations. Therefore, the interband or intervalley carrier-scattering rate sensitively affects the real *ZT* improvement. For the majority of thermoelectric systems, the interband or intervalley carrier-scattering rate is, however, unknown, but first-principles calculations would indeed provide some useful information about the scattering rate and the effect on transport properties.[106]

Building a proper potential barrier height can realize the selective transmit of the higher-energy carriers and the effective screen of the lower-energy carriers,[101] thereby resulting in the remarkably increased Seebeck coefficient. This is based
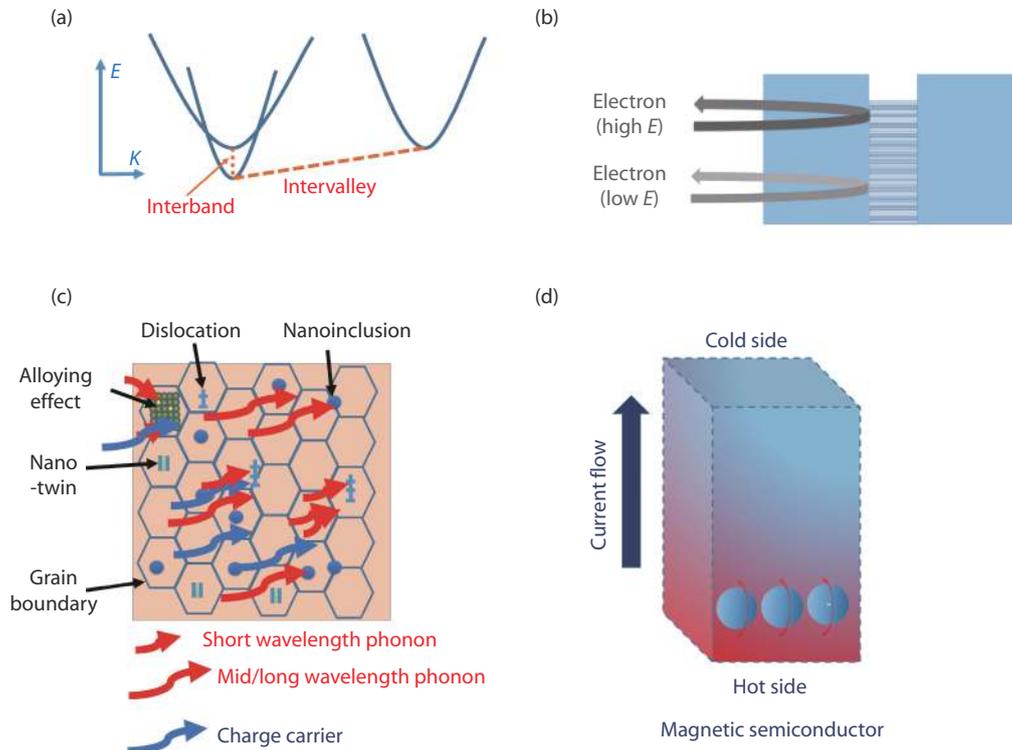
Fig. 4 Schematic diagrams of the ineffectiveness of several strategies in thermoelectrics: (a) the interband or intervalley scattering in band convergence; (b) strong carrier scattering in energy filtering; (c) phonon and electron co-scattering by microstructural engineering; (d) electrons with the same direction spins in the magnetic semiconductor.

on the assumption that the energy filtering effect does not induce the reduction of electrical conductivity. In reality, the introduced energy barrier definitely scatters carriers with low energy and high energy, as shown in Figure 4b, and thus reduces the carrier mobility that has been frequently observed in the experimental results. Theoretical stimulations also highlighted the ineffectiveness of the energy filtering at grain boundaries due to the role of high chemical potential in the realistic model.[107] More importantly, a long-standing problem is the experimental demonstration of the energy filtering effect in bulk material because current explanations and mechanisms about the energy filtering effect come from logical deduction based on the obtained experimental results. In addition, hot debates still exist in the thermoelectric community about whether charge carriers can bounce against "another parabolic extended states".

For thermal properties, electronic thermal conductivity is proportional to the Lorenz number and electrical conductivity, as $\kappa_e = L\sigma T$ defined by the Wiedemann-Franz relation. Lorenz number is difficult to directly measure experimentally and in thermoelectric it is usually theoretically calculated by using the band model and measured Seebeck coefficients. Currently, no report aims at tuning the Lorenz number to achieve high thermoelectric performance. For the most part, reducing electrical conductivity is controversial to the requirement of maximizing the power factor. The κ_{lat} is a relatively independent parameter, but it is impossible to significantly suppress the κ_{lat} via the microstructural defects without satisfying the electrical transport properties.[16,18,19,41] It should be mentioned that microstructural engineering not

only impedes the phonon transport but also certainly acts as the carrier scattering center considering the difference between carrier and phonon mean free path range, as shown in Figure 4c.[41] The overall ZT enhancement, therefore, will be offset by the deterioration of carrier mobility. Recently, sub-nanostructures (interstitials, clusters, and dislocations) are found to be effective to maintain the high carrier mobility in n-type PbTe and PbSe, in addition to the strong phonon scattering.[99,108–110] Besides, the analysis of the phonon-scattering mechanism or contribution commonly depends on the modified Debye-Callaway model in the thermoelectric area. However, too many fitting parameters in the model may not give the real physical picture, which is subject to the qualitative level.

Recently, the spin effect has been reconsidered and is under active investigations in thermoelectric by doping magnetic atoms in the lattice or adding magnetic second phases in the matrix.[111–116] Here it should be mentioned that under magnetic field thermoelectric performance can be increased for some systems at the low-temperature range due to the intriguing thermomagnetic phenomenon, which is beyond our present discussion. Traditionally, magnetic semiconductors are not considered as the promising thermoelectric material due to the low carrier mobility originating from strong magnetic scattering. For materials in the magnetic state, the spins of electrons are in the same direction that would lead to the lower Seebeck coefficients because the magnitude of the Seebeck coefficient can be approximately understood by the entropy of electrons, as shown in Figure 4d. On the other hand, this carrier-magnon interaction may lead to the en-

hanced effective carrier mass that may be helpful for high power factor, as reported in $Yb_{14}MnSb_{11}$ and $CuFeS_2$. Doping atoms to change the magnetic properties show the distinct and controversial influence on thermoelectric properties, which is still in the debate. For example, the nonmagnetic $Zn^{[2+]}$ ions replacing the magnetic $Mn^{[2+]}$ ions in $Yb_{14}MnSb_{11}$ reduced the spin disorder, lowered the resistivity, and enhanced ZT[111] while magnetic $Mn^{[2+]}$ ions doping into nonmagnetic $CuGaTe_2$ resulted in the increase of carrier effective mass and significant enhancement of power factor.[113] Magnetic composites enable the delicate control of electron and phonon behavior,[115,117] leading to the enhanced ZT. However, whether it is a universal strategy is still an open question.[118,119]

1.3 The multi-criteria of good materials

The conventional view about the criterion of good thermoelectric material is the high ZT, which far deviates from the real situation. Herein, we try to define the multi-criteria of good thermoelectric materials for power generation applications, mainly including the four following aspects.

1.3.1 High thermoelectric performance

Nowadays, thermoelectric devices are at an inferior position for power generation, which is primarily ascribed to the material's low performance. Additionally, there should be no theoretical up limit for the material's ZT value. Thus, achieving a high ZT is always the main motivation for thermoelectric research. Here it should be addressed that the material's average ZT, rather than the peak ZT, at the investigated temperature range dominates the device's final conversion efficiency. For example, n-type In_4Se_{3-x} crystal shows a high peak ZT~1.5 at 700 K, but the strong temperature dependence leads to the low theoretical conversion efficiency of ~ 0.6%.[120] For power generation applications, the output power, dominated by the material's power factor and device's leg length, should be as significant as the conversion efficiency, or more important for the unlimited heat source, like solar heat, or free heat source, like waste heat of steel factories.[121,122] Shortening the leg length would increase the temperature gradient that may speed up the device failure for some sensitive systems. In addition, materials with low thermal conductivity under fixed heat flow conditions are unsuitable to maximize the output power because thermal shunts may be needed to maintain the required heat dissipation.[121] Therefore, a high power factor is a big advantage in the thermoelectric area. Practically, the conversion efficiency of thermoelectric devices, consisting of multiple pairs, is dominated by the real performance of n- and p-type legs. Under the consideration of leg geometry and thermal expansion coefficient, it is strongly recommended to simultaneously realize high performance based on the same parent. However, some materials with high performance only show one type of conduction above room temperature.[55,59,65,123] This asymmetrical thermoelectric performance is critically related with native point defects as the killer effect and/or distinct electronic band structure of conduction band and valence band. For example, as a consequence of high-concentration cation vacancy, some thermoelectric compounds, e.g. GeTe,[65] SnTe,[123] β-Zn_4Sb_3,[20] α-MgAgSb,[55] and most Zintl phases,[57] possess persistent p-type conductivity.

Figure 5a and 5b present the relationship between total thermal conductivity κ_{tot} and power factor PF at room temperature for advanced n-type and p-type thermoelectric systems, respectively, where the bubble color represents the highest calculated Z that is a direct indicator of material performance to getting rid of the measured temperature influence. From this figure, we can conclude that: (1) few candidates show both high power factor and large Z; (b) Recently discovered new materials still could not compete with the traditional materials; (c) few materials show large Z for both n-type and p-type.

1.3.2 Strong mechanical properties

In reality, high thermoelectric performance is not the only concern for energy harvesting. Generally, thermal cycling during the long-time service, as well as the manufacturing and assembling processes, results in significant thermal stress on the thermoelectric materials.[124,125] Materials with poor mechanical properties would experience the appearance of scratches, cracks, or other flaws on the surface or inside, which consequently deteriorates the real performance and more serious leads to device failure. Therefore, mechanical properties should be good, at least not bad, to accomplish the measured superior thermoelectric performance. Common examples of mechanical properties measurement include hardness, elastic modulus, flexural and compressive strengths, fracture toughness, creep properties, and fatigue limit.[126–131] Some of the mechanical properties, like Poisson's ratio, are the material's intrinsic parameter, not sensitive to microstructure whereas strength properties closely relate
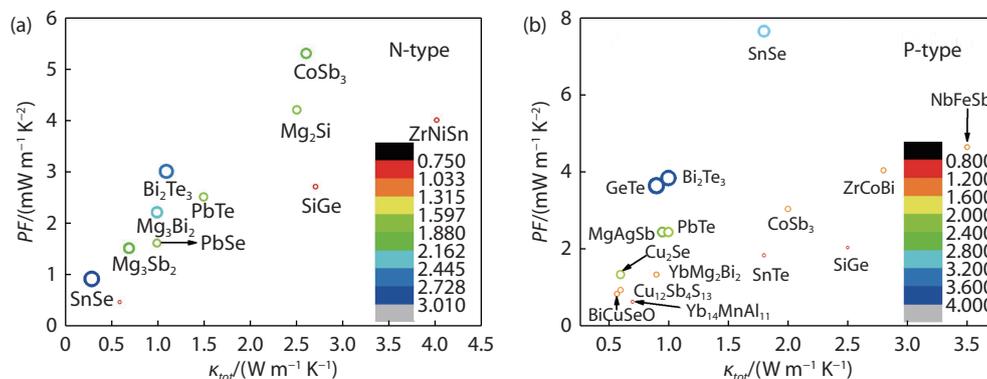
Fig. 5 (a) and (b) The relationship between total thermal conductivity κ_{tot} and power factor PF at room temperature for advanced n-type and p-type thermoelectric systems, respectively, where the bubble color represents the highest calculated Z ($\times 10^{-3}$ K^{-1}).[72-75]

with its microstructure. However, it is impossible to improve all of the indicators of mechanical properties at the same time. In metallurgy, conventional mechanisms of strengthening metals and alloys by reducing dislocation movement include solid-solution strengthening,[132,133] grain refinement strengthening,[134–136] dispersion hardening,[137,138] and strain hardening.[139] Figure 6 displays the relationship between Hardness and elastic modulus of typical thermoelectric materials in comparison to polymers, metals and ceramics.[129] The majority of thermoelectric materials behave like brittle ceramic with poor mechanical properties due to the complex structure and bonding, as well as non-metallic constituted elements, especially for materials with low thermal conductivity, such as PbTe[126] and $AgSbTe_2$.[140] In contrast, filled skutterudite and Half-Heusler alloys exhibit quite good mechanical properties,[128,129,141,142] both of which can well service under adverse working conditions, like automotive exhaust waste heat harvesting.
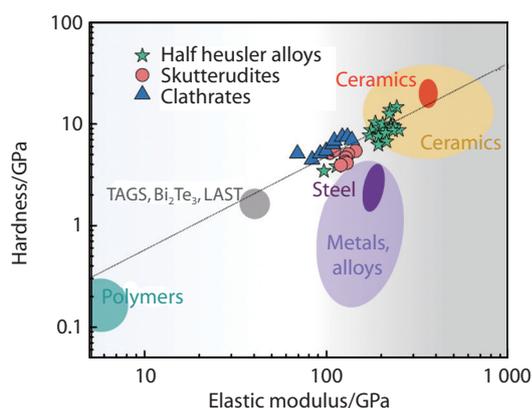
Fig. 6 Hardness vs. elastic modulus of typical thermoelectric materials in comparison to polymers, metals and ceramics. [129]

1.3.3 Good thermal stability

Thermal stability describes the material's ability to withstand temperature and maintain its composition, microstructure, and properties. Since thermoelectric materials suffer large electric fields, high thermal gradient, and high working temperature, materials with poor thermal stability would not maintain stable properties, even in a short service time. Generally, thermal stability is evaluated using temperature-dependent structure analysis techniques (X-ray diffraction, neutron scattering, scanning electron microscopy (SEM), TEM, *etc.*), thermal analysis techniques (thermogravimetric analysis (TGA), thermogravimetry (TG), *etc.*), and temperature-dependent properties measurements. For testing the long-time thermal stability, performing a thermal-cycling or annealing process to stimulate the real work conditions will give more solid conclusions.

From the viewpoint of thermodynamics, some materials intrinsically suffer poor thermal stability due to the unstable or metastable energy state and chemical bonding. For example, the liquid-like compound shows the quick small ions immigration rate in real applications.[59,143] Recently, n-type Mg_3(Bi, Sb)$_2$ is found to tend to decompose after the first heating cycle from 300 K to 725 K since elemental bismuth release from the crystal structure.[144] Also, the significant phase change, due to the Mg evaporation, during the in situ meas-

urements of their thermoelectric properties at 673 K and 773 K is displayed in Figure 7a.[145] Besides, some materials are extremely sensitive to oxygen, moisture, or high temperature. For example, BiCuSeO shows the obvious oxidation behavior in the air that dramatically deteriorates the thermoelectric properties.[146,147] Some Zintl compounds, like $Yb_{14}MnSb_{11}$, are air and water-sensitive, so the synthesis should be handled in argon or nitrogen-filled glovebox with low water levels.[21] Na-doped $BaCu_2Se_2$, an air and water stable compound, shows a high *ZT* around 1 at 773 K, but it volatilizes at
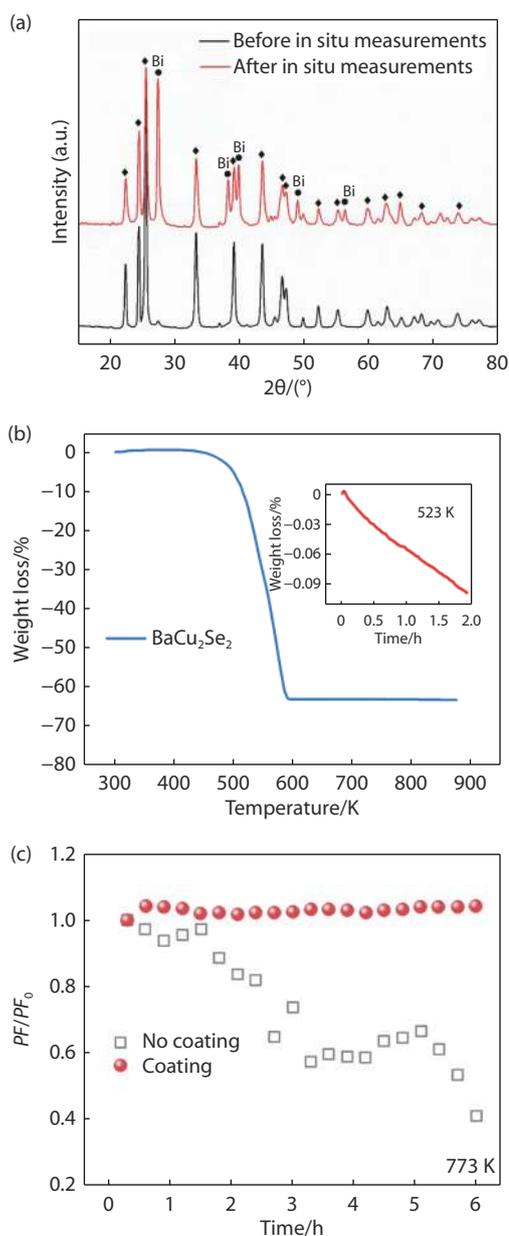
Fig. 7 (a) Comparison of XRD patterns for $Mg_{3.2}Sb_{0.49}Bi_{1.5}Te_{0.01}$ after *in situ* measure- ments of its electronic thermoelectric properties at 773 K.[145] (b) thermogravimetric analysis of $BaCu_2Se_2$ powder and densified pellet (inset) under the Ar atmosphere.[148] (c) comparison of the measured power factor at 773 K by the long-term in situ measurements for $Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}$ (without and with the boron nitride coating).[145]

473 K based on the thermogravimetric analysis, shown in Figure 7b.[148] Using some protective coatings, e.g., boron nitride, glass, is the most-effective method to avoid or suppress the oxidation or sublimation of high-vapor-pressure elements in the thermoelectric legs at elevated temperature[145]. Figure 7c displays the critical role of boron nitride coating on the measured power factor at 773 K by the long-term in situ measurements for $Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}$, in which the utilization of boron nitride coating help to achieving the good stability. For nanostructured thermoelectric materials, microstructure stability is always a critical issue for real applications. Enthalpy stored in the grain boundaries and high residual strain during the heavily deformed process provides a remarkable driving force for grain coarsening, even at ambient temperature. Besides, single-dispersed nanoinclusions that are intentionally added tend to aggregate on the matrix surface to reduce the total system energy. For example, PbS-rich precipitates within a PbTe-rich matrix fabricated by water quenching shows a high thermoelectric performance than thermally stable specimens, but precipitates grow significantly with several thermal cycles that reduce the performance.[149]

1.3.4 Earth-abundant, cheap, nontoxic element

In Jan 2019, the European Chemical Society released a new periodic table with curves and lumps, which clearly depicted element scarcity in the Earth's crust and addressed these Earth's elements in danger of disappearing thanks to human overuse. A number of the elements on the endangered list, such as tellurium, indium, germanium, and hafnium, are important materials for thermoelectric applications. In light of this critical issue, there needs to be a greater emphasis on the development of promising thermoelectric materials using earth-abundant elements. The cost of raw materials is a big component for thermoelectric modules, which also includes the fabrication and manufacturing cost, as well as the heat exchanger and ceramic plate cost.[150] Of course, most of the scarce elements show a high raw material price. That is why Bi_2Te_3 and SiGe show much higher materials costs compared with other materials.[150] Reducing or suspending to use of these elements with high prices would be welcomed and become a big advantage from the cost consideration for real applications, but the high thermoelectric performance is the prerequisite. In practical reality, the power-generation cost metric in ＄/W is are equivalent to maximizing ZT. However, the current cost of thermoelectric system (above 10 ＄/W) is much higher than other clean power-generation technologies, like photovoltaics (＄0.5/W), concentrated solar power and geothermal power (＄3-4/W), and organic Rankine cycle (＄4-5/W).[151] This critical fact further confines the thermoelectric application in niche markets when and other alternatives are not feasible or reliable.

1.4 New materials discovery

Thermoelectric research of searching for new promising thermoelectric materials rely on laborious trial-and-error experiments that are bound by high costs and time-consuming procedures of synthesis, but few promising alternatives are identified eventually. Over the past 60 years, traditional thermoelectric materials, including Bi_2Te_3, lead chalcogenides, and SiGe, still dominate the research activity and application market. For medium and high-temperature applications, both filled $CoSb_3$ skutterudite and half-Heusler alloys developed in the last two decades are considered as the new promising thermoelectric materials.[63,152,153] Recently, compounds featured with wide bandgap, layered and low symmetry, including BiCuSeO and SnSe crystal, are identified to be promising thermoelectric materials.[53,60,154] However, new materials could not rival the monster position of Bi_2Te_3 based materials for room-temperature and low-temperature applications yet. Although some new materials synthesized in the lab exhibit the comparable peak or average ZT with commercial n-type or p-type Bi_2Te_3 ingot, these inherent shortcomings, such as only one type conduction for Zn_4Sb_3 and α-MgAgSb,[20,55] poor performance for p-type Mg_3Sb_2,[56] bad thermal stability for Ag_2Te and Cu_2Se,[59] toxic elements for thallium-based chalcogenides,[155] limits the real application. Currently, fulfilling all these criteria of promising thermoelectric materials we proposed in the previous section seems to be impossible.

Over the past decades, theory and computations started to come into play. With the guide of empirical and semi-empirical models as well as *ab initio* calculations,[156,157] some novel thermoelectric materials with complex structures have been discovered and designed. Recently, high-throughput computational materials design based on existing databases is an emerging area to quickly identify promising thermoelectric compounds,[96,158,159] especially for materials with the simple crystal structure, such as half-Heusler alloys.[160,161] Figure 8 describes the high-throughput materials design framework for the discovery of promising thermoelectric materials. This approach has greatly shortened the period and cost of thermoelectric research.

High-throughput materials design framework
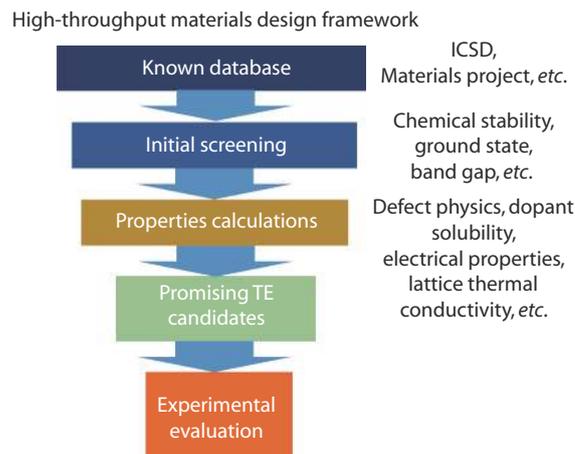
Fig. 8 High-throughput materials design framework for the discovery of promising thermoelectric materials.

According to these theoretical predictions, discovering materials with the intrinsically low thermal conductivity κ_{lat} becomes straightforward.[43,162] Very recently, a new crystallographic parameter, namely the site occupancy factor, is proposed as an effective indicator to identify a material catalogue with low κ_{lat} in the Crystallography Open Database, leading to the discovery of 1587 compounds containing the partial occupancy feature with the possible low κ_{lat}.[163] However, the majority of these materials with low κ_{lat} usually show the quite low power factor less than 10 μW cm^{-1} K^{-2}, bad mechanical properties, as well as the poor data reprodu-

cibility, which significantly limit their further application for energy harvesting. In contrast, DFT calculations of electrical transport properties are routinely performed assuming the constant relaxation time approximation, so there is a big difference between theoretical and experimental electrical conductivity and Seebeck coefficient. Therefore, it remains difficult to discover materials with both high power factor and high *ZT*.

1.5 Material synthesis challenges

During the last two decades, mechanical alloying, melting spinning, self-propagating high-temperature synthesis, and solution chemistry synthesis have been developed to successfully fabricate high-performance thermoelectric materials. These advanced methods are continued to be frequently used that will help to produce some good materials with high *ZT* in the future. Traditional fabrication methods of thermoelectric materials usually involve a long and/or complex annealing procedure, but materials can reach the most thermodynamic ground state. Mechanical alloying,[16,48,164–167] melting spinning,[168–170] self-propagating high-temperature synthesis,[84,171–173] and solution chemistry synthesis[174–177] have demonstrated the potential of the synthesis of high-performance materials in the lab scale. These three former methods can realize fast synthesis and reduce energy consumption. In most cases, this represents the strongly out-of-equilibrium synthesis condition, leading to thermodynamically unstable microstructure or composition if no post-annealing treatments are performed. Especially for working at the elevated temperature, these synthesized materials often possess poor thermal stability since these behaviors like grain coarsening, particle/nanoinclusion aggregation, and nanoprecipitate redissolution, tend to occur, displayed in the schematic diagram in Figure 9, driven by decreasing the total interfacial energy against high working temperature or thermal cycling. Therefore, the measured high thermoelectric properties may not be maintained for a long period in real service conditions. The main drawbacks of solution chemistry synthesis include the low yield, high synthetic cost, difficulty in the precise control of the stoichiometry, and easy contamination. Specifically, the nanocomposite concept receives intensive research attention from the thermoelectric community.[48,178] The synthesis of nanocomposite materials requires delicate treatment and procedures, especially for the intentional introduction of second phases, to ensure microstructural homogeneity. In addition, nanocomposite materials may suffer microstructure instability at high temperature that would degrade the performance.

Grain coarsening
Particle aggregation
Nanoprecipitates redissolution

Low temperature   High temperature
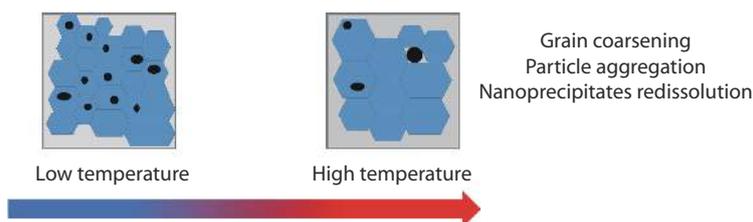
Fig. 9 The schematic diagram of microstructural instability of nanostructured materials at high working temperature.

Scalability is the dominant factor from lab-scale synthesis to industrial production in material science. However, the upscaling of high-*ZT* thermoelectric materials without obvious performance loss is still a key issue. These recently developed fabrication methods are difficult to realize this upscale process and few reports enable the one-batch weight over 100 grams for high-performance powder.[84] More importantly, fabricating the large-size sample with homogeneous properties is another critical challenge for the subsequent sintering process,[179] especially for spark plasma sintering (SPS). A batch synthesis of high-performance half Heusler alloys, namely n-type $Zr_{0.5}Hf_{0.5}NiSn_{0.985}Sb_{0.015}$ and p-type $Zr_{0.5}Hf_{0.5}CoSb_{0.8}Sn_{0.2}$, over 100 grams were enabled by the self-propagating high-temperature synthesis method. Very recently, a scalable preparation method, based on Simoloyer ball-milling, enables to obtain of over 1 kg $Mg_{3.1}Sb_{1.5}Bi_{0.49}Te_{0.01}$ powder in a single batch and the sintered samples with different diameters, ranging from a half-inch to two inches, show the comparable thermoelectric properties.[180]

1.6 Reliable and valid measurement

Although commercial instruments are commonly employed to measure the individual thermoelectric parameters, big experimental errors ~20% can be observed from sample to sample and from person to person. Wang *et al.* performed an international round-robin study on n-type and p-type bulk Bi_2Te_3 compounds from Marlow Industries around ten years ago observed the large discrepancies of measurement data and demonstrated the importance of reliable measurement for the thermoelectric community.[181,182] In this insightful study, it was found that the probe distance determination is the main source of error for electrical transport properties while several complex factors, such as measurement instruments, standard test method, analysis model, etc., critically affect the measurement data of thermal properties.

It is known that reliability and validity are extremely important for a convincing analysis and conclusion. Figure 10 shows the relationship between reliability and validity for experiment results. In reality, it is difficult to obtain both reliable and valid data for thermoelectric properties. Recently, Borup *et al.* and Wei *et al.* gave a comprehensive review of measurement theory and deeply discussed the origin of measurement accuracy for each thermoelectric parameter, which is useful and meaningful for new researchers or students in the thermoelectric field. Here we just highlighted some important aspects from these two reviews and added some of our own experience and perspective. First, in most cases, the homemade instruments for simultaneously measurements electrical conductivities and Seebeck coefficients usually show larger uncertainty than commercial instruments, especially for Seebeck coefficients measurement due to the contribution from thermal couples. Secondly, careful maintenance and regular calibration of commercial instruments

are highly recommended, therefore avoiding the big error from the damaged thermocouple or chamber contamination. Thirdly, a van der Pauw configuration is recommended for resistance measurement during the hall coefficient measurement process, but the measurements for samples with high carrier concentration and/or at high temperature still make difficulties for researchers. Fourthly, since heat capacity measurement is the most challenging task among the measurements of all the thermoelectric parameters, a comparison of the measured data with the modified corrected Dulong-Petit value including from the thermal expansion is highly required. Fifthly, for some special materials, like phase transitions, ultralow thermal conductivities, and bad mechanical properties, all the thermoelectric parameter measurements need to be conducted carefully enough, especially for the measurements of the Seebeck coefficient and thermal conductivity. Last, but not least, reading the user manual from the commercial instruments before use is appreciated, because measurement requirements for materials with distinct properties may be different. A reliable and valid measurement of thermoelectric properties is the prerequisite for assessing final performance. There are always great concerns regarding the reproducibility of the published high-ZT works in the thermoelectric area and thereby the international round-robin study is welcomed again to elaborate on the true situation.
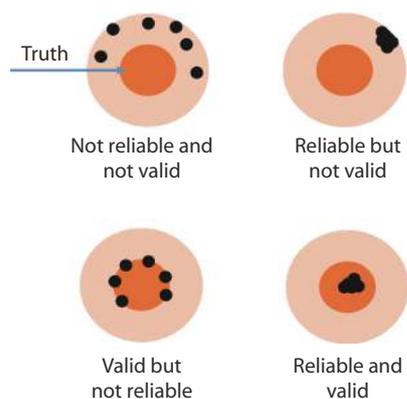
Fig. 10 The relationship between reliability and validity for experiment results.

2 Summary

During the last two decades, we have developed some novel thermoelectric materials and witnessed the remarkable improvement of materials' ZT, especially for the peak ZT, thanks to the deeper understanding of thermoelectric fundamental theory and advanced fabrication methods. However, for material science research, its motivation, development, and evaluation must rely on the real-application prospect. Thermoelectric devices still do not compete with conventional heat engines as a consequence of low performance. This awkward situation would strongly limit further development due to the faded or killed confidence and support from governments and enterprises. Therefore, from the viewpoint of material level, future critical challenges are discussed and emphasized, including the role of point defect physics, new the-

ories to decouple the thermoelectric parameters, the multi-criteria of good thermoelectric materials, discoveries of new materials, material synthesis challenges, and reliable and valid measurement. To address these challenges in the thermoelectric area, efforts are underway to enrich current understanding, design promising materials, and eventually develop high-performance devices towards realizing sustainable development of thermoelectric science and widespread industrial applications of thermoelectric devices.

Conflict of interest

The authors declare no conflict of interest.

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414

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