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Recent progress in thermoelectric materials

Abstract

Direct conversion of heat into electricity through advanced thermoelectric (TE) materials has been one of the most attractive solutions to the severe environmental and energy issues facing humanity. In recent years, great progress has been made in improving their dimensionless figure of merit (ZT), which determines the conversion efficiency of TE devices. ZT is related to three “interlocked” factors—the Seebeck coefficient, electrical conductivity, and thermal conductivity. These three factors are interdependent in bulk TE materials, and altering one changes the other two. The difficulty in simultaneously optimizing them caused TE research to stagnate, until great reductions in thermal conductivity were both theoretically and experimentally proven in nanomaterials in 1993. In this review, we first introduce some TE fundamentals and then review the most recent improvements in ZT in different kinds of inorganic and organic TE materials, which is followed by an investigation of the outlook for new directions in TE technology.

Keywords

recent, materials, progress, thermoelectric

Disciplines

Engineering | Physical Sciences and Mathematics

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Recent progress in thermoelectric materials

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Keywords Thermoelectrics · Functional materials · Nanostructures · Energy conversion

1 Introduction

Growing energy demands, concerns over climate change and depletion of fossil fuel resources have led to a concerted effort

to develop sustainable technologies for the efficient use, conversion, and recovery of energy. One such technology is the use of thermoelectric (TE) materials to directly convert heat into electricity, based on the Seebeck effect [1–7], which was discovered in 1836 by Thomas Johann Seebeck. It should be noted that TE materials can also convert electricity into cooling through the Peltier effect. The detailed principles of TE conversions have been described elsewhere [4–7]. This technology has distinct advantages, including: (1) TE conversion is reliable and operates in silence compared with other energy conversion technologies, as it works without mechanical movement; (2) TE devices are simple, compact, and safe; (3) it is an environmentally friendly green technology, because no heat and no gaseous or chemical waste are produced during operation; and (4) it can be widely used in places where other energy conversion technologies are unavailable, such as in the remote outer space [1, 2].

Although TE technology possesses many merits and has been known for more than one century, it has only been applied in narrow fields because of its low conversion efficiency (typically less than 6 %) [6]. The conversion efficiency strongly depends on the figure of merit (ZT) of the TE material, as described by Eq. (1),

$$\eta = \eta_c \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_h}, \quad (1)$$

where η is the conversion efficiency of heat to electricity, T_c and T_h are the temperatures of cold and hot sides of a TE generator, respectively, η_c represents the Carnot efficiency and can be expressed as $\eta_c = 1 - T_c/T_h$. ZT is given by Eq. (2),

$$ZT = \frac{S^2 \sigma T}{\kappa}, \quad (2)$$

where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and $S^2 \sigma$ is

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called the power factor. The dependence of the conversion efficiency on ZT is shown in Fig. 1. It clearly shows that ZT of TE materials should be at least above 3 in order to ensure that the device conversion efficiency is competitive with that of traditional power generators, which can reach 40 % of Carnot efficiency.

Equation (2) demonstrates that high ZT can be obtained by improving the Seebeck coefficient and electrical conductivity while reducing the thermal conductivity as much as possible. σ of TE materials can be expressed by Eq. (3),

$$\sigma = ne\mu, \quad (3)$$

where n is the density of charge carriers, μ is the mobility of charge carriers, e is the charge of unit carrier. The electrical conductivity can be significantly improved through chemical doping. Each dopant atom can have one more (less) valence electron than its host atoms and hence, can increase the density of charge carriers. Meanwhile, the dopants can also reduce the mobility of the charge carriers due to the enhanced scattering between dopants and carriers. The ideal density of charge carriers should be in a range from 10^{19} to 10^{21} cm^{-3} [8].

Simple doping of impurities may also improve the Seebeck coefficient by changing the electron density of states (DOS) [9]. As shown in Eq. (4),

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}, \quad (4)$$

the Seebeck coefficient is mainly controlled by the carrier concentration and effective mass of the charge carriers (m^*), which usually decreases with increasing carrier mobility. k_B and h are Boltzmann constant and Planck constant, respectively. Another way to enhance the Seebeck coefficient is by the use of external field effects [10].

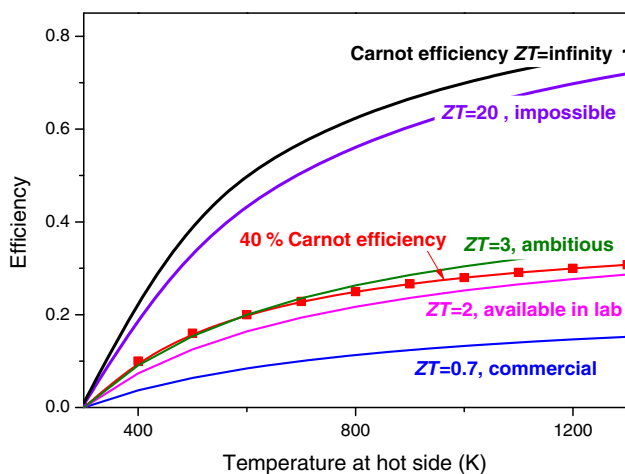


Fig. 1 (Color online) Conversion efficiency of TE materials with changing temperature difference and ZT , assuming that the cold side temperature is 300 K. The red curve is the 40 % Carnot efficiency

Thermal conductivity is decreased by enhancing phonon scattering (i.e., phonon-boundary scattering, phonon-defect scattering, and phonon-phonon scattering). The thermal conductivity includes electron thermal conductivity (k_e) and lattice thermal conductivity (k_c), as shown in Eq. (5),

$$k = k_e + k_c, \quad (5)$$

k_e is proportional to the electrical conductivity according to the Wiedemann–Franz Law [11, 12]. In semiconductors, usually >90 % of thermal conductivity comes from the lattice thermal conductivity (k_c), which is independent of the electrical conductivity. Hence, reducing the lattice thermal conductivity will lead to a pronounced enhancement in the TE performance.

According to the above description, the Seebeck coefficient, the thermal conductivity, and the electrical conductivity are strongly dependent on each other, and it is very challenging to improve them simultaneously in bulk TE materials. Research on TE materials was nearly frozen from the 1960s to the 1990s. In 1993, Dresselhaus and co-workers [13, 14] theoretically proved that low-dimensional materials can have higher ZT than their bulk analogs due both to their lower thermal conductivity and to quantum confinement effects. Their work rekindled research interest in TE materials and provided a strategy to improve the ZT values of TE materials by nanotechnology. Currently, the highest ZT value ($ZT = 3.6$ at 580 K) was obtained in $\text{PbSe}_{0.98}\text{Te}_{0.02}/\text{PbTe}$ quantum-dot superlattices (QDSLs) grown by molecular beam epitaxy (MBE), which was reported by Harman et al. [15] in 2005. Figure 2 shows the trends in both publications and patents on TE materials since 1965. It shows a blossoming in publications since 1995, and the publications from 2010 to 2013 are almost as numerous as those published within the previous 5 years (Fig. 2a), in which over 85 % are focused on inorganic TE materials, and only 15 % are about organic TE materials (Fig. 2b). Among all publications on inorganic TE materials, there are 32 % and 25 % of them are about silicon-based and oxide-based TE materials, respectively. Compared with publications, there are only about 450 patents on TE materials and related technology (Fig. 2c) since 1965, and most patents were filed during 1995–2010.

With the soaring interests in TE materials, there are many good reviews on the different types [16–22], including oxide based [16], organic based [17], and so on. For examples, as early as in 1986, Rowe [18] published a review on different kinds of potential TE materials; in 2009, Sootsman et al. [19] also summarized TE materials in different kinds; Chen and co-workers [20] have reviewed the progress on nanocomposite TE materials, and Li et al. [21] have highlighted the potential application of semiconductor nanowires in TEs, including the colloidal

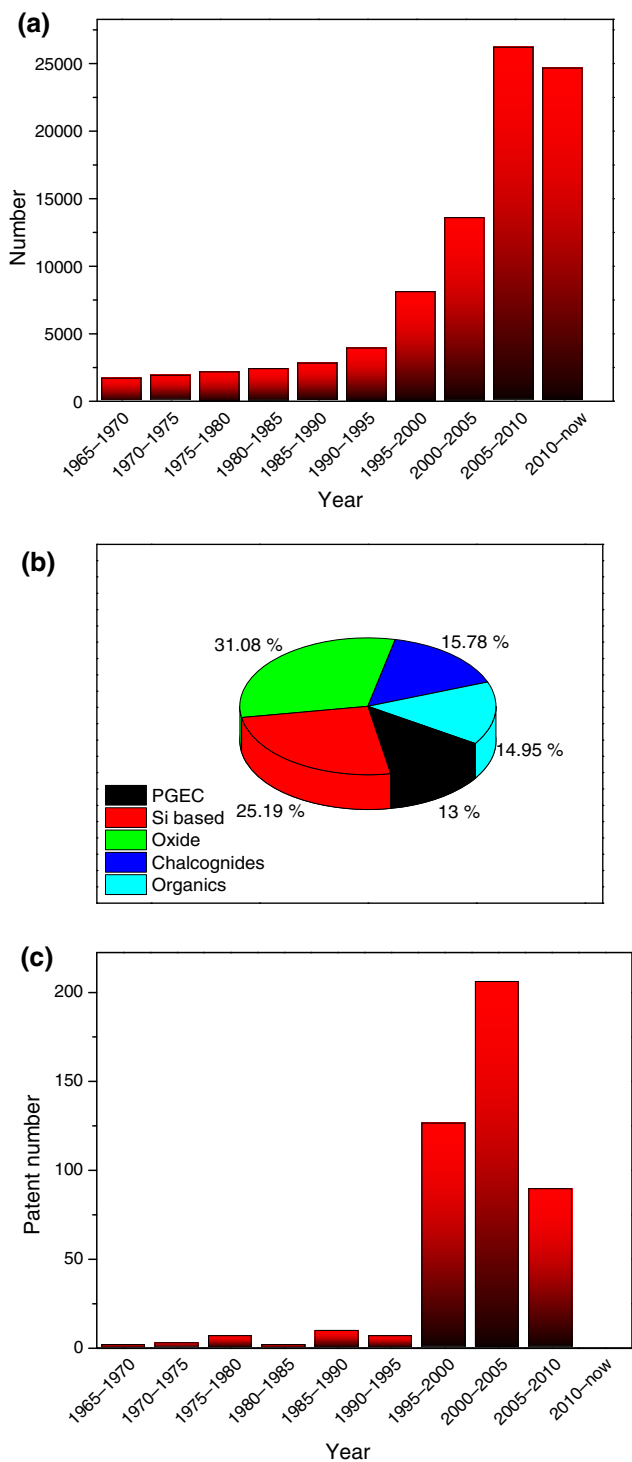


Fig. 2 (Color online) **a** Publications in the area of TE materials and related technology from 1965 to 2013; **b** Publications on different types of TE materials from 2010 to 2013; **c** Patents in the area of TE materials and related technology from 1965 to 2013. The data were collected from Science Direct data library by using “TE” as the key word

nanowires synthesized from wet chemistry [22–27]. On the basis of previous reviews, we summarize the latest progress for all the different types of TE materials in the past several

years. We also show our perspectives on the future of TE materials and TE technology.

2 Recent progress in inorganic TE materials

There are many kinds of TE materials, from semiconductors to ceramics, from oxides to organics, from bulk to superlattice, and from nanoparticles to nanowires [16–27].

Figure 3 shows the application temperature ranges of different TE materials and the natural abundance of the relevant elements. Most state-of-the-art high-performance TE materials contain some toxic or low abundance elements. Here, we want to address the scientific progress made in different kinds of TE materials rather than their cost, toxicity, and effects on the environment during actual application.

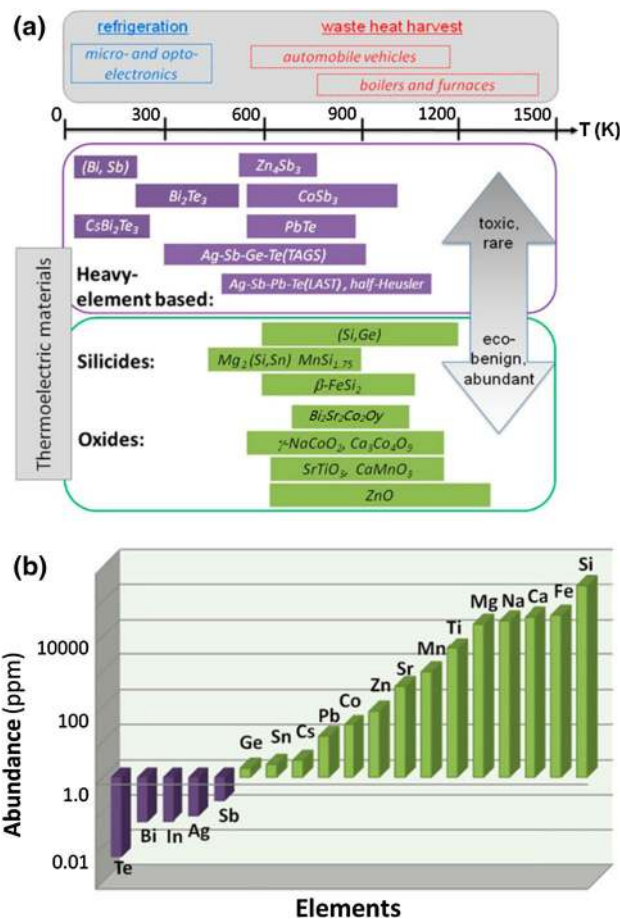


Fig. 3 (Color online) **a** Application temperature ranges of different kinds of TE materials; and **b** abundance of elements in the Earth's crust that is used in TE materials. Reprinted with permission from [16] Copyright 2011, Cambridge University Press

2.1 Metal chalcogenides

Metal chalcogenides have been extensively applied in many energy conversion and storage devices, such as solar cells, lithium ion batteries, fuel cells, supercapacitors, and TE generators and coolers [28–33]. In fact, metal chalcogenides, such as lead and bismuth-based selenides, and tellurides are prime candidates for TE applications due to their better and reliable performance in comparison with other TE materials. Their TE modules have been successfully commercialized with a ZT of around 1 [34]. Recently, their ZT values have been drastically improved to new records in the laboratory through nanotechnology, chemical doping, and engineering of their electrical structure. Some ZT values are above 2 or even 3 [35–38]. These breakthroughs and advances will be discussed in the following sections.

2.1.1 Lead chalcogenides

Lead is one of the most useful elements in good TE materials, as it has great natural abundance in the Earth's crust and can be easily processed. More importantly, it possesses a heavy atomic weight, which has benefits for the reduction of lattice vibration and thermal conductivity. Lead chalcogenides have been playing a dominant role in TE power generation for more than 50 years. Harman et al. [15] reported PbTe/PbTeSe quantum-dot superlattices with a ZT of 3.0 at 550 K. Although PbTe has been well investigated and synthesized by all kinds of methods, the ZT of bulk PbTe has been underestimated for a long time due to the difficulty in precisely measuring its thermal conductivity at high temperature until 2006, when the Snyder and co-workers [39] at the California Institute of Technology carefully studied the thermal conductivity of PbTe using an advanced laser flash technique. They corrected the ZT of p-type Na-doped PbTe and n-type I-doped PbTe from 0.8 and 0.7 to 1.5 and 1.4 at 750 K, respectively [39–41].

Another important advance was the use of nano-inclusions to reduce the thermal conductivity of PbTe [42–49]. The nano-inclusions usually come from a well-dispersed second phase and can be divided into “coherent” precipitates, which are slightly mismatched with the matrix, and “incoherent” precipitates, which show a clear boundary with the host. Both kinds of nano-inclusions can significantly reduce the thermal conductivity of PbTe-based TE materials, but they work by different mechanisms and show different effects. The coherent nano-inclusions act as point defects and scatter short wavelength phonons due to their slight mismatch with the matrix. Since the incoherent ones possess a large mismatch with the matrix, they work as nanoparticles and selectively scatter mid to long

wavelength phonons. A ZT of 1.7–1.8 for both n-type and p-type PbTe has been realized through the use of coherent nano-inclusions of AgSbTe₂ [43], NaSbTe₂ [44], and SrTe [45]. While a ZT of 1.4–1.5 has been achieved in n-type PbTe by incoherent nano-inclusions of Sb and Ag₂Te [46, 47], it is slightly lower than that obtained by using coherent nano-inclusions due to their adverse effects on charge carrier mobility.

By improving phonon scattering on all relevant length scales in a hierarchical system (i.e., from atomic-scale lattice disorder and nanoscale-endotaxial precipitates to mesoscale grain boundaries), Kanishka et al. [50] achieved the maximum reduction in the lattice thermal conductivity and a ZT of 2.2 at 915 K in p-type PbTe doped with 4 % SrTe (molar concentration). Figure 4 shows the maximum ZT values for all length scales of scattering centers: the atomic scale (alloy scattering, dopant), the nanoscale (SrTe nanocrystals) to the mesoscale (grain-boundary scattering). By combining the effects of atomic-scale alloy doping, endotaxial nanostructuring, and mesoscale grain-boundary control, maximum phonon scattering can be achieved at high temperature, and the ZT can be increased beyond the values obtained from nanostructures alone. Use of multi-scale phonon scattering is a new strategy to minimize the thermal conductivity of TE materials.

Besides the conventional route of reducing thermal conductivity, enhancement of the power factor ($S^2\sigma$) has also been achieved by chemical doping. Biswas et al. [45] found that doping Se into p-type PbTe can increase carrier mobility without decreasing carrier concentration due to the convergence of electronic bands. Finally, they obtained a ZT of 1.8 in Na_{0.02}Pb_{0.98}Te_{0.85}Se_{0.15}.

In addition to lead chalcogenide nanocomposites made by solid-state reaction, there are more and more reports on nanostructured TEs made from wet-chemical approaches. For instance, Ibanez et al. [51] synthesized core-shell PbTe@PbS nanoparticles in organic solvent using a hot injection method. They tested the TE properties of the resultant nanoparticles after consolidating them into a pellet and obtained a ZT of 1.07 at 700 K. The high ZT of core-shell PbTe@PbS nanoparticles is because: (1) The

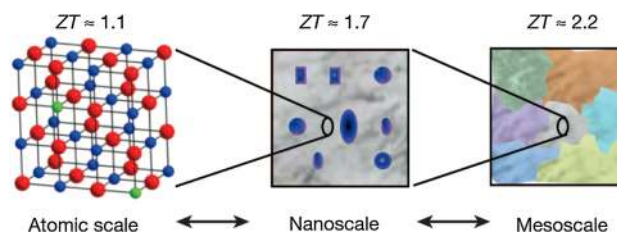


Fig. 4 (Color online) All-length-scale hierarchy in TE materials. Reprinted with permission from [50]. Copyright 2012, Nature Publishing Group

PbTe core functions like a p-type semiconductor, while the PbS shell acts as an n-type one, so that the compensation of the two kinds of charge carriers makes the electrical conductivity and the Seebeck coefficient relatively lower than those of pure PbTe and PbS at low temperature. With increasing temperature, however, the energy-activated charge carrier mobility is greatly enhanced and finally leads to an electrical conductivity that is one order of magnitude higher than those of pure PbTe or PbS. (2) The thermal conductivity is greatly reduced, not only by nanoscale effects and the lattice mismatch between PbTe and PbS, but also by partial alloying of PbS and PbTe, which can introduce a high density of point defects.

The other lead chalcogenides apart from PbTe, such as PbSe and PbS, have a similar structure to PbTe and a slightly larger band gap. Se and S are cheaper and less toxic than Te, and there are more opportunities to explore PbSe and PbS as alternatives. It was predicted that p-type PbSe would be a good TE material too [52]. This prediction was recently confirmed by Wang et al. [53], who doped PbSe with Na and got a ZT of 1.2 at 850 K. Zhang et al. [54] also doped PbSe with Al to obtain n-type PbSe with a high ZT of 1.3 at 850 K. In contrast to PbSe, only a moderate ZT of 0.8 at 900 K was obtained in PbS, even though some PbTe nano-precipitates were introduced into it [55].

2.1.2 Bismuth chalcogenides

Since their discovery in the 1950s, Bi_2Te_3 and its alloys with Sb and Se, with a ZT of 0.6 at 300 K, have been commercialized and used in TE refrigerators. Advances in nanotechnology have recently boosted the ZT of this conventional TE material to a new record, as demonstrated by a ZT of 2.4 at 300 K obtained from a superlattice of $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$ films in 2000 [56]. This breakthrough not only demonstrates how nanoscale effects can improve the performance of conventional TE materials but also has led to a burst of research on TE nanomaterials.

Similar to lead chalcogenides, the introduction of nanostructures into the bismuth chalcogenide matrix can improve its TE performance. Chen and co-workers [57] and Xie et al. [58] increased the ZT of p-type $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$ from 1 to 1.4–1.5 by employing nano-inclusions during powder metallurgy synthesis. The same process did not work for n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, because the high carrier concentration decreases the average carrier mobility, and it increases the thermal conductivity. Another reason lies in the formation of Te vacancies during the ball-milling process, which affects the electrical conductivity.

The use of different well-dispersed particles to simultaneously enhance the phonon scattering, and the Seebeck coefficient can improve the ZT of Bi_2Te_3 -based TE

materials. Liu et al. [59] achieved a ZT of 0.94–0.99 in n-type $\text{Cu}_{0.01}\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, which is higher than that of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ ($ZT = 0.85$). Besides the reduction of thermal conductivity resulting from nano-inclusions, Ko et al. [60] also observed an increase in the Seebeck coefficient due to a carrier-selective scattering effect in Pt-doped Sb_2Te_3 . Liu et al. [61] investigated the effect of SiC on the transport properties of n-type and p-type Bi_2Te_3 and found a selective carrier scattering effect caused by the SiC particles. Ren and co-workers [62] successfully increased the ZT of n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ to 1.04 by improving its electrical conductivity through the reorientation of the *ab*-planes of small crystals during multiple-step hot pressing of ball-milled nanopowders.

In 2010, Ferdows and Roger [63] theoretically calculated the ZT of Bi_2Te_3 thin films (five atomic layers thick) to be as high as 7.2 at room temperature. The high ZT results from the change in the distribution of the valence band density due to the quantum confinement in the thin film. There is no experimental result supporting this calculation, however. In addition to thin films, the ZT of Bi_2Te_3 nanowires has also been theoretically calculated, and the results show a strong diameter dependence, e.g., the ZT value can be over 6 if the nanowire diameter is smaller than 5 nm. Inspired by the high ZT of nanowires from theoretical predictions, Zhang et al. [64] synthesized uniform 8-nm Bi_2Te_3 nanowires and achieved a ZT of 0.96 at 380 K. The authors also designed Bi_2Te_3 nanowire-based heterostructures, such as $\text{Te@Bi}_2\text{Te}_3$, $\text{Bi}_2\text{Te}_3\text{@PbTe}$, although the ZT of the $\text{Te@Bi}_2\text{Te}_3$ heterostructure was only around 0.23 at 400 K. This value was two times higher than that of pure Te nanowires, but much lower than that of pure Bi_2Te_3 nanowire (0.96 at 380 K) [65].

Besides the use of zero-dimensional nanoparticles or one-dimensional (1D) nanowires to improve their TE performance, introduction of two-dimensional (2D) nanosheets into bismuth chalcogenides can also lead to a high ZT . Li et al. [66] mixed graphene with Bi_2Te_3 to improve its conductivity, resulting in a 1.5 times higher ZT (0.3 at 350 K) for the composites than for single crystal Bi_2Te_3 . Although the ZT value is low, their work provides an idea to prepare hybrid TE composites with enhanced performance.

2.2 Superionic conductors

An ideal TE material should be a phonon glass and an electron crystal (PGEC), which can simultaneously exhibit high electrical conductivity and low thermal conductivity, and thus show high ZT . Some superionic conductors such as cuprous and silver chalcogenides have similar properties. In contrast to the structure of lead and bismuth chalcogenides, cuprous and silver chalcogenides have a

special structure where the chalcogen anions form a crystalline lattice and provide a pathway for charge carriers, while the cuprous or silver cations (i.e., Cu^+ and Ag^+) are highly disordered around the chalcogen sublattice at high temperature. Cu^+ or Ag^+ ions can move fast like liquid at high temperature, which leads to extremely low thermal conductivity. The liquid-like behavior of Cu^+ and Ag^+ makes their chalcogenides phonon liquid and electron crystal (PLEC), essentially similar to PGEC. Therefore, they exhibit outstanding TE performance, demonstrated by the ZT of p-type Cu_{2-x}Se (1.6 at 1,000 K), the highest value among all bulk TE materials [67]. In 2013, Liu et al. [68] got an even higher ZT (2.3 at 400 K) in n-type Cu_2Se . This specific high ZT was obtained by the critical scattering of electrons and phonons during the second-order phase transition in Cu_2Se . The temperature fluctuation near phase transition temperature can lead to the “critical scattering”, which can selectively scatter phonons without influence on electrons. This offered a new strategy to get a high ZT at phase transition temperature.

Figure 5 shows the structure of cuprous selenide. The Se atoms form a rigid face-centered cubic lattice, and the Cu^+ ions are highly disordered around the Se sublattice.

It should be noted that the copper and chalcogen can form various compounds with complicated structures. Figure 6 is the binary Cu–Se phase diagram, clearly showing the variation of crystal phases and compositions that can occur with increasing temperature and ratio of elements. Nevertheless, there are few compounds (e.g., Cu_2Se or Cu_{2-x}Se) that are suitable for TE application.

The low thermal conductivity of cuprous and silver chalcogenides is attributed to the liquid-like behavior of Cu^+ or Ag^+ , which is due to their fast movement arising from the crystal phase transition. Their high electrical conductivity is due to the deficiency of Cu^+ or Ag^+ . As cuprous and silver chalcogenide nanostructures have smaller size and higher surface to volume ratio than their bulk analogs, they have a higher degree of deficiency and disorder and are expected to show better performance.

Although different copper and silver chalcogenide nanostructures have been synthesized in different ways [69–72], there are only few reports on their TE properties due to difficulties in large-scale preparation of their nanostructures with well-defined compositions and crystal structures, as well as uniform size and morphology. Recently, Xiao et al. [73] synthesized monodispersed Ag_2S , Ag_2Se , and Ag_4SeS nanocrystals through a solvothermal method and then investigated the TE properties of these nanocrystals, especially at the phase transition temperature. Their ZT at the corresponding transition temperature is in an order of $ZT_{\text{Ag}_4\text{SeS}} (0.33) > ZT_{\text{Ag}_2\text{Se}} (0.23) > ZT_{\text{Ag}_2\text{S}} (0.12)$. Later on, the authors successfully doped Ag_2Se nanocrystals with Bi^{3+} to switch the conductivity from p-type into n-type, and they obtained a ZT of 1.5 at 700 K [74]. Compared with silver chalcogenide nanostructures, there is much less reports on the TE properties of copper chalcogenide nanomaterials. Zhang et al. [75] prepared Cu_{2-x}Se nanowires by a hydrothermal method in the Teflon-lined autoclaves and measured their Seebeck coefficient to be $180 \mu\text{V/K}$. Unfortunately, there is nothing about the ZT value of these nanowires.

The above research suggests that superionic conductors could be high-performance TE materials, especially in nanostructured form. There is considerable scope for investigating the TE application of cationic and anionic superionic conductors.

2.3 Metal oxides

Metal oxide-based TE materials have several advantages in comparison with metal chalcogenides. First, they possess good chemical and thermal stability, and thus can be used in a large temperature gradient in air. Second, they are environmentally friendly and cost-effective. Third, they could exhibit novel non-linear, non-local TE effects (i.e., the Benedicks effect) induced by a large temperature gradient, which may be thermoelectrically favorable [76, 77]. Fourth, their TE performance can be tuned over a wide

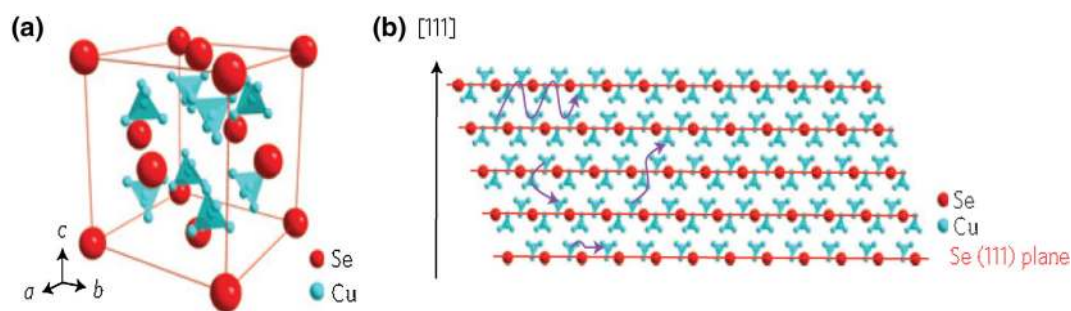


Fig. 5 (Color online) Crystal structure of $\beta\text{-Cu}_2\text{Se}$ with a cubic anti-fluorite structure: **a** unit cell; **b** projected plane along the cubic $[110]$ direction. The arrows indicate that the Cu ions can freely travel among the interstitial sites. Reprinted with permission from [67]. Copyright 2012, Nature Publishing Group

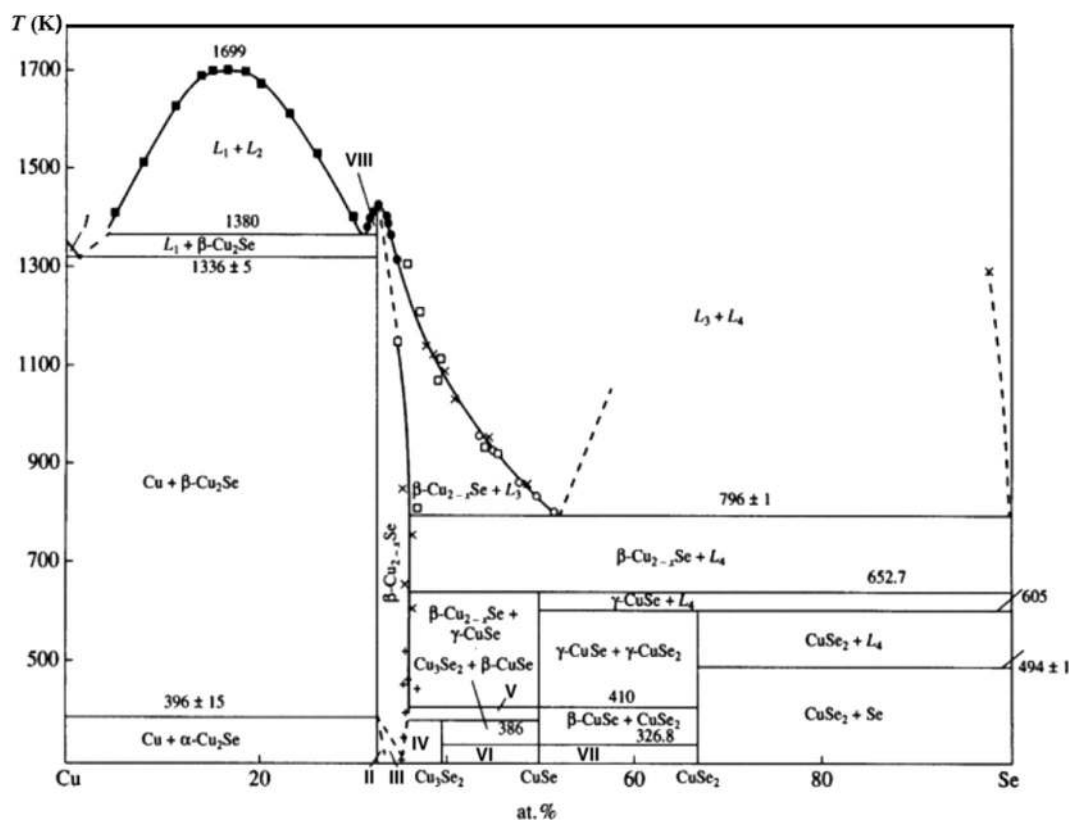


Fig. 6 Phase diagram of Cu–Se system. Phase (I) Cu+L₁, (II) α -Cu_{2-x}Se, (III) α -Cu_{2-x}Se+ β -Cu_{2-x}Se, (IV) β -Cu_{2-x}Se+Cu₃Se₂, (V) β -Cu_{2-x}Se+ β -CuSe, (VI) Cu₃Se₂+ α -CuSe, (VII) α -CuSe+CuSe₂, and (VIII) L₂+ β -Cu₂Se. Reprinted with permission from [67]. Copyright 2012, Nature Publishing Group

range by engineering their structure and composition. In addition, they can be also used in other energy conversion devices (e.g., solar cells and lithium ion batteries), which could improve the performance of these devices.

Despite the above advantages, oxide-based TE materials have lower ZT compared with conventional TE materials such as Bi₂Te₃ due to their relatively higher thermal conductivity. There are several types of TE oxides, including cobalt oxides (p-type), manganese oxides (n-type), and zinc oxides (n-type semiconductors). In 1997, research interest in oxide-based TE materials was ignited when p-type Na_xCoO₂ with a ZT around 1 was discovered. Since then, some layered oxide materials have been predicted to show a reasonably high ZT if different kinds of layers (unit nanoblocks) with different compositions, and symmetries are integrated into hybrid crystals or superlattices, in which each layer can play its own role in realizing independent control of electrons and phonons.

The oxide layer structure can be strongly influenced by the processing method that is used. Noudem et al. [78] investigated the effect of spark plasma sintering (SPS) on the morphology of Ca_{0.95}Sm_{0.05}MnO₃ and its TE performance. They got a higher power factor than in previous reports by optimizing the sintering parameters. Inspired by

these findings and the fact that nanostructures can effectively decrease thermal conductivity, investigations on layered oxide-based TE materials have rapidly increased and made great progress. He et al. [16] have summarized the progress achieved in oxide-based TE materials from 2000 to 2010. Figure 7 displays some representative oxide TE materials investigated in this period. Since now, the highest ZT obtained in oxides was around 2.4 at room temperature which was realized on SrTiO₃ superlattice [79].

In 2011, Jood et al. [80] successfully doped Al into ZnO nanoparticles using a microwave solvothermal approach (Fig. 8). The resultant doped ZnO nanoparticles showed a ZT of 0.44 at 1,000 K, 50 % higher than that of the best non-nanostructured counterpart at the same temperature. Their work again proved the effectiveness of nano-inclusions in decreasing thermal conductivity.

In addition to ZnO, BiCuSeO was also found to be a potential candidate as an oxide-based TE material by Li et al. [81] in 2012. A ZT of 0.7 was obtained in this material at 773 K. This oxide not only possessed good electrical conductivity and a large Seebeck coefficient, but also showed extremely low thermal conductivity due to its low speed of sound and Young's modulus. In addition, by

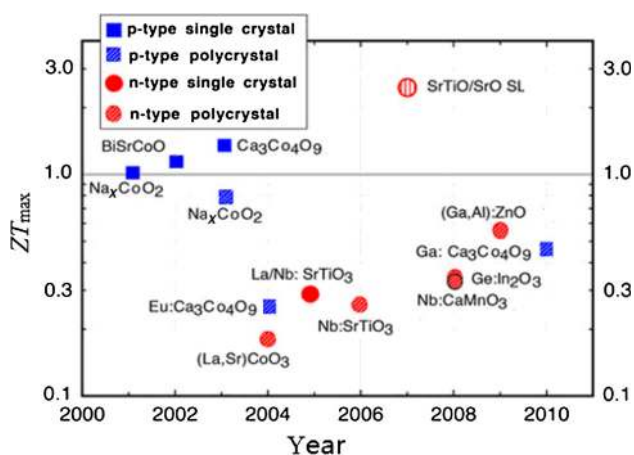


Fig. 7 (Color online) Maximum figure of merit values of p-type and n-type TE oxides from 2000 to 2010. Reprinted with permission from [16]. Copyright 2011, Cambridge University Press

purifying the constitutive phase and reducing grain size, the electrical conductivity could be significantly enhanced while maintaining a large Seebeck coefficient. Later, Li et al. [82] reported a higher ZT value of 1.1 at 923 K for $\text{Bi}_{0.875}\text{Ba}_{0.125}\text{CuSeO}$. This high ZT value was achieved by the combined effect of heavy doping with Ba and refinement of grain size (200–400 nm). Guided by the previously existing TE phases, Constantinescu et al. [83] used the phase diagram equilibrium to design new thermoelectric TE oxides based on other transition metals. They synthesized cobalt-free BaFeO_x which has the same perovskite structure as Na_xCoO_2 . Although the obtained power factor is too low for practical applications, their work provides an idea for designing new TE materials, due to the higher abundance and lower toxicity of Ba, Fe in comparison with cobalt, lead, bismuth, and the other heavy elements used in conventional TE materials.

Although there are many investigations on the TE properties of oxide materials, the development of

nanotechnology and doping techniques would provide new opportunity for them. Their ZT values would be drastically improved in near future, and they would become more competitive than other TE materials, because they have high thermal and chemical stability, in addition to their low fabrication cost.

2.4 Silicon-based materials

Silicon is cheap, environmentally friendly, and has been widely used in semiconductor devices and solar cells. Bulk silicon was proved not a good TE material, as it has high thermal conductivity (around $150 \text{ W}/(\text{m K})$). This drawback has been successfully overcome by reducing its grain size down to nanoscale dimensions. Recently, a ZT of 0.6 at room temperature was achieved in B-doped Si nanowires (50 nm in diameter) which were fabricated by etching silicon wafers [84]. Akram et al. [85] also reported the efficient TE performance of silicon nanowires with cross-sectional areas of $10 \text{ nm} \times 20 \text{ nm}$ and $20 \text{ nm} \times 20 \text{ nm}$. A ZT of 1 at 200 K was achieved by varying the nanowire diameter from 10 to 20 nm and by varying the impurity doping level. In addition to nanowires, Sabah et al. [86] employed a simple high energy ball-milling method to synthesize doped Si nanoparticles on a large scale and then consolidate them into pellets. A ZT of 0.7 at 1,275 K was measured for this n-type bulk nanostructured Si, which is 3.5 times larger than that of heavily doped single-crystal Si.

Besides experimental research, theoretical investigations on the TE properties of nanoscale Si have been carried out in parallel. Lee et al. [87] computed the room temperature TE properties of nanoporous silicon using a combination of classical molecular dynamics for the lattice thermal conductivity and ab initio density functional theory for the electrical conductivity, Seebeck coefficient, and electronic contribution to the thermal conductivity. They predicted that the ZT could increase by 2 orders of magnitude over

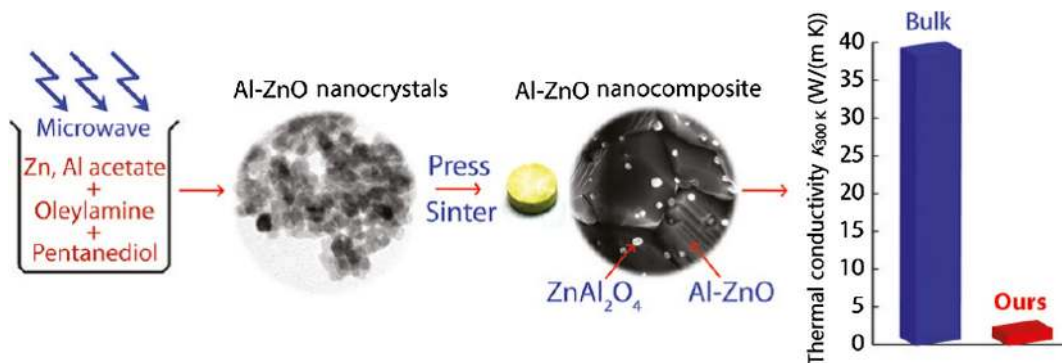


Fig. 8 (Color online) Schematic illustration of the fabrication of Al containing ZnO nanocomposites with low thermal conductivity, obtained by the cold-pressing and sintering of Al-doped ZnO nanocrystals synthesized by the microwave-stimulated solvothermal method. Reprinted with permission from [80]. Copyright 2011, American Chemistry Society

that of the bulk due to the combination of the nanometer size pores, which can greatly reduce the thermal conductivity, and the ordered arrangement of pores which allows for only a moderate reduction in the power factor. Yang et al. [88] calculated the lattice thermal conductivity of nanocrystalline, nanoporous, and superlattice Si. The results show that (1) the lattice thermal conductivity can be remarkably reduced through the boundary scattering effect and intrinsic size effect in these nanomaterials; (2) nanoporous Si exhibits smaller lattice thermal conductivity than Si nanowires due to the porosity effect; (3) fully dense Si nanocomposites have comparable lattice thermal conductivity to that of Si nanowires; and (4) periodic quantum structures, such as superlattices, are not necessary for the reduction of thermal conductivity.

Silicon nanostructures have a bright prospect in TE applications, as they can be easily fabricated using the existing semiconducting industry. Their TE device can be easily combined with electronic devices. More importantly, their TE performance can be significantly improved by doping with germanium, although it is very expensive. How to improve their ZT without use of expensive elements would be an important subject in this area. Here, we want to address two important types of silicon-based TE materials (i.e., SiGe and Mg_2Si) in detail in the following section.

2.4.1 SiGe-based TE materials

The addition of germanium into the silicon matrix can effectively reduce the lattice thermal conductivity. The SiGe alloys that are thus formed are currently the best TE materials at high temperature (around 1,000 °C) and are therefore used in radioisotope TE generators (RTG) and some other high temperature applications. For example, SiGe TE modules with a material ZT of 0.5 (p-type) and 0.9 (n-type) have been used in RTGs by NASA in the United States since 1976 [88].

Recently, a pronounced enhancement in ZT values has been demonstrated for both n- and p-type SiGe alloys by using them in nanostructured form, which can increase the phonon scattering [89–91]. One example is that the thermal conductivity was greatly reduced, and the maximum ZT of p-type nanostructured $Si_{80}Ge_{20}B_5$ was improved from 0.5 to 0.95 [89], while the ZT of n-type $Si_{80}Ge_{20}P_2$ was increased from 0.93 to around 1.3 [90]. The concentration of Ge is still too high, however, leading to high fabrication cost. It should be noted that omitting the Ge would lead to a drop in ZT value. In 2009, Zhu et al. [92] added 5 % Ge into GaP and P co-doped Si to achieve a ZT of 0.94 at 900 °C. Yu et al. [93] also achieved a ZT of 1.3 at 900 °C for nanocomposites of $(Si_{95}Ge_5)_{0.65}(Si_{70}Ge_{30}P_3)_{0.35}$ by using a modulation doping method. The mechanism of modulation doping is shown in Fig. 9. The dopants (P) in

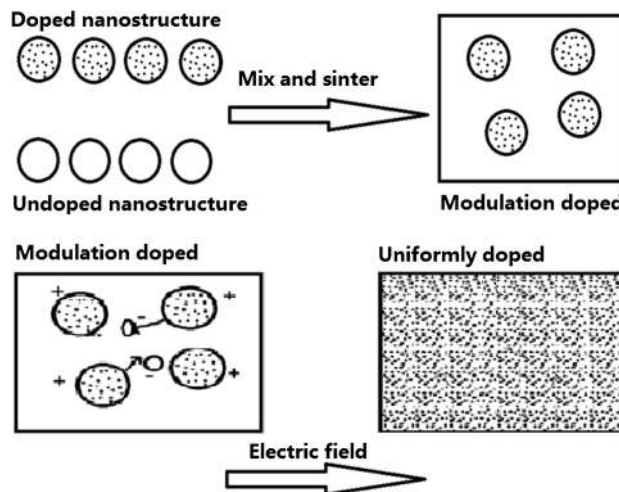


Fig. 9 Schematic diagram of modulation doping and uniform doping

the nanoparticles of $Si_{70}Ge_{30}$ offer extra charge carriers, while the scattering between the charge carriers and the ionized dopants is greatly reduced, as the dopants are localized in the nanoparticles. Hence, the power factor is greatly enhanced. Their work provides a new approach to increase the concentration of charge carriers while reducing the loss of mobility.

In 2009, Mingo et al. [94] proposed a “nanoparticle-in-alloy” approach to enhance the TE performance of SiGe. With nanosized silicide and germanide fillers in the SiGe matrix, a fivefold increase in the ZT at room temperature and a 2.5 times increase at 900 K were achieved. They also predicted that there must be an optimal nanosize that can minimize the nanocomposite’s thermal conductivity. Meanwhile, the nanoparticles do not impair the electrical conductivity because of size control. Finally, a ZT of 1.7 at 900 K was obtained through this approach.

In 2012, a ZT of 2 at 800 K was reported by Lee et al. [95] who simultaneously tested the thermal conductivity, electrical conductivity, and power factor of a single SiGe nanowire. The high ZT arises from the huge reduction in thermal conductivity due to the quantum confinement effect. This result demonstrates the great potential of nanostructured SiGe-based TE materials.

2.4.2 Mg_2Si -based TE materials

Despite the high performance of SiGe-based TE materials, the use of Ge results in high cost. Alternative TE materials could be Mg_2B_{IV} ($B_{IV} = Si, Ge, \text{ and } Sn$) compounds and their alloys, among which, Mg_2Si -based materials have been extensively investigated, as they can be used in the engine operating temperature range (i.e., 500–800 K). More importantly, they have lower density, higher resistance to oxygen, non-toxicity, and environmental friendliness in

comparison with other TE materials used in the same temperature range, such as CoSb_3 and PbTe [96, 97]. The huge abundance of Mg and Si [98–100] leads to low fabrication cost, which would enable their wide application.

Mg_2Si is an intermetallic compound or Zintl salt with a high melting point and metallic luster at room temperature. It is a poor n-type semiconductor and sensitive to water. Vining et al. [101] proposed that Mg_2Si could possess a higher ZT due to the fact that the material factor ($\beta = (T/300)(m^*/m_e)^{3/2}$) of Mg_2Si (14) is much larger than those of SiGe (1.2–2.6) and FeSi_2 (0.05–0.8). Later experiments proved that the ZT of intrinsic Mg_2Si is relatively low, i.e., smaller than 0.2 [102–106]. The reason for the low ZT is its high thermal conductivity due to the light weight of the Si atoms. Another drawback of this material is the difficulty in preparing highly pure Mg_2Si due to the similar properties of Mg and Si. The boiling point of Mg (1,380 K) is the same as the melting point of Mg_2Si (1,380 K). In addition, Mg and Si have poor solubility in each other and very different vapor pressures. The separation of elements usually leads to a degradation of performance during the application of Mg_2Si as a TE material.

There are mainly three routes to improve the ZT of Mg_2Si : (1) doping with various elements such as Al, Sb, Bi, and Na; (2) formation of a homogeneous solid solution of $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ and $\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x$; and (3) the use of nanostructures. Nikhil et al. [107] investigated the effect of crystallite size on the TE properties of nanoscale Mg_2Si . They thought that nanostructure in Mg_2Si may not be effective to increase ZT because of the detrimental loss of carrier mobility at the grain boundaries, but Yang et al. [108, 109] reported that the ZT of nano- Mg_2Si can be increased to 0.36 at 811 K by the use of mechanical alloying and SPS methods. They further increased the ZT to 0.8 at 823 K by doping nano- Mg_2Si with Bi. Using a similar strategy, Zaitsev et al. [110] doped $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ with Sb and got a ZT of 1.1 at 780 K. Noda et al. [111] doped $\text{Mg}_2\text{Si}_{0.6}\text{Ge}_{0.4}$ with Sb and Ag, and achieved a ZT of 1.07 at 663 K for Sb-doped $\text{Mg}_2\text{Si}_{0.6}\text{Ge}_{0.4}$ and 1.68 at 629 K for its Ag-doped analog, respectively.

2.5 PGEC TE materials

One type of high performance bulk TE materials is the PGEC, as identified by Slack et al. [12], which can scatter most phonons to result in low thermal conductivity, as well as conducting electrons to promote high electrical conductivity, by forming a complex cage-like structure filled with heavy atoms. Skutterudites, clathrates, and half-Heusler alloys are such TE materials. They are mainly prepared by casting or powder metallurgic method, and their TE performance can be improved by chemical doping or substitution.

2.5.1 Skutterudites

As shown in Fig. 10, skutterudites are bulk TE materials with the structure of $(\text{Co, Ni, Fe})(\text{P, Sb, As})_3$ and cubic space group $\text{Im}\bar{3}$. They contain vacancies into which low-coordination ions (usually rare earth elements) can be inserted to decrease the thermal conductivity by enhancing phonon scattering without reducing electrical conductivity. Such a structure makes them exhibit PGEC behavior. The chemical formula of skutterudites can be expressed as $\text{ReM}_4\text{X}_{12}$, where Re is a rare earth element, M is a transition metal element, and X is a non-metal element from Group V, such as phosphorus, antimony, or arsenic. ZT of skutterudites can be significantly improved by double, triple, and multiple filling of elements into the vacancies in their structure. Usually, alkali metals, alkaline-earth metals, lanthanides, and similar elements are selected as “fillers” or “dopants” for skutterudites because of their moderate atom size. Hence, the selection and combination of different “fillers” is very crucial for achieving high TE performance. Replacement of host atoms in lattice sites, such as substitution for Co and Fe, has also been identified as an effective way to reduce thermal conductivity.

The merits of skutterudites include (1) the ZT is relatively high and can be easily tuned by controlling their compositions and structures; (2) components are relatively cheap and non-toxic; (3) the application temperature can be up to 600 °C. The sublimation of Group V elements (e.g., antimony), however, and poor resistance to oxidation limit their wide application, as oxidation and volatilization easily take place in harsh environments such as in air at high temperature, which lead to a rapid degradation of TE properties and shortens the lifetime of TE generators [112–118].

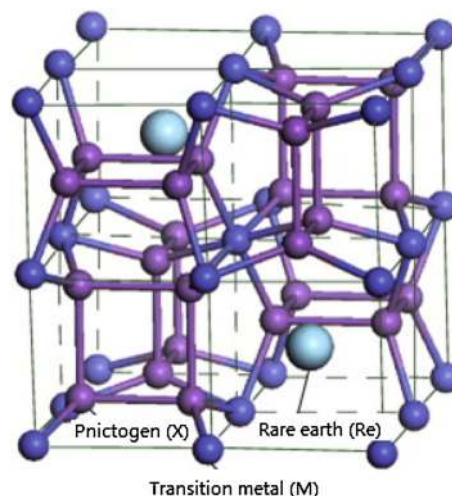


Fig. 10 (Color online) Crystal structure of skutterudites and element distribution in the unit cell

Recently, great progress has been achieved in improvement of the TE properties of skutterudites. In 2011, CoSb_3 with multiple fillers of Ba, La, and Yb were synthesized, and a high ZT of 1.7 at 850 K was realized [119]. The dependence of skutterudite TE properties on the filled fraction and a comparison of their ZT with those other TE materials are shown in Fig. 11.

In addition to the tuning with fillers, a ZT of 1.8 has been achieved in Sr-, Ba-, Yb-filled CoSb_3 by employing a high pressure torsion process, which can refine the grain size of the material via severe plastic deformation [120]. The refinement of grain size increases the amount of interfaces and leads to further reduction in thermal conductivity.

2.5.2 Clathrates

Compared with skutterudites, clathrates possess a more complex cage-like structure and a wider variation in composition. They have a general formula of $\text{A}_x\text{B}_y\text{C}_{46-y}$

(type I) and $\text{A}_x\text{B}_y\text{C}_{136-y}$ (type II), in which B and C are elements from Groups III and IV and can form a framework serving as host for “guest” atoms of element A (alkali or alkaline-earth metal), which are encapsulated between two different polyhedra. The structure of Type I clathrates is shown in Fig. 12. The yellow atoms denote the guest atoms, with the light yellow at the 6d position and the dark yellow at the 2a position. The host structure is also shown with varying color intensity: 6c (light blue), 16i (medium blue), and 24k (dark blue). Figure 12a illustrates the unit cell with its large tetrakaidecahedral (24-atom) cage in blue and dodecahedral (20-atom) cage in red. Figure 12b depicts the bonding arrangements of the different host structure sites, where the atom size is intended to enhance the clarity. In Fig. 12c, the different guest atom sites in the large cage are illustrated: 12h (light red), 24j (medium red), and 24k (dark red). The main differences between types I and II clathrates are the number and size of the vacancies in their unit cells.

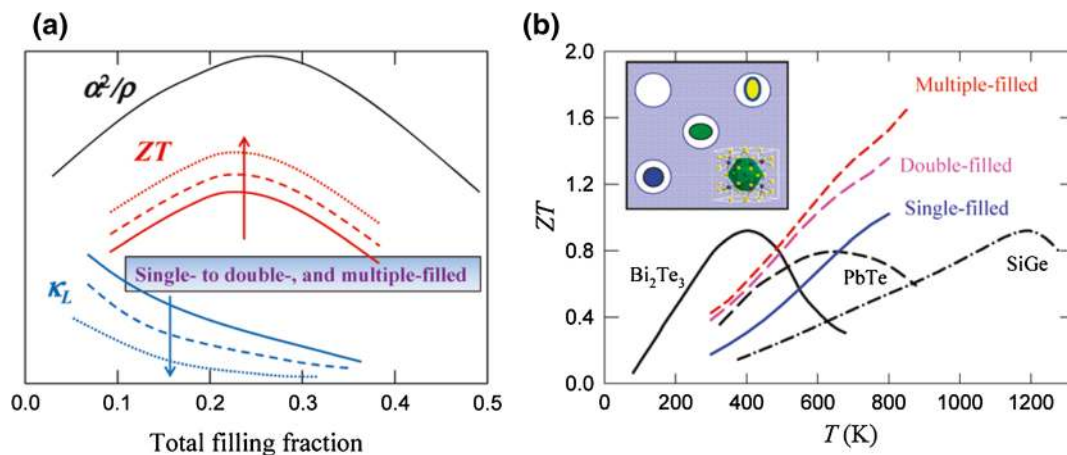


Fig. 11 Relationship between TE properties and the filled fraction of skutterudites (a) and comparison of ZT with other TE materials (b). α^2/ρ is power factor; κ_L is the lattice thermal conductivity. Reprinted with permission from [119]. Copyright 2011, American Chemical Society

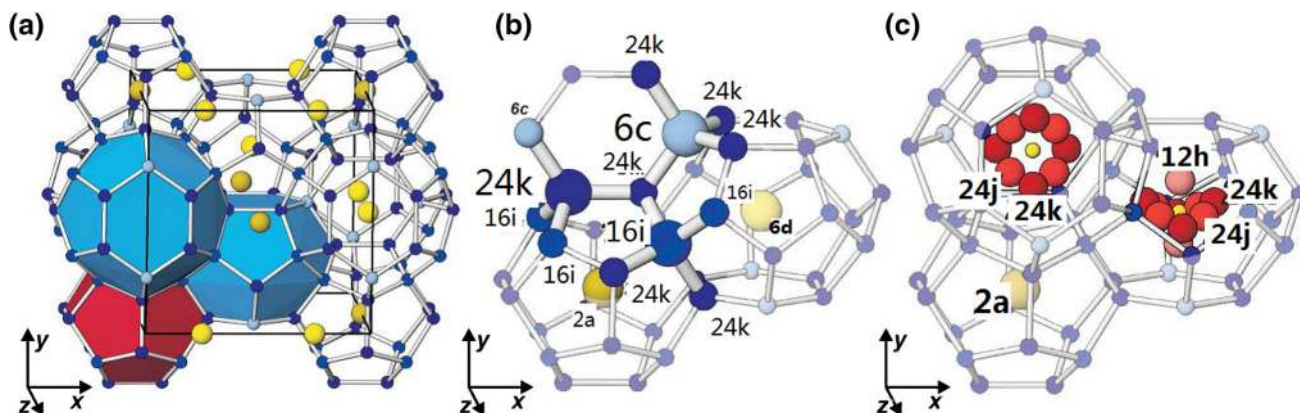


Fig. 12 Crystal structure of Type I clathrate (a) unit cell; (b) bonding arrangements of the different host structure sites; (c) different guest sites. Reprinted with permission from [121]. Copyright 2007, American Chemical Society

Their complex unit cells allow a significant reduction in the thermal conductivity and lead to a high ZT . Unlike skutterudites, both single crystals and polycrystalline powders of clathrates can have high ZT and can be tuned over a wide range. In addition, they are highly stable at high temperature, both chemically and thermally. They also show excellent compatibility with other devices in multimodal applications.

Powder metallurgical and crystal growth techniques have been well developed to synthesize clathrates. A direct approach to optimize the TE properties of semiconducting type I clathrates is substitutional doping, where some framework atoms are replaced by dopant atoms. Compared with type I clathrates, their type II analogs have not been intensively studied and would be an interesting subject, because a partial filling of their polyhedra allows a better tuning of their electrical properties and a better control of the dopant concentration. Some important progress in this area was reviewed by Christensen et al. [121].

The highest ZT of 1.35 at 900 K was reported in the n-type clathrate $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ in 2006 [122]. Because they are limited by the “Zintl rule” [123–125], optimization of the power factors of stable clathrates is very difficult, and there are rare reports on the reduction of lattice thermal conductivity in clathrates by nano-engineering approaches [126]. Inspired by the successful use of high pressure torsion (HPT) on skutterudites, Yan et al. [127] tried to obtain a higher ZT for $\text{Ba}_8\text{Cu}_{3.66}\text{Ge}_{40.30}\text{In}_{1.65}$ by the same HPT method. Unfortunately, their results showed that compared with hot-pressed samples, the carrier concentration was reduced, and the increase in ZT was negligible, although a higher electrical resistivity and Seebeck coefficient were achieved after HPT processing.

2.5.3 Half-Heusler alloys

Half-Heusler alloys (ABX) have potential in high temperature power generation, especially as n-type material. These alloys have three components selected from different element groups or from the same group. A and X are transition metals, and B may be a metal or non-metal. The crystal structure of a half-Heusler alloy could be considered as a simple rock salt structure formed by A and X, which is filled with B at one of the two body diagonal positions (1/4, 1/4, 1/4) in the unit cell, leaving the other one (3/4, 3/4, 3/4) unoccupied [128]. Figure 13 shows the structure of a typical half-Heusler ABX alloy and the element sources of A, B, and X. The structure allows doping on each of the three occupied face-centered cubic (fcc) sublattices to tune the TE properties individually. These alloys are relatively cheap and have a promising ZT in the temperature range from 600 to 1,000 K.

Figure 14 shows the recent progress in both n-type and p-type half-Heusler alloys. In 2010, Yan et al. [129]

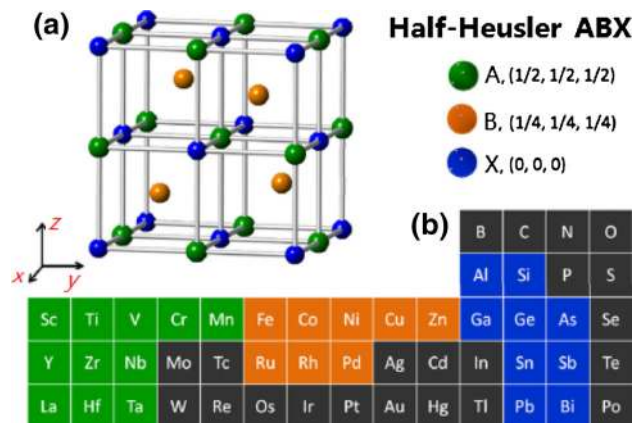


Fig. 13 (Color online) Structure of a typical Half-Heusler ABX alloy and the element sources of A, B, X. Reprinted with permission from Ref. [20]. Copyright 2012, Elsevier

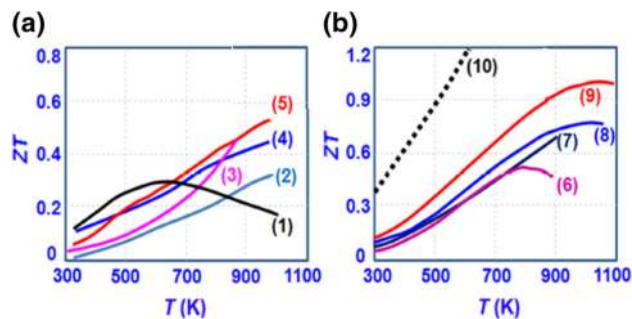


Fig. 14 (Color online) Overview of the most promising p- (a) and n-type (b) half-Heusler alloys. (1) $\text{ErNi}_{1-x}\text{Pd}_x\text{Sb}$; (2) $\text{ZrNi}_{0.8}\text{Ir}_{0.2}\text{Sn}$; (3) $\text{TiCo}_{0.85}\text{Fe}_{0.15}\text{Sb}$; (4) $\text{ZrCoSn}_{0.1}\text{Sb}_{0.9}$; (5) $\text{Zr}_{0.5}\text{Hf}_{0.5}\text{CoSb}_{0.8}\text{Sn}_{0.2}$; (6) $\text{Ti}_{0.5}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Co}_{0.95}\text{Ni}_{0.05}\text{Sb}$; (7) $\text{Ti}_{0.6}\text{Hf}_{0.4}\text{Co}_{0.87}\text{Ni}_{0.13}\text{Sb}$; (8) $\text{Zr}_{0.75}\text{Hf}_{0.25}\text{NiSn}_{0.975}\text{Sb}_{0.025}$; (9) $\text{Zr}_{0.4}\text{Hf}_{0.6}\text{NiSn}_{0.98}\text{Sb}_{0.02}$; (10) $\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Ti}_{0.5}\text{NiSn}_{0.998}\text{Sb}_{0.002}$. Reprinted with permission from [131]. Copyright 2012, MDPI

reported p-type $\text{Zr}_{0.5}\text{Hf}_{0.5}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ with a ZT of 0.8 at 973 K. The ZT enhancement comes from a simultaneous increase in the Seebeck coefficient and a decrease in the thermal conductivity due to nanostructures. The samples were made in three steps: (1) preparation of alloyed ingots using the arc melting method; (2) ball milling of the resultant ingots into nanopowders; and (3) preparation of a dense bulk by hot pressing of nanopowders.

One common approach to enhancing TE performance is partial replacement of elements by their neighbors from the same group or the same row to form nano-inclusions. Benjamin et al. [130] substituted one neighboring atom with fewer valence electrons and one with more electrons. The amounts of the fillers or dopants were adjusted so that the deficiency and excess electrons were compensated. Therefore, the amount of valence electrons was not changed, and the semiconducting properties were retained. They obtained a solid solution of $\text{TiCo}_x(\text{Ni}_{0.5}\text{Fe}_{0.5})_{1-x}\text{Sb}$, in which Co was substituted equally by Fe and Ni, and ZT was

enhanced by a factor of about seven to a value of 0.04 at 400 K for $\text{TiCo}_{0.8}(\text{Ni}_{0.1}\text{Fe}_{0.1})\text{Sb}$ due to the reduction in the thermal conductivity and the retention of a high Seebeck coefficient. Although the ZT value is still relatively low, their work demonstrates a new way of substitution: the use of one neighboring atom with fewer valence electrons and one with more electrons to improve the ZT of half-Heusler alloys. More progress in nanostructured half-Heusler materials has been summarized in [131].

3 Organic TE materials

As described above, the advances in the engineering of inorganic nanostructures have resulted in notable improvement in ZT . Nevertheless, inorganic TE materials have issues of either high fabrication cost or toxicity. The conducting-polymer-based TE materials offer a new solution with low cost and environmental friendliness. Figure 15 shows the chemical structures of some conducting polymers. The conducting polymers usually have backbones of contiguous sp^2 hybridized carbon centers. One valence electron on each center resides in a p_z orbital, which is orthogonal to the other three sigma-bonds. p_z orbitals conjugate with each other to form delocalized orbitals. In principle, these materials can be doped by reduction, which adds electrons to unfilled bands. Undoped conjugated polymers are semiconductors or insulators. Their energy gap can be above 2 eV, which is large for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes and polyacetylenes, have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Their electrical conductivity can increase by several orders of magnitude up to values of around 0.1 S/cm, even at a very low level of doping (<1 %) [132].

Although possessing a relatively low electrical conductivity, the intrinsically low thermal conductivity of polymers, which is usually 1–3 orders of magnitude lower than for inorganics [133, 134] (usually in the range of 0.1–1 W/(m K)) makes them potential candidates for high-

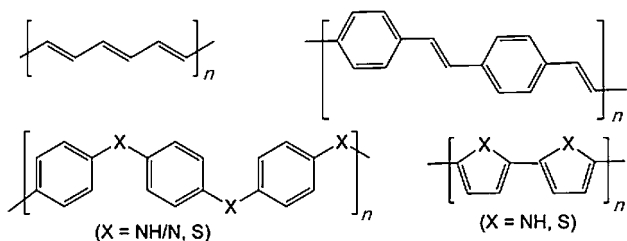


Fig. 15 Chemical structures of some conducting polymers. From top left clockwise: polyacetylene; polyphenylene vinylene; polypyrrole ($X = \text{NH}$) and polythiophene ($X = \text{S}$); and polyaniline ($X = \text{NH/N}$) and polyphenylene sulfide ($X = \text{S}$)

performance TE applications. In addition, their thermal conductivity mainly depends on their chemical compositions [135–139], thereby offering an opportunity for realizing higher ZT via tuning the power factor without heavily increasing thermal conductivity. It has theoretically been shown that under certain conditions, some quasi 1D organic crystal may have a ZT of 20 at room temperature [140]. In addition, the organic TE materials possess light weight, large surface areas, good flexibility, and can be prepared or modified in solution. Their application temperature is around room temperature. These properties agree well with the requirements of future applications that are geared toward personal and portable polymer-based flexible electronics [141–145]. Also, their well-investigated carbon or organic chemistry provides a good theoretical basis for these materials.

As described above, the weakness of organic TE materials mainly comes from their low power factor. Similar to inorganic TE materials, there exists a trade-off between their electrical conductivity and their Seebeck coefficient. For more details on the theory and mechanisms of polymer TE materials, there are already a few good reviews [146, 147], including the latest one published by He et al. [148] in 2013. Here, we briefly introduce some breakthroughs in this area. Table 1 roughly summarizes the TE performance for eight polymers up to 2010.

In 2011, Yu et al. [151] improved the TE performance of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) by addition of different concentrations of single-wall carbon nanotubes, resulting in a large TE power factor in the in-plane direction of the composites ($-160 \mu\text{W}/(\text{m K}^2)$) and high electrical conductivity (105 S/m) at room temperature. These properties make the composites very promising for various electronic applications. Although the ZT of their material was unavailable, their work suggested that the addition of carbon nanomaterials (graphene sheets, carbon nanotubes (CNTs), and fullerene) into organic TE materials is a good way to improve their electrical conductivity.

Chen et al. [152] investigated the electrical and thermal transport properties of a novel macro three-dimensional (3D) CNT network (as shown in Fig. 16). They found that its electrical conductivity could be adjusted through a convenient gas-fuming doping process. For example, when doped with potassium (K), the original p-type CNT network could be converted into an n-type semiconductor with a changed electrical conductivity, while iodine (I_2) doping enhanced its electrical conductivity. They used the modified CNTs to improve the TE performance of polyaniline (PANI). This work provides a good example of fabrication of low-cost polymer-based TE materials.

Another two kinds of promising organic TE materials are polyacetylene and poly(3,4-ethylenedioxythiophene).

Table 1 The electrical conductivity, Seebeck coefficient, thermal conductivity, and ZT of various polymers [149]

Polymer	σ (S/cm)	S ($\mu\text{V/K}$)	κ (W/(m K))	ZT at 300 K
Polyacetylene	4,990–11,560	11.4–28.4	0.7	0.047–0.38
Polypyrrole	100	12	0.1–0.2	0.002
Polyaniline	7,000	7	0.1–0.2	0.051
Polythiophene	100	21	0.1–0.2	0.0066
Poly(paraphenylene)	10^{-5}	12	0.1–0.2	2.1×10^{-10}
Poly(<i>p</i> -phenylenevinylene)	10^{-5}	7	0.1–0.2	7.2×10^{-11}
Poly(carbazolenevinylene)	0.005	230	0.1–0.2	8×10^{-5}
PEDOT:PSS	55	13	0.1–0.2	0.0014
PEDOT:PSS ^a	900	75	0.24	0.42

^a Data from ref. [150]

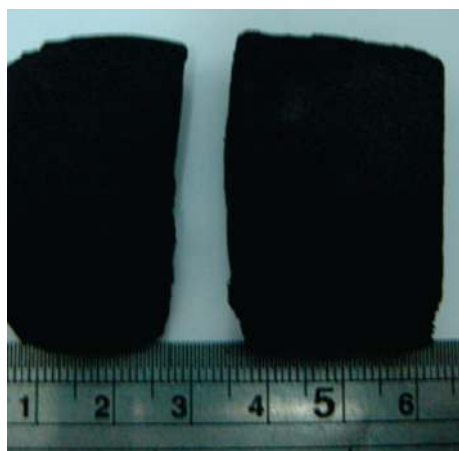


Fig. 16 (Color online) 3D CNT Network. Reprinted with permission from [152], Copyright 2012, American Chemical Society

In doped acetylene [149], a ZT of 0.38 has been observed at room temperature, but this material is not even stable in air. In poly(3,4-ethylenedioxythiophene), a ZT of 0.25 has been measured at room temperature, and this material is air stable [153].

Another possible solution to the low power factor of polymer-based TE materials is the formation of hybrids or composites by adding conductive inorganic nanomaterials. Toshima et al. [154] tried to directly mix polyaniline with pristine Au nanoparticles and improved its electrical conductivity to 350 S/cm at 50 °C while keeping a relatively high Seebeck coefficient. They also added dodecanethiol protected Au nanoparticles (NPs) to improve the electrical conductivity of poly(3,4-ethylenedioxythiophene) film to increase its ZT from 0.0062 to 0.0163 at 50 °C. Du et al. [155] have published a good review on inorganic–organic hybrid TE materials.

According to their calculated results, Kim et al. [150, 156] concluded that reducing the dopant concentration (represented by the product of the subunit volume ratio and the subunit concentration ratio) is as important as

optimizing carrier concentration to maximize ZT for organic semiconductors. This is because the exponential dependence of carrier mobility on dopant volume leads to a variation in over-typical doping concentrations in organic semiconductors, which is much larger than the variation in over-typical doping concentrations in inorganic semiconductors. By employing this strategy to dope poly(styrenesulphonate) in poly(3,4-ethylenedioxythiophene), they achieved a ZT of 0.42 at room temperature. This is the highest ZT obtained among organic semiconductor-based TE materials at present.

4 Summary

We have summarized the recent advances in both inorganic and organic TE materials from experimental and theoretical perspectives. Detailed ZT values for these TE materials were listed in Table 2. In most cases, the enhancement of TE performance is attributed to the introduction of nanostructures into the host matrix, including nano-inclusions, nanocomposites, nanowires, nanopores, nanograins, point defects, etc. Therefore, the development of TE performance is reliant on the advances in nano-science and nanotechnology.

Nanostructures can significantly reduce thermal conductivity by enhancing the phonon scattering of materials. Unfortunately, the decrease in thermal conductivity is at the cost of carrier mobility in some cases. The deterioration in carrier mobility results from the disturbance arising from various types of phonon scattering, such as the scattering between the nanostructure and the charge carriers. In order to increase carrier mobility without raising thermal conductivity, reconstructing the electron transport channel is necessary (i.e., increasing the ratio of ordered structure). A good example of such reconstruction is modulation doping. Although the current TE nanomaterials show high performance, they face the following challenges: (1) large-scale

Table 2 Some representatives of high-performance inorganic TE materials

Type	Material	Temperature (K)	ZT	Reference	Mechanism
Metal chalcogenides	PbTe(SrTe) ₄ Na ₂	915	2.2	[50]	Full scale phonon scattering
	Bi ₂ Te ₃ -Sb ₂ Te ₃	300	2.4	[56]	Superlattice
Superionic conductor	p-type Cu _{2-x} Se	1,000	1.6	[67]	Structure, dope, phase transition
	n-type Cu _{2-x} Se	400	2.3	[68]	
Oxides	SrTiO ₃	~300	2.4	[79]	Superlattice
Silicon based	Silicon	1,275	0.7	[86]	Nanowire
	SiGe	800	2	[95]	
	Mg ₂ Si _{0.4} Sn _{0.6}	800	1.1	[110]	
PGEC	(Sr, Ba, Yb) _{0.07} Co ₄ Sb ₁₂	800	1.8	[120]	Dope, nanostructure
	Ba ₈ Ga ₁₆ Ge ₃₀	900	1.35	[122]	Extrinsic to intrinsic transition
	Zr _{0.5} Hf _{0.5} CoSb _{0.8} Sn _{0.2}	973	0.8	[129]	Nano inclusion

preparation of size, shape, and composition tunable nanomaterials; (2) poor stability of nanostructures, as they can be destroyed during compression into highly dense pellets at high temperature or high pressure; (3) although 1D nanowires and 2D nanosheets provide excellent samples for investigating TE properties on the individual material level, large-scale fabrication of TE devices from them without destroying the structure for practical application is a big issue; and (4) the formation of ordered nanostructures as desired.

Similar to TE nanomaterials, bulk superionic conductors can also have high *ZT* values (e.g., Cu₂Se has a *ZT* of 1.5 at 1,000 K) due to their unique PLEC properties. The PLEC is attributed to the fast movement of cations (or anions in anionic superionic conductors) and their deficiency. The introduction of nanotechnology into this field would significantly boost their TE performance and spark their practical application, as producing them in nanostructured form not only can reduce their thermal conductivity but also can promote high electrical conductivity due to higher deficiency and faster movement of cations (or anions).

It should be noted that most TE materials have issues of low *ZT*, high cost, or environmental unfriendliness. Many high *ZT* materials produced in the laboratory have no commercial potential due to the difficulties in large-scale preparation, as well as high fabrication cost and poor stability. In order to commercialize those mid-*ZT* materials with low price and high stability, more attention should be paid to the design and optimization of high-performance TE devices, while great efforts are devoted to improving their *ZT*. This is because the real conversion efficiency of TE devices is much lower than the theoretical value, even if the *ZT* of a TE material is as high as 4 [157].

In order to improve the overall energy conversion efficiency, TE devices are combined with other devices such as solar cells. Many TE materials can be also used in solar cells, such as Si and metal chalcogenides. Recently,

Kraemer et al. [158] reported a flat-panel solar TE generator (STEG) with a system efficiency of 4.6 %–5.2 % generated from a temperature difference of 180 °C ($T_c = 20$ °C, $T_h = 200$ °C). This efficiency is 7–8 times higher than the best value previously reported. Wang et al. [159] developed a novel photovoltaic-TE (PV-TE) hybrid device composed of a series-connected dye-sensitized solar cell (DSSC), a solar selective absorber, and a TE generator. The overall conversion efficiency is over 13 %. This work highlights the potential of hybrid devices in conversion of abundant solar energy into electricity. The wide application of clean solar energy would significantly reduce fossil fuel consumption, our CO₂ footprint, and environmental deterioration, so the use of multiple energy conversion devices to yield maximal output would be an important direction in this area.

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