Eliciting High-Performance Thermoelectric Materials via Phase Diagram Engineering: A Review

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Thermoelectric (TE) materials and devices have been a promising green technology since the 1960s. Enormous research efforts bring forth TE generator and TE refrigerator, in which the former specializes in waste heat recovery while the latter advances the spot-cooling technology. For both TE applications, the thermoelectric figure-of-merit $zT = (S^2\sigma T)/k$ is keen to be raised, where the Seebeck coefficient $S$, electrical conductivity $\sigma$ and thermal conductivity $k$ are correlated. In complex TE materials, the stoichiometry modulation and maximal solubility of foreign atoms play vital roles. Phase diagram engineering bridges the equilibrium phase diagrams with transport properties, opening a new avenue of thermodynamic-based optimization. This article reviews the phase diagram engineering, which tunes the TE performance for the state-of-art TE materials, including the bismuth-tellurides, the zinc-antimonides, the lead-tellurides, and the germanium-tellurides. Examples of I–V–VI$_2$ and I–III–VI$_2$ (I = Ag, Cu; III = Ga; VI$_2$ = S, Se, Te) compounds incorporated with phase diagram engineering are also discussed. All the cases aim to validate that phase diagram engineering could be a general approach for TE materials.

1. Introduction

Alongside the evolution of technology timeline, environmental protection and energy sustainability significantly guide the research feast toward the high-performance green energy resources and technologies.$^{[1,2]}$ Alternatives to the fossil fuels that emit harmful greenhouse gases become desired, in which the thermoelectric (TE) materials have played an inevitable role since the 1960s.$^{[3]}$ One of TE technology features is the waste heat recovery via the Seebeck effect,$^{[4]}$ which allows the conversion between thermal energy and electricity. Such a TE generator produces precious electrical energy from any arbitrary interfaces where a temperature gradient exists, simultaneously boosting energy usage efficiency while eases global warming.

Many TE materials are being explored for power generation applications, such as GeTe,$^{[5]}$ PbTe$^{[6,7]}$, Bi$_2$Te$_3$,$^{[8]}$ and silicides.$^{[9]}$ Moreover, the TE cooler, which utilizes the Peltier effect,$^{[10]}$ emerges as a vital spot-cooling device assembled by all-solid-state materials. With the advantages of refrigerant-free and size-minimization, the TE cooler exhibits the advantages of refrigerant-free and size-minimization, which can be used as the next-generation cooling technology.$^{[10]}$

After more than 60 years of development, the practical application and potential coverage of TE technology are comprehensive. Nevertheless, a TE material’s thermal-to-electric efficiency is still required to be boosted. In general, the TE figure-of-merit $zT = (S^2\sigma T)/k$ positively relates to the performance of TE materials, in which the $z$ is the Seebeck coefficient, $\sigma = \rho^{-1}$ refers to the electrical conductivity, and $k = k_\| + k_\perp + k_\delta$ comprises the total thermal conductivity $k_\|$, lattice thermal conductivity $k_\delta$, and bipolar thermal conductivity $k_\perp$, respectively. Most importantly, the $S$, $\sigma$, and $k_\|$, have the carrier concentration $n_H$ as a common factor, which correlates and depends on each other. Therefore, the counterbalance between the thermal and electrical transport properties is essential to attain high $zT$ values, which could be fulfilled by band structure engineering,$^{[11]}$ carrier optimization,$^{[12,13]}$ filtering effect,$^{[14]}$, and so on. In parallel, the reduction in $k_\|$, also paves the way toward high-performance TE materials, mainly accomplished by all-scale defect engineering$^{[15]}$ and alloying effect.$^{[16]}$ Those imperfections introduce multiscale roadblocks, such as the interstitial/antisite defect, dislocations, nanoprecipitates, and grain boundaries, aiming to impede the phonons with different wavelengths.

Countless efforts bring the breakthroughs of $zT$ value in succession. The peak $zT$ grows less than unity in the 1960s to greater than 2.5 after 2015$^{[17]}$ whose progress is slow yet steadily. Complex TE materials with various dopants are the primary targets, while different approaches can be adopted.$^{[18,19]}$ The
chemical concentration, homogeneity, and microstructure for those multicomponent systems, which can be altered by different synthesis processes, affect the resultant TE properties and raise the concern in reproducibility. In recent years, the thermodynamic routes[28] emerge as the new paradigm for realizing the high-performance TE materials, which explore the equilibrium states followed by the transport properties optimization. For instance, the high-entropy engineering and the liquid-like concept both yield the ultralow $\kappa_{\text{L}}$[23] in which the former induces severe lattice distortion while the latter fulfills the ionic conduction.

In line with the thermodynamic approach, the phase boundary mapping[22] and the phase diagram engineering[23–30] both make great use of the equilibrium phase diagrams, while the latter emphasizes the homogeneity regions and the phase transformations. It shall be noted that the phase boundary mapping has been exploited to the n-type Mg$_2$Sb$_2$[31–34] which yields the enhanced TE performance within an optimal compositional region. Both phase diagram engineering and phase boundary mapping rely on the thermodynamic phase diagram, in which the equilibrium solubility plays a critical role. The related work[31–34] and an up-to-date review[20] can be found somewhere else.

The phase boundary on a phase diagram infers a specific dopant’s maximal solubility, where the electronic transport properties can be significantly tuned. Moreover, the existence of nanoprecipitates or mass fluctuations is expected when the alloys are located across the phase boundaries, which reduces the $\kappa_{\text{L}}$ notably. This review discusses and summarizes the high-performance TE materials in view of phase diagram engineering. By exploring the compositional regions that are less studied before, the state-of-the-art bismuth telluride alloys,[23,24] the germanium telluride alloys,[15] the zinc antidotinum alloys,[26] and the lead telluride alloys[27] show outperforming TE performance by adopting this approach. Moreover, the optimization of ternary TE compounds, such as the n-type rock-salt AgBiSe$_2$[28] p-type rock-salt Ag$_2$Sb$_2$Te$_5$[29] and p-type chalcogenite Cu$_3$Ga$_2$Te$_6$[10] suggests that the phase diagram engineering is feasible in general materials. The high-performance TE materials discovered alongside the adventure open up a new avenue for advancing this research area, as confirmed through the following case-by-case studies.

2. Revisiting the State-of-the-Art TE Alloys via Phase Diagram Engineering

2.1. Bi$_2$Te$_3$-Based Alloys

Bi$_2$Te$_3$ is the most well-established room temperature TE cooler,[35] which crystallizes in a rhombohedral structure (R3m) with the lattice constants of $a = 4.385$ Å and $c = 30.44$ Å. Being an anisotropic layer–structure material,[26–38] the Bi$_2$Te$_3$ comprises a quintuple layer of Te$^{6\text{th}}$–Bi$_{\text{II}}$–Te$^{6\text{th}}$–Bi$_{\text{II}}$–Te$^{4\text{th}}$, in which the weaker Van der Waals force bonds two adjacent Te$^{4\text{th}}$ atoms. The pristine Bi$_2$Te$_3$ has a narrow homogeneity region,[39] while the defect formation mainly determines its conduction type. The Bi$_{\text{II}}$ antisite defect dominates the Bi-rich Bi$_2$Te$_3$, which produces an extra hole that enables the p-type conduction.[40] By contrast, the Te$_{\text{II}}$ antisite defect in the Te-rich Bi$_2$Te$_3$ accompanying with additional electron carrier yields the n-type conduction.[10] Typically, the incorporation of Sb or Se in Bi$_2$Te$_3$ stabilizes the p-type[41] or n-type[40,42–43] conducting, respectively, because the dopant antisite defect Sb$_{\text{II}}$ and selenium vacancy V$_{\text{Se}}$ exhibit lower formation energy than the pristine defects Bi$_{\text{II}}$ and Te$_{\text{II}}$, respectively. As known, the p-type (Bi, Sb)$_2$Te$_3$ has been reported with an extraordinary peak $\kappa T \approx 1.86$ at 320 K,[45] while the n-type Se-Bi$_2$Te$_3$ exhibits a much lower peak $\kappa T < 1.2$. The addition of Ag, Cu, Co, S, In, and so on boosts the TE performance of n-type Bi$_2$Te$_3$ (Table 1)[44–45]. Furthermore, the modification of synthesis routes, including the solvothermal,[44] Bridgman growth,[45] zone melting (ZM),[46] spark plasma sintering (SPS),[47] hot pressing (HP),[48] melt-centrifugation (MC),[41,49] and so on, also influences the resultant transport properties. It is worth noting that the MC emerges as a new and effective synthesis route that introduces the dense dislocation arrays and grain boundaries within a porous microstructure through the liquid-phase compaction process. A significant reduction in $\kappa_{\text{L}}$ in the p-type Sb-Bi$_2$Te$_3$ has been fulfilled through such a microstructure engineering.[41,49]

2.1.1. Cu-Bi$_2$Te$_3$ (Phase Diagrams and TE Properties)

Copper has been an effective n-type dopant for Bi$_2$Te$_3$, and much previous work has investigated the Cu-Bi$_2$Te$_3$[57,59,61,63,64] thoroughly. Nevertheless, the discrepancy in the reported $\kappa T$ peak values still exists. Given that the stoichiometry in Bi$_2$Te$_3$ matters, the homogeneity region of Cu-Bi$_2$Te$_3$ shall be well understood, making the phase diagram important. From the previous works,[33] the isothermal section of the Bi–Cu–Te ternary system at 523 K is constructed by collecting the phase equilibria information from ternary alloys that underwent a postannealing for at least 6 months (Figure 1a). Selective equilibrium microstructures (Figure 1b–d) confirm the existence of three-phase Bi$_2$Te$_3$ + CuTe + Te, the two-phase Bi$_2$Te$_3$ + Cu$_2$Te$_5$ and the phase Bi + Bi$_2$Te$_3$ + Cu$_2$Te, respectively. With the phase diagram in hand, the maximal solubility in Bi$_2$Te$_3$ could be determined less than 3 at% Cu. The homogeneity region of Bi-soluble Bi$_2$Te$_3$, as shown by the magnified isothermal section (Figure 1e), extends asymmetrically toward the Bi-rich side. Also, the color map in Figure 1e reveals the distribution of (S) for two series alloys (Bi$_2$Te$_3$)$_{1-x}$(Cu$_2$Te)$_x$ and Bi$_{0.966}$Cu$_{0.034}$Te at 300 K, where the blue ribbons indicate the p-type behavior and the red ribbons refer to the n-type conducting, respectively. Moreover, the green ribbons infer the p–n transition zone, which coincides well with the phase boundary of the single-phase Bi$_2$Te$_3$.

The TE properties for (Bi$_2$Te$_3$)$_{1-x}$(Cu$_2$Te)$_x$ and the Bi$_{0.966}$Cu$_{0.034}$Te are shown in Figure 1f–j. It shall be noted that filled symbols denote the p-type Cu-Bi$_2$Te$_3$, while open symbols represent the n-type Cu-Bi$_2$Te$_3$. The $\rho(T)$ curves (Figure 1g) lift with the increasing $x$ and then drops when $x = 0.07$, which corresponds to the p–n transition. For the heavily doped samples $(x \geq 0.07)$, the conduction type transits to completely n-type semiconducting $(S < 0)$ in the temperature range of 300–550 K (Figure 1h).

Both the $\alpha(T)$ and $\kappa_{\text{L}}(T)$ curves drop with increasing $x$ and $y$, attributing to the alloying effect that leads to the enhanced phonon scattering. As a result, the (Bi$_2$Te$_3$)$_{0.9925}$(Cu$_2$Te)$_{0.01}$ and the Bi$_{0.99}$(Cu$_{0.01}$Te) achieve the highest peak values of 1.2–1.3 at 300 K. Although the n-type $x = 0.09$ only attains the peak $\kappa T \approx 1.0$ at 300 K, the temperature-independent $\kappa T$ curve

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**Table 1**

| Alloy                  | $\kappa T$ (K) |
|-----------------------|----------------|
| Bi$_2$Te$_3$          | 1.30           |
| Bi$_2$Te$_3$ + CuTe   | 1.86           |
| Bi$_2$Te$_3$ + Cu$_2$Te$_5$ | 1.25 |
| Bi + Bi$_2$Te$_3$ + Cu$_2$Te | 1.05 |

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**Figure 1**

(a) Selective equilibrium microstructures for two series alloys (Bi$_2$Te$_3$)$_{1-x}$(Cu$_2$Te)$_x$ and Bi$_{0.966}$Cu$_{0.034}$Te at 300 K. The blue ribbons indicate the p-type behavior and the red ribbons refer to the n-type conducting, respectively. Moreover, the green ribbons infer the p–n transition zone, which coincides well with the phase boundary of the single-phase Bi$_2$Te$_3$.

(b) The $\rho(T)$ curves (Figure 1g) lift with the increasing $x$ and then drops when $x = 0.07$. Both the $\alpha(T)$ and $\kappa_{\text{L}}(T)$ curves drop with increasing $x$ and $y$, attributing to the alloying effect that leads to the enhanced phonon scattering. As a result, the (Bi$_2$Te$_3$)$_{0.9925}$(Cu$_2$Te)$_{0.01}$ and the Bi$_{0.99}$(Cu$_{0.01}$Te) achieve the highest peak values of 1.2–1.3 at 300 K. Although the n-type $x = 0.09$ only attains the peak $\kappa T \approx 1.0$ at 300 K, the temperature-independent $\kappa T$ curve
Table 1. The $zT$ peak values of Bi$_2$Te$_3$-based, GeTe-based, Zn$_2$Sb$_3$-based, PbTe-based, I–V–VI$_2$-based, and I–III–VI$_2$-based materials reported by the literature.\([15–30,33–41]\) The corresponding synthesis method and nominal composition are also shown later. Reproduced (Adapted) with permission.\([27]\)

| Stoichiometry | $zT_{\text{max}}$ | $T$ (K) | $zT_{\text{ave}}$, $T = 300$–773 K | Conduction type | Synthesis |
|---------------|-----------------|--------|--------------------------------|-----------------|-----------|
| Bi$_2$Te$_3$-based alloys | Bi$_2$Te$_2$.Sb$_2$.Te$_3$ | 1.23 | 480 | – | N | ST |
| | Bi$_2$(Te$_0.95$Sb$_0.05$)Te$_3$ | 1.13 | 308 | – | N | B |
| | Bi$_2$Te$_{3-z}$Sb$_{2z}$.Te$_3$ | 1.2 | 357 | – | N | BM + ZM + HD |
| | Bi$_2$Sb$_{0.84}$Te$_{0.16}$.Se$_3$.Te$_3$ | 0.82 | 400 | – | N | HP |
| | (Bi$_2$Te$_0.90$.Co$_{0.10}$)Sb$_2$.Te$_3$ | 0.77 | 398 | – | N | SPS |
| | Zn$_{0.00}$Bi$_2$(Te$_{0.95}$.Sb$_{0.05}$)Te$_3$ | 1.1 | 340 | – | N | ZM |
| | Sn$_{0.02}$Bi$_2$.Te$_{2}$.Se$_2$.Te$_3$ | 1.11 | 370 | – | N | ST + HP |
| | Bi$_2$Te$_2$.Se$_2$.J.1.47 vol% SnS$_2$ | 0.93 | 450 | – | N | ST + SPS |
| | Bi$_2$Te$_2$.Se$_2$.J.0.25 wt% Sb$_2$I$_3$ | 1.1 | 625 | – | N | ZM + HD |
| | Bi$_2$Te$_2$.Se$_2$.J.1.5 vol% InSb | 1.22 | 323 | – | N | BM + HP |
| | Lu$_2$.Bi$_2$.Te$_2$.Se$_2$.Te$_3$.Te$_3$ | 1.37 | 373 | – | N | HT + HP |
| | (Bi$_2$Te$_2$.Se$_2$.J.9.95).MgB$_2$.Te$_3$.Te$_3$ | 0.96 | 325 | – | N | SPS |
| | Cu$_{0.01}$Bi$_2$(Te$_{0.95}$.Se$_{0.05}$)Te$_3$ | 1.15 | 340 | – | N | ZM |
| | Bi$_2$Te$_2$.Se$_2$.J.0.007 wt% | 1.13 | 423 | – | N | HP |
| | Cu$_{0.13}$Bi$_2$.Te$_2$.Se$_2$.Te$_3$.Te$_3$ | 0.97 | 423 | – | N | HD |
| | Bi$_2$Te$_2$.Se$_2$.J.0.15 wt% Ag$_{0.005}$ | 1.24 | 323 | – | N | ST + SPS |
| | Bi$_2$Te$_2$.Se$_2$.J.0.15 vol% Cu@Ag$_{0.005}$ | 0.91 | 320 | – | N | SPS |
| | Bi$_2$Te$_2$.J.7.5 wt% Ag$_{0.02}$ | 1.48 | 300 | – | N | CP |
| | Cu$_{0.01}$Bi$_2$.Te$_2$.Te$_3$.Te$_3$ | 1.15 | 300 | – | N | B |
| | Bi$_2$Te$_2$.J.1 vol% Cu@Ag$_{0.005}$ | 0.69 | 450 | – | N | HT + SPS |
| | La$_{0.1}$.Bi$_2$.Te$_2$.Te$_3$.Te$_3$ | 0.9 | 470 | – | N | ST + SPS |
| | Bi$_2$Te$_2$.Sb$_2$.Se$_2$.Te$_3$.Te$_3$ | 0.8 | 573 | – | N | BM + HP |
| | Bi$_2$Te$_2$.J.0.15 vol% InSb | 0.38 | 400 | – | N | SPS |
| | Bi$_2$Te$_2$.J.0.15 vol% Cu@Ag$_{0.005}$ | 1.1 | 420 | – | N | ST + SPS |
| GeTe-based alloys | Ge$_{0.80}$Sb$_{0.20}$.Te$_3$.Te$_3$ | 2.35 | 773 | 1.2 | P | A |
| | Sb$_2$.Te$_2$.GeTe$_2$.Te$_3$.Te$_3$ | 2.4 | 773 | 1.51 | P | SPS |
| | Ge$_{0.80}$.Pb$_{0.20}$.Te$_3$.Te$_3$ | 1.3 | 623 | 0.9 | P | SPS |
| | Ge$_{0.95}$Bi$_{0.05}$.Te$_3$.Te$_3$.Te$_3$ | 1.8 | 700 | 1.05 | P | HP |
| | Ge$_{0.95}$Bi$_{0.05}$.Te$_3$.Te$_3$.Te$_3$ | 2.4 | 773 | 1.28 | P | SPS |
| | Ge$_{0.95}$Bi$_{0.05}$.Te$_3$.Te$_3$.Te$_3$ | 2.0 | 650 | 1.2 | P | SPS |
| | Ge$_{0.30}$Mn$_{0.70}$.Sb$_{0.40}$.Te$_3$.Te$_3$.Te$_3$ | 1.61 | 823 | 1.1 | P | SPS |
| | Ge$_{0.30}$Pb$_{0.70}$.Bi$_{0.40}$.Te$_3$.Te$_3$.Te$_3$ | 2.4 | 600 | 1.6 | P | HP |
| | Ge$_{0.30}$Sb$_{1.00}$.Sb$_{0.40}$.Se$_{0.60}$.Te$_3$.Te$_3$.Te$_3$ | 2.0 | 700 | 1.1 | P | HP |
| | Ge$_{0.30}$Sb$_{0.50}$.Bi$_{0.50}$.Te$_3$.Te$_3$.Te$_3$ | 2.2 | 650 | 1.65 | P | SPS |
| | (GeTe)$_{0.37}$.Bi$_2$.Se$_2$.J.0.05$.Te$_3$.Te$_3$.Te$_3$ | 2.0 | 773 | – | P | SPS |
| | Ge$_{0.85}$Pb$_{0.15}$.Sb$_{0.05}$.Te$_3$.Te$_3$.Te$_3$ | 2.2 | 800 | – | P | HP |
| | Ge$_{0.85}$Pb$_{0.15}$.Sb$_{0.05}$.Te$_3$.Te$_3$.Te$_3$ | 2.3 | 800 | 1.4 | P | HP |
| | Ge$_{0.85}$Bi$_{0.05}$.Bi$_{0.40}$.Te$_3$.Te$_3$.Te$_3$ | 2.3 | 750 | 1.6 | P | SPS |
| | (GeTe)$_2$.J.0.15$(AgSbTe$_2$)$_3$.Te$_3$.Te$_3$.Te$_3$ | 1.4 | 773 | 0.9 | P | VM |
| | (GeTe)$_{0.75}$.PbSe$_{0.25}$.Te$_3$.Te$_3$.Te$_3$ | 2.2 | 800 | 1.21 | P | HP |
| | (CoGe)$_{0.25}$.GeTe$_2$.J.0.15$.Sb$_2$.Te$_3$.Te$_3$.Te$_3$ | 1.9 | 723 | – | P | VM |
| | Ge$_{0.50}$Sb$_{0.10}$.Sb$_{0.40}$.Te$_3$.Te$_3$.Te$_3$ | 2.2 | 800 | – | P | SPS |
| | Sb$_2$.Te$_3$.Ge$_{0.78}$.Re$_{0.01}$.Te$_3$.Te$_3$.Te$_3$ | 2.25 | 773 | – | P | SPS |
| | (GeTe)$_{0.75}$.AgSbSe$_{0.25}$.Te$_3$.Te$_3$.Te$_3$ | 1.9 | 600 | 1.4 | P | VM |
| Stoichiometry | $zT_{\text{max}}$ | $T$ [K] | $zT_{\text{ave}}$ | Conduction type | Synthesis |
|---------------|-----------------|--------|-----------------|----------------|-----------|
| Ge$_{0.9}$Sb$_{0.1}$Te$_0.75$S$_{0.25}$Se$_{0.05}$ | 2.1 | 630 | – | P | SPS |
| CeTe–$1.5\%$Cu$_2$Te–$2\%$Bi$_2$Te–$8\%$PbTe | 2.4 | 650 | 1.2 | P | HP |
| Ce$_{0.5}$Sn$_{0.5}$Bi$_{0.125}$Sb$_{0.125}$Te$_{0.6}$ | 1.7 | 700 | 1.23 | P | PAS |
| Zn$_{1.5}$Sb$_{0.7}$-based alloys | | | | | |
| A$_{0.05}$Zn$_{1.05}$Sb$_{0.7}$ | 0.5 | 605 | – | P | QA |
| (Zn$_{0.97}$Ag$_{0.03}$)$_{0.45}$Sb$_{0.55}$ | 1.19 | 575 | – | P | SPS |
| (Zn$_{0.99}$Ag$_{0.01}$)$_{0.45}$Sb$_{0.55}$ | 0.106 | 300 | – | P | HP |
| (Zn$_{0.97}$Ag$_{0.03}$)$_{0.45}$Sb$_{0.55}$ | 0.63 | 290 | – | P | QA |
| (Zn$_{0.97}$Ag$_{0.03}$)$_{0.45}$Sb$_{0.55}$ | 0.23 | 260 | – | P | QA |
| (Zn$_{0.99}$Ag$_{0.01}$)$_{0.45}$Sb$_{0.55}$ | 0.123 | 310 | – | P | HP |
| Zn$_{1.2}$Cd$_{0.2}$Sb$_{0.7}$ | 1.09 | 673 | – | P | HP |
| Zn$_{1.2}$Cd$_{0.2}$Sb$_{0.7}$ | 1.3 | 673 | – | P | VA |
| (Zn$_{0.9}$Ge$_{0.04}$)$_{0.45}$Sb$_{0.55}$ | 1.4 | 670 | – | P | C |
| Cu$_{0.05}$Zn$_{0.95}$Sb$_{0.7}$ | 0.84 | 631 | – | P | SPS |
| (Zn$_{0.99}$Ge$_{0.01}$)$_{0.45}$Sb$_{0.55}$ | 1.2 | 670 | – | P | C |
| (Zn$_{0.98}$Gd$_{0.02}$)$_{0.45}$Sb$_{0.55}$ | 1.2 | 655 | – | P | HP |
| (Zn$_{0.98}$Ga$_{0.02}$)$_{0.45}$Sb$_{0.55}$ | 0.65 | 310 | – | P | HP |
| Zn$_{0.01}$Ge$_{0.04}$Sb$_{0.7}$ | 1.2 | 650 | – | P | HP |
| (Zn$_{0.97}$Ge$_{0.03}$)$_{0.45}$Sb$_{0.55}$ | 1.35 | 680 | – | P | QA |
| Hg$_{0.04}$Zn$_{0.96}$Sb$_{0.7}$ | 0.51 | 390 | – | P | VA |
| Zn$_{1.1}$In$_{0.9}$Sb$_{0.7}$ | 0.17 | 360 | – | P | SPS |
| Zn$_{1.1}$In$_{0.9}$Sb$_{0.7}$ | 1.4 | 700 | – | P | B |
| (Zn$_{0.97}$In$_{0.03}$)$_{0.45}$Sb$_{0.55}$ | 1.8 | 698 | – | P | B |
| In$_{0.02}$Zn$_{0.98}$Sb$_{0.7}$ | 0.6 | 605 | – | P | QA |
| Zn$_{1.1}$In$_{0.9}$Sb$_{0.7}$ | 0.38 | 673 | – | P | VA |
| (Zn$_{0.98}$In$_{0.02}$)$_{0.45}$Sb$_{0.55}$ | 0.09 | 310 | – | P | HP |
| Mg$_{0.04}$Zn$_{0.96}$Sb$_{0.7}$ | 0.3 | 300 | – | P | VA |
| (Zn$_{0.99}$Nb$_{0.01}$)$_{0.45}$Sb$_{0.55}$ | 1.1 | 680 | – | P | HP |
| Pb$_{0.02}$Zn$_{0.98}$Sb$_{0.7}$ | 1.12 | 605 | – | P | VA |
| (Zn$_{0.98}$Pb$_{0.02}$)$_{0.45}$Sb$_{0.55}$ | 0.65 | 615 | – | P | HP |
| (Zn$_{0.99}$Sn$_{0.01}$)$_{0.45}$Sb$_{0.55}$ | 1.1 | 615 | – | P | HP |
| Zn$_{0.5}$Sb$_{0.5}$Te$_{0.05}$ | 1.07 | 680 | – | P | HP |
| Zn$_{0.5}$Sb$_{0.5}$Te$_{0.05}$ | 1.0 | 673 | – | P | HP |
| PbTe-based alloys | | | | | |
| (Pb$_{0.5}$S$_{0.5}$)$_{0.45}$–(Te$_{0.5}$Se$_{0.05}$)$_{0.45}$ | 1.4 | 773 | 0.56 | N | SPS |
| PbTe$_{0.98}$S$_{0.02}$–$3\%$ Sb | 1.8 | 773 | 0.81 | N | SPS |
| PbTe–$2\%$ Cu$_2$Te | 1.5 | 723 | 0.87 | N | SPS |
| Cu$_{0.02}$PbTe | 1.3 | 773 | 0.87 | N | HP |
| Pb$_{0.98}$Ga$_{0.02}$Te$_{0.02}$ | 1.28 | 673 | 1.01 | N | B |
| Pb$_{0.98}$Ga$_{0.02}$Te$_{0.02}$ | 1.34 | 766 | 0.86 | N | SPS |
| Pb$_{0.98}$Ga$_{0.02}$Te$_{0.02}$ | 1.3 | 823 | 0.69 | N | SPS |
| Pb$_{0.98}$Ga$_{0.02}$Te$_{0.02}$ | 1.6 | 773 | 0.79 | N | SPS |
| (Pb$_{0.98}$S$_{0.02}$)$_{0.45}$–(Te$_{0.5}$Se$_{0.05}$)$_{0.45}$ | 1.52 | 700 | 0.81 | N | HP |
| Pb$_{0.98}$Ge$_{0.02}$Te–$5\%$ GeTe | 1.47 | 673 | 1.14 | N | SPS |
| Cu$_{0.02}$PbTe$_{0.98}$Te$_{0.02}$ | 1.6 | 750 | 0.69 | N | QA |
| Pb$_{0.98}$In$_{0.02}$Te$_{0.05}$ | 1.2 | 673 | 0.57 | N | HP |
| Pb$_{0.98}$In$_{0.02}$Te$_{0.05}$ | 1.4 | 773 | 0.93 | N | HP |
Table 1. Continued.

| Stoichiometry | $zT_{\text{max}}$ | $T$ [K] | $zT_{\text{avg}}$, $T = 300$–773 K | Conduction type | Synthesis |
|---------------|-----------------|--------|---------------------------------|----------------|-----------|
| (PbLa$_{0.01}$Te$_{0.99}$Ag$_{2}$Te$_{2}$)$_{0.05}$ | 1.6 | 775 | 0.32 | N | HP |
| (Ag$_{0.00}$Pb$_{0.99}$Ag$_{2}$Te$_{2}$)$_{0.05}$ | 1.3 | 750 | 0.62 | N | HP |
| PbTe/7% PbTe@Ca$_{2}$Ag$_{3}$ | 1.6 | 723 | 0.61 | N | FHC |
| S$_{7}$Zn, PbI$_{2}$ | 1.35 | 650 | 0.89 | N | AC |
| PbTe$_{0.999}$Ag$_{0.001}$ | 1.2 | 800 | 0.48 | N | SPS |
| (PbTe$_{0.75}$S$_{0.25}$)$_{0.05}$Ag$_{2}$Te$_{0.05}$ | 1.2 | 773 | 0.48 | N | SPS |
| Pb$_{0.95}$Bi$_{0.05}$Te$_{2}$ | 0.75 | 700 | 0.26 | SPS |
| Pb$_{0.925}$Bi$_{0.015}$Te$_{2}$ | 1.1 | 800 | 0.50 | N |
| Pb$_{0.905}$Sb$_{0.015}$Te$_{2}$ | 1.4 | 900 | 0.34 | N |
| C$_{0.0}$Pb$_{0.99}$Te$_{0.25}$Se$_{0.75}$ | 1.0 | 573 | 0.77 | N | HP |
| PbTe-0.5% Pb-2% Sb | 1.4 | 673 | 0.66 | N | RC |
| PbTe$_{0.998}$Ag$_{0.002}$ | 1.4 | 720 | 0.75 | N | HP |
| PbTe-6% PbSn$_{2}$ + 0.005% PbI$_{2}$ | 1.1 | 625 | 0.79 | N | FC |
| La$_{0.95}$Bi$_{0.05}$Te$_{2}$ | 1.05 | 700 | 0.46 | N |
| PbTe$_{0.998}$Ag$_{0.002}$ | 1.4 | 723 | 0.63 | N |
| Pb$_{0.95}$In$_{0.05}$Te$_{2}$ | 0.66 | 800 | 0.27 | N | HP |
| AgBi$_{0.05}$Sb$_{0.95}$Te$_{2}$ | 1.04 | 570 | – | N | SPS |
| Ag$_{0.96}$Nb$_{0.04}$Bi$_{2}$Se$_{2}$ | 1.0 | 773 | – | N | SPS |
| AgBiSe$_{1.0}$Cl$_{0.0}$ | 0.9 | 810 | – | SPS |
| AgBiSe$_{0.75}$Cl$_{0.25}$ | 1.0 | 823 | – | N | HP |
| Ag$_{0.95}$In$_{0.05}$Bi$_{2}$Se$_{2}$ | 0.7 | 773 | – | N | B |
| AgBiSe$_{1.0}$Te$_{0.1}$ | 0.6 | 573 | – | N | SPS |
| AgSb$_{0.25}$Te$_{0.75}$ | 1.37 | 565 | – | N | SPS |
| AgBiS | 0.7 | 820 | – | N | SPS |
| AgSb$_{0.25}$Zn$_{0.75}$Te$_{2}$ | 1.9 | 585 | – | P | VA |
| CuGaTe$_{2}$ + 3 vol% Cu$_{2}$Se | 1.2 | 834 | – | P | HP |
| Cu$_{0.98}$Ga$_{0.02}$Se$_{2}$ | 1.07 | 721 | – | P | SPS |
| CuGax$_{0.02}$Fe$_{0.02}$Te$_{2}$ | 0.92 | 870 | – | P | SPS |
| Cu$_{0.98}$Ag$_{0.02}$Ge$_{0.02}$ | 1.0 | 750 | – | P | QA |
| CuGax$_{0.02}$Mn$_{0.02}$Te$_{2}$ | 0.83 | 870 | – | P | SPS |
| (CuGaSe)$_{0.98}$In$_{0.02}$Te$_{2.00}$ | 0.8 | 850 | – | P | HP |
| (CuGaSe)$_{0.98}$In$_{0.02}$Ga$_{0.00}$Te$_{2.00}$ | 0.8 | 850 | – | P | HP |
| Cu$_{0.5}$Sb$_{0.5}$Ga$_{0.02}$Te$_{2}$ | 0.82 | 800 | – | P | HP |

Synthesis abbreviation: A, annealing; AC, air cooling; B, Bridgman; C, calculation; CP, cold pressing; CS, chemical synthesis; FHC, facile hydrothermal route; HD, hot deformation; HP, hot pressing; MC, melt-centrifugation; QA, quench annealing; RC, rapid cooling; ST, solvothermal method; SPS, spark plasma sintering; THM, traveling heater method; VA, vacuum melting; ZM, zone melting.

(Figure 1f) suggests a satisfactory average $zT_{\text{avg}} \approx 1.0$ in the temperature range of 300–500 K, which could be beneficial for a TE module.

2.1.2. Ge-Bi$_{2}$Te$_{3}$/Ga-Bi$_{2}$Te$_{3}$ (Phase Diagrams and TE Properties)

The isothermal section of the ternary Bi–Ge–Te system (Figure 2a) confirms the maximal $\approx 3.0$ at% solubility of Bi in GeTe and the $\approx 5.0$ at% solubility of Ge in Bi$_2$Te$_3$.[99] Moreover, at least four ternary compounds, the Ge$_{1.8}$Bi$_{2.5}$Te$_{3}$, Ge$_{1.5}$Bi$_{2.3}$Te$_{4}$, and Ge$_{1.5}$Bi$_{4}$Te$_{7}$, are stabilized at 523 K. The S mapping (Figure 2e) also reveals a clear p–n transition when analyzing the Bridgman grown Bi$_{100-y}$Ge$_{y}$Te$_{60-y}$ alloys. The temperature-dependent TE properties (Figure 2f–i) suggest that the p-type Bi$_{39.0}$Ge$_{1.0}$Te$_{60.0}$ attains the peak $zT \approx 0.9$ at 325 K, while the n-type Bi$_{32.5}$Ge$_{10.0}$Te$_{57.5}$ only reaches peak $zT \approx 0.45$ at 525 K, respectively. The superposition of the nominal composition on the phase diagram reveals that the p-type Bi$_{100-y}$Ge$_{y}$Te$_{60-y}$ falls in the single-phase Bi$_{2}$Te$_{3}$, while the n-type Bi$_{32.5}$Ge$_{10.0}$Te$_{57.5}$ locates in Bi$_{2}$Te$_{3}$ + Ge$_{1.5}$Bi$_{2}$Te$_{4}$ + Ge$_{1.5}$Bi$_{4}$Te$_{7}$ three-phase region. The presence of secondary phases seems to alter the conduction type in Ge-Bi$_{2}$Te$_{3}$ alloys dramatically.
A very similar case has later been found in the Ga-Bi2Te3. The isothermal section of the ternary Bi–Ga–Te system at 523 K (Figure 3a) suggests that the solubility in Bi2Te3 is less than 1 at% Ga. Unlike the isothermal section of Bi–Te–Ge (Figure 2a), the Bi–Ga–Te system contains no ternary compounds at 523 K. The thermally equilibrated microstructures (Figure 3b and 3c) further confirm the existence of three-phase Bi2Te3 + Bi4Te5 + Ga2Te3 and Bi2Te + Bi4Te5 + Ga2Te3 region. The thermally equilibrated microstructure of alloy #8 (Bi–15.0 at%Ga–57.5 at%Te) reveals three equilibrium phases (Figure 3b). The compositional analysis demonstrates that the darkest phase is the Ga2Te3 phase, while the gray matrix phase is composed of the brightest lamella and the gray lamella, which are the Bi4Te5 phase and Bi2Te3 phase.

Following a similar procedure, the homogeneity region of Bi2Te3 can be mapped out. The enlarged isothermal section (Figure 3d) is superimposed with four series Ga-containing Bi2Te3 alloys, which are (Bi2Te3)1–x(Cu2Te) x (x = 0.01, 0.03, 0.05, 0.07, and 0.09) and Bi2–xCu x Te (y = 0.01, 0.03, 0.05, 0.07, and 0.09). Their TE properties (Figure 3e–i) can also be explained by using the phase diagram. For example, the ρ increases with the increasing Ga content (Figure 3f), and then drops suddenly in the a = 0.03 or b = 0.07 alloys, whose nominal composition coincides with the p–n transition zone. The S at 300 K.
transits from positive (p-type) to negative (n-type) when a and b are larger than 0.03. The κ_L for a = 0.07 and a = 0.09 alloys achieves low-lying κ_L/C^251Wm^-1K^-1 at 300 K due to a strong alloying effect (Figure 3i). Consequently, the n-type (Bi₂Te₃₀.03(Ga₂Te₅₀.07) alloy shows a peak zT ≈ 1.5, while the p-type Bi₁₋₀.₀₉Ga₀.₀₁Te₃ has a peak zT ≈ 1.2 at 300 K. Both n- and p-type Ga-Bi₂Te₃ reveal outstanding TE performance, in which their compositions and conduction type can be predicted by using the phase diagram.

2.2. GeTe-Based Alloys

The p-type germanium tellurides (GeTe) rise as the most popular midtemperature TE generator owing to its outstanding TE performance. In addition to TE application, the GeTe-based alloys have been widely used as phase change materials because they undergo successive phase transitions from low-temperature rhombohedral α-GeTe to the high-temperature cubic β-GeTe. For a pristine GeTe, the enormous amount of Ge vacancy induces a high hole carrier concentration of ≈10¹⁴ cm⁻³, which makes it possess an intrinsically high κ. To overcome this disadvantage, doping with group IB (Cu, Ag, Cu) to group VIA (Se, Te) elements or the transition metals effectively prevents the excess Ge vacancy while reducing the κ_L by increasing lattice distortion. Table 1 shows the peak zT values along with the synthesis methods from previous work. It shall be mentioned that the TE performance for GeTe-based alloys varies with different synthesis routes reported by different groups. The discrepancy is
likely to originate from its complex phase transformation behavior that influences the transport properties when different synthesis procedure or dopant is adopted. Therefore, the thermodynamic route\[^{25}\] that probes an equilibrium pathway might lead to reliable and reproducible TE properties.

As shown in Table 1, many breakthroughs have been reported by adopting different synthesis routes or incorporating different dopants. Usually, the doping elements bring severe lattice distortion that reduces the $\kappa_L$. Among them, the incorporation of copper (Cu) in GeTe decreases the charge carrier concentration and produces a high density of stacking fault, which advances the power factor and reduces $\kappa_L$ simultaneously.\[^{92,93}\] The $\alpha$ to $\beta$ phase transition temperature is decreased in Sn-GeTe\[^{95}\] and Sb-GeTe\[^{96}\] alloys, which also accompanies the reduction in $\kappa_L$. For In-GeTe alloys, the addition of In introduces the distorted density of states (DOS) near the Fermi level ($E_F$), which enhances the power factor.\[^{94}\] Among all the dopants, the Sb-GeTe alloys yield a remarkable peak $zT$ value at $T > 700$ K, enabling the GeTe-based alloys to be promising midtemperature TE generators.\[^{97}\]

### 2.2.1. Sb-GeTe (Phase Diagrams and TE Properties)

There have been extensive reports upon the high TE performance of Sb-GeTe, and several of them even reach $zT > 2$ via

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**Figure 3.** a) The isothermal section of the ternary Bi–Ga–Te system at 523 K. The back scattered images and WDS elemental mapping: b) alloy #8 (Bi–15.0 at%Ga–57.5 at%Te), c) alloy #15 (Bi–10.0 at%Ga–45.0 at%Te). d) Magnified isothermal section superimposed with color contour of Seebeck ($S$) coefficient measured at 300 K. The temperature-dependent e) $zT$ values, f) electrical resistivity ($\rho(T)$) curves, g) Seebeck coefficient ($S(T)$) curves, h) thermal conductivity ($\kappa(T)$) curves, and i) lattice thermal conductivity ($\kappa_L(T)$) curves for the two series of Ga-Bi$_2$Te$_3$ alloys, which are (Bi$_2$Te$_3$)$_{1-a}$Ga$_a$Te$_3$ (a = 0, 0.01, 0.03, 0.05, 0.07, and 0.09) and Bi$_2$Ga$_b$Te$_3$ (b = 0.01, 0.02, 0.03, 0.07, 0.09, 0.14, and 0.18). The inset (e) showed the reproducibility for three $a = 0.07$ samples. Adapted with permission.\[^{25}\] Copyright 2020, Wiley-VCH GmbH.
different approaches. For example, an alloy of Ge$_{0.6}$Sb$_{0.4}$Te$_{11.91}$ attains a peak $zT \approx 2.1$ at 775 K$^{[99]}$ owing to the synergistically alloying effect and carrier optimization. High-density stacking fault reduces the $\kappa_i$ while manipulating the vacancy level through the deficient Te enhances the $S$.$^{[99]}$ On the contrary, Xu et al.$^{[12]}$ consolidated the TE alloys by different annealing process durations. During annealing, the Ge vacancies would migrate and reconstruct into the long-range van der Waals gaps, suppressing the carrier concentration and bringing down the electron thermal conductivity $\kappa_e$. The highest $zT \approx 2.4$ at 773 K was found in Sb$_{0.95}$Te$_{0.05}$GeTe$_{17}$. For the Sb-substituted Ge$_{1-x}$Sb$_x$Te, Perumal et al.$^{[99]}$ and Bayikadi et al.$^{[97]}$ both revisited the Ge$_{0.9}$Sb$_{0.1}$Te alloy through various sample preparation processes. Under a slow annealing process, the rhombohedral lattice distorts toward the cubic nature with a decreasing $n_i$. Meanwhile, the Sb dopant increases the valence band degeneracy in Ge$_{0.9}$Sb$_{0.1}$Te, which leads to higher power factor (PF = $S^2\rho^{-1}$).$^{[99]}$ On the contrary, the herringbone structure is typically observed on a GeTe-based material$^{[96]}$ in which the high-density twin boundaries induce a strong phonon scattering and yield an ultralow $\kappa$. As a result, a peak $zT \approx 1.85$ at 725 K was reported by Perumal et al.$^{[99]}$ A higher peak $zT \approx 2.35$ at 800 K for the identical Ge$_{0.9}$Sb$_{0.1}$Te was suggested by Bayikadi et al.$^{[97]}$ which was accomplished by a two-step cooling process. A brief conclusion can be made that the stoichiometry and synthesis process affect the resultant TE performance for a GeTe-based alloy, as the former determines the cation concentration level while the latter manipulates the microstructure. Therefore, the GeTe-based phase diagrams are critical because they illustrate the relationship between stoichiometry, phase transformation, and microstructural evolution.

Lately, Tsai et al.$^{[23]}$ report an ultrahigh peak $zT \approx 2.69$ in a (GeTe)$_{0.095}$(Sb$_2$Te)$_{0.05}$ alloy via a thermodynamic approach. In this work, the isothermal section for Ge–Sb–Te ternary system at 623 K (Figure 4a) is well constructed by experiments. Taking alloy #22 as an example, the backscattered image (Figure 4d) reveals three different phase contrasts, indicating the coexistence of the $\beta$-GeTe, the $\delta$, and the Ge. The microstructures for selective thermally equilibrated $\theta^9$ (two-phase region Ge$_{0.95}$Sb$_{0.05}$Te$_{0.05}$GeTe$_{0.05}$), $\#17$ (three-phase region $\beta$-GeTe + Ge$_{0.95}$Sb$_{0.05}$Te$_{0.05}$ + $\gamma$), $\#22$ (three-phase region $\beta$-GeTe + Sb + Ge), and $\#31$ (two-phase region $\delta$ + Sb) are shown in Figure 4b–e, respectively. The phase diagrams (Figure 4a–j) affirm the coexistence of $\alpha$-GeTe and $\beta$-GeTe at the low-temperature region for the Sb-GeTe alloys. Most importantly, a spinodal region forms on the top of the two-phase $\alpha+\beta$, explaining the microstructural evolution (Figure 4f–i) in the best-performing (GeTe)$_{0.095}$(Sb$_2$Te)$_{0.05}$ alloy. In other words, the temperature-dependent diffusion-driven spinodal fluctuations are locked by the diffusionless athermal $\alpha$ to $\beta$ phase transition. The compositional line scan (an inset of Figure 4j) indicates the inhomogeneous Sb distribution for the 723 K annealed sample (within the spinodal region), reflecting an uphill diffusion feature. As suggested by the isopleth section (Figure 4j), the (GeTe)$_{0.095}$(Sb$_2$Te)$_{0.05}$ ($y = 0.05$) alloy passes through a bimodal region while cooling, and the phase separation takes place, leading to the formation of the Sb-deficient $\beta$-GeTe ($6\text{ at%} \text{ Sb}$) and Sb-rich $\beta$-GeTe ($11\text{ at%} \text{ Sb}$) with the blurred phase boundaries. The Sb-deficient $\beta$-GeTe further transforms into the low-temperature $\alpha$-GeTe via the athermal reaction, and the inhomogeneity causing by the coexistence of Sb-rich $\beta$-GeTe and $\alpha$-GeTe can thus be maintained. In addition to the best-performing (GeTe)$_{0.095}$(Sb$_2$Te)$_{0.05}$ alloys, Tsai et al.$^{[23]}$ also investigated the TE performance of Ge$_{1-x}$Sb$_x$Te ($x = 0.02$, 0.05, and 0.10) and Ge$_{0.9}$Sb$_{0.1}$-Z$_2$ ($z = 0.02$, 0.05, and 0.10), as shown in Figure 4i–p. The $S$ and $\rho$ increase with the increasing Sb content, simultaneously, while the $\kappa$ is dramatically decreased. The $zT$ value elevates from 0.8 to 2.69 at 723 K (Figure 4i), revealing a significant improvement in the Sb-GeTe alloys by adopting the phase diagram engineering.

2.3. $\text{ZnSb}_x\text{Based Alloys}$

ZnSb-based compounds are cost-effective and environment-friendly p-type TE material.$^{[1,100,101]}$ In the recent decade, several Zn–Sb binary compounds, including the ZnSb, Zn$_3$Sb$_3$ (Zn$_{13}$Sb$_{10}$), Zn$_3$Sb$_2$, Zn$_4$Sb$_7$, and Zn$_5$Sb$_7$, draw attention as a nontoxic alternative to the lead tellurides.$^{[102,103]}$ In particular, the ZnSb has a higher $S$, a larger $\rho \approx 110 \text{ m}\Omega\text{ cm}$ and a moderate $\kappa = 2.3 \text{ W m}^{-1} \text{ K}^{-1}$ when compared with $\beta$-Zn$_3$Sb$_2$.$^{[109,112]}$ The existence of ZnSb inclusion in $\beta$-Zn$_3$Sb$_2$ would significantly lift the $S$ and $\rho$. By contrast, the excess Zn in $\beta$-Zn$_3$Sb$_2$ lowers the $S$ and $\rho$. Nevertheless, the presence of either ZnSb ($\approx 2.3 \text{ W m}^{-1} \text{ K}^{-1}$) or Zn ($\approx 116 \text{ W m}^{-1} \text{ K}^{-1}$) in the $\beta$-Zn$_3$Sb$_2$ leads to a higher $\kappa$. Therefore, the counterbalance between the impurities (ZnSb or Zn) and the matrix $\beta$-Zn$_3$Sb$_2$ greatly influences its TE properties. Many strategies,$^{[15]}$ such as doping and nanostructuring, have been proposed to improve its TE performance.

Zintl phase, featuring electron crystal phonon glass, possesses low $\kappa_i$ without low electrical properties, such as Mg$_2$Sb$_3$,$^{[31–34]}$ Zn$_4$Sb$_6$,$^{[26]}$ and so on. Recent studies of $\beta$-Zn$_3$Sb$_2$ focus on its structural complexity, including the diffusion and disordered channels of Zn atoms and localized dumbbell vibration of the Sb–Sb dimers in the $\beta$-Zn$_3$Sb$_2$.$^{[100,106]}$ There are four crystallographic structures of Zn$_3$Sb$_2$, which exist at different temperature ranges, i.e., the $\alpha'$-phase (below 230 K), $\alpha$-phase (230–263 K), $\beta$-phase (263–765 K), and $\gamma$-phase (765–837 K).$^{[106–108]}$ Among these four structures, only the $\beta$-Zn$_3$Sb$_2$ fulfills the “phonon-glass electron-crystal [PGE]” concept, which possesses low $\kappa_i \approx 0.4–0.6 \text{ W m}^{-1} \text{ K}^{-1}$ and moderate $\sigma$. The reported zT values of $\beta$-Zn$_3$Sb$_2$ range from 0.8 to 1.3 at 673 K.$^{[100,106]}$ In addition, the Zn vacancy ($V_{Zn}$) in Zn$_3$Sb$_2$ brings abnormal transport properties. In a pristine Zn$_3$Sb$_2$, an $\approx 0.3\%$ $V_{Zn}$ exists and acts as the center for Zn migration, which makes the Zn$_3$Sb$_2$ disordered and reduces $\kappa_i$ by $70\%$.$^{[110–112]}$ Like other TE materials, doping optimizes the carrier concentration and stabilizes the crystal structure of $\beta$-Zn$_3$Sb$_2$. Table 1 shows the TE properties for Zn$_3$Sb$_2$-based alloys incorporated with different dopants.

Despite all the efforts,$^{[113–118]}$ the thermal stability of Zn$_3$Sb$_2$ is still the main concern for practical applications. Lo et al.$^{[119]}$ provide a comprehensive study regarding the phase relationship and phase transformation for the binary Zn–Sb system. The phase boundary mapping and phase diagram engineering illustrates the relationship between TE performance and phase stability for the doped Zn$_3$Sb$_2$.$^{[20]}$ Both help locate the stabilization regions for the Zn$_3$Sb$_2$. In short, a phase diagram plays a crucial role in determining the stoichiometry of $\beta$-Zn$_3$Sb$_2$ and depicting the solubility region when a dopant is added.$^{[120]}$ Therefore, the...
Figure 4. a) Isothermal section of Ge–Sb–Te ternary system at 623 K overlaid with nominal compositions of thermally equilibrated alloys. SEM micrographs of Ge–Sb–Te alloys equilibrated for over 60 days at 623 K: b) alloy #9 (Ge–55.0 at%Te–25.0 at%Sb), c) alloy #17 (Ge–45.0 at%Te–30.0 at%Sb), d) alloy #22 (Ge–40.0 at%Te–10.0 at%Sb), e) alloy #31 (Ge–15.0 at%Te–80.0 at%Sb). Phase decomposition and athermal transformation in the (GeTe)\(_1\)–\(_y\) (Sb\(_2\)Te\(_3\))\(_y\) pseudobinary system. The elemental mapping of Sb for \(y = 0.05\) samples annealed at f) 773 K, g) 723 K, h) 673 K, and i) 623 K for 72 h. j) Isoplethal section of pseudobinary (GeTe)\(_1\)–\(_y\) (Sb\(_2\)Te\(_3\))\(_y\), revealing the temperature and composition ranges of the phase decomposition and diffusionless athermal transformation. The insets: line scan results for Sb concentration for \(y = 0.05\) samples annealed at 773 and 723 K are shown as an inset, together with the Gibbs free energy curves (G) versus composition (y) for the spinodal decomposition (right panel, upper image) and the athermal transformation (right panel, lower image). k) A schematic showing the mechanism leading to the strong composition fluctuation and the coexistence of α and β. Thermoelectric properties for the four series of GeTe-based alloys, which are Ge\(_{1-x}\)Sb\(_x\)Te \((x = 0.02, 0.05, \text{ and } 0.10)\), Ge\(_{1-x}\)Sb\(_x\)Te \((y = 0.05, 0.06, 0.07, \text{ and } 0.10)\), and Ge\(_{1-x}\)Sb\(_x\)Te \((z = 0.02, 0.05, \text{ and } 0.10)\). l) The temperature-dependent figure-of-merit (\(zT\) value) and the inset show the temperature profile of the synthesis process. m) Electrical resistivity \(\rho(T)\), n) Seebeck coefficient \(S(T)\), o) power factor \(\sigma S^2(T)\) (where \(\sigma = 1/\rho\)), p) thermal conductivity \(\kappa(T)\) and the inset show the enlarge thermal conductivity. Adapted with permission.\(^{[26]}\) Copyright 2019, American Chemical Society.
phase diagrams for those Zn$_4$Sb$_3$-based alloys are essential to understand the homogeneity region and phase relation.\cite{121}

### 2.3.1. In-Zn$_4$Sb$_3$ (Phase Diagrams and TE Properties)

Several prospective dopants for Zn$_4$Sb$_3$ have been reported, which not only enhance the $zT$, but stabilize its crystal structure in the midtemperature range.\cite{122} Furthermore, light doping cases easily generate nanoprecipitation, leading to $\kappa_L$ reduction or the $S$ improvement via the filtering effect.\cite{26,122} In particular, the In-Zn$_4$Sb$_3$ reveals an enhanced $zT$ due to the low-lying $\kappa$.\cite{26,123,124} Most previous work agrees that indium can effectively increase the phase stability and boost the peak $zT$ value of Zn$_4$Sb$_3$, and that makes the phase diagram of Zn–Sb–In important. Recently, the phase diagram of Zn–Sb–In at 623 K (Figure 5a) was constructed by experiments,\cite{26} in which the solubility range of $\beta$-Zn$_4$Sb$_3$ can be depicted (Figure 5b). The maximal solubility in $\beta$-Zn$_4$Sb$_3$ is approximate $\approx 2\%$ In, and the homogeneity region of $\beta$-Zn$_4$Sb$_3$ extends asymmetrically toward the Zn-rich side. In addition to the $\beta$-Zn$_4$Sb$_3$, the phase diagram identifies a ternary compound Zn$_5$Sb$_4$In$_2$. Evidence can be shown by the thermally equilibrated In–Zn–Sb alloy (Figure 5c), which reveals three distinct phases of Zn$_4$Sb$_3$, Zn, and Zn$_5$Sb$_4$In$_2$. The equilibrium phase diagram acts as a map guiding the doping direction. The

Figure 5. a) The isothermal section of the ternary Zn–Sb–In system at 623 K. b) The enlarged isothermal section superimposed with the color contour of peak $zT$ values at 623 K. The WDS maps for individual elements of Zn, Sb, and In for c) alloy #21 (In–65.0 at%Zn–27.5 at%Sb), and d) elemental mapping conducted by EPMA of Zn$_{3.95}$In$_{0.05}$Sb$_3$. Temperature-dependent e) $zT$ curves, f) Seebeck coefficient ($S(T)$) curves, g) electrical resistivity ($\rho(T)$) curves, h) thermal conductivity ($k(T)$) curves, g) thermal conductivity ($k(T)$) curves, and i) lattice thermal conductivity ($k_L(T)$) curves for the Zn$_{4-x}$In$_x$Sb$_3$ ($x = 0–0.07$), the (InSb)$_y$(Zn$_4$Sb$_3$)$_{1-y}$ ($y = 0.03–0.15$). Adapted with permission.\cite{69} Copyright 2017, Elsevier.
high $zT$ zones can be identified by superimposing the peak $zT$ values of In$_2$Sb$_3$ alloys on the magnified isothermal section (Figure 5b), highlighting the two-phase Zn$_4$Sb$_3$ + Zn, the two-phase Zn$_4$Sb$_3$ + ZnSb$_4$ + In$_2$, and the three-phase Zn$_4$Sb$_3$ + ZnSb$_4$ + In$_2$ + In$_4$ regions. An alloy of Zn$_{0.95}$In$_{0.05}$Sb$_3$ achieves a remarkable $zT$ of $\approx$1.8 at 698 K (Figure 5e), which falls in a Zn$_4$Sb$_3$ + ZnSb$_4$ + In$_2$ two-phase region (Figure 5d). The microstructure of Zn$_{0.95}$In$_{0.05}$Sb$_3$ further confirms the coexistence of the Zn$_4$Sb$_3$ matrix, InSb nanoincipient, and ZnSb$_4$ + In$_2$ inclusions (Figure 5d). A closer observation reported by Wu et al.[26] further suggests the modulation distribution of InSb nanoincipient in the Zn$_4$Sb$_3$ + In$_2$. That might be responsible for the ultralow $\kappa_L$ and high peak $zT$. In other words, the secondary phase-free Zn$_4$Sb$_3$ provides the channels for the hole carrier to pass without disruption, while the InSb-embedded Zn$_4$Sb$_3$ + In$_2$ scatters the phonons to an extent. The TEM image verification can be found somewhere else.[26] Such an exquisite microstructure for the best-performing Zn$_{0.95}$In$_{0.05}$Sb$_3$ could only be precisely located using phase diagram engineering.[26]

Furthermore, the increasing substitution of Zn by In degrades the peak $zT$ value ($\kappa = 0.07; \text{ Figure 5e}$), attributing to the higher $\kappa$ and $\kappa_L$ (Figure 5h,i). The increased $\kappa$ could result from the excess amount of secondary Zn$_4$Sb$_3$ + In$_2$, which both possess higher $\kappa$. By contrast, the (InSb)$_4$Zn$_4$Sb$_3$$_{1-\gamma}$ reveal much lower peak $zT$ values until the heavily alloying $\gamma = 0.013$ and $\gamma = 0.015$ alloys (Figure 5e) whose composition also falls across the Zn$_4$Sb$_3$ + Zn$_4$Sb$_3$ + In$_4$ + In$_2$. Low-lying $\kappa$ (Figure 5h) and optimized $S$ (Figure 5f) are also attained in $\gamma = 0.013$ and $\gamma = 0.015$ alloys.

2.4. PbTe-Based Alloys

Lead tellurides have been widely used in a space rover since the 1960s. The breakthroughs in both peak $zT$ and $zT_{ave}$ have been fulfilled by adopting various approaches, including band structure engineering and defect engineering. However, most of them are effective for p-type PbTe only. The progress in the n-type PbTe was much slower than the p-type counterpart in the last decade, and that drives the research interests toward high-performance n-type lead tellurides. In the recent decade, innovative strategies, including dynamic doping,[143,144] phase diagram engineering,[27] lattice strain engineering,[145–147] and so on, are utilized to improve the $zT$ values of n-type PbTe, which yields outstanding results.[147–150] For example, alloyed defects in a doped lead telluride could manipulate the charge transport and atomic vibrational properties, resulting in the optimized TE properties.[151,152]

Among these potential strategies, the phase diagram engineering emerges as a new approach to disclose the relationship between the TE performance, microstructure, and phase stability.[143,153,154] As known, the stoichiometry in the pristine PbTe significantly affects its transport properties given that it only tolerates a small mutual solubility.[154] As further revealed by a density functional theory (DFT) calculation,[145] the vacancies ($V_{Te}$ or $V_{Po}$) have lower formation energies rather than antisite or interstitial defects. When a dopant is involved, a phase diagram can predict the optimal compositional region and could be further supported by first-principles defect calculation.[154]

Examples can be found in the I-PbTe.[154] and the Cu-PbTe[143] systems. The Cu-PbTe even shows an abnormal jog of carrier concentration around $T \approx 500$ K.[156] A Cu$_{0.09}$PbTe alloy exhibits an outstanding peak $zT = 1.3$ at 773 K[143] Phase diagram engineering is also feasible for boosting the TE performance for the codoped PbTe. For the (Cu, Se)-PbTe, the phase diagram illustrates the solubility of Cu inside the Se-PbTe,[153] which marks an optimal region for compositional manipulation. The best-performing (Cu, Se)-PbTe achieves an extraordinary peak $zT \approx 1.6$ at 750 K.[153]

The evolution of the microstructure, strain field, and defects significantly influences the $\kappa_L$.[147,157–162] The strain field can effectively reduce $\kappa_L$ due to the severe lattice distortion.[149,155,156] The formation of point defects,[163] dislocations,[160] grain boundary,[162] and precipitates[164] induces the strain field, which affects the phonon traveling to different levels. Taking the MnTe–PbTe as an example, the MnTe alloying generates various kinds of defects, including the Mn interstitial, the line defect, and the grain boundary, leading to a significant reduction of $\kappa_L$.[148] The $zT$ value of PbTe–4% MnTe alloy reaches 1.6 at 773 K. Moreover, the $zT_{ave}$ of PbTe–4% MnTe is boosted to $\approx 1.05$ in the temperature range of 300–873 K. The Sb-incorporated PbTe also reveals reduced $\kappa_L$ alongside the carrier concentration optimization.[165] It is worth mentioning that Sb dopant gives rise to complex effects, such as forming a nanoscale precipitate with the coherent interface between matrix and simultaneously substituting the two closest Pb and Te sites as temperature elevated.[163] The mass fluctuations and strain field inside the PbTe lattice induced by dissolved Sb partly scatter phonons that lower the $\kappa_L$. Those phenomena synergistically boost the $zT$ value of PbTe$_{0.998}$Ge$_{0.002}$–3% Sb to 1.8 at 773 K. Another high-performance codoped PbTe can be found in (Ga, Ge)-PbTe.[159] Ga is an effective n-type dopant, while the Ge atoms distort the PbTe lattice, and therefore the codopant (Ga, Ge)-PbTe shall yield extraordinary TE performance. With the addition of Ge, the $\kappa_L$ shows a $\approx$34% reduction at 300 K compared with the Pb$_{0.998}$Ga$_{0.002}$Te. Consequently, the $zT$ value of Pb$_{0.998}$Ga$_{0.002}$Te–5% GeTe reaches $\approx$1.47 at 673 K with an enhanced $zT_{ave}$ attains $\approx$1.27 within the temperature range of 400–773 K.[150]

2.4.1. Ga-PbTe (Phase Diagrams and TE Properties)

The Ga atoms serve as a strong electron donor and introduce a deep impurity level in the band structure in PbTe.[151] Incorporated Ga induces two kinds of impurity states in the valence band (VB) and conduction band (CB), separately, resulting in an optimal carrier concentration.[152] The peak $zT$ of an n-type Pb$_{0.998}$Ga$_{0.002}$Te attains $\approx$1.34 at 766 K with an outperforming $zT_{ave} \approx 0.86$ in the temperature range of 300–673 K.[111] Wang et al.[134] revisit the same system with an emphasis upon the relation between the TE properties and microstructure; they reported a similar peak $zT$ value in an n-type Pb$_{0.998}$Ga$_{0.002}$Te but with a lower $zT_{ave} \approx 0.69$ in the same temperature range. As shown in Table 1, the PbTe-based materials generally possess varying TE performance, mainly due to different synthesis routes. Nevertheless, the thermodynamic approach might minimize the inconsistency by determining the equilibrium
solubility. To seek the optimal composition with better TE performance, the phase diagrams for the PbTe-based alloys are in need. Deng et al.\(^\text{[27]}\) constructed the Pb–Te–Ga phase diagram (Figure 6a) at 673 K by experiments and realized that the solubility of Ga in PbTe is asymmetric and is as minor as 1.0 at% (Figure 6b). The equilibrium microstructures and the wavelength dispersive X-ray spectroscopy (WDS) elemental mapping (Figure 6c and d) for various ternary Ga–Pb–Te alloys help depict the phase diagram through a long-term postannealing process. The magnified isothermal section (Figure 6b) is further superimposed with the color contour of peak $zT$ values, inferring that the high $zT$ zone for Ga-PbTe falls across the maximum solubility of Ga in Te-enriched PbTe.

Compared with the previous Ga-PbTe alloys,\(^\text{[151,152]}\) the Ga$_{0.02}$Pb$_{0.98}$Te reported by Deng et al.\(^\text{[27]}\) reveals a similar peak value yet with an outperforming $zT_{ave}$ = 1.01 within 300–673 K (Table 1). To elucidate the relevance between phases and transport properties, the temperature-dependent $\rho$, $S$, $\kappa$, and $\kappa_L$ curves for Ga-PbTe alloys are shown in Figure 6f–i. The $\rho(T)$ curves (Figure 6f) dramatically move downward with the increasing Ga content. For the undoped and minor doped samples ($x = 0$ and $x = 0.004$), the $\rho(T)$ curves transit from the metallic to

![Figure 6](https://www.advancedsciencenews.com/figure/6-1024x1024.png)

**Figure 6.** a) The isothermal section of the ternary Pb–Te–Ga system at 673 K. b) The enlarged isothermal section superimposed with the color contour of peak $zT$ values at 673 K. The WDS maps for individual elements of Pb, Ga, and Te for c) alloy #33 (Ga–25.0 at%Pb–55.0 at%Te), and d) alloy #28 (Ga–10.0 at%Pb–55.0 at%Te) underwent a 30-day postannealed at 673 K. Temperature-dependent e) $zT$ curves, f) electrical resistivity ($\rho(T)$) curves, g) Seebeck coefficient ($S(T)$) curves, h) thermal conductivity ($\kappa(T)$) curves, and i) lattice thermal conductivity ($\kappa_L(T)$) curves for the Ga$_{x}$Pb$_{1-x}$Te ($x = 0–0.02$), the Ga$_{y}$(PbTe)$_{1-y}$ ($y = 0.004–0.012$), and the Ga$_{x}$PbTe$_{1-x-y}$ ($x = 0.006, 0.01$).\(^{[27]}\) The Debye–Callaway model well predicts the temperature-dependent lattice thermal conductivity ($\kappa_L(T)$) and is included in (i). The high-temperature lattice thermal conductivity ($\kappa_L$) of Ga$_{0.02}$Pb$_{0.98}$Te approaches the amorphous limit of cubic structure ($\approx 0.4$ W m$^{-1}$ K$^{-1}$). Adapted with permission.\(^{[27]}\) Copyright 2020, Wiley-VCH GmbH.
semiconductor conducting with increasing temperature. Meanwhile, the S(T) curves for these two alloys (inset of Figure 6g) also reveal the transition from p-type to n-type conducting. By contrast, the heavily doped x = 0.06 exhibits a decreasing ρ(T) and S(T) due to the increasing Ga⁺ contribution. Nevertheless, its κ and κ₁ are significantly lifting owing to the presence of secondary phases. The Ga₄(PbTe)₂₋₁₋ₓ also reveals a similar increasing n₁₋ₓ with increasing y. Nevertheless, the increasing z in the Te-deficient Ga₄PbTe₁₋ₓ oppositely leads to a decrease in n₁₋ₓ, which leads to the higher ρ(T) curves (Figure 6f). As the temperature elevates, the κ(T) and κ₁(T) curves (Figure 6h,i) decline except for the undoped x = 0. In particular, the κ₁ is greatly reduced from κ₁ = 1 to κ₁ = 0.85 W m⁻¹ K⁻¹ at 673 K as the composition shifting from x = 0.01 to x = 0.02. The reduction in κ₁ can be explained by the defect evolution,[27] which changes from a dislocation loop to nanoprecipitates. The low-κ₁ and high-zTregion can be properly probed by the as-constructed phase diagram (Figure 6b).

3. Advances in Ternary TE Compounds via Phase Diagram Engineering

3.1. n-Type AgBiSe₂ (Phase Diagrams and TE Properties)

Among all mid-temperature TE materials, the I–V–I₂ compounds (I = Ag, Cu, or alkali metal; V = Sb, Bi; and I₂ = S, Se, Te) are the potential ones, such as AgSbTe₂[29,175] or AgSbSe₂.[176] The AgSbVI₂-based materials crystallize in a NaCl crystal structure where Ag or Sb randomly occupies the Na site.[177] This characteristic structure leads to low κ owing to the anharmonicity that enhances the phonon scattering without affecting the electronic transport properties. As featured with low κ[176–178] and high S,[179] the AgSbTe₂ possesses high TE performance with a reported peak zT of 0.9 at 570 K.[180–183] Doping or alloying could further bring up the TE performance for the I–V–I₂ compounds. For example, the p-type AgSb₀.₇₅Bi₀.₂₅Te₂ exhibits a reduced κ and a peak zT ≈ 1.04 at 570 K,[177] while the p-type AgSbSe₀.₇₄Te₀.₃₄ achieves a peak zT ≈ 1.37 at 565 K.[186]

Most of the I–V–I₂ compounds are p-type semiconductors, except for the n-type AgBiSe₂.[187] At room temperature, the n-type AgBiSe₂ crystallizes in a hexagonal structure with the space group of Pmまい (a = 4.194 Å, c = 19.65 Å) and undergoes a phase transition to a rhombohedral structure with a space group of R₃ (a = 4.184 Å, c = 19.87 Å) at 523 K. As the temperature is higher than 723 K, the AgBiSe₂ transforms into a cubic structure with a space group of Pm₃m (a = 5.930 Å).[188] Owing to the strong anharmonicity, the AgBiSe₂ possesses an intrinsically low κ ≈ 0.45 W m⁻¹ K⁻¹ at 300 K.[188] Nevertheless, the moderate PF of an undoped AgBiSe₂ limits the peak zT to less than 0.5 at 723 K. To raise its PF, doping with Nb fulfills the carrier optimization and decreases the ρ significantly. The n-type Na-AgBiSe₂, therefore, shows a peak zT = 1 at 773 K.

It is noted that the stoichiometry in those I–V–I₂ compounds influences the resultant transport properties. The ratio between the cation (Ag⁺ or Cu⁺) and anion (Te²⁻ or Se²⁻) highly affects the electronic transport properties. The Ag–Bi–Se icosahedral section (Figure 7a) at 773 K[28] further maps out the homogeneity region of AgBiSe₂, which is 52.7–45.3 at% Se and 16.4–26.5 at% Ag. Similarly, the construction of an equilibrium phase diagram relies on various equilibrium results from postannealing alloys. For instance, the equilibrium microstructure of alloy #1 confirms the existence of liquid Bi and Ag₉Se (Figure 7b), while the selective microstructures for other thermally equilibrated samples are shown in Figure 7c–e. The single-phase AgBiSe₂ region probes the possible high-zT area for further investigation. For all the ternary alloys, the ρ is relatively low, ranging from 2 to 5 mΩ cm, while the value of S ranges from ≈40 to ≈70 μV K⁻¹, as shown in Figure 7g,h. Among them, the Ag₂Sb₃Se₁₀ displays peak zT ≈ 0.75 at 748 K (Figure 7f), accompanying with low κ ≈ 0.7 W m⁻¹ K⁻¹ at 748 K. Further alloying with GeSe, the absolute value of S increased from 60 to 130 μV K⁻¹ and the n-type (Ag₂Sb₃Se₁₀)ₐ₋₀.ₙ₉₃₃(GeSe)ₐ₋₀.ₙ₃ has a peak zT value of 1.05 at 748 K, attributing from its ultralow κ ≈ 0.3 W m⁻¹ K⁻¹. Therefore, a well-constructed phase diagram helps locate the homogeneity region for complex TE materials, narrowing the potentially high-zT zones for multicomponent alloys.

3.2. p-Type CuGaTe₂ (Phase Diagrams and TE Properties)

Apart from the I–V–I₂ compounds, the chalcopyrite I–III–Vₐ compounds are also considered promising in the fields of optoelectronic facilities and solar cells.[192–195] In recent years, chalcopyrite materials show their potential as TE materials.[196–200] The p-type CuGaTe₂, which has low ρ and high S, reveals a peak zT of 1.4 at 950 K.[201] The stoichiometry of Cu and Ag in Cu₁₋ₓGaTe₂,[197] Cu₁₋ₓInTe₂[202], and Ag₁₋ₓGaTe₂[198] affects the resultant TE properties notably. Moreover, alloying with 3 vol% of Cu₃Se enhances the phonon scattering, which leads to low κ and high peak zT of 1.2 at 825 K.[203] Ag-doped CuGaTe₂ also reveals a low-lying κ of 0.6 W m⁻¹ K⁻¹ at 610 K.[199] The same results can be found in the Sn-doped Cu₁₋ₓGaSnₐₓTe₂, Gd-doped Cu₃Ga₁₋ₓGdₓTe₂, and so on, whose maximum zT value is 1.07 at 721 K[204] and 0.75 at 737 K.[200] Even though the CuGaTe₂ shows great potential as a TE generator, the information, such as the homogeneity region with or without doping, the thermal stability, the intrinsic transport property, and so on, is still inadequate. Phase diagram engineering provides a feasible solution to unveiling the relationship between phases and TE properties. The previous study[28] indicates that the ternary CuGaTe₂ phase can stabilize within a compositional region of 48.0–53.0 at% Te and 25.0–30.0 at% Cu, as confirmed by the Cu–Ga–Te phase diagram (Figure 8a). The equilibrium microstructure of alloy #8 reveals a two-phase feature (Figure 8b) after 30 days postannealing. Optimizing the nominal composition of CuGaTe₂ based on the phase diagram infers that the Ga-rich Cu₃Ga₂Se₄ outperforms all the other CuGaTe₂ alloys. At 750 K, the Cu₃Ga₂Se₄ attains a peak zT ≈ 0.6 and a low-lying κ ≈ 1.1 W m⁻¹ K⁻¹ (Figure 8f and 8j). By contrast, the Cu-rich Cu₃Ga₂Se₄ has a much lower peak zT of 0.08, meaning that a small variation in nominal composition yields a huge difference in the TE performance (Figure 8g–i). In short, one shall have a phase diagram in hand to navigate toward the correct compositional regions where high-performance chalcopyrite materials can be located.
4. Summary and Prospect

In summary, this review introduces the incorporation of phase diagram engineering in TE materials, which underlines the relationship between chemical composition, phase stability, microstructural evolution, and transport properties. Moreover, phase diagram engineering acts as a practical way to develop high-performance TE materials that are less addressed before. Various examples have been reviewed and discussed, including those state-of-the-art TE coolers/generators or promising yet less-studied ternary compounds. By means of isothermal sections, the temperature-dependent solubility of a complex TE material can be depicted, which guides the doping or alloying directions. Through an isoplethal section, the phase transformations of a TE material could be revealed, explaining the possible compositional fluctuations or crystal structure distortion. Combining different phase diagrams with thermal/electrical transport properties yields various optimization strategies that either rejuvenate the well-established TE materials or develop new and promising TE candidates from a thermodynamic perspective.

Figure 7. a) The isothermal section of the ternary Ag–Bi–Se system at 773 K. b) Backscattered electron image of alloy #1 (Ag–20.0 at%Bi–20.0 at%Se), c) alloy #10 (Ag–20.0 at%Bi–60.0 at%Se), d) alloy #28 (Ag–40.0 at%Bi–50.0 at%Se), and e) alloy #2 (Ag–20.0 at%Bi–35.0 at%Se) and underwent a 45-day postannealed at 773 K. Temperature-dependent f) $zT$ curves, g) Seebeck coefficient ($S(T)$) curves, h) electrical resistivity ($\rho(T)$) curves, i) thermal conductivity ($\kappa(T)$) curves, and j) lattice thermal conductivity ($\kappa_L(T)$). Adapted with permission.[28] Copyright 2017, Elsevier.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords

figure-of-merit, phase diagram engineering, TE generators, TE refrigerator, thermoelectric materials

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[1] E. S. Toberer, G. J. Snyder, Nature 2008, 7, 105.
[2] F. J. DiSalvo, Science 1999, 285, 703.
[3] L. E. Bell, Science 2008, 321, 1457.
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