High thermoelectric performance of Bi-Te alloy: Defect engineering strategy

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A B S T R A C T

Waste-to-energy conversion generally means incineration, and the combustion of organic waste material for energy recovery involves generation of carbon dioxide. In contrast, thermoelectric energy conversion from waste heat is another way of green energy harvesting without generating pollution. Heat sources around room temperature are omnipresent in portable electronics and home appliances. The Bi-Te alloy system has been known to produce relatively high thermoelectric performance around room temperature. Here, we review the current state-of-the-art defect engineering strategies for Bi-Te alloy systems used to achieve high thermoelectric figure of merit performance. These include alloying effects, grain refinement, and nanocomposites; when used together they are commonly referred to as an all-scale hierarchical architecture. The alloying effect generates point impurities in the host matrix, grain refinement creates a large density of grain boundaries, while nanocomposites create a large amount of new interfaces. Inclusion of such effects significantly reduces the lattice thermal conductivity by enhanced phonon scattering at point defects, interfaces, and grain boundaries. Nonetheless, these types of defects scatter only low or high frequency phonons. Research on scattering of mid-range frequency phonons has rarely been reported. We propose an approach of plastic deformation that generates dislocations, which scatters mid-range frequency phonons. A material engineered using an all-scale hierarchical architecture with plastic deformation is able to scatter full spectrum phonons.

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1. Introduction

The expected depletion of fossil fuels and their production of carbon dioxide raise questions about the ability of current technologies to sustain energy and electricity production. This problem applies to nuclear technologies as well given the recent Fukushima accident. Energy harvesting from non-polluting natural resources has been investigated for decades. For example, hydraulic power plants, solar energy, wind, and earth heat are good examples of green energy harvesting. While these have been intensively investigated and partially utilized, the cost of implementing such systems and their low conversion efficiency still delay their full-scale realization in modern society. On the other hand, reusing waste is another key topic in energy harvesting. Waste-to-energy conversion generally refers to incineration. However, the combustion of organic waste materials for energy recovery again involves significant generation of carbon dioxide.

Thermoelectric energy conversion from waste heat is another way of green energy harvesting without producing undesirable by-products. Thermoelectric (TE) materials could be used to realize solid-state devices for power generator that are soundless and scalable, making them ideal for small-scale portable electronics and large-scale plant technology [1,2]. In addition, TE Peltier devices could replace mechanical compression-based refrigeration and fossil fuel-based heating systems, which are localized cooling and heating systems [3,4].

The established state-of-the-art bulk materials that have high thermoelectric (TE) performance are summarized in Fig. 1a, b. The performance of TE materials is evaluated using a dimensionless figure of merit $zT = \frac{\alpha^2 s}{k}$. Here $\alpha$, $s$, $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively, which are explained in detail below in the theory section. For near room temperature applications (room temperature to 200 °C), Bi$_2$Te$_3$ and Sb$_2$Te$_3$ alloys are typically used due to their higher figure of merit for n- and p-type TE systems.
respectively. To enhance the TE performance, the n-type Bi$_2$Te$_3$ is alloyed with Se to Bi$_{0.5}$Te$_{0.5}$Se$_{0.5}$, the p-type Sb$_2$Te$_3$ is alloyed with Bi to Bi$_{1-x}$Sb$_x$Te$_3$; these are commonly referred to as Bi-Te alloy systems. For mid-temperature applications (200–700 °C), CoSb$_3$ has been shown to possess high figure of merit for n-type TE materials [2], and (GeTe)$_2$(AgSbTe$_2$)$_y$ alloy (TAGS) demonstrates good performance in p-type TE materials [5]. On the other hand, PbTe is used for both n- and p-type TE materials [6]. SiGe alloys are typically used in high-temperature (>700 °C) applications for both n- and p-type TE materials [7]. In addition, Yb$_{14}$MnSb$_{11}$ has been used in p-type TE materials because it has the highest TE performance at high temperature [8].

Among various TE materials, low temperature operating materials have attracted much interest recently due to the possibility of using them in real life environments. Relatively low temperature (RT-200 °C) waste heat from homes, building heating, home appliances, and portable electronics could be converted to electricity by using TE devices [5]. In the last two decades, CsBi$_4$Te$_6$ (zT = 0.62 at RT) [9], Ca$_2$CoO$_{3.34}$CoO$_2$ (zT = 0.035 at RT) [10] and Ba$_8$Ga$_{16}$Sn$_{30-x-y}$Sb$_y$ (BGSS, zT$_p$ = 1.0, zT$_n$ = 0.9 at near 175 °C) [11] TE materials have been reported for low temperature TE applications. Moreover, a maximum zT of 1.1 is achieved near RT in Bi$_{0.5}$Sb$_{1.5}$Te$_3$ p-type TE materials [12], and n-type Bi$_2$Te$_2$Se$_3$ had a zT of 1.04 at 125 °C [13]. The Bi-Te alloy materials have been considered to be by far the most suitable materials for power generators or cooling devices at near room temperature [1,2,13,14].

Most bismuth chalcogenide compounds have an unusual layer structure, including Bi$_2$Te$_3$, Bi$_2$Se$_3$, and their alloy systems [15]. In the case of Bi$_2$Te$_3$, they have various types of binding characteristics including covalent bonding, ionic bonding, and van der Waals interactions. Their various characteristics result in anisotropic electrical and thermal properties. Bi$_2$Te$_3$ has two bonding types: a covalent–ionic type in a quintuple layer (Te$^{4+}$-Bi–Te$^{4+}$-Bi–Te$^{4+}$) and van der Waals interactions between two Te$^{4+}$-Te$^{4+}$ layers of two different quintuple layers [16]. Due to the structural anisotropy, the thermal conductivity in the ab-plane is higher than that in the c-axis (the ab-plane is perpendicular to the c-axis). Phonon propagation is impeded due to weak van der Waals interactions between two different quintuple layers, so that the thermal conductivity is greatly reduced. In contrast, the Seebeck coefficient is nearly isotropic [16].

Two general strategies have been suggested for enhancing TE performance: alloying effect and grain refinement. The alloying effect generates point impurities in a host matrix, and grain refinement creates a large density of grain boundaries. The point impurities and grain boundaries significantly reduce the lattice thermal conductivity (zT ∝ 1/k), resulting in an enhanced zT [14,17,18]. Recently, a nanostructured approach was reported that can strongly enhance the zT by addition of nanometer scale inclusions. SrTe nanocrystals (inclusions) improve the phonon scattering in the Na-doped PbTe matrix, and the zT reaches 1.7 at 540 °C [19]. Since then, the development of nanocomposites in TE materials has opened up new avenues of research for high TE performance. A nanocomposite strategy has been suggested to maximize zT with typical strategies including the alloying effect and grain refinement; this strategy is referred to as the all-scale hierarchical architecture [20].

The concept of the Bi-Te alloy based nanocomposites has been adopted for TE systems to enhance the TE properties in recent years. As mentioned before, the n-type Bi$_2$Te$_3$, Se$_x$ and p-type Bi$_{1-x}$Sb$_x$Te$_3$ are known to be the best materials due to alloying effects (a Bi-Te system can easily form alloys with Sb or Se elements) and structural anisotropy [21]. The alloy based nanocomposite system also includes grain refinement effects because of the dispersion of nano inclusions induced by ball milling or the chemical growth process. These methods are explained in detail in the methods section. Thus, the nanocomposite system in TE materials has an all-scale (atomic, nano, meso) hierarchical architecture [20].

In this review, we summarize the reported results related to the improvement in zT in Bi-Te alloy systems by nanocomposite. We focus on ex-situ nanoinclusion composites only, because in-situ nanocomposites cannot be unambiguously compared with doping and alloy effects. Tables 1 and 2 provide summaries of the n-type and p-type Bi-Te alloy nanocomposites, respectively, and these tables list the materials involved, processing details, electrical properties (carrier concentration, mobility, and resistivity), thermal properties, and the maximum figure of merit (zT). We propose that plastic deformation that has been introduced to improve mechanical strength by accumulating dislocations in the matrix can also be applied to improve TE properties. Finally, perspectives on Bi-Te systems are also discussed.

2. Theory

The performance of TE materials is evaluated using a dimensionless figure of merit (zT) that incorporates the Seebeck coefficient (α), electrical conductivity (σ), thermal conductivity (κ), and absolute temperature (T), as expressed in Eqn. (1) [1,2,22].

\[ zT = \frac{\alpha^2 \sigma}{\kappa} T \]  

(1)
<table>
<thead>
<tr>
<th>Inclusion</th>
<th>Ref. No.</th>
<th>Matrix</th>
<th>Process</th>
<th>Concentration</th>
<th>Carrier density ($10^{19}$/cm$^3$)</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>Seebeck coefficient ($\mu$V/K)</th>
<th>Resistivity ($\Omega$m)</th>
<th>Thermal conductivity (W/mK)</th>
<th>Max. $zT$</th>
<th>Max. $zT$ temp. (K)</th>
<th>Improvement of $zT$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>CNT 44</td>
<td>Bi$_2$Te$_3$</td>
<td>CR, SPS</td>
<td>Raw</td>
<td>8.1</td>
<td>250</td>
<td>-298</td>
<td>8.8</td>
<td>0.00</td>
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<td>473</td>
<td>55.22</td>
</tr>
<tr>
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<td>Ref. No.</td>
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<td>0.75</td>
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<td>-121</td>
<td>12.9</td>
<td>0.67</td>
<td>0.80</td>
<td>473</td>
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<td>-105</td>
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<td>MA, BM, HP</td>
<td>Raw</td>
<td>0.3 vol%</td>
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<td>3400</td>
<td>-127</td>
<td>14.8</td>
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<td>473</td>
<td>11.46</td>
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<tr>
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<td>1.07</td>
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<td>Melt, Mix, HP</td>
<td>Raw</td>
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<td>80.4</td>
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<td>1.00</td>
<td>0.56</td>
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<td>79.15</td>
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<td>0.9</td>
<td>0.09</td>
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<td>Raw</td>
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<td>ZM, BM, SPS</td>
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<td>0.1 vol%</td>
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<td>ZnO:Al 50 Bi$_2$Te$<em>2.7$Se$</em>{0.3}$</td>
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<td>0.9</td>
<td>0.85</td>
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<table>
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<th>Inclusion</th>
<th>Ref. No.</th>
<th>Matrix</th>
<th>Process</th>
<th>Concentration</th>
<th>Carrier density (*10^19/cm^3)</th>
<th>Mobility (cm^2/Vs)</th>
<th>Seebeck coefficient (μV/K)</th>
<th>Resistivity (μΩm)</th>
<th>Thermal conductivity (W/mK)</th>
<th>Max. zT</th>
<th>Max. zT temp. (K)</th>
<th>Improvement of zT (%)</th>
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<td>12</td>
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<td>181</td>
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<td>18.6</td>
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<td>24.6</td>
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<td>Bi_0.5Sb_1.5Te_3</td>
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<td>1 vol%</td>
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<td>0.78</td>
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<tr>
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<td>184</td>
<td>6.3</td>
<td>1.52</td>
<td>1.27</td>
<td>360</td>
<td>7.81</td>
</tr>
</tbody>
</table>

* MW: Micro-Wave treatment, γRI: γ-ray Irradiation.
For maximizing TE performance, a high voltage output (high Seebeck coefficient), a low electrical loss (low resistivity, high electrical conductivity), and a large thermal gradient between the hot and cold side (low thermal conductivity) are essential [23,24]. The Seebeck coefficient and electrical conductivity are related to the carrier concentration. The Seebeck coefficient ($\alpha$) is given by Eqn. (2),

$$\alpha = \frac{8n^2k_B^2\pi}{3e\hbar^2} \frac{x^0}{T} \left( \frac{\pi}{3n} \right)^{\frac{1}{2}}$$

where $k_B$ is the Boltzmann constant, $h$ is Planck's constant, $m^*$ is the effective mass of the carrier, and $n$ is the carrier concentration. The electrical conductivity ($\sigma$) can be expressed by Eqn. (3),

$$\sigma = ne\mu$$

where $\mu$ is the carrier mobility and $e$ is the charge of an electron. Low carrier concentration simultaneously leads to a large Seebeck coefficient (Eqn. (2)) and low electrical conductivity (Eqn. (3)). This trade-off seems to be unavoidable if one modifies the carrier concentration. Fig. 1c shows the compromise between the Seebeck coefficient and electrical conductivity with carrier concentration. Maximizing the figure of merit $zT$ requires a compromise between the Seebeck coefficient and the electrical conductivity by carefully controlling carrier concentration. The optimized carrier concentration range is between 10$^{10}$ and 10$^{20}$ cm$^{-3}$, which is typical for heavily doped semiconductors [2]. By substituting Eqns. (2) and (3) into Eqn. (1), the figure of merit shows the following relationship: $zT \sim n^{-1/3} \mu$. This strongly suggests that it is desirable to increase carrier mobility instead of engineering the carrier concentration, which involves the aforementioned trade-off. In fact, at high carrier concentration, carrier-carrier scattering comes into play, thus reducing mobility. High crystal quality is required to give high mobility. Nevertheless, the thermal conductivity should be high for high quality crystals, which again reduces the figure of merit.

3. Lattice thermal conductivity

Thermal conductivity ($\kappa_T$) is determined by two sources, carriers transporting heat (carrier thermal conductivity, $\kappa_c$) based on drift and phonons travelling through the lattice (lattice thermal conductivity, $\kappa_L$), as shown in Eqn. (4).

$$\kappa_T = \kappa_c + \kappa_L$$

The carrier thermal conductivity is directly proportional to the electrical conductivity according to the Wiedemann–Franz Law, as can be seen in Eqn. (5).

$$\kappa_c = L_\text{G}T = ne\mu LT$$

where $L$ is the Lorenz number. The lattice thermal conductivity is independent of the electrical conductivity. In semiconductors, lattice thermal conductivity dominates the total thermal conductivity. Hence, selectively reducing the lattice thermal conductivity will effectively enhance $zT$ [2].

The lattice thermal conductivity is explained using Callaway's model (Eqn. (6)) [25],

$$\kappa_L = \frac{k_B}{2\pi^2\nu} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{\theta/T} \frac{\tau_C(x)}{(e^x - 1)^2} \, dx$$

where $\nu$ is the phonon-group velocity, $\theta$ is the Debye temperature, $x = \hbar\theta/k_BT$, and $\tau_C$ is the combined relaxation time. $\tau_C$ has two main terms including acoustic phonon dispersion branch (resistive scattering process, $\tau_R$) and independent scattering process (normal process, $\tau_N$). However, a large amount of defects exist in polycrystal (real sample), thus resistive process becomes dominant ($\tau_R \approx \tau_N$) [26,27]. $\tau_R$ is a reciprocal sum of all resistive scattering process, as shown in Eqn. (7),

$$\tau_R^{-1} = \tau_D^{-1} + \tau_B^{-1} + \tau_S^{-1} + \tau_D^{-1} + \tau_F^{-1} + \tau_B^{-1}.$$

Here, $\tau_D$, $\tau_B$, $\tau_S$, $\tau_D$, $\tau_B$, $\tau_B$ are the relaxation times that correspond to scattering from Umklapp processes, point defects, boundaries, strains, dislocations, particles (precipitates), and bipolarons, respectively. To reduce the lattice thermal conductivity, it is necessary to control the scattering mechanisms by tuning the phonon relaxation time.

Three defect engineering strategies have been suggested for reducing lattice thermal conductivity [22,25], as shown in Fig. 2a–c. The alloying effect at the atomic scale is related to the point impurities (Fig. 2a). The relaxation time associated with point impurities is given by Eqn. (8) [27],

$$\tau_{PD}^{-1} = \frac{G}{4\pi^3\nu^4}.$$  

Here, $\Omega_0$ is the unit cell volume, and $\nu$ is the phonon angular frequency. $I$ is the phonon scattering parameter, which depends on the two main parameters. One is the mass difference between impurity atom (guest) and matrix atom (host), $I = \Sigma\{1 - M/M_{av}\}$. Another is the radii difference (elastic strain filed) between impurity atom and matrix atom, $I = \Sigma f_i(1 - M/M_{av})^2$. Here $f_i$ is the fractional concentration of impurity atom, $M_i$ is the atomic mass of impurity, $M_{av}$ is the average atomic mass, $\gamma$ is the average anharmonicity of the bonds, $R_i$ is the atomic radius of impurity, $R_{av}$ is the average atomic radius [26]. The point defects effectively scatter high frequency phonons (short wavelength) [3]. For example, the Bi-Te based alloys, such as n-type Bi$_2$Te$_3$, $\text{Se Mexicans}$, and p-type Bi$_2$Sb$_2$Te$_3$ are known to be the best materials among those used around room temperature [21].

Another defect engineering strategy is the nanocomposite approach (Fig. 2b). Phonon scattering occurs for nanometer-scale particles. The relaxation time associated with particles is given by Eqn. (9) [28,29],

$$\tau_p^{-1} = \frac{\sigma_c^{-1} + \sigma_i^{-1}}{V_p}.$$  

where $\sigma_c = 2\pi R^2$, $\sigma_i = \pi R^2/8(\Delta D/\Delta D')^2(nR/b)^4$, $R$ is the particle average radius, $\Delta D$ is the density difference between the particle and matrix, $D$ is the matrix density, and $V_p$ is the volume fraction of the nanoparticles. The density, size, and volume fraction of inclusions affect the phonon scattering. The nano-SiC powder dispersed into Bi$_2$Te$_3$ reduced the lattice thermal conductivity [30]. Other nanocomposites, such as ZrO$_2$ in CoSb$_3$ [31], TiO$_2$ in skutterudite [32] and core shell structures of PbTe@PbS [33], have also shown the capability of enhancing phonon scattering by nanoparticles.

Grain refinement at the meso-scale is related to the phonon scattering by grain boundaries (Fig. 2c). The relaxation time associated with the boundary scattering is given by Eqn. (10) [18],

$$\tau_B^{-1} = \frac{\nu}{d}.$$  

where $d$ is the grain size. The grain boundary effectively scatters the low frequency phonons (long wavelength) [11]. Grain refinement generates numerous boundaries, which leads to the strong scattering of phonons due to the lattice mismatch. Grain refinement...
has been realized by ball milling (fracture and micro-rolling) [14] and melt spinning (limited crystal growth by rapid quenching) [34].

However, these three kinds of strategies to reduce only the lattice thermal conductivity affect not only electrical conductivity but also the Seebeck coefficient due to carrier scattering at defect sites such as point defects, interfaces between inclusions and the matrix, and grain boundaries. Moreover, the carrier concentration, effective mass, and density of states are modified [1,3,14,35]. Therefore, enhancing TE properties requires appropriate strategies that take into account the matrix and inclusions.

4. Method

In ex-situ nanocomposites, a homogenous dispersion of nano-inclusions in the matrix is a key factor for effectively improving the thermoelectric properties because nanoparticles tend to agglomerate due to high surface energy. The non-uniform dispersion causes imbalanced characteristics [36–38]. To obtain a uniform dispersion, nanocomposites are fabricated by solid or liquid dispersion processes.

4.1. Solid process

In solid processes, the solid state matrices (Bi-Te alloys) and inclusions are mechanically mixed together. The matrices are synthesized separately by melting processes or mechanical alloying. Stoichiometric amounts of Bi, Te and Sb or Se granules are placed in a quartz tube and are vacuum sealed. The mixture is homogeneously mixed and melted in a furnace and slowly cooled. The cooled ingot of Bi-Te alloy is crushed into a powder for effective mixing with nano-inclusions [23]. In contrast, a mechanical alloying process is performed using high energy ball milling with a Spex mill [37,38]. A schematic illustration of the solid process, which includes the mechanical alloying process of the matrix and the mixing process of matrix-nano-inclusions. During ball milling, high energy impacts increase the defect density in the nano-inclusions as well as the matrix [36,39,40]. If the electrical properties of the inclusions depend on the intrinsic geometry structure or size (C60, CNT, nanowires, etc.), then their properties might change during the dispersion process.

4.2. Liquid processing

Liquid processing is based on a wet chemical reaction, and it can improve the dispersion of nano-inclusions in a matrix compared with solid processing. The Bi-Te alloy can be directly precipitated and grown on the surface of nano-inclusions which act as growth templates. Molecular level mixing is achieved using a liquid state and grown on the surface of nanoinclusions which act as growth templates. Molecular level mixing is achieved using a liquid state.

Finally, the mixture powder is consolidated (by solid or liquid processes) using spark plasma sintering equipment or a hot press machine under non-oxidation conditions.
5. Bi-Te alloy with nanoinclusions

5.1. n-type Bi-Te alloy nanocomposites

The n-type nanocomposites typically have a Bi$_2$Te$_3$ [24,30,37,38,41,44,47,48] or Bi$_2$Te$_{3-x}$Se$_x$ alloy matrix [21,44–46,49,50] with nanoinclusions made mostly of carbon materials (CNT [37,38,44,45] or graphene [41]), metals (Cu [21,46], Ag [24]) or other compounds (SiC [30,47], Bi$_2$Se$_3$ [48], Al$_2$O$_3$ [49], ZnO:Al [50]). These nanocomposite systems lead to improved TE properties (Table 1). A major improvement is the reduction in the lattice thermal conductivity, which is attributed to the enhancement of phonon scattering at the many interfaces that newly form by an addition of the nanometer-size inclusions. Fig. 4a shows a schematic illustration of the phonon scattering mechanism. The point impurity and nano-scale inclusion effectively scatter high frequency phonons. Moreover, the grain boundaries effectively scatter low frequency phonons [1].

The ex-situ composite system forms incoherent interfaces due to the lattice mismatch between the matrix and inclusions. The incoherent interface deteriorates the phonon propagation more severely than the coherent interface (in-situ precipitation), which effectively reduces the lattice thermal conductivity [51]. As a result, the lattice thermal conductivity significantly changes from 0.66 to 0.23 W/mK with Ag nanoinclusions [24], and from 0.68 to 0.48 W/mK with Al$_2$O$_3$ inclusions [49] due to interface scattering. The addition of CNTs in the Bi$_2$Te$_3$ matrix reduces the lattice thermal conductivity from 0.21 to 0.14 W/mK [44]. In addition, by changing the matrix from Bi$_2$Te$_3$ to Bi-Te-Se, the lattice thermal conductivity is reduced more drastically to 0.1 W/mK. This observation is ascribed to the combination of the alloying effect and nano-composite approach. Point defects and nanometer-scale particles affect the phonon relaxation time, thus the lattice thermal conductivity is effectively reduced. Nevertheless, the maximum $zT$ of
Bi$_2$Te$_3$, Bi$_2$Te$_3$-CNT, and (Bi-Te-Se)-CNT composite systems are still low, 0.52, 0.8, and 0.9, respectively [44].

The interface between the matrix and inclusions change both phonon propagation and carrier mobility, which result in changes in the electrical conductivity and Seebeck coefficient. The newly formed interface cause a reduction in the carrier mobility due to the carrier scattering, which slightly reduces the electrical conductivity [21, 30, 38, 41, 44, 47, 48, 50]. The p-type carriers stemming from CNTs offset the concentration of n-type carriers in the Bi$_2$Te$_3$ matrix [44], thereby increasing the Seebeck coefficient (Eqn. (2)). Moreover, the interface between metal inclusions and the semiconductor matrix generate an energy filtering effect in the metal nanoinclusions [21,24,46]. Metal/semiconductor interfaces lead to band-bending as indicated in the interface potential: $V_B = \Phi_i - \chi + E_F$. Here, $\Phi_i$ is the inclusion work function, $\chi$ is electron affinity, and $E_F$ is the Fermi energy. This interface potential generates a new carrier scattering mechanism, which affects the relaxation times of the carriers. The total relaxation time of a carrier $\tau_{\text{total}}$ is given by Eqn. (11) [52],

$$\tau_{\text{total}}^{-1} = \tau_{\text{bulk}}^{-1} + \tau_i^{-1}$$ (11)

where $\tau_{\text{bulk}}$ is the relaxation time in the bulk, and $\tau_i$ is the relaxation time associated with the inclusion (interface potential). Low energy carriers selectively impede the interface potential because $\tau_i$ is energy dependent: on the other hand, carriers with high energy are unaffected. This behavior is referred to as the energy filtering effect [46,52], as can be seen in Fig. 4b. Therefore, the high energy carriers only participate in transport due to the selective repression of the low energy carriers, so that the average carrier energy increases, resulting in the enhanced Seebeck coefficient. Moreover, the carrier thermal conductivity ($\kappa$) is also reduced in heavily doped semiconductors by the same mechanism [52]. The maximum $zT$ of Bi$_2$Te$_2$Se$_0.3$ with Cu nanoinclusions is improved from 0.56 to 0.98 due to the enhanced Seebeck coefficient and reduced thermal conductivity [46]. In the Bi$_2$Te$_3$-Ag composite case, the metal inclusion provides carriers into the matrix, leading to an increase in the carrier concentration. Although the Seebeck coefficient may increase due to the energy filtering effect, the total Seebeck coefficient decreases due to a high carrier concentration. Nevertheless, the maximum $zT$ is improved from 0.23 to 0.77 by the increased electrical conductivity with reduced lattice thermal conductivity [24].

Another behavior similar to the energy filtering effect (called the potential barrier effect) occurs at the interface between non-metallic inclusions and a semiconductor matrix [49,53]. If the Fermi level at the interface between the matrix and inclusion is higher than the grain inside, a potential barrier is generated. While carriers pass through the interface, low energy carriers are scattered or filtered. This behavior also occurs at the grain boundary [53]. The introduction of the $\gamma$-Al$_2$O$_3$ nanoparticles in the Bi$_2$Se$_0.3$Te$_2$ matrix generates a potential barrier at interface, leading to an increased potential barrier height, so that the Seebeck coefficient is enhanced by scattering the low energy carriers. As a result, the maximum $zT$ is increased from 0.73 to 0.99. This improvement also includes a reduction in thermal conductivity by interface scattering [49].

In graphene inclusions, the graphene acts as a growth template for Bi$_2$Te$_3$ grains in a liquid process. A number of nucleation sites are generated during hydrothermal processing, which reduce the crystal size and consequently reduce the lattice thermal conductivity. As a result, the maximum $zT$ is improved from 0.15 to 0.21 [41]. A comparison of the maximum $zT$ values from nanocomposites and raw materials are shown in Fig. 5a, and the individual maximum $zT$ and the rate of improvement are summarized in Table 1. The improvements of Ref. [24] and Ref. [37] after adding nanoinclusions are over 200%. The noticeable improvements are related to the fabrication method. However, the maximum $zT$ values of the composites are too low, 0.77 [24] and 0.14 [37], which are not satisfactory results. As mentioned above, liquid state processing can lead to a lower $zT$ due to the remaining residual and low temperature growth. The maximum $zT$ values of the matrix without inclusions are 0.23 [24] and 0.04 [37], respectively.

In addition, the Vickers hardness and Young’s modulus are improved from 0.62 to 0.79 GPa with 1.0 vol% SiC and from 32.8 to 42.7 GPa for the sample with 0.5 vol% SiC nanoinclusions, respectively, due to high intrinsic mechanical properties of SiC [30]. The improvement of mechanical properties by nanoinclusions already studied is ascribed to dispersion hardening. Nanoinclusions with high intrinsic mechanical properties prevent the movement of plastic deformation, consequently improving the hardness and Young’s modulus by generating back stress [54,55].

5.2. p-type Bi-Te alloy nanocomposites

The p-type nanocomposites are based on a Bi$_2$-Sb$_2$Te$_3$ alloy matrix with nanoinclusions which consist of various carbon materials (C$_{60}$ [39,40], CNT [36] graphene [42,56]), metals (Cu [23,57], Au [43] metalloids (Si [58]) and other compounds (SiC [59,60], ZnSb$_3$ [61], ZnAlO [62], Al$_2$O$_3$ [63], WS$_2$ [64], Si$_3$N$_4$ [65]). These nanocomposites also improve TE properties (Table 2, Fig. 5b) due to the reduced thermal conductivity or enhanced electrical conductivity.

The high energy ball milling process transforms C$_{60}$ to a layered-type structure on the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ matrix particle surface. The nanocrystalline matrix is covered with a layer of C$_{60}$. This specific structure prevents recrystallization and grain growth during high temperature processing such as sintering and subsequent annealing. This phenomenon leads to enhanced phonon scattering at the grain boundaries with newly formed interfaces, so that thermal conductivity decreases and the maximum $zT$ increases from 0.86 to 1.15 [39]. Addition of graphene and CNTs induce similar behavior for the C$_{60}$ inclusions. Graphene acts as a growth site, which provides the grain refinement effect. Although the Seebeck coefficient decreases due to the intrinsic properties of graphene (high carrier concentration, $n = 6.00-14.5 \times 10^{19}$/cm$^3$ [66]), the maximum $zT$ values are improved from 0.77 to 1.13 [42] and 1.15–1.40 [56] due to decreased thermal conductivity. In the Bi$_2$Te$_3$-Ag composite case, the metal inclusion significantly reduces lattice thermal conductivity from 0.59 to 0.33 W/mK while reducing the carrier thermal conductivity from 0.40 to 0.35 W/mK, so that the maximum $zT$ is changed from 1.03 to 1.47 [36]. SiC nanoinclusions also slightly enhance the $zT$ value by reducing the thermal conductivity due to phonon scattering at interfaces [59,60].

In Bi$_2$Sb$_{1.5}$Te$_3$-Cu composites, the effect of improved electrical conductivity dominates the enhancement of $zT$ from 0.86 to 1.1 due to the doping effect by Cu particles [57]. Likewise, the inclusions affect carrier transport. A potential barrier effect also occurs in p-type nanocomposites. SiC nanoinclusions increase the Seebeck coefficient by the potential barrier effect [58]. The large amount of new interfaces between Si and the matrix decrease the thermal conductivity. As a consequence, a maximum $zT$ of 1.32 is achieved [58]. The maximum $zT$ of Bi$_2$Sb$_{1.5}$Te$_3$ with Al$_2$O$_3$ is 1.5 ($zT_{\text{max}} = 0.95$) due to a similar mechanism [63].

In contrast, tuning the carrier concentration in defects is considered in p-type Bi-Te alloy systems. In the defect region, the Bi could replace Te (commonly referred to as a Bi anti-site), or Sb could replace Te (Sb anti-site). This region is slightly Bi or Sb rich [67]. Furthermore, inside the grain, the Bi vacancy and Te anti-site (Te replaced Bi) exist. The Bi or Sb anti-sites create a hole carrier
[68], and a Bi vacancy creates three holes [67]. On the other hand, the Te anti-site creates an electron [69]. Therefore, increasing hole concentration is probabilistically dominant in Bi-Te alloy system. The carrier concentration tuning is realized by the point defect engineering which is performed by alloy strategy (control of alloy concentration) [70] or hot deformation strategy (control of micro-structure) [71] in Bi-Te based alloys system. In addition, the carrier concentration is tuned by addition of nanoinclusion. Increasing carrier concentration by addition of a ZnAlO nanoinclusion leads to a decrease in resistivity from 10.6 to 5.1 μΩm, which improves the maximum \( zT \) from 0.98 to 1.33 [62].

The nanoinclusions are able to decompose and diffuse in the matrix. Some elements replace Bi, Sb, Te or form a second phase in ex-situ composites [43,64]. Formation of the second phase generates the interfaces and defects. For example, some of the added Au inclusions react with a Bi_{0.4}Sb_{1.6}Te_3 matrix forming the AuTe_2 phase during the high temperature process, which modify the carrier concentration [43]. When WSe_2 is introduced into the Bi_{0.4}Sb_{1.6}Te_3 alloy system, the W reacts with the Te and also replaces Sb or Bi, which allow for tuning the carrier concentration [64]. Although the Seebeck coefficient decreases due to the increased carrier concentration, the increase in electrical conductivity and decrease in thermal conductivity are dominant. The Bi_{0.4}Sb_{1.6}Te_3-Au composite achieves a maximum \( zT \) of 1.01 from 0.85 [43]. The lattice thermal conductivity also decreases from 0.9 to 0.75 W/mK with WSe_2 nanoinclinations, and the maximum \( zT \) is improved from 1.05 to 1.27 [64].

In Bi_{0.5}Sb_{1.5}Te_3-Zn_{0.4}Sb_{3} composites, some Zn replace Bi or Sb in the boundary regime, resulting in an increase in the hole concentration. A p-type Zn_{0.4}Sb_{3} inclusion forms a p-p-type heterojunction at the interface, which further increases carrier concentration. As a result, the electrical conductivity significantly increases, and the maximum \( zT \) also increases from 0.2 to 0.6, which is also due to the reduced lattice thermal conductivity (from 1.55 to 0.77 W/mK) [61]. The individual maximum \( zT \) values and the rate of improvement are summarized in Table 2. A comparison of maximum \( zT \) values for the nanocomposites and raw materials is provided in Fig. 5b. The improvement observed in Ref. 61 is over 200%. However, the maximum \( zT \) value is 0.6. Even when solid state processing (melting and ball milling) is used, the maximum \( zT \) of the matrix without any inclusions is only 0.2.

6. Discussion

For comparing trends, the abnormal improvements in \( zT \) from Refs. [24,37,61] and \( zT \) values that are too low [41] are filtered out. The \( zT \) of the raw materials without nanoinclinations are under 0.25, making them too low to be compared with other materials (n-type
raw $zT = 0.5-0.99$, $p$-type raw $zT = 0.77-1.28$). Reasonable data ranges of $n$- and $p$-type Bi-Te alloy nanocomposites are indicated in the blue box in Fig. 5c and the orange box in Fig. 5d, respectively. The $n$-type Bi-Te alloy nanocomposites show higher improvements (5–79%) compared with $p$-type Bi-Te alloy nanocomposites (8–56%). The maximum $zT$ values of $n$-type Bi-Te alloy nanocomposites are generally below 1 ($zT = 0.66-1.04$). These $zT$ performances are not satisfactory results compared with the $p$-type Bi-Te alloy nanocomposites ($zT = 0.97-1.50$). This behavior is caused by an intrinsically low $zT$ matrix of Bi$_2$Te$_3$ and Bi$_2$Te$_3$S$_x$Se$_{1-x}$ alloy systems that do not have nanoinclusions.

In the $n$- and $p$-type Bi-Te alloy nanocomposites, different factors are responsible for the improvement in TE performance. The $zT$ values are clearly enhanced in both $n$- and $p$-type Bi-Te alloy nanocomposites. The major determining factor is the thermal conductivity. Introduction of nanoinclusions result in a large quantity of interfaces, which enhance the phonon scattering. Moreover, solid processing and liquid processing to obtain a uniform dispersion of nanoinclusions effectively reduce the grain size, generating grain boundaries. Some inclusions prevent recrystallization and grain growth [39,40,56]. These types of grain refinement also enhance phonon scattering at the grain boundary. The alloy (guest) elements provide point impurities in the Bi-Te (host) matrix, which also change the relaxation time of the phonons. These three strategies effectively reduce the lattice thermal conductivity.

Addition of nanoinclusions affects the phonon propagation and carrier mobility. The interface between the inclusion and semiconductor matrix create a potential barrier due to differences in intrinsic properties such as work function, electron affinity, and Fermi energy. This phenomenon results in selective scattering of low energy carriers. Therefore, the average carrier energy increases and, as a result, the Seebeck coefficient increases (energy filtering effect, potential barrier effect) [52]. The carrier concentration is also influenced by the inclusions. In the $n$-type Bi-Te matrix, a $p$-type inclusion offset the carrier, resulting in a decrease in carrier concentration [44]. In contrast, $p$-type inclusions generate a $p$-$p$-type heterojunction, which increase carrier concentration [61]. The intrinsic high carrier concentration of inclusions increases the carrier concentration in the matrix [42,56]. The carrier concentration is also related to defects in the Bi-Te alloy matrix. Defects such as boundaries, interfaces, and the formation of a second phase lead to a stoichiometric imbalance, often creating anti-sites and vacancies. This behavior change the carrier concentration, typically increasing hole carriers. In a $p$-type Bi-Te matrix, the electrical conductivity is significantly increased due to increasing carrier concentration. However, this phenomenon also causes a decrease in the Seebeck coefficient. Thus, the strategy to control the carrier concentration by defects operates more effectively in the $p$-type Bi-Te matrix. In contrast, the strategy employing energy filtration or the potential barrier effect for increasing the Seebeck coefficient operate more effectively in the $n$-type Bi-Te matrix.

7. Conclusions

The Bi$_2$Te$_3$ materials have good TE performance ($zT$) at near room temperature. A high Seebeck coefficient, high electrical conductivity and low thermal conductivity are necessary for enhancement of TE performance in Bi-Te. Among these, reducing the lattice thermal conductivity effectively leads to an enhancement of $zT$ because the lattice thermal conductivity is independent of the electrical conductivity. The all-scale hierarchical architecture strategy that includes the alloying effect, grain refinement, and nanocomposites is proposed to decrease the lattice thermal conductivity. This strategy is realized by uniformly dispersing nano-inclusions in the Bi-Te alloy. Introduction of nano-inclusions in the Bi-Te alloy matrix creates a large density of interfaces, which effectively enhance phonon scattering and improved $zT$. Furthermore, the interaction between the matrix and inclusion increases the Seebeck coefficient in an $n$-type Bi-Te matrix by energy filtering and potential barrier effects. In contrast, tuning the carrier concentration by control of defects effectively improves electrical conductivity in the $p$-type Bi-Te matrix. While the Bi-Te alloy nanocomposite strategy successfully increases $zT$, the absolute value of $zT$ is still far less than the desired one. A strategic plan is essential for further improvement.

8. New direction: defect engineering strategy

The aforementioned all-scale hierarchical architecture strategy improves the TE properties because it effectively reduces the lattice thermal conductivity. However, the point defect, grain boundary, and nano-scale inclusions can scatter only the high or low frequency phonons. Thus, to more effectively reduce the lattice thermal conductivity, mid-frequency phonon scattering is necessary. The mid-frequency phonons are effectively scattered at dislocations [1]. Three main types of dislocations scatter phonons: core and screw and edge dislocations. The relaxation time associated with dislocations is given by Eqn. (12) [72],

$$\tau_D^{-1} = \tau_D^{1}_{\text{core}} + \tau_D^{1}_{\text{screw}} + \tau_D^{1}_{\text{edge}}$$

Here, the relaxation time associated with core dislocations ($\tau_D^{1}_{\text{core}}$) is given by Eqn. (13) [11], and the screw dislocation time ($\tau_D^{1}_{\text{screw}}$) is given by Eqn. (14) [72]. The edge dislocation $\tau_D^{1}_{\text{edge}}$ is given by the same expression as $\tau_D^{1}_{\text{screw}}$, but with a different Burgers vector,

$$\tau_D^{1}_{\text{core}} = ND_D\frac{\nabla^4}{p^2}\omega^3$$

$$\tau_D^{1}_{\text{screw}} = 0.06Nb^2\gamma^2\omega$$

Here, $N_D$ is the dislocation density, $\nabla$ is the average atomic volume of the matrix, $b$ is the magnitude of the Burgers vector, and $\gamma$ is the Grüneisen parameter. An increase in dislocation density can lead to reductions in the lattice thermal conductivity. Recently, a technique to engineer grain boundaries with dislocations is proposed to enhance mid-frequency phonon scattering at dislocations. Fig. 6 shows a schematic illustration of the liquid-phase compaction process for generating dislocation arrays in the grain boundaries of the Bi$_0.5$Sb$_{1.5}$Te$_3$ matrix. The dislocation arrays are localized at the grain boundaries, as can be seen in Fig. 6b–e, effectively reducing the lattice thermal conductivity without significantly decreasing the electrical conductivity, resulting in a maximum $zT$ of ~2 [1].

Dislocation density is typically controlled by the plastic deformation process. Frank–Read provides a well-known mechanism of dislocation generation [73], which is known to improve mechanical strength. Fig. 7 shows the schematic illustration of dislocation generation by a Frank–Read source mechanism. A straight dislocation (red line) is shown with ends pinned at A and B in a slip plane (a). During plastic deformation, a shear stress (black arrow, $\tau$) is exerted. The straight dislocation line, located on the slip plane, is curved into an arc (b–c). If a sufficient shear stress is applied, the dislocation spontaneously grows (d), and then two opposite dislocations meet (e) and make a loop (f). The loop and newly formed dislocation are separated (f). The separated loop spontaneously grows (d), and then two opposite dislocations meet (e) and make a loop (f). The loop and newly formed dislocation are separated (f).
remarkable for composite materials. During the high temperature consolidation process, the mismatch in thermal expansion coefficients between the inclusion and the matrix generates dislocations in the matrix; consequently, the dislocation density is already high before plastic deformation [55]. The pinning effect, wherein the dislocation ends are immovable, occurs more effectively with added inclusions. Therefore, the Frank–Read source mechanism will accelerate during the plastic deformation process in a composite system.

The Bi-Te alloys are easily crushed due to the low mechanical properties caused by van der Waals interactions between two Te(1) layers [30]. Thus, open die processes such as rolling and forging are not appropriate for plastic deformation of Bi-Te alloys. Extrusion is a typical plastic deformation method similar to the die process. Severe plastic deformation (SPD) processes including equal channel angular pressing (ECAP) and high pressure torsion (HPT) are the most commonly use processes for generating high dislocation density and ultra-fine grains (UFGs) [74]. In extrusion, the sample is forced to pass through the mold, which has a gradient in the cross sectional area (starting area is larger, \( A_0 > A_1 \)). During extrusion, the cross sectional area is reduced, and therefore plastic deformation occurs with grain refinement and increased
dislocation density. The basic principle of extrusion is illustrated in Fig. 8a. In the ECAP process (Fig. 8b), the sample is forced to pass through the mold, which has an abrupt angle ($\Phi$) bended channel. A severe shear strain is introduced in the sample during processing through the mold. Repetitive processes lead to grain refinement and increased dislocation density due to accumulated shear strain in the sample. In the HPT process (Fig. 8c), the coin-shaped sample is placed between the upper anvil and lower anvil, and then a high hydrostatic pressure is induced with torsional strain based on the rotation of the lower anvils. As a result, an extremely high shear strain is introduced in the sample.

So far only a few studies have reported the influence of plastic deformation on skutterudites for enhancing $zT$. The dislocation density of a $\text{Sr}_{0.07}\text{Ba}_{0.07}\text{Yb}_{0.07}\text{Co}_{4}\text{Sb}_{12}$ sample is increased from $1.4 \times 10^{12}$ to $3.1 \times 10^{12}$ m$^{-2}$, and the $zT$ value also increases from 1.4 to 1.8 at 530 °C after the plastic deformation process [75]. In the case of $\text{DD}_{0.08}\text{Fe}_{3}\text{Co}_{4}\text{Sb}_{12}$ (DD is an abbreviation for didymium), 152 nm grains are reduced to 53 nm, whereas the dislocation density increases from $2.8 \times 10^{13}$ to $2.0 \times 10^{14}$ m$^{-2}$ using the HPT process. The $zT$ of the HPT-processed improves from 1.2 to 1.6 at 530 °C [76]. After the SPD process, an excessive enhancement in defects such as dislocations, grain boundaries, and microcracks causes high electrical resistivity, resulting a low $zT$ in $\text{Pr}_{0.67}\text{Fe}_{3}\text{Co}_{4}\text{Sb}_{12}$, $\text{Pr}_{0.71}\text{Fe}_{3.5}\text{Ni}_{0.5}\text{Sb}_{12}$ and $\text{Ba}_{0.06}\text{Co}_{4}\text{Sb}_{12}$ [77].

A few papers report plastic deformation effects in the Bi-Te alloy system. Using extrusion processing in $\text{Bi}_{2}\text{Te}_{2.85}\text{Se}_{0.15}$ with SbI$_3$ doping, a maximum figure of merit ($z$) of $3.05 \times 10^{-3}/K$ is achieved (the $1/K$ unit means that there is no information on the temperature dependence of TE performance) [78]. The $z$ value of $n$-type $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{Te}_{2.7}\text{Se}_{0.3}$ reaches a maximum of $3.04 \times 10^{-3}/K$ with 6 passes of ECAP processing [79]. After 4 passes of ECAP processing, the figure of merit is $3.85 \times 10^{-3}/K$ in $(\text{Bi}_{0.24}\text{Sb}_{0.76})\text{Te}_{3}$ due to the

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**Fig. 8.** Schematic illustration of the principle of plastic deformation: (a) extrusion, (b) equal channel angular pressing (ECAP), and (c) high pressure torsion (HPT).

**Fig. 9.** Schematic illustration of phonon scattering mechanism in defect engineering strategy: point impurity (alloy element) and nanoinclusion interaction for high-frequency phonon scattering, dislocation for mid-frequency phonon scattering, and grain boundary for low frequency phonon scattering.
Using plastic deformation for dislocation engineering with the all-scale hierarchical architectures strategy may become a new direction for achieving high TE performance of a Bi-Te system. In an all-scale hierarchical architectures strategy, the alloying effect generates the 0-dimensional defects (point impurities), the grain refinement enhances the 2-dimensional defects (boundaries), and the nanocomposite approach induces the 3-dimensional defects (nanoparticles). Further, plastic deformation is used to control the 0-dimensional defects (dislocations). Consequently, our newly proposed direction for high TE performance covers all aspects of defect engineering including point impurities, dislocations, grain boundaries, and second phase particles. Using this strategy, we can expect that the lattice thermal conductivity significantly reduce due to full spectrum phonon scattering by engineered defects. Fig. 9 shows schematic illustrations of the concept of full spectrum phonon scattering based on our suggested defect engineering strategy.

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References
