# Chapter 3

## Materials for Near-Room Temperatures

Weishu Liu, Yucheng Lan, Jiehe Sui, Zihang Liu, and Zhifeng Ren

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3.1 Bismuth Chalcogenides
Weishu Liu, Yucheng Lan, and Zhifeng Ren

3.1.1 Introduction
The history of V2–VI3 compounds for thermoelectric application near-room temperature started from Bi2Te3 and later moved to its alloys with element Sb at Bi site and Se at Te site.1–3 The early works mainly focused on the well-grown single crystals or casted ingots, which were already well reviewed by many authors over the past decades.4–6 However, the Bi2Te3-based ingots are mechanically brittle due to the intrinsic laminar crystalline structure characterized with van der Waals bonds. In contrast, their polycrystalline counterparts were proved to be more mechanically robust because the grain boundaries work well as a block to the propagation of fracture cracks.7,8 The decreased lattice thermal conductivity was widely observed in both the p-type (Bi, Sb)2Te3 and n-type Bi2(Te, Se)3 polycrystalline bulks made by various nanoapproaches. However, the thermoelectric figure of merit (ZT) values of these nanostructured materials were not inevitably enhanced due to various reasons. One of the challenges was the controllable charge carrier concentration, which was sensitive to the native defects, grain boundaries, and protection atmosphere. In this chapter, we will focus our discussion on the latest advances in the performance enhancement and puzzle understandings for the p-type (Bi, Sb)2Te3 and n-type Bi2(Te, Se)3 polycrystalline bulks.

3.1.2 p-Type (Bi, Sb)2Te3
The classic compositions of the p-type BiₓSb₂₋ₓTe₃ ranged from x = 0.3–0.6, in which the antisite defects were identified as the dominant charge carrier provider. Generally, BiₓSb₂₋ₓTe₃ with more Bi has less positive charge carriers because of the decreased concentration.9 Here, the Kröger–Vink notations were used to describe the electric charge and lattice position for point defect species in crystals. The prime (’) represents the negative charge, the dot (‘) represents the positive charge, and the cross (‘×’) for the neutral charge. A recent theoretical calculation for Sb₂Te₃ suggests that the dominant native defect is antisite defect in Sb-rich case while vacancy in a Te-rich case,10 as shown in Figure 3.1.10 The native acceptor behavior makes a well explanation for the reason why Sb₂Te₃-rich BiₓSb₂₋ₓTe₃ is usually a p-type semiconductor.

3.1.2.1 Early Works
The early efforts in the polycrystalline p-type BiₓSb₂₋ₓTe₃ achieved notable enhancements in mechanical strength rather than thermoelectric performance compared with its state-of-the-art single crystal counterpart.11–17 Tokiai et al.7 fabricated a polycrystalline p-type BiₓSb₂₋ₓTe₃ with significantly enhanced mechanical strength by using ball milling (BM) (dry process + wet process) with hot pressing (HP) (cold isostatic press + hot isostatic press) with elemental powders as the raw materials. Nevertheless, some oxide impurities, such as Bi₂O₃, TeO₃, and Sb₂O₃, were observed in their p-type polycrystalline
FIGURE 3.1 The formation energy of $\Delta H$ as a function of anion chemical potential for all the possible defects in (a) Bi$_2$Se$_3$, (b) Bi$_2$Te$_3$, (c) Sb$_2$Te$_3$. $V_{Bi}$, $V_{Sb}$, $V_{Se}$, and $V_{Te}$ stand for the bismuth vacancy, antimony vacancy, selenium vacancy, and tellurium vacancy, respectively, while Bi$_{Se}$, Bi$_{Te}$, Sb$_{Te}$, Se$_{Bi}$, and Te$_{Bi}$ are the antisite defects. 1 and 2 are labeled to distinguish Se(Te) in different layers. X-rich ($X$ for Bi, Sb, Se, or Te) indicates the extreme growth conditions. Vertically lines highlight the boundary of the carrier types. (Reprinted with permission from Zhang, M. et al., Physical Review B, 88, 235131, 2013. Copyright 2013 by the American Physical Society.)
Bi<sub>x</sub>Sb<sub>2−x</sub>Te<sub>3</sub> which could have resulted from the usage of wet BM process. Furthermore, the Seebeck coefficient of Bi<sub>0.5</sub>Sb<sub>1.5</sub>Te<sub>3</sub> continuously increased from 50 to 280 μV/K, together with an increased electrical resistivity from 10 to 41 μΩm, when the BM time increased from 1 to 10 h. The maximum power factor (PF) of this polycrystalline Bi<sub>0.5</sub>Sb<sub>1.5</sub>Te<sub>3</sub> (PF = 19 μW/cm K<sup>2</sup> for the 10 h BM sample) was much lower than that of the single crystal counterpart (PF = 32–46 μW/cm K<sup>2</sup>), which therefore led to a low ZT value of 0.48 at 25°C. By adding extra Sb in Bi<sub>x</sub>Sb<sub>2−x</sub>Te<sub>3</sub> and using less Bi content, the enhanced PF of ~40 μW/cm K<sup>2</sup> and ZT of 0.78 at 25°C were reported in the Bi<sub>0.45</sub>Sb<sub>1.55</sub>Te<sub>3</sub> by the same group. Even so, the ZT value of this polycrystalline Bi<sub>0.45</sub>Sb<sub>1.55</sub>Te<sub>3</sub> was still inferior compared with its single crystalline counterpart (ZT = 0.96 in Bi<sub>0.45</sub>Sb<sub>1.55</sub>Te<sub>3</sub>). Navratil et al. synthesized a polycrystalline Bi<sub>0.45</sub>Sb<sub>1.55</sub>Te<sub>3</sub> with a ZT value of 0.93 at 27°C through the fabrication route of grinding, cold pressing, and annealing by using corresponding ingot as the raw material. The sintered Bi<sub>x</sub>Sb<sub>2−x</sub>Te<sub>3</sub> powders were sieved into two size scales. The sintered Bi<sub>x</sub>Sb<sub>2−x</sub>Te<sub>3</sub> sample, by using the finer grinding powders (grain size <130 μm), displayed higher Seebeck coefficient and electrical resistivity than that of the one by using coarser grinding powders (grain size 130–300 μm), which suggested that a donor-like effect of grinding and pressing process. This donor effect even changed the p-type Bi<sub>x</sub>Sb<sub>2−x</sub>Te<sub>3</sub> into n-type. One of the possible reasons was that Te vacancies generated from the mechanical deformation in the grinding process annihilated the antisite defects and, hence, reduced the hole concentration. Oh et al. conducted a systematic investigation in the Bi<sub>x</sub>Sb<sub>2−x</sub>Te<sub>3</sub> system and got optimized ZT values of 0.92 and 0.88 at room temperature in polycrystalline Bi<sub>0.4</sub>Sb<sub>1.6</sub>Te<sub>3</sub> by using ingots and elemental powders as raw materials, respectively. Additionally, a donor-like effect of oxygen was confirmed in polycrystalline Bi<sub>0.4</sub>Sb<sub>1.6</sub>Te<sub>3</sub> by Oh et al. Seo et al. reported that an enhanced ZT value from 0.81 to 0.88 was obtained in polycrystalline Bi<sub>0.45</sub>Sb<sub>1.55</sub>Te<sub>3</sub> by a thermal extrusion process. It was believed that the texture developed by the thermal extrusion process increased carrier mobility. These early efforts failed to get superior ZT values in polycrystalline Bi<sub>x</sub>Sb<sub>2−x</sub>Te<sub>3</sub> bulks compared with their single crystal counterpart. However, they outlined the most important factors that govern the thermoelectric performance of a p-type Bi<sub>x</sub>Sb<sub>2−x</sub>Te<sub>3</sub> polycrystalline bulk: (1) Bi/Sb ratio, (2) extra Te or Sb, (3) BM conditions, (4) HP conditions, (5) protection atmosphere, and (6) morphology of grain boundaries. Systematically considering all these factors is a big challenge to make the polycrystalline p-type Bi<sub>x</sub>Sb<sub>2−x</sub>Te<sub>3</sub> with a better thermoelectric performance over their single crystalline counterpart.

3.1.2.2 BM-HP Route

In 2008, high peak ZT values of 1.3 and 1.4 near 100°C were reported in p-type Bi<sub>x</sub>Sb<sub>2−x</sub>Te<sub>3</sub> nanostructured bulks by using elemental chucks and high-quality BiSbTe ingot as raw materials, respectively. These nanostructured Bi<sub>x</sub>Sb<sub>2−x</sub>Te<sub>3</sub> bulks were made by a joint route of high-energy BM and direct current (dc) HP. Here, the dc HP is a current assistant HP technique utilizing
the self-heating effect of joule heat for heating when current passes through the sample within a graphite die, which was also called spark plasma sintering (SPS) or plasma activate sintering technique by different groups. The importance of the fast-speed HP to obtain the nanostructured or nanocrystalline thermoelectric bulk materials has been explained in our previous work.21 Shortly, the fast-sintering technology is the key to ensure that the nanostructures of the ball milled powders remain in the final sintered bulks because of the limited grain growth. Figure 3.2 shows the temperature-dependent thermoelectric properties of the nanostructured Bi$_x$Sb$_{2-x}$Te$_3$ bulks and their ingot counterpart. Because of well protection atmosphere and systematic fabricate condition optimization, the room-temperature PF of both nanostructured bulks is comparable to their ingot counterpart (~46 μW/cm K$^2$). Since the carrier mobility of the polycrystalline bulks is lower than that of their single crystal counterpart, a higher carrier concentration is necessary for the polycrystalline materials to achieve the comparable PF. The carrier concentration of the polycrystalline Bi$_x$Sb$_{2-x}$Te$_3$ was adjusted by the BM and HP conditions and other dopants. The combination of high-energy BM and dc HP (BM-HP) endowed the polycrystalline Bi$_x$Sb$_{2-x}$Te$_3$ bulks with finer nanostructures and, hence, lower lattice thermal conductivity. Figure 3.3 shows some general features of the nanostructured Bi$_x$Sb$_{2-x}$Te$_3$.22 Firstly, the bulks consisted of widely size-distributed grains ranging from 10 nm to 3 μm, as shown in Figure 3.3a and b. At the fine grain end of the distribution, there were 12% of the grains with a diameter less than 20 nm and 5% with a diameter in the 20–40 nm range in one bulk made from BiSbTe ingot. Secondly, there were many nanoinclusions either embedded in the grains or located at the grain boundaries with size from 10–100 nm, as shown in Figure 3.3c and d. In the nanostructured Bi$_x$Sb$_{2-x}$Te$_3$ synthesized from ingot, some of interesting nanoinclusions were identified: one was the Te-poor Bi$_x$Sb$_{2-x}$Te$_{3-δ}$ without clear boundary from the matrix (coherent inclusion) and another was the pure Te with a high-angle boundary from the surrounding materials (incoherent inclusion). The simultaneous appearance of these two types of nanoinclusions suggested that the BM-HP process could create some kind of local compositional fluctuation. Furthermore, the microstructure of the nanostructured Bi$_x$Sb$_{2-x}$Te$_3$ made from the elemental chunks is quite similar to the one made from ingot, having many Te-poor coherent Bi$_x$Sb$_{2-x}$Te$_{3-δ}$ nanoinclusions. However, the difference is that Sb nanoprecipitations rather than Te nanoprecipitations were found in the nanostructured Bi$_x$Sb$_{2-x}$Te$_3$ bulk made from the elemental chunks. Thirdly, some atomic level defects, such as point defects and threading dislocations were identified, as shown in Figure 3.3e through f. For example, the dislocation concentration of nanocrystalline Bi$_x$Sb$_{2-x}$Te$_3$ was ~10$^{11}$ cm$^{-2}$, at least 10 times higher than the value of ~5 × 10$^9$ cm$^{-2}$ found in the single crystalline ingot. However, it is too challenging to numerically consider these scale defects to clarify the reason why the nanostructured Bi$_x$Sb$_{2-x}$Te$_3$ synthesized from ingot has ~10% lower thermal conductivity. Recently, similar BM-HP routes were used for reinvigorating the polycrystalline Bi$_x$Sb$_{2-x}$Te$_3$ by several other groups.23–26 However,
FIGURE 3.2 Temperature-dependent thermoelectric properties of nanocrystalline Bi$_x$Sb$_{2-x}$Te$_3$ bulks made by high-energy BM and dc HP: (a) electrical resistivity, (b) Seebeck coefficient, (c) PF, (d) thermal conductivity, and (e) figure of merit. The data of the commercial BiSbTe ingot and nanocrystalline BiSbTe bulk made from ingots are from Poudel et al., while those for nanocrystalline BiSbTe bulk made from elements are from Ma et al. (Reprinted with permission from Ma Y. et al., Enhanced thermoelectric figure-of-merit in p-type nanostructured bismuth antimony telluride alloys made from elemental chunks. Nano Letters 8, 2580. Copyright 2008. American Chemistry Society.)
Materials for Near-Room Temperatures

FIGURE 3.3 Multisize scale crystalline structure in the Bi$_x$Sb$_{2-x}$Te$_3$ bulks made by high-energy BM and dc HP: (a) TEM image of large grains; (b) HRTEM image of small grains; (c) HRTEM image of a tellurium-poor nanoinclusion without a boundary; (d) HRTEM image of a tellurium nanoinclusion with a high-angle boundary; (e) HRTEM images of dislocation in grains with excited [003] reflections (left), along the [210] zone (right) (numbers 5 and 7 represent five- and seven-layer lamellae, respectively); and (f) inverse FFT (IFFT) of dislocation in grains with excited [105] reflections (Wiener-filtered) (white arrows indicate threading dislocations). Grain size distribution histogram in two size scales are present in the lower panel of a and b, respectively. (Reprinted with permission from Lan Y. C. et al., Structure study of bulk nanograin thermoelectric bismuth antimony telluride. Nano Letters, 9, 1419–1422. Copyright 2009. American Chemical Society.)
only few of the nanostructured Bi$_x$Sb$_{2-x}$Te$_3$ with a Seebeck coefficient closed to 190–210 μV/K$^{-1}$ had a high $ZT > 1.2^{24,26}$ which suggested the importance of synergistically tuning the thermal and electrical properties.

### 3.1.2.3 MS-HP Route

Besides the high energy BM, rapid solidification through melt spinning (MS) was another good way to get the nanostructured precursors before sintering. Kim et al.\cite{27} fabricated Bi$_{0.5}$Sb$_{1.5}$Te$_3$ ribbons early by melt spinning the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ ingot with 3–4% extra Te on a Cu wheel rotating at a surface speed of 47 m/s, and then fast-speed (5 min) hot pressed into the polycrystalline bulks at different temperatures. Microscale compositional inhomogeneity was identified in both casted ingot and the final hot pressed bulks. Due to the low PF (~33 μW/cm K$^2$), only a $ZT$ of 0.92 at room temperature was obtained. Later, Xie et al.\cite{28,29} reported a nanocrystalline Bi$_{0.52}$Sb$_{1.48}$Te$_3$ bulk made by using similar melting spinning plus spark plasma sintering. Compared with the BM-ed powders, the MS-ed ribbons has wider size scale structures, including amorphous phase, nanocrystalline phase, and microcrystalline phase due to the different cooling rate from the contact surface with cooper roller to the free surface with air.\cite{30} Furthermore, slight compositional variation was identified along the cross section of ribbons from contact surface to contact surface (Te = 57.7 at.%; Sb = ~ 28.0 at.%; Bi = 14.4 at.%) to free surface (Te = 61.6 at.%; Sb = ~ 29.5 at.%; Bi = 9.2 at.%),\cite{29} as shown in Figure 3.4. Compared

![Figure 3.4](image-url)
with Kim’s sample, Xie’s nanostructured sample has a comparable PF (~35 μW/cm K²) but much lower thermal conductivity and, hence, a superior $ZT$ value of 1.56 at 300 K. They later clarified that the measurement direction is vertical to the SPS pressure direction for electrical properties while parallel to the SPS pressure direction for the thermal conductivity. The real thermal conductivity vertical to the SPS pressure direction is slightly higher than that parallel to the SPS pressure direction. Recently, the same group conducted a more systematic investigation of the MS-SPS effect has on the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, as shown in Figure 3.5. Compared to the ingot counterpart, an enhanced $ZT$ value of 1.22 at 340 K was achieved in MS-SPS-ed $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ with a significantly reduced lattice thermal conductivity of 0.55 W/m K and a mildly reduced PF (~34 μW/cm K²). Multisize scale structural features were also identified in the MS-SPS-ed bulk, including fine grains, nanoinclusions, and dislocations, which is generally similar to the one made by the BM-HP route. Compared with their ingot counterpart, the MS-SPS-ed bulk is more

![Graphs showing temperature-dependent properties](image-url)

**FIGURE 3.5** Temperature-dependent thermoelectric properties of nanocrystalline $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ made by the MS and plasma activate sintering: (a) electrical conductivity, (b) Seebeck coefficient, (c) thermal conductivity, (d) figure of merit. (Continued)
mechanically robust with a 26–40% enhanced fracture toughness of $K_{IC}$. It is noted that the PF of the MS-SPS-ed nanocrystalline bulks is lower than that of the one fabricated from the BM-HP process. Ivanova et al.\textsuperscript{32} suggested that an anneal in Ar or H\textsubscript{2} process could improve the PF of the MS-HP-ed Bi$_{0.5}$Sb$_{1.5}$Te$_{3}$, as a result, an enhanced $ZT$ of 1.3 near-room temperature. In addition to BM and melting spinning to obtain the nanostructured precursors, there are also other methods to synthesize the Bi$_{x}$Sb$_{2-x}$Te$_{3}$ nanopowders such as bottom-up chemical synthetic methods.\textsuperscript{33,34} However, it is too challenging for these chemical metallurgy routes to get a high PF comparable with the MS-HP-ed and MA-HP-ed nanocrystalline Bi$_{x}$Sb$_{2-x}$Te$_{3}$. Recently, Nguyen et al.\textsuperscript{35} reported a new spark erosion (SE) technique for producing high-quality p-type Bi$_{0.5}$Sb$_{1.5}$Te$_{3}$ nanoparticles at a production rate as high as 135 g/h and very low energy consumption (<2.0 kWh/kg). The nanoparticles subjected to SE were observed to be well defined and round with an average size of 20–50 nm. The SE-SPSed nanocrystalline Bi$_{0.5}$Sb$_{1.5}$Te$_{3}$ shows a comparable PF and reduced thermal conductivity and, hence, a significantly
enhanced $ZT$ value of 1.36 at 87°C compared with the starting ingot ($ZT = 1$ at 50°C).

### 3.1.2.4 GB Engineering

In addition to tuning the size and shape of the precursor particles or ribbons, the final nanostructures can be further refined by dispersing extra nanoparticles or modifying particle surfaces. A notable suppression of the grain growth was observed by using the extra nanoparticles in the Bi$_x$Sb$_{2-x}$Te$_3$, such as SiC (100 nm),$^{36,37}$ C$_{60}$,$^{38}$ and B$_4$C.$^{39}$ The enhanced phonon scattering comes from the increased concentration of grain boundaries and newly formed phase boundaries. However, the carrier mobility of Bi$_x$Sb$_{2-x}$Te$_3$ was also reduced by these nanoparticles. SiC has been considered as a stable and inert secondary phase to Bi$_x$Sb$_{2-x}$Te$_3$. However, the carrier concentration of Bi$_{0.3}$Sb$_{1.7}$Te$_3$ was reduced by these nanoparticles. SiC has been considered as a stable and inert secondary phase to Bi$_x$Sb$_{2-x}$Te$_3$. However, the carrier concentration of Bi$_{0.3}$Sb$_{1.7}$Te$_3$ + $x$ (vol%) SiC showed a notable increase from $1.8 \times 10^{19}$ cm$^{-3}$ to $3.5 \times 10^{19}$ cm$^{-3}$ when the content of SiC increases from $x = 0$ to $x = 0.6$,$^{37}$ as shown in Table 3.1. There are two possible reasons: (1) Some of SiC nanoparticles decomposed during high-energy BM, and then the Si or C got into the Bi$_{0.3}$Sb$_{1.7}$Te$_3$ lattice as a new acceptor. (2) Some of the native defects at the phase boundaries (SiC/ Bi$_{0.3}$Sb$_{1.7}$Te$_3$) behaved as new acceptor. Zhang et al.$^{40}$ reported a more effective way to suppress the grain growth of p-type Bi$_{0.3}$Sb$_{1.7}$Te$_3$ by using the some oleic acid (OA) in the MA-HP route. It was found that the OA significantly reduced the particle agglomeration during BM and, hence, suppressed grain growth during HP process. In contrast to having a flake-like grains, Bi$_{0.3}$Sb$_{1.7}$Te$_3$ with OA had more round grains with the random distribution, creating less anisotropy between the directions vertical/parallel the pressure direction. Furthermore, slight increases in both the Seebeck coefficient and electrical resistivity were observed. A combination of small grains (200–500 nm) and nanopores leads to a decrease in lattice thermal conductivity, therefore reaching an optimized $ZT$ of 1.3 at 100°C for the sample with 2.0 wt% OA.

Recently, a group of researchers from South Korea reported that a large amount of extra Te liquid phase (25 wt.%) could significantly modify the grain boundary of nanocrystalline Bi$_{0.5}$Sb$_{1.5}$Te$_3$ by MS-SPS route.$^{41}$ Dense dislocation

### TABLE 3.1  Seebeck Coefficient, Carrier Concentration, and Mobility of the Canocomposite Bi$_{0.3}$Sb$_{1.7}$Te$_3 + X$ vol% SiC ($X = 0, 0.1, 0.4, \text{and } 0.6$) at 323 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seebeck Coefficient ($\mu$V/K)</th>
<th>Carrier Concentration (10$^{19}$ cm$^{-3}$)</th>
<th>Carrier Mobility (cm$^2$/V s)</th>
<th>$m^<em>/m_0^</em>$</th>
</tr>
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<tr>
<td>$x = 0$</td>
<td>187.94</td>
<td>1.81</td>
<td>365.4</td>
<td>1</td>
</tr>
<tr>
<td>$x = 0.1$</td>
<td>186.14</td>
<td>2.48</td>
<td>284.2</td>
<td>1.222</td>
</tr>
<tr>
<td>$x = 0.4$</td>
<td>196.18</td>
<td>3.39</td>
<td>212.1</td>
<td>1.586</td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>187.52</td>
<td>3.51</td>
<td>164.1</td>
<td>1.552</td>
</tr>
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FIGURE 3.6  (a through c) Schematic illustration showing the generation of dislocation arrays during the liquid phase compacting process. The Te liquid (red) between the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ grains flows out during the compacting process and facilitates the formation of dislocation arrays embedded at the grain boundaries.  
(d through g) TEM images of dislocation array from low resolution to high resolution. (Reprinted with permission from Kim, S. I. et al., Science 348, 109–114, 2015. Copyright 2015. AAAS.)
arrays were formed at the low-energy grain boundary when the extra Te liquid was expelled out during spark plasma sintering process, as shown in Figure 3.6. The novel nanostructures were claimed for the very low lattice thermal conductivity (0.33–0.34 W/m K) and, hence, the new record ZT of 1.67 (∥, parallel to the pressure direction) and 1.85 (⊥, vertical to the pressure direction). Anisotropic electrical conductivity \( \sigma \) was observed in their Te-MS-ed Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) in which \( \sigma_\perp \) is 16.5% higher than \( \sigma_\parallel \). In contrast, only 6.5% difference in thermal conductivity was detected. The real role of the dense dislocation arrays is still unclear. The extremely low lattice thermal conductivity desires more experimental confirmations and theoretical understandings. Besides the low thermal conductivity, the Te-MS-ed Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) showed a clear enhanced PF of (\( PF_\perp \sim 40 \mu \text{W/cm K}^2 \)) compared with previous MS-HP-ed Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) bulks. Grain boundary engineering was used to tailor not only the transport of the phonons, but also the transport of electrons. Ko et al.\(^{42}\) observed a significantly increased Seebeck coefficient in the Pt/Sb\(_2\)Te\(_3\) nanocomposite from 115.6 to 151.6 \( \mu \text{V/K} \). Enhanced PF in the Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) was reported by embedding a few selected metal (Ag, Co, Cu, Mn, Mo, Ni, Pd, Tb, Zn) nanoparticles, in which the Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3/\)Ag nanocomposite showed the largest incensement of 25%.\(^{43,44}\) The Hall coefficient measurement suggested an increased effective carrier mass from \( m^* = 0.8m_0 \) to \( m^* = 1.2m_0 \). At the same time, a decreased lattice thermal conductivity was observed due to the increased phonon scattering by the phase boundary. As a result, a high ZT of 1.35 was obtained in the Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3/\)Ag nanocomposite. A similar increased effective carrier mass \( m^* \) was also observed in the Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\)-expanded graphene.\(^{45}\) Additionally, Zhang et al.\(^{46}\) observed a significant reduction in the lattice thermal conductivity in the Ag nanoparticle-dispersed (60 nm) Bi\(_2\)Te\(_3\) made from a chemical metallurgy route.

3.1.3 n-Type Bi\(_2\)(Te, Se)\(_3\)

The classic compositions of the n-type Bi\(_2\)Te\(_3\)-Se\(_x\) ranged from \( x = 0.2 \) to 0.8. A recent theoretical calculation for Bi\(_2\)Se\(_3\) suggests that the dominant native defect is vacancy \( V_{\text{Se}}^\ast \) in Bi-rich case while anti-site defect \( Se_{\text{Bi}}^\ast \) in a Se-rich case, which makes Bi\(_2\)Se\(_3\) a very strong n-type. Parker and Singh\(^{47}\) theoretically suggested that a p-type Bi\(_2\)Se\(_3\) could have a potential high ZT of 1.5. However, it is too challenging to experimentally achieve a p-type Bi\(_2\)Se\(_3\) with high hole concentrations of \( \sim 10^{19} \text{ cm}^{-3} \). On the other hand, the main charge carriers type of Bi\(_2\)Te\(_3\) was stoichiometric ratio dependent.\(^{10,48}\) It suggests that the dominant native defect is Bi\(_{\text{Te}}^\ast \) in Bi-rich case (p-type), while Te\(_{\text{Bi}}^\ast \) in a Te-rich case (n-type), as shown in Figure 3.1. Furthermore, in an alloy of Bi\(_2\)Te\(_{1-x}\)Se\(_x\), the real dominant defect is more complicated. In the Bi rich case, the donor-like \( V_{\text{Se}}^\ast \) and acceptor-like Bi\(_{\text{Te}}^\ast \) coexisted. Besides stoichiometric ratio (Te, Se)/Bi and alloying ratio Te/Se, the defect related to the plastic deformation also needs to be taken into account.

3.1.3.1 Equivalent Doping Effect of BM-HP

Similar to the p-type Bi\(_{x}\)Sb\(_{2-x}\)Te\(_3\), the early works to prepare fine-grained n-type Bi\(_2\)Te\(_{2-x}\)Se\(_x\) materials were also motivated by the expectation to improve
the mechanical strength for more robust and reduced thermal conductivity for higher thermoelectric $ZT$ values.\textsuperscript{15,49,50} However, it was even more challenging to achieve an enhanced $ZT$ in the fine-grained n-type Bi$_2$Te$_{2-y}$Se$_y$ materials than in the p-type Bi$_x$Sb$_{2-x}$Te$_3$ materials. One of the challenges is controllable carrier concentration. The BM-HP process was not a pure donor-like effect in the n-type Bi$_2$Te$_{2-y}$Se$_y$ materials. For example, the BM time and HP temperature were most widely investigated; however, there were still many conflicting experimental results that puzzle the readers,\textsuperscript{49–62} as shown in Table 3.2. Some results suggested that BM and HP have a donor-like effect on the n-type Bi$_2$Te$_{2-y}$Se$_y$ which corresponds to decreased Seebeck coefficient and increased carrier concentration, while others just suggested an opposite acceptor-like effect. Kanatzia et al.\textsuperscript{50} observed an acceptor-like behavior for the BM time (from 1 to 15 h) based on the cold pressed bulks, while a donor-like behavior for the BM time based on hot pressed bulks. Unfortunately, they did not give enough explanations to clarify this puzzle. However, we would also like to give the credits to these early works. Besides the main factors that determined the thermoelectric properties, similar to what was summarized for the p-type Sb$_x$Bi$_2$Te$_3$, they also additionally indicated the main challenges for n-type Bi$_2$Te$_{2-y}$Se$_{0.3}$ polycrystalline or nanostructured materials: (1) carrier concentration heavily depends on the plastic deformation and thermal history and (2) a notable side effect from grain boundary to the transport of electrons.

First, we will uncover these puzzles by understanding the evaluation of the dominant atomic defects due the plastic deformation and thermal history. Mechanical BM does not only reduce the particle size but also results into heavy plastic deformation within each particle. Heavy plastic deformation produces many line defects and point defects. Schultz et al.\textsuperscript{63} described a simple experiment by sharply bending a single crystal Bi$_2$Te$_3$ about an axis parallel to the basal plane to introduce the dislocations; however, these dislocations did not make the concentration change of the charge carrier. The plastic deformation usually produces vacancy–interstitial pair together due to the dislocation intersections. In Bi$_2$Te$_3$, the nonbasal slip gives the average vacancy–interstitial pair of Te and Bi in a ratio of 3/2, while a slip along the basal plane only produces the Te vacancy–interstitial pair. Due to the van de Waals bonds, the dislocation slip along the basal plane is much easier than that along nonbasal plane. It was therefore believed that the concentration of the $V_{\text{Te}}^{\text{m}}$–$\text{Te}_i$ pair was more than that of $V_{\text{Bi}}^{\text{m}}$–$\text{Bi}_i$ vacancies. According to the net increase in the negative charge carrier after subjecting a pure plastic deformation, Schultz et al.\textsuperscript{63} further suggested that the interstitials were undoubtedly present but apparently not as electrically active as the vacancies. This dominant donor effect of $V_{\text{Te}}^{\text{m}}$ was therefore widely accepted for the Bi$_2$Te$_3$ ingot changed from p-type to n-type after being directly subjected to hot extrusion,\textsuperscript{63} or BM and then HP.\textsuperscript{50,51} The thermal treatment process, such as HP or annealing, has two major effects: (1) loss of Te making Bi$_2$Te$_3$ more Bi-rich and (2) annihilation of the high-energy state defect pair $V_{\text{Te}}^{\text{m}}$–$\text{Te}_i$. The loss of Te or Se of Bi$_2$Te$_{3-x}$Se$_x$ during the HP and annealing process was widely confirmed.\textsuperscript{58,63,64} It is noted that the loss
### TABLE 3.2 Effects of BM Time and HP or Annealing Temperature on the Seebeck Coefficient or Carrier Concentration in n-Type Bi$_{2}$Te$_{3-y}$Se$_{y}$ Fine-Grained Materials

<table>
<thead>
<tr>
<th>Start Material before BM-HP</th>
<th>BM Time (h)</th>
<th>HP Temperature °C</th>
<th>S (μV/K)</th>
<th>N (10$^{19}$ cm$^{-3}$)</th>
<th>Equal Effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>{2}$Te$</em>{3}$ ingot</td>
<td>1 → 15</td>
<td>CP</td>
<td>-191 → -236</td>
<td></td>
<td>Acceptor</td>
<td>Kanatzia et al.$^{50}$</td>
</tr>
<tr>
<td></td>
<td>1 → 15</td>
<td>400</td>
<td>-168 → -150</td>
<td></td>
<td>Donor</td>
<td></td>
</tr>
<tr>
<td>Bi$<em>{2}$Te$</em>{3}$ mix</td>
<td>3 → 9</td>
<td>300</td>
<td></td>
<td>7 → 13</td>
<td>Donor</td>
<td>Kuo et al.$^{52}$</td>
</tr>
<tr>
<td></td>
<td>1 → 80</td>
<td>400</td>
<td></td>
<td>6.2 → 1.6</td>
<td>Acceptor</td>
<td>Zhao et al.$^{53}$</td>
</tr>
<tr>
<td>Bi$<em>{1.94}$Sb$</em>{0.01}$Te$<em>{2.76}$Se$</em>{0.29}$ ingot</td>
<td>0.5 → 10</td>
<td>420</td>
<td>-120 → -208</td>
<td>9.5 → 4.2</td>
<td>Acceptor</td>
<td>Oh et al.$^{48}$</td>
</tr>
<tr>
<td>Bi$<em>{2}$Te$</em>{2.7}$Se$_{0.3}$ mix</td>
<td>12 → 18</td>
<td>500</td>
<td>-154 → -133</td>
<td></td>
<td>Donor</td>
<td>Liu$^{54}$</td>
</tr>
<tr>
<td>Bi$<em>{2}$Te$</em>{2.7}$Se$<em>{0.3}$S$</em>{0.01}$ mix</td>
<td>10 → 18</td>
<td>500</td>
<td>-208 → -224</td>
<td></td>
<td>Acceptor</td>
<td>Liu$^{55}$</td>
</tr>
<tr>
<td>Bi$<em>{2}$Se$</em>{0.21}$Te$_{2.79}$ ingot</td>
<td>1 → 8</td>
<td>CP</td>
<td>9 → 12</td>
<td></td>
<td>Donor</td>
<td>Lin et al.$^{58}$</td>
</tr>
</tbody>
</table>

**HP or Annealing**

| Bi$_{2}$Te$_{3}$ mix       | 3           | 350 → 450         | -112 → -127 | 6.9 → 6 | Acceptor | Zhao et al.$^{59}$ |
| Bi$_{2}$Te$_{2.85}$Se$_{0.15}$ mix | 6   | 320 → 440         | -147 → -135 |           | Donor     | Fan et al.$^{61}$ |
| Bi$_{2}$Te$_{2.79}$Se$_{0.21}$ ingot | 15  | 250 → 350         | -155 → -110 | 4.5 → 6 | Donor     | Lu and Liao$^{62}$ |
| Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ mix | 12  | 300 → 500         | -214 → -294 |           | Acceptor | Liu$^{56}$ |

**Note:** CP: cold press; ingot: melting ingot; mix: elemental mixtures.
of Te and Se in the conventional Bi$_2$Te$_{3-x}$Se$_x$ could generate both donor $V_X^\cd$ $(X = \text{Te, Se})$ and acceptor $\text{Bi}'_{\text{Te}}$ in the conventional Bi$_2$Te$_{3-x}$Se$_x$ depending on the content of Se. At the same thermal history, the loss of the Te and Se in a BM- or grinding-derived power compact would be much higher than that in the casted ingot or well-grown single crystals because the former one has more escape channels than the latter one. Generally, BM and HP would creative extra $V_{\text{Te}}^\cd$ and $V_{\text{Se}}^\cd$ in the final polycrystalline bulks. The chalcogen vacancies are the well-known donors; however, they could further react with some native antisite defects and result in the opposite effect, as shown in Figure 3.7. In a highly Te-rich case, the chalcogen vacancies could cancel the dominant defect $\text{Te}_{\text{Bi}}^{\cd}$, leading to a decreased n-type carrier concentration. This was the reason why the increasing BM time resulted into a Seebeck coefficient increase in the chalcogen-rich Bi$_{1.94}$Sb$_{0.01}$Te$_{2.76}$Se$_{0.29}$ and Bi$_{2}$Te$_{2.7}$Se$_{0.3}$S$_{0.01}$. Besides artificially starting with chalcogen-rich samples, oxygen is another source for turning a stoichiometric Bi$_2$Te$_{3-x}$Se$_x$ into a chalcogen-rich case. In the case without well protection, oxygen was easily absorbed on the grinding particles and left in the final sintered pucks as a strong n-type donor. It was suggested that oxygen resolved into Bi$_2$Te$_3$ and took up the place of Te(2) position with the smallest electronegativity, consequently forming Bi$_2$Te$_{3-x}$O$_x$ solid solution. The oxygen could make an original stoichiometric Bi$_2$Te$_{3-x}$Se$_x$ become the chalcogen-rich and high

![Figure 3.7](image-url)

**FIGURE 3.7** Schedule picture for the effect of BM time and HP temperature for the Bi$_2$Te$_3$. Shown in (a) is the plot of Seebeck coefficient versus charge carrier concentration. Shown in (b) is the composition-dependent domains. Domain a is p-type, Te-rich range with dominant defect of $V_{\text{Bi}}^{\cd}$; domain b is p-type depletion range with coexisting $V_{\text{Bi}}^{\cd}$ and $\text{Te}_{\text{Bi}}^{\cd}$; domain c is n-type depletion range with coexisting $V_{\text{Bi}}^{\cd}$ and $\text{Te}_{\text{Bi}}^{\cd}$; domain d is n-type depletion range with coexisting $V_{\text{Bi}}^{\cd}$ and $V_{\text{Te}}^{\cd}$; and domain e is n-type, Bi-rich range with dominant defect of $V_{\text{Te}}^{\cd}$. 
n-type carrier concentration. This explains why Zhao et al. had a Bi$_2$Te$_3$ with a high carrier concentration and a low Seebeck coefficient and observed acceptor-like BM (1–80) and HP processes (from 350°C to 450°C).

### 3.1.3.2 Reproducibility from Batch to Batch

The second challenge for the n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$ connects with the reproducibility of the thermoelectric properties from batch to batch. This is a question that has not yet received enough attentions. Figure 3.8a and b shows the temperature-dependent electrical resistivity and Seebeck coefficient of 10 batches of Bi$_2$Te$_{2.7}$Se$_{0.3}$ made by BM and HP methods under the same fabrication conditions, indicating a poor reproducibility from batch to batch. The coefficient of deviation for the electrical resistivity of 10 batches was larger than 13%, suggesting an uncontrollable carrier concentration. However, the application of the same fabrication route to the p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ achieved a good reproducibility.

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**FIGURE 3.8** (a and b) Temperature dependence of electrical resistivity and Seebeck coefficient of 10 batches of Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples made by BM plus dc-HP method. (c and d) Temperature dependence of electrical resistivity and Seebeck coefficient of 8 batches of Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples made by the same method and conditions as those shown in a and b. (Liu, W. S. et al.: Thermoelectric property studies on Cu doped n-type Cu$_x$Bi$_2$Te$_{2.7}$Se$_{0.3}$ nanocomposites. *Advanced Energy Materials*. 2011. 1. 577–587. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.)
with coefficient of deviation less than 3%. The puzzle is that both the high-energy BM and the fast-speed HP processes are a nonthermodynamic process. Generally, ball milled powders are homogenous in macroscale, but inhomogeneous in microscale, characterized with a broad particle size distribution, nanoinclusions, and atomic defects. The later fast-speed HP does not give enough time to recover all the charge active defects because we intentionally expect that such defects or nanostructures could be left as the effective phonon scattering centers. Furthermore, the evaporation of Te or Se was another important factor to cause the scattering from batch to batch. Liu et al.\textsuperscript{60} gave an explanation for the reproducibility difference puzzle between n-type Bi\textsubscript{2}Te\textsubscript{3}\textsubscript{−y}Se\textsubscript{y} and p-type Bi\textsubscript{x}Sb\textsubscript{2}−xTe\textsubscript{3} by considering the dominant defect under a metal rich case due to loss of the chalcogen elements as follows:

\begin{equation}
\text{Bi}_2\text{Te}_3 = 2\text{Bi}^x + (3-x)\text{Te}^x + x\text{Te}(g) \uparrow + xV_{\text{Te}}^+ + 2xe, \quad (3.1)
\end{equation}

\begin{equation}
\text{Bi}_2\text{Te}_3 = \left(2 - \frac{2}{5}x\right)\text{Bi}^x + (3-x)\text{Te}^x + x\text{Te}(g) \uparrow

+ \left(\frac{2}{5}xV_{\text{Bi}}^\text{V} + \frac{3}{5}xV_{\text{Te}}^\text{V} \right) \uparrow + \frac{2}{5}x\text{Bi}^\prime_{\text{Te}} + \frac{2}{5}xh. \quad (3.2)
\end{equation}

For the n-type Bi\textsubscript{2}Te\textsubscript{3}−ySe\textsubscript{y}, the loss of Te or Se will be favorable to form the donor-like V\textsubscript{Te}\textsuperscript{V} as shown in Equation 3.1. However, the loss of Te will be favorable to form the acceptor-like Bi\textsubscript{Te}\textsuperscript{V} as shown in Equation 3.2. Considering that both the n-type Bi\textsubscript{2}Te\textsubscript{3}−ySe\textsubscript{y} and p-type Bi\textsubscript{x}Sb\textsubscript{2}−xTe\textsubscript{3} have the same amount of chalcogen element loss at the same BM and HP conditions, it is found that the free carrier concentration with Te vacancy dominant is five times higher than that when Bi antisite is dominant. Hence, a little random fluctuation of missing Te generates more serious irreproducible electrical resistivity and Seebeck coefficient in n-type Bi\textsubscript{2}Te\textsubscript{3} rather than p-type Bi\textsubscript{2}Te\textsubscript{3}. It is worth pointing out that both the situations described by Equation 3.1 for n-type and Equation 3.2 for p-type are the ideal cases. In the real case, there are minor acceptor-like Bi\textsubscript{Te}\textsuperscript{V} or Bi\textsubscript{Se}\textsuperscript{V} antisite defects besides the major donor-like V\textsubscript{Te}\textsuperscript{V} and V\textsubscript{Se}\textsuperscript{V} vacancies in n-type Bi\textsubscript{2}Te\textsubscript{3} alloying, while there is also minor donor-like V\textsubscript{Te}\textsuperscript{V} besides the major acceptor-like Sb\textsubscript{Te}\textsuperscript{V} or Bi\textsubscript{Te}\textsuperscript{V} antisite defects in p-type Bi\textsubscript{2}Te\textsubscript{3}. The alloy with Sb usually increases the concentration of antisite defect on Te-site (Sb\textsubscript{Te}\textsuperscript{V}) and hence gives more holes due to the smaller electronegativity difference between Sb (2.05) and Te (2.10) than that between Bi (2.02) and Te (2.10). The alloy with Se usually increases the concentration of vacancy on the Te site (V\textsubscript{Se}\textsuperscript{V}) and, hence, gives more electrons because Se has a lower energy of evaporation (37.70 kJ/mol) than Te (52.55 kJ/mol). The concentration of vacancy (V\textsubscript{Te}\textsuperscript{V} and V\textsubscript{Se}\textsuperscript{V}) in n-type Bi\textsubscript{2}Te\textsubscript{2}−xSe\textsubscript{x} will be higher than that in p-type Sb\textsubscript{2}−xBi\textsubscript{x}Te\textsubscript{3}, which is another reason why we have a more serious reproducibility problem in n-type Bi\textsubscript{2}Te\textsubscript{3}−xSe\textsubscript{x} rather than in p-type Sb\textsubscript{2}−xBi\textsubscript{x}Te\textsubscript{3}.
The key to improve the reproducibility of n-type Bi₂Te₂.₇Se₀.₃ was to suppress the generation of Te vacancy, including both whole V₆₀ and fractional V₆₀. Reducing the energy of the BM process, such as decreasing BM rotation speed and adjusting the BM medium filling parameter, would decrease the mechanical deformation and thus, reduce, the generation of Te vacancy. However, we desired the high BM energy to achieve finer grains and high hot press temperature to optimize grain boundaries. One of the alternative choices was to raise the formation energy of the \( V_{Te}^{\bullet\bullet} \) and \( V_{Se}^{\bullet\bullet} \) by doping. Figure 3.8c and d presents the temperature dependence of electrical resistivity and Seebeck coefficient for eight batches of Cu₀.₀₁Bi₂Te₂.₇Se₀.₃. The reproducibility of the Cu-added n-type Cu₀.₀₁Bi₂Te₂.₇Se₀.₃ is obviously improved. The coefficient of variation of electrical resistivity, Seebeck coefficient, and PF for Cu₀.₀₁Bi₂Te₂.₇Se₀.₃ were 1.₉₂%, 1.₀₀% and 0.₉₈%, respectively, which is much lower than 1₃.₂₃%, 6.₅₀%, and 3.₄₇% for Bi₂Te₂.₇Se₀.₃, respectively. Here, the Cu was believed to raise the formation energy of chalcogen vacancy and suppress escaping Te and Se. However, it is worthy to point out that Cu ion is mobile which could lead to some thermal stability problem under a thermal gradient. Instead, slight extra Se or S was used to suppress the appearance of Te vacancy and, hence, minimize the performance fluctuation from batch to batch.

### 3.1.3.3 Texture for the Enhanced ZT

Besides the challenges mentioned earlier, the simple BM-HP route is still not enough to achieve an enhanced \( ZT \) in the n-type Bi₂Te₃₋ₓSeₓ material compared with the single crystalline counterpart. The significantly decreased lattice thermal conductivity is offset by the reduced PF due to the decreased carrier mobility. Here, we use the Bi₂Te₃₋ₓSeₓ single crystals grown by Scherrer and Sherrer⁴,⁵ as a reference. The optimized PF of Bi₂Te₃₋ₓSeₓ single crystals is around 5₀ μW/cm K² for \( x = 0.₇₅ \), 4₆ μW/cm K² for \( x = 0.₁₅ \), and 4₂ μW/cm K² for \( x = 0.₄₅ \) when the Seebeck coefficient is around −₂₀₀ μV/K. However, many of the early efforts on fine-grained or nano-structured Bi₂Te₃₋ₓSeₓ by the BM-HP route only resulted into a PF less than 2₀ W/cm K².⁴₈,⁴₉,₅₃,₆₁–₆₄ The deteriorated effect of the oxygen could be one of the reasons for the low PF.⁶₅–₆₈ However, even with a well protection, the nanocrystalline Bi₂Te₃₋ₓSeₓ with randomly distributed grains only reach a power of 2₄–₂₈ μW/cm K².¹₉,₅₄–₅₇,₆₀ The Cu-doped nanocrystalline Bi₂Te₂.₇Se₀.₃ was reported to have slightly superior PF of 3₁ μW/cm K².⁶₀ However, it is still ~3₀% lower than the PF of Scherrer an Sherrer’s⁴,⁵ single crystals. It is worthy to point out that the similar BM-HP could make a nanocrystalline Bi₀.₄Sb₁.₆Te₃ having a PF of 4₅ μW/cm K² comparable with its single crystal counterpart.²⁰ It was well known that the n-type Bi₂Te₂.₇Se₀.₃ has higher anisotropic electrical transport properties between the in-plane and out-of-plane directions than the p-type Bi₀.₄Sb₁.₆Te₃ (use the basal plane containing the van der Waals bonds).⁴,⁵ This fact leads to the n-type Bi₂Te₂.₇Se₀.₃ suffering more from the randomly distributed grains. An effective way to reconstruct the transport channel of the electrons is to further align the randomly distributed grains. Two general approaches were reported to achieve the
texture in the Bi$_2$Te$_3$-based materials: hot extrusion and hot forging. The hot extrusion route is characterized when the material flowing direction is parallel to the pressure. Figure 3.9 illustrates two main hot extrusion routes: one is the unequal channel linear extrusion (Figure 3.9a); another is equal channel angular extrusion (Figure 3.9b). For the unequal channel linear extrusion, the deformation is mainly determined by the channel size reduction ratio (or extrusion ratio). Seo et al.\textsuperscript{70} fabricated n-type Bi$_2$Te$_{2.85}$Se$_{0.15}$ by hot extrusion in the temperature range of 300–440°C under an extrusion ratio of 20:1. The hot extrusion gave rise to a slightly preferred orientation of grains with an orientation factor \(F(0 \ 0 \ l)\) of 0.16. Here, the orientation factor was calculated by the Lotgering method using the following:\textsuperscript{71}

\[
F = \frac{P - P_0}{1 - P_0}, \quad (3.3)
\]

where \(P = I(0 \ 0 \ l)/\sum I(b \ k \ l), \ P_0 = I_0(0 \ 0 \ l)/\sum I_0(b \ k \ l)\). \(P\) and \(P_0\) are the ratios of the integrated X-ray intensities of all \((0 \ 0 \ l)\) planes to those of all \((b \ k \ l)\) planes for the preferentially oriented and randomly oriented samples, respectively. At a higher temperature of 450°C, Hong et al.\textsuperscript{72} obtained stronger texture with an orientation factor of 0.17–0.2 in the n-type Bi$_2$Te$_{2.85}$Se$_{0.15}$ at an extrusion ratio of 16:1. By using an even higher temperature of 480°C and high extrude ratio of 25:1, Hong and Chun\textsuperscript{73} got a higher orientation factor of 0.23, which also resulted in a marked PF of 53 \(\mu\)W/cm K$^2$. Besides the extrusion ratio and temperature, Yang et al.\textsuperscript{74} showed that the extrusion angle also played an important role in plastic deformation. The die with lower extrusion angle had longer or larger regions of deformation, resulting in lower deformation and, thence, less micropores.\textsuperscript{74} It was found that hot extruded material had a ringlike texture in which the normal to the basal plane orient to the radial direction and [110] orient to the extrusion direction.\textsuperscript{75} Equal channel

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.9.png}
\caption{Schematic figure of the hot extrusion: (a) unequal channel linear extrusion and (b) equal channel angular extrusion.}
\end{figure}
angular extrusion (ECAE) is another widely used thermal extrusion process.\textsuperscript{76,77} For example, Fan et al.\textsuperscript{76} reported an orientation factor of 0.26–0.28 in n-type Bi\textsubscript{2}Te\textsubscript{2.85}Se\textsubscript{0.15} by performing ECAE under a ram speed of 2.5 mm/min in the temperature range 380–480°C in argon atmosphere. The stainless steel die was used for the extrusion process, and graphite powders were coated with the extrusion die to reduce the friction force. Hayashi et al.\textsuperscript{77} observed continuously improved carrier mobility from 140 cm\textsuperscript{2}/V s (without ECAE) to 240 cm\textsuperscript{2}/V s (six times of ECAE) by applying multitime ECAE. The orientation imaging microscopy confirmed the formation of textured grains and twin boundaries, which also explains the high PF of 40 \textmu W/cm K and an improved $ZT$ of 0.9 near-room temperature in the sample after six times of ECAE. The thermal extrusion has also been used in the p-type Bi\textsubscript{2−x}Sb\textsubscript{x}Te\textsubscript{3} materials.\textsuperscript{70,78}

Compared with hot extrusion, hot forging involves slightly simple and easy processing and also has two common modes: radial flow hot forging and uniaxial flow hot forging as shown in Figure 3.10. The (00l) texture has been early identified in the hot pressed Bi\textsubscript{2}Te\textsubscript{3}-based bulks. It was found that the hot pressed bulk from the spherical particles (by gas atomizing method) showed an isotropic thermoelectric properties, while the hot pressed bulk from the flake-like particles showed anisotropic behavior.\textsuperscript{79} Jiang et al.\textsuperscript{80} obtained a strong texture ($F = 0.8$) in the n-type Bi\textsubscript{2}Te\textsubscript{0.79}Se\textsubscript{0.21} by using big grinding

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure310.png}
\caption{Schematic figure of the hot forging: (a) radial flow hot forging and (b) uniaxial flow hot forging.}
\end{figure}
particles (180–380 μm). However no notable enhancement in the $ZT$ was observed due to the comparable thermal conductivity and reduced PF compared with as-grown ingot. The orientation factor was almost independent of sintering temperature in the range of 400–440°C. Furthermore, the orientation factor was significantly reduced from 0.85 to 0.4 when the particles size reduced from 180–380 to 90–120 μm, which suggested that these textures are controlled by the size and morphology of the starting particles. Besides the plastic flow, similar compacting texture was also observed in a p-type $Bi_{0.4}Sb_{1.6}Te_3$ case (100–175 μm) with strong morphological anisotropy. When the particle size went down in nanoscale, the texture due to the particle morphology become much weaker. In order to get a high orientation in fine-grained $Bi_2Te_3$, a flowing assistant hot forging is necessary. Usually, a hot pressed bulk was used for the hot forging to develop the strong texture. Zhao et al. reported a highly textured $Bi_2Te_3$ with an orientation factor of $F = 0.67$ by radial flowing hot forging from φ15 mm rod into φ20 mm, which corresponds to a PF of 33 μW/cm K$^2$, with 70% enhancement compared with the originally pressed bulk. Hu et al. reported that multitime radial flow multitime hot-forging could continuously improve the grain alignment of the $Bi_2Te_2Se_1$. They also named their process a repetitive hot deformation. In their experiment, casted ingots were ground into fine powders and then hot pressed into a φ10 mm rod at 400°C for 30 min. Subsequently, the HP bulk was placed in the center of a larger die with an inner diameter of 16 mm and re-pressed at 550°C (HD1). Then, a disk of φ10 mm was cut from the φ16 mm HD1 bulk, and the φ 16 mm die was put back for the second time, hot forging into φ 16 mm bulk (HD2). These processes were repeated to get the HD3 bulk, which shows a higher orientation factor of 0.48 compared with $F = 0.2$ for the HP bulk. However, a further hot forging cannot get notable higher orientation factor ($F = 0.46$ for the HD4). Figure 3.11 shows the temperature-dependent thermoelectric properties of the multitime radial flowing hot forged $Bi_2Te_2Se_1$. The PF was continuously increased from 13 μW/cm K$^2$ (HP bulk) to 29 μW/cm K$^2$ (HD4 bulk), and the peak $ZT$ was improved from 0.57 (HP) to 1 (HD4). Besides the developed texture, the same group of authors also suggested that the re-pressed process might further introduce some new lattice defect resulting in decreased lattice thermal conductivity because of a recrystallization process. It was noted that they might overestimate the electronic thermal conductivity by using an empirical Lorenz number $2.0 \times 10^{-8}$ V$^2$/K$^2$. The sample with higher texture would have an overestimated electrical conductivity and an underestimated $\kappa_{carr}$ ($\kappa_{carr} = L\sigma T$); as a result, it could lead to a underestimated $\kappa_{latt}$ from the relationship, i.e., $\kappa_{latt} = \kappa_{tot} - \kappa_{carr}$. The new developed lattice defect might cause a decreased thermal conductivity for some special case, such as a zone melt ingot as a start rod for the hot deformation. In contrast to the radial flow hot forging, we developed the uniaxial flow hot forging (W. S. Liu and Z. F. Ren, unpublished, 2012), as shown in Figure 3.12a. Firstly, BM-ed nanopowders were hot pressed into a rod (φ = 0.5” and length = 0.5”) at 500°C, which was referred to as as-pressed (AP) bulk. Then half of the
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A rod was placed in a big die and was uniaxial repressed into a plate (length = 1” and width = 0.5”) at 525°C, which was identified as first re-pressed (RP1) bulk. Then, the plate was polished, cleaned, and then cut into two identical pieces and stacked together for re-pressing into a plate (length= 1” and width = 0.5”) again, which was referred as second re-pressed (RP2) bulk. Then, the RP2 plate was repetitively polished, cleaned, cut, stacked, and re-pressed into the third re-pressed (RP3) bulk. The advantage of uniaxial flow hot forging is that it is easy to execute the multitime repressing. Figure 3.12b through e shows the thermoelectric properties of multitime repressed Cu_{0.005}Bi_{2}Te_{2.7}Se_{0.3} and their X-ray powder diffraction (XRD) patterns. The significant increased peak PF from 28.7 μW/cm K^2 (AP) to 42.2 μW/cm K^2 (RP3) was consistent with the developed (00l)-texture by the multitime repressing. The (00l) orientation factor from the XRD pattern was 0.22 for RP1 bulk, 0.30 for RP2 bulk, and 0.38 for RP3 bulk. In our case, the lattice thermal conductivity was slightly increased with the improved texture, finally reaching a highest peak ZT of 1.1 at 100°C in RP3 Cu_{0.005}Bi_{2}Te_{2.7}Se_{0.3}, which is near 30% higher than that of the AP one (0.85 at 100°C).

FIGURE 3.11 Thermoelectric properties and (00l) texture of the multitime radial flow hot forged Bi_{2}Te_{2}Se_{1}: (a) electrical conductivity, (b) Seebeck coefficient, and (c) PF. (d) XRD patterns of textured Bi_{2}Te_{2}Se_{1}. (Reprinted from Acta Materialia, 60, Hu, L. P. et al., Improving thermoelectric properties of n-type bismuth-telluride-based alloys by deformation induced lattice defect and texture enhancement, 4431–4437, Copyright (2012), with permission from Elsevier.)
3.1.4 Outlook

In this section, we reviewed the most recent advances in Bi$_2$Te$_3$-based materials by using the powder metallurgy routes, such as BM-HP and MS-SPS. We did not have enough space to give enough praise for the efforts on the chemical metallurgy routes for the nanostructured Bi$_2$Te$_3$-based thermoelectric materials. We also discussed some challenges met in the n-type nanocrystalline Bi$_2$Te$_3$-$\text{Se}_x$, such as the equivalent doping effect of BM-HP, reproducibility from batch to batch, and texture for the enhanced $ZT$. It is noted that the highest temperature usage for Bi$_2$Te$_3$ is around 250°C due to poor thermoelectric performance and thermal stability at higher temperature. Some new V$_2$- to VI$_3$-type compounds, such as Bi$_2$Te$_2$S, and Bi$_2$SeS$_2$, have shown to be promising for overcoming the usage temperature limit, which desires more some attentions.
3.2 MgAgSb Low-Temperature Thermoelectric Materials

Jiehe Sui, Zihang Liu, and Zhifeng Ren

3.2.1 Introduction

For low-temperature applications, p-type Bi$_x$Sb$_{2-x}$Te$_3$ thermoelectric materials have received dominant attentions since 1950s. The highest $ZT$ could surpass the benchmark of ~1 by nanostructuring or hot deformation. Nevertheless, the strong bipolar effect above 373 K severely degrades its performance, which restricts the utilization merely around room temperature. Even worse, due to the fact that tellurium (Te) is an extremely scarce element on the earth’s crust, this further limits the widespread application. Therefore, searching for a better alternative without Te that can work at higher temperature is necessary and critical in thermoelectric field.

Recently, MgAgSb-based materials have been developed as a promising p-type candidate for power generation below 550 K, possessing an exciting conversion efficiency of about 8.5% for $T_c = 293$ K and $T_h = 518$ K. The heavy valence band and intrinsically weak electron–phonon scattering contribute to the relatively high PF; meanwhile, the distorted crystal structure and multiscale microstructure result in low thermal conductivity, which will be discussed in detail later.

3.2.2 Crystal Structure and Band Structure

3.2.2.1 Crystal Structure

As first reported by Kirkham et al., pristine MgAgSb has complicated phase transitions from room-temperature $\alpha$ phase to intermediate-temperature $\beta$ phase and finally to high-temperature $\gamma$ phase. $\alpha$-MgAgSb has a tetragonal structure with space group $I4\bar{1}2$, as shown in Figure 3.13a. Sb atoms form a face-centered cubic closely packing sublattice, with Mg and Ag atoms lying in the centers of all the Sb octahedrons and half of the Sb tetrahedrons, respectively. The filled sites form one-dimensional chains, running in all three primary directions. But the Mg–Sb rock salt lattice is a distorted structure, rotated by 45° about the $c$ axis. $\beta$-MgAgSb phase is also tetragonal.

FIGURE 3.13 Crystal structure of MgAgSb: (a) $\alpha$ phase, (b) $\beta$ phase, and (c) $\gamma$ phase.
with space group P4/nmm (129) shown in Figure 3.13b. Mg and Sb atoms form a distorted rock salt lattice, as in the low-temperature phase, and Ag atoms fill half of the distorted Mg–Sb pseudocubes. The structure is similar to the Cu₃Sb structure with Mg and Ag each replacing one of the two Cu sites. γ-MgAgSb is cubic with space group F43m (216), as shown in Figure 3.13c. In fact, this crystal structure is identical to half-Heusler structure. Mg and Sb atoms form the rock salt sublattice, and Ag atoms fill half of the tetrahedral interstices, alternating between filled and empty sites.

### 3.2.2.2 Band Structure

Since α-MgAgSb has an excellent thermoelectric performance, the following discussions mainly focus on its structure, properties, and their relationship. Ying et al.⁹⁹ first calculated the band structure within the density functional theory (DFT) using the projector augmented wave method. The result showed that α-MgAgSb was a narrow bandgap semiconductor with an indirect gap energy of ~0.1 eV. The top of the valence band was at the X-point, while the bottom of the conduction band was located at the G-point. Moreover, the DOSs of the valence band edge was much higher than that of the conduction band edge. Similarly, Li et al.¹⁰⁰ performed the band structure calculation of α-MgAgSb based on DFT plus Generalized Gradient Approximation-Perdew Brueke Ernzerhof (GGA-PBE) function, which had an indirect bandgap of ~0.063 eV. Sheng et al.¹⁰¹ also predicted that α-MgAgSb was a semiconductor using the Becke–Johnson (mBJ) and Heyd–Scuseria–Ernzerhof (HSE) methods, while it was a semimetal using PBE method, as shown in Figure 3.14.

However, Miao et al.¹⁰² presented a comprehensive theoretical study of the structural, electronic, and thermoelectric properties of MgAgSb by combining first-principles calculations and Boltzmann transport theory. They claimed that the α phase was better classified as a semimetal with highly dispersive conduction and valence bands overlapping slightly and crossing the Fermi level at distinct k-points using different calculation methods, including GGA-PBE, local-density approximation (LDA), and GGA-PBEsol. They assumed that previous investigations restricted their calculations to a limited path within the primitive Brillouin zone that did not cross the hole pockets. Moreover, a semimetal–to-semiconductor transition in α-MgAgSb had been predicted with raising the pressure.¹⁰³ The true band structure needed to be clarified by further optical properties measurement.

### 3.2.3 Synthesis Method

Kirkham et al.⁹⁸ first tried to prepare the pristine MgAgSb using a normal method, including vacuum melting, long-time annealing, and hot pressing procedures. However, there were high contents of secondary phases based on the XRD pattern analysis, namely, Sb and Ag₃Sb. Then, Ying et al.⁹⁹ used a similar controlled fabrication process and finally obtained a much lower content of impurity phases and the mass fraction of around 2%. Zhao et al.⁹² first employed a simple and novel two-step BM and quick hot press method,
finely tuned the composition from MgAgSb to MgAg\textsubscript{0.97}Sb\textsubscript{0.99} and obtained the pure phase of nanostructured MgAgSb within the detection limit of the XRD analysis.

### 3.2.4 Microstructure

The following part mainly focuses on the microstructure of nanostructured MgAgSb. The SEM image and medium-magnification transmission electron microscopy (TEM) image showed the typical grain size of around 150 nm (Figure 3.15a). Moreover, some nanoinclusions ranging from 5 to 10 nm...
FIGURE 3.15  (a) Medium-magnification TEM image showing mesoscale grains; (b) high-magnification TEM image of the grain boundary showing good crystallization; the inset corresponds the FFT image along the \( c \) zone axis direction; (c) high-magnification TEM image showing nanoinclusions; (d) high-magnification TEM image showing high-density stacking faults; (e) high-magnification TEM image showing specific morphology of stacking fault; (f) FFT image along the [021] direction; (g) high-magnification TEM image showing a large quantity of dislocations inside the grain; (h) corresponding IFFT images showing a density of dislocation \( \sim 3.3 \times 10^{11} \) cm\(^{-2} \) with the enlarged dislocations and GPA images as insets. (Reproduced with permission from Liu, Z. et al.: Lithium doping to enhance thermoelectric performance of MgAgSb with weak electron–phonon coupling. *Advanced Energy Materials*. 6. 1502269. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.)
under high magnification can also be observed (Figure 3.15c). Moreover, a high number of defects could be seen in some grains, mainly including a high density of nanoscale stacking faults and dislocations. Careful investigations of the stacking faults showed that the typical morphology of the nanoscale stacking fault is about 20 nm in length (Figure 3.15d and e). The corresponding fast Fourier transformation (FFT) image further demonstrated the existence of stacking faults, playing a vital role in scattering those short to medium wavelength phonons. More importantly, a large quantity of dislocation could be clearly observed inside the grain, as shown in Figure 3.15g. To study the surrounding strain field around the dislocation cores, a high-quality high-resolution transmission electron microscopy (HRTEM) image was analyzed via geometric phase analysis (GPA), as shown in the inset in Figure 3.15h, both of which could act as effective scattering centers for short-wavelength phonons.

3.2.5 Thermoelectric Properties

3.2.5.1 Thermoelectric Properties of Pristine MgAgSb

Because there are some differences about thermoelectric properties between unheated and heated MgAgSb samples, it should be noted that all the thermoelectric properties discussed later are about the heated sample. As shown in Figure 3.16a, the electrical resistivity first increases from $3.6 \times 10^{-5} \, \Omega \cdot m$ at 300 K to $4.3 \times 10^{-5} \, \Omega \cdot m$ at 348 K and then sharply decreases to $2.1 \times 10^{-5} \, \Omega \cdot m$ due to the strong bipolar effect. Moreover, it shows a dependence of temperature ($\rho$ versus $T^{3/2}$), which confirms a carrier transport mechanism dominated by acoustic phonon scattering before the intrinsic excitation. The relatively high electrical resistivity is ascribed to the low carrier concentration, e.g., $2.7 \times 10^{19} \, cm^{-3}$ at 300 K. As expected, the Seebeck coefficients show the same tendency with the electrical resistivity. The large Seebeck coefficients, e.g., 255.8 $\mu$V/K at 300 K, are due to the typical heavy band feature, as shown in Figure 3.16b. The high DOS effective mass at the Fermi level ($m^*$) at 300 K can be roughly calculated assuming a single parabolic band model and an acoustic phonon scattering mechanism. The obtained value is around 2.4 $m_e$ at 300 K, as shown in Figure 3.16c, which can be ascribed to the flat valence band ($m^*_v = 1.3m_0$) rather than a highly degenerated electronic band. The deformation potential $E_{def}$ can be roughly estimated by the following equation when the acoustic phonon scattering is dominant:

$$E_{def}^2 = \frac{(8\pi)^{1/2}(h/2\pi)^4 e \rho v_L^2}{3(m^*_v)^{5/2}(k_B T)^{3/2} \mu_H},$$

(3.4)

where $\rho$ is density ($\sim 6.2 \, g/cm^3$), $v_L$ is the longitudinal velocity of sound ($\sim 3708 \, m/s$), and $\mu_H$ is the drift mobility ($\mu_H = \mu_{H_{14}}$). The obtained deformation potential $E_{def}$ is about 6.6 eV. Typically, the reported deformation potential $E_{def}$ for thermoelectric materials ranges from 5 to 35 eV, which means
that the deformation potential $E_{\text{def}}$ of MgAgSb is at the lower end, demonstrating weak electron–phonon coupling. The calculated PF maintains a relatively high value at the whole measured temperature range, e.g., 18.2 $\mu$W/cm K$^2$ at 300 K and 21.8 $\mu$W/cm K$^2$ at 548 K. As shown in Figure 3.16d, the total thermal conductivity $\kappa_{\text{total}}$ first decreases at a low-temperature range due to the Umklapp scattering process and then increases at a higher temperature because of the bipolar effect. The difference between the total thermal conductivity $\kappa_{\text{total}}$ and the electronic thermal conductivity $\kappa_{\text{ele}}$ before intrinsic excitation can be approximately estimated as the lattice thermal conductivity $\kappa_{\text{lat}}$, neglecting the contribution of bipolar effect. From the W-F relationship,
κ_{ele} can be calculated (κ_{ele} = LσT), where L is the Lorenz number calculated based on the single parabolic model with an acoustic phonon scattering mechanism. As shown in Figure 3.16e, room-temperature κ_{lat} is around 0.66 W/m K, much lower than that of the state-of-art thermoelectric materials. This intrinsically low κ_{lat} is due to the combination of weak bonding and intricate microstructure. Finally, the obtained ZT is shown in Figure 3.16f, with peak ZT and average ZT of around 1.2 and 1.0, respectively. Furthermore, it is a very promising candidate to fill the gap in the p-type ZT spectrum between low-temperature BiSbTe alloys and medium to high temperature CoSb3-based and PbTe-based materials.

### 3.2.5.2 Optimizing the Thermoelectric Properties upon Doping

Due to the relatively low carrier concentration of pristine MgAgSb, effective doping aims to increase the carrier concentration and optimize the electrical transport properties. As shown in Figure 3.17, Li doping is more...
effective to supply holes as an acceptor dopant in the MgAgSb system, compared to Na and Cu dopings or Sb content tuning. The highest carrier concentration has already exceeded $10^{20}$ cm$^{-3}$ with 2% Li doping concentration or more. That is why Li doping can lead to the lowest electrical resistivity and highest PF in the MgAgSb system. Assuming the single parabolic band model and an acoustic phonon scattering mechanism, the calculated carrier concentration dependence of PF at room temperature is shown in Figure 3.17. The optimum carrier concentration for PF is around $9 \times 10^{19}$ cm$^{-3}$, in good agreement with the measured Li doping data. Furthermore, the average PF from 300 to 548 K somewhat increases upon doping, e.g., 19.6 $\mu$W/cm K$^2$ for pristine MgAgSb and 24.6 $\mu$W/cm K$^2$ for 1% Li doping.

Although the electrical transport properties show a regular change upon extrinsic doping, the thermal transport properties seem to be abnormal. For example, doping with Ni or Cu observably suppresses the lattice thermal conductivity compared with other methods, especially in the low-temperature range. The underlying mechanism for this phenomenon is still unknown that needs further investigations through first principles calculations or neutron diffraction. Due to the point defect scattering, doping slightly decreases the lattice thermal conductivity except for Ni or Cu doping. Since weak chemical bonding and intricate microstructure scatter the heat-carrying phonons from atomic scale to microscale, extrinsic doping would not significantly affect the phonon transport in general.

### 3.2.6 Contact and Conversion Efficiency

Silver pad has been demonstrated as a proper electrical contact with low electrical resistance for MgAgSb using a simple one-step hot press technique, as shown in Figure 3.18a. The obtained sample is given in Figure 3.18b, with a size of $3 \times 3 \times 5$ mm$^3$. The reason for choosing silver contact mainly includes two parts: First, the coefficients of thermal expansion with $19.5 \times 10^{-6}$/°C for silver and $20 \times 10^{-6}$/°C for the MgAgSb are well matched; second, silver is one of the component elements of MgAgSb that reduces elemental diffusion due to the smaller concentration gradient. A clean and well-defined interface between MgAgSb and silver contact indicates that there is only minimal elemental interdiffusion during the fabrication process.

Due to the combination of high average $ZT$ and low electrical resistance, the measured single thermoelectric leg device efficiency of MgAgSb compound with hot pressed silver contacts is around 8.5% operating between 293 and 538 K using home-designed system (Figure 3.18c). The high efficiency value substantially outperforms the previous reports of other thermoelectric modules in the same temperature range, including commercial p-type Bi$_2$Te$_3$-based material shown in Figure 3.18d.
3.2.7 Conclusion

Pristine $\alpha$-MgAgSb exhibits typical semiconductor properties and possesses excellent thermoelectric performance at the low-temperature range. Proper doping increases the carrier concentration and thus optimizes the electrical transport properties. In addition, the combination of weak chemical bonding and multiscale microstructure scatters the heat-carrying phonons. Therefore, a high peak $ZT$ and average $ZT$ can be finally achieved. More importantly, a record high conversion efficiency of 8.5% for $T_c = 293$ K and $T_h = 518$ K has been experimentally demonstrated for hot pressed MgAgSb with Ag contact, which highlights the realistic potential of MgAgSb for power generation in the low-temperature range.
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