Thermoelectric Property Studies on Cu-Doped n-type Cu$_x$Bi$_2$Te$_{2.7}$Se$_{0.3}$ Nanocomposites

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Combining high energy ball-milling and hot-pressing, significant enhancements of the thermoelectric figure-of-merit (ZT) have been reported for p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanocomposites. However, applying the same technique to n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$ showed no improvement on ZT values, due to the anisotropic nature of the thermoelectric properties of n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$. Even though texturing was effective in improving peak ZT of Bi$_2$Te$_{2.7}$Se$_{0.3}$ from 0.85 to 1.04, reproducibility from batch to batch remains unsatisfactory. Here, we show that good reproducibility can be achieved by introducing an optimal concentration of 0.01 copper (Cu) per Bi$_2$Te$_{2.7}$Se$_{0.3}$ to make Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples. A peak ZT value of 0.99 was achieved in Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples without texturing. With texturing by re-pressing, the peak ZT was increased to 1.06. Aging in air for over 5 months did not deteriorate but further improved the peak ZT to 1.10. The mechanism by which copper improves the reproducibility, enhances the carrier mobility, and reduces the lattice thermal conductivity is also discussed.

1. Introduction

Thermoelectric effects involve direct conversion between thermal and electrical energy by employing electrons and holes as energy carriers. Such effects are potentially useful for waste heat recovery and for thermal management of microelectronics and biological systems.[1] The energy conversion efficiency of thermoelectric devices is governed by the dimensionless thermoelectric figure-of-merit (ZT) defined as $ZT = (S^2\sigma/k)T$, where $S$, $\sigma$, $k$, and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature. Since $S$, $\sigma$, and the electronic contribution to $k$ are coupled via band structures (energy gap $E_g$, charge carriers’ effective mass $m^*$, etc.) and scattering mechanisms, it is difficult to control the parameters independently.[2] Therefore, ZT-1 has been regarded as a benchmark for many thermoelectric materials for a long time.

Bi$_2$Te$_3$-based alloyed thermoelectric materials have been studied extensively since the 1960s.[3] Single-crystal p-type Bi$_2$Sb$_{1-x}$Te$_3$ alloys and n-type Bi$_{1-x}$Te$_x$Se$_3$ alloys are still the best commercially available thermoelectric materials for applications at or near room temperature. Nevertheless, the lamellar structure and weak van der Waals bond between the two quintets makes them susceptible to easy cleavage along their basal planes, perpendicular to the c-axis, and hence impart very poor mechanical properties. For this reason, their polycrystalline counterparts are also used in commercial devices, despite their worse thermoelectric performance.[4–6]

Recently, ZT values of 1.3 using elemental chunks[7] and 1.4 using crystalline ingots[8] as the feedstocks were achieved in nanostructured p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanocomposites by combining high-energy ball milling (BM) and direct current hot-pressing (dc-HP). These values correspond to a 30–40% improvement in the peak ZT values compared with their single-crystal counterpart. Microstructure analysis by transmission electron microscopy (TEM) demonstrated that the high ZT values resulted from a significantly decreased lattice thermal conductivity arising from the scattering of grain boundaries and nanoprecipitates.[9] Nanoengineering has now become the preferred approach in enhancing thermoelectric materials’ performance.[10–12] This simple BM-HP route was also applied to fabricate polycrystalline n-type Bi$_{1-x}$Te$_x$Se$_3$ nanocomposites. However, no obvious improvement in ZT value was obtained since the gain from the decreased lattice thermal conductivity was offset by the reduced power factor due to the decreased carrier mobility and the increased carrier thermal conductivity due to the increased carrier concentration. It is reported that the n-type Bi$_2$Te$_{1-x}$Se$_x$ ingots have similar high power factor to that of p-type Bi-Sb-Te ingots.[13] However, the power factor of n-type Bi$_2$Te$_{1-x}$Se$_x$ single crystals is more sensitive to the lattice directions.[14] The power factor along the basal plane is much higher than that perpendicular to the basal plane. This high electrical anisotropy results in a much lower average power factor for polycrystalline samples with randomly oriented grains than that of single crystals grown along the basal plane. Since the p-type
Bi₂Sb₂Te₅ single crystals are less sensitive to lattice directions, the polycrystals have a similar power factor to the single crystals. It has been experimentally confirmed that reorientation of randomly oriented grains can improve the carrier mobility of n-type Bi₂Te₅S₅ polycrystalline samples and hence enhance their ZT values. However, the significantly increased carrier concentration is probably related to the lattice defects generated from the heavy deformation during the BM process, such as Te vacancies (V_{Te}) that can provide two free electrons. Recently, Jiang et al. conducted an experiment in which they crushed Bi₂Te₃₋₅Seₓ ingots fabricated by zone-melting into powders, sieved them into three grades of size 96–120, 120–180 and 180–380 μm, and finally sintered them into bulk samples. The results showed that the samples formed from finer particles had higher electron concentrations. Jiang et al. attributed this increased carrier concentration from reduced starting particle size to the increase of the V_{Te} concentration. Another possible explanation for increased carriers is defect states related to dangling bonds at the grain boundary of Bi₂Te₃₋₅Seₓ. Donor-like defect states increase the carrier concentration, and therefore decrease the Seebeck coefficient. Furthermore, these donor-like defects are extremely difficult to control, and hence probably lead to the serious irreproducibility problem related to the fabrication parameters, such as BM time, BM energy, HP temperature, heat treatment, etc. For industrial large scale production, good process reproducibility is equally as important as the high ZT value.

The effect of copper as a donor in Bi₂Te₃-based alloys has been widely investigated in both single-crystal bulk (via direct addition and electrochemical intercalation) and polycrystalline samples. Increased carrier mobility and aging problems have been noted in copper-doped Bi₂Te₃-based alloys. Our investigation concerned the effect of copper on reproducibility and thermoelectric properties of CuₓBi₂Te₂₋₅Seₓ nanocomposite fabricated by combining BM and dc-HP. Re-orientation of random grains was also conducted to further improve the ZT value of Bi₂Te₃-based nanocomposites, as demonstrated previously and the effect of aging time on thermoelectric properties was also investigated. We also try to explain why copper can simultaneously improve the reproducibility, increase the carrier mobility, and decrease the lattice thermal conductivity.

2. Results

2.1. Processing Reproducibility

Figure 1(a,b) shows the temperature-dependent electrical resistivity and Seebeck coefficient of ten batches of Bi₂Te₂₋₅Seₓ fabricated by ball-milling and hot-pressing methods under the same fabrication conditions. It clearly shows that both the electrical resistivity and Seebeck coefficient are highly irreproducible from batch to batch. It seems that some batches show typical semiconductor behavior while others behave as semimetals, which indicates that the carrier concentration of the as-fabricated Bi₂Te₂₋₅Seₓ samples changes from batch to batch. After extensive experimentation, we found that the irreproducibility issue is related to the ball-milling rather than the hot-pressing process. It has been reported that the grain size reduction and solid-state reaction during the ball-milling process are driven by the accumulation of mechanical energy as a result of random ball-to-ball and ball-to-wall collisions. Ball-milled powers are homogenous on the macroscale, but inhomogeneous in microscale due to a broad particle size distribution, presence of nanoscale inclusions, and atomic defects. The uncontrollable atomic defects in Bi₂Te₂₋₅Seₓ arising from mechanical deformation are therefore considered a direct reason for the carrier concentration fluctuation from batch to batch. The most common defects in Bi₂Te₃-based alloys include antisite defects of Bi in Te-sites (Bi₅Te, contributes one hole per defect), vacancies at the Te-sites (V_{Te}, contributes two electrons per defect), and vacancies at Bi-sites (V_{Bi}, contributes three holes per defect). Since the energy of evaporation for Te (52.55 kJ/mol) is much lower than that of Bi (104.80 kJ/mol), the evaporation of Te is much easier than that of Bi. The evaporation of each Te leaves one Te vacancy (V_{Te}) with two free electrons, as indicated in Equation (1).

\[
B_{i_3}T_{e_3} = 2B_{i_5}^{m} + (3 - x) Te^{g} + xTe^{+} + 2xe^{-}
\]

(1)

Because of the small difference in electronegativity between Te (2.1) and Bi (2.02), Bi can easily jump from Bi-sites to Te-sites to form antisite defects, contributing one hole as a free carrier. Most Bi₂Te₃ single crystals or ingots with large grains are therefore intrinsically p-type. For fine-grained polycrystalline samples, the dangling bonds at grain boundaries due to Te deficiencies can also be considered as fractional-V_{Te}, and also work as n-type doping in the same manner as the whole-V_{Te} defects inside the grains. We also noted that vacancies at the Bi-sites and Te-sites can cancel each other out at a ratio of V_{Bi}/V_{Te} = 2.3, and contribute to zero net free charge. We therefore arrive at a defect formation equation, Equation (2), where vacancies at the Te-sites are totally neutralized by antisites at Te-sites and vacancies at Bi-sites.

\[
B_{i_3}T_{e_3} = \left(2 - \frac{2}{5}x\right)B_{i_5}^{m} + (3 - x)Te^{g} + \frac{2}{5}xTe^{+} + 3xV_{Bi}^{-} + \frac{3}{5}xV_{Te}^{-}
\]

\[
+ \frac{3}{5}xV_{Bi}^{-} + \frac{3}{5}xV_{Te}^{-}
\]

(2)

Finally, we find that the free carrier concentration when Te vacancies are the dominant type is five times higher than when Bi antisite defects are dominant, even with the same concentration of Te evaporation. Hence, a small random fluctuation of missing Te will generate more serious irreproducibility problems in n-type Bi₂Te₃ than in p-type Bi₂Te₃. It is worth noting that the situations described by Equation (1) for n-type materials and Equation (2) for p-type materials are ideal cases. In a real case, there are minor acceptor-like Bi₅Te or Sb₅Te antisite defects as well as the major donor-like V_{Te} or V_{Se} vacancies in n-type Bi₂Te₃ alloying, while there are also minor donor-like V_{Bi} or V_{Se} vacancies alongside the major acceptor-like Bi₅Te or Sb₅Te antisite defects in p-type Bi₂Te₃. Alloying with Sb usually increases...
the concentration of antisite defects at Te-sites (Sb$_{Te}$) and hence results in more holes, due to the smaller electronegative difference between Sb (2.05) and Te (2.10) than between Bi (2.02) and Te (2.10). The alloy with Se usually increases the concentration of vacancies at Te-sites (V$_{Se}$) 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 vacancies (V$_{Te}$ and V$_{Se}$) in n-type Bi$_2$Te$_{3-x}$Se$_x$ will be higher than that in p-type Sb$_{2-x}$Bi$_x$Te$_3$, which is another reason why we have a more serious reproducibility problem in n-type Bi$_2$Te$_{3-x}$Se$_x$ than in p-type Sb$_{2-x}$Bi$_x$Te$_3$.

The key to improving the reproducibility of n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$ is to suppress the generation of Te vacancies, both whole-V$_{Te}$ and fractional-V$_{Te}$. Reducing the energy of the ball-milling process, for example by decreasing ball-milling rotation speed or adjusting the ball-milling medium filling parameter, is one method of decreasing the mechanical deformation and thus reducing Te vacancy generation. However, to achieve fine

**Figure 1.** Temperature dependence of electrical resistivity (a) and Seebeck coefficient (b) of ten batches of Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples fabricated by the BM plus dc-HP method. Temperature dependence of electrical resistivity (c) and Seebeck coefficient (d) of eight batches of Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples made by the same method and under the same conditions as shown in (a) and (b). (e) Coefficient of variation for room temperature thermoelectric properties of ten batches of Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples and eight batches of Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples, and (f) Seebeck coefficient at room temperature as a function of natural logarithm electrical conductivity for ten batches of Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples and eight batches of Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples.
of eight batches of Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ is less scattered and narrowing data. The Seebeck coefficient of eight batches of Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$. The reproducibility of the Cu added n-type Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ is obviously improved. In order to quantify the scattering behavior of the thermoelectric properties from batch to batch, a coefficient of variation (C$_v$) is calculated. Here, the C$_v$ is defined as the root of mean-square-deviation normalized by the mean value ($\bar{\theta}$) of scattering data $\theta$.

$$C_v = \sqrt{E \left( (\bar{\theta} - \theta)^2 \right)} / \bar{\theta},$$

where $E$ is an operator to solve the mean value. The coefficient of variation of electrical resistivity, Seebeck coefficient, and power factor for Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ is 1.92%, 1.00% and 0.98%, respectively, much lower than 13.23%, 6.50% and 3.47% for Bi$_2$Te$_2$Se$_{0.3}$, as shown in Figure 1(e).

Figure 1(f) shows the Seebeck coefficient at room temperature as a function of the natural logarithm of electrical conductivity for Bi$_2$Te$_2$Se$_{0.3}$ and eight batches of Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ prepared under identical ball-milling and hot-pressing conditions. It is interesting to note that the Seebeck coefficient of the ten batches of Bi$_2$Te$_2$Se$_{0.3}$ spans a wide range, while falling into a linear relationship with natural logarithm electrical conductivity. This linear relationship between electrical conductivity and Seebeck coefficient demonstrates that the as-pressed Cu$_{x}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ compounds produced by ball-milling and hot-pressing possess a pure Bi$_2$Te$_3$ phase, and no special preferred orientation is observed in comparison with the standard spectra of random powder samples, indicating the randomness of the grains. The lattice constants of Cu$_x$Bi$_2$Te$_{2.7}$Se$_{0.3}$ compounds are calculated by Rietveld refinement and are shown in Figure 1(c). The lattice parameter $c$ of Bi$_2$Te$_3$-phase increases from 30.364 to 30.402 Å with increasing Cu content from $x = 0$ to $x = 0.03$ in Cu$_x$Bi$_2$Te$_{2.7}$Se$_{0.3}$.

### 2.2. Optimization of Cu Doping Concentration

Figure 2(a) shows the typical lattice structure of Bi$_2$Te$_3$-based alloys in a hexagonal cell, which is characterized by the stacking layers perpendicular to the $c$-axis in a sequence, -Te$(1)$-Bi-$Te$(2)-. Here the superscripts refer to the type of Te with different chemical bonding environments. The interstitial sites formed by four-Te$(1)$ atoms are also highlighted in Figure 2(a). Figure 2(b) shows the X-ray diffraction (XRD) patterns of Cu$_x$Bi$_2$Te$_{2.7}$Se$_{0.3}$ for different copper contents. The XRD spectra demonstrates that the as-pressed Cu$_x$Bi$_2$Te$_{2.7}$Se$_{0.3}$ compounds produced by ball-milling and hot-pressing possess a pure Bi$_2$Te$_3$ phase, and no special preferred orientation is observed in comparison with the standard spectra of random powder samples. The Cu$_{x}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples consist of nanograins with diameter of less than one micrometer, as shown in Figure 3(a).
Figure 3 (b) shows a typical TEM images containing parallel black and white stripes observed under the diffraction conditions shown as the inset. These stripes are horizontal across the <001> direction and their periodicity is about 30 nm. Previous HRTEM work indicated that a strain field induces black and white stripes.\cite{29,30} For inherent strain fields caused by dislocation or composition fluctuation, the periodicity of the induced black and white stripes is 10 nm and those stripes are parallel to (10\(\bar{1}0\)) in single crystals.\cite{29} Hot-pressed Bi\(_2\)Te\(_3\) nanocomposites,\cite{19} and Bi\(_2\)Te\(_3\) superlattices.\cite{30} Here the observed black and white stripes are 30 nm wide and perpendicular to the <001> direction. Therefore the black and white stripes observed here should be caused by another kind of strain field.

In order to find the origin of the strain field, EDS is measured from several pairs of black and white stripes. EDS signals were collected from small regions with a diameter of 5 nm. The calculated average concentration of copper in the black stripes at different locations across many grains is 0.4 at.\% higher than that in the adjacent white stripes. It is probable that the interstitial copper in the lattice causes the strain field, resulting in the intensity contrast between the black stripes and white stripes.

Figure 3(c) shows a line profile along the dotted line in the HRTEM images, which identifies a clear interface between a black stripe (left segment) and a white stripe (right segment). The copper concentration in the black stripe is 0.8 at.\% higher than that in the white stripe. The average width of 15 fringes is \(d = 3.09\) nm in black stripe while \(d = 3.04\) nm in the white stripe. Obviously the lattice is expanded along the c-axis in the copper-rich regions. The lattice parameter c is 0.05 nm longer in the black stripe than that in the white stripe. The expansion along the c axis should come from the interstitial copper in Cu\(_x\)Bi\(_2\)Te\(_2\)Se\(_{0.3}\). It is worth pointing out that the expansion of
the fringe width depends on the copper concentration. When the copper concentration in the black stripes is close to that in the white stripes, likely 0.2 at.% difference, the change of the fringe width is too small to be measured from HRTEM images.

We also noted that the lattice expansion along $<001>$ direction observed by HRTEM is much larger than that observed by XRD. This is attributable to the difference between a local expansion in each unit cell and an average expansion of the bulk. Since the copper content in our sample Cu$_x$Bi$_2$Te$_2.7$Se$_{0.3}$ is only 1–3 at.%, the large local expansion in the region with Cu is reduced by the non-expansion region without Cu, resulting in a smaller average expansion. This lattice distortion is likely to work as new phonon scattering center.

Figure 4 shows the temperature-dependent thermoelectric properties of Cu$_x$Bi$_2$Te$_2.7$Se$_{0.3}$ with different copper contents. The data for the copper-free sample used here is from a sample fabricated at the same time as the copper-doped samples. The decreased electrical resistivity and Seebeck coefficient with increased copper content clearly demonstrates a donor behavior, as shown in Figure 4 (a,b). The positive temperature-dependent behavior of electrical resistivity demonstrates that all the copper-doped samples are degenerated semiconductors except the copper-free sample. We also note that the peak 

![Figure 4](attachment:image.png)
Seebbeck coefficient shifts from 25, to 75, 125 and 175 °C as the copper content increases from x = 0 to 0.01, 0.02, and 0.03 in CuₓBi₂Te₂Se₀.₃, respectively. This is a typical behavior in thermoelectric materials since the increased external major carriers suppress the generation of minor carriers and hence increase the onset temperature of bipolar effect. The power factor (S²/T) is calculated from the measured electrical resistivity and Seebeck coefficient, which is shown in Figure 4(c). The optimized content of copper is x = 0.01 in CuₓBi₂Te₂Se₀.₃, which shows the highest power factor of 3150 μWm⁻¹K⁻². This value is much higher than the 2060 μWm⁻¹K⁻² of the copper-free sample Bi₂Te₂Se₀.₃. It is noted that the as-pressed Bi₂Te₂Se₀.₃ is not optimized for carrier concentration due to the irreproducibility issue. The maximum power factor of the copper-free Bi₂Te₂Se₀.₃ with an optimized carrier concentration is ~2500 μWm⁻¹K⁻², about 20% less than that of the optimized Cu₀.₀₁Bi₂Te₂Se₀.₃. The room temperature mobility, calculated from the Hall coefficient and electrical conductivity, increases from 173, to 245, 245, and 184 cm²V⁻¹s⁻¹ as copper content increases from x = 0 to 0.01, 0.02, and 0.03, respectively. It clearly demonstrates that the enhancement in power factor is due to the improved charge carrier mobility. In order to quantify the number of free electrons contributed from each copper, the carrier concentration of as-pressed CuₓBi₂Te₂Se₀.₃ (x = 0, 0.01, 0.02, 0.03) is plotted as a function of copper concentration, as shown in Figure 4(d). The carrier concentration of the as-pressed Cu₀.₀₁Bi₂Te₂Se₀.₃ is about (1–7) × 10¹⁹ cm⁻³, depending on the copper concentration. Calculating the slope of carrier concentration as a function of copper concentration, we obtained a value of 0.3 electrons/copper. This value is comparable to 0.4 electrons/copper obtained in copper-doped Bi₂Te₂Se₀.₃ single crystals by direct copper addition,[22] but less than the 0.65 electrons/copper obtained in copper-doped Bi₂Te₂Se₀.₃ by electrochemical intercalation.[24]

Figure 4(e,f) shows the temperature-dependent thermal conductivity and dimensionless thermoelectric figure-of-merit (ZT) of CuₓBi₂Te₂Se₀.₃ for different copper contents. The thermal conductivity of Cu₀.₀₁Bi₂Te₂Se₀.₃ at room temperature is 0.846, 1.041, 1.156 and 1.574 Wm⁻¹K⁻¹, as Cu content increases from x = 0 to 0.01, 0.02, and 0.03 respectively. It is well known that the total thermal conductivity κₗat comprises three parts, i.e., lattice thermal conductivity κₗat, carrier thermal conductivity κₗcar, and bipolar thermal conductivity κₗbipolar. For most heavily doped semiconductors, κₗbipolar near room temperature is negligible, and κₗat is therefore estimated by directly subtracting κₗcar from κₗat. However, κₗat/κₗcar with increasing temperatures, in a large amount of references, is a typical phenomenon that bipolar effect starts to contribute to the thermal conduction. The direct calculation of κₗbipolar is difficult because it involves many band structure parameters, such as mobility μ and effective mass m∗ for both valence band and conduction band, and forbidden bandgap E₀ that cannot be directly measured.[33,34] For semiconductors with large band gap or heavy doping, κₗcar/κₗat can be used as a good estimation of κₗat in a wide temperature range. As a result, κₗat in intrinsic excitation region can be estimated by extrapolating the linear relationship in extrinsic region between κₗat and T⁻¹ when phonon-phonon scattering is the dominant scattering mechanism, finally κₗat/κₗcar/κₗat can be considered as an indirect evaluation of κₗbipolar in intrinsic excitation region.[34] Nevertheless, both methods are not accurate enough for the estimation of κₗat for as-pressed CuₓBi₂Te₂Se₀.₃ in the intrinsic excitation region, so only κₗat near room temperature is calculated from κₗat = κₗat-κₗcar. Here the κₗat is calculated by the Wiedemann-Franz law, i.e., κₗat = LσT, where L is the Lorenz number. For free electrons, L = 2.45 × 10⁻⁸ V²K⁻². However, for most thermoelectric materials, the real Lorenz number is lower than 2.45 × 10⁻⁸ V²K⁻², depending on the reduced Fermi energy ξ = E_F/κₗat and scattering parameter r as shown in the following.[13]

\[
L = \left( \frac{k_B}{e} \right)^2 \left( \frac{(r + 7/2) F_{r,1/2}(\xi)}{(r + 3/2) F_{r,1/2}(\xi)} \right) - \left( \frac{(r + 5/2) F_{r,1/2}(\xi)}{(r + 3/2) F_{r,1/2}(\xi)} \right)^2 \right)
\]

where \( F_{r}(\xi) \) is the Fermi integration

\[
F_{n}(\xi) = \int_{0}^{\infty} \frac{x^n}{1 + e^{x-\xi}} \, dx
\]

The reduced Fermi energy can be derived from both the carrier concentration and Seebeck coefficient on the basis of single band approximation,

\[
n = 4\pi \left( \frac{2m^*k_B T}{\hbar^2} \right)^{3/2} F_{1/2}(\xi)
\]

\[
S = \pm \frac{k_B}{e} \left( \frac{(r + 5/2) F_{r,1/2}(\xi)}{(r + 3/2) F_{r,1/2}(\xi)} \right) \xi
\]

It is noted that the carrier concentration is usually obtained through the Hall measurement, by the relationship \( n = qn_{H} / (eR_{H}) \), where \( R_{H} \) is the Hall coefficient and \( e \) is free charge, and \( R_{H} \) is a parameter related to the scattering parameter \( r \) and \( \xi \). It is clearly shown that the evaluation of \( \xi \) from the measured \( S \) is only related to scattering parameter \( r \) while the estimation of \( \xi \) from the measured \( n \) is associated with two unknown parameters \( m^* \) and \( r \). So the calculation of \( \xi \) is derived from the measured \( S \) by using Equation (4) and (6), as shown in Table 1. Here, acoustic phonon scattering has been assumed as the main carrier scattering mechanism near room temperature, i.e., \( r = -0.5 \) . By applying the calculated \( \xi \) into Equation (3), the Lorenz number is obtained as 1.54 × 10⁻⁸, 1.63 × 10⁻⁸, 1.73 × 10⁻⁸, and 1.84 × 10⁻⁸ V²K⁻² as the copper content increases from x = 0 to 0.01, 0.02, and 0.03, respectively. The \( \kappa_{at} \) of copper-free Bi₂Te₂Se₀.₃ is 0.728 Wm⁻¹K⁻¹ which is consistent with our previous data.[38] There is a considerable decrease in \( \kappa_{at} \) at room temperature from 0.728 to 0.606, 0.546, and 0.501 Wm⁻¹K⁻¹ when copper content increases from x = 0 to 0.01, 0.02, and 0.03, respectively. Our observation of nano scale strain domains (i.e., nano stripes) due to composition fluctuation of copper, as shown in Figure 3, could be the most possible reason for this significant reduction in thermal conductivity. As a result, an enhancement in ZT is observed due to the addition of copper, as shown in Figure 4(f). The sample Cu₀.₀₁Bi₂Te₂Se₀.₃ shows an optimized ZT values with peak ZT value of 0.99 at 175 °C, which is higher than 0.73 at 25 °C for the copper free sample.
This value is also higher than 0.85 at 150 °C of the copper free sample with an optimized carrier concentration.[18] This enhanced ZT value suggests that slight copper addition is beneficial to the Bi$_2$Te$_2$Se$_0.3$ system. This also explains why barrier layers are needed to prevent excessive diffusion of Cu from the circuit contacts into the thermoelectric legs for commercial thermoelectric cooling modules.[15]

2.3. Further Enhancement of ZT by Texturing

Our previous work has shown that partial texturing of random grains of as-pressed Bi$_2$Te$_2$Se$_0.3$ nanocomposites by a pressing process significantly enhanced the ZT value in the perpendicular direction due to enhanced electrical conductivity.[18] Thus, similar texturing fabrication processes were applied to the as-pressed Cu$_{0.01}$Bi$_2$Te$_2$Se$_0.3$ samples. Firstly, an as-pressed sample with dimensions 19.05 mm in diameter and 22.7 mm in thickness was pressed at 500 °C under the protection of flowing nitrogen gas C under the protection of flowing nitrogen gas and then subjected to re-pressing at 530 °C under the protection of flowing nitrogen gas into a bulk sample with dimensions of 25.4 mm in diameter and 12.7 mm in thickness, allowing us to conduct an anisotropy investigation on the thermoelectric properties for the same sample. The XRD pattern shows that a similar degree of orientation was achieved as before.[18] For simplicity, the detailed XRD patterns are not given here. Figure 5 shows the comparison of temperature-dependent thermoelectric properties of as-pressed and re-pressed Cu$_{0.01}$Bi$_2$Te$_2$Se$_0.3$ samples. Shown in Figure 5 are the comparison of temperature-dependent thermoelectric properties between a re-pressed Cu$_{0.01}$Bi$_2$Te$_2$Se$_0.3$ sample that was measured immediately following sample preparation and then measured again after being stored in air for five months. The slightly increased electrical conductivity and Seebeck coefficient of the aged sample indicate a slightly decreased carrier concentration and possible copper diffusion. However, no obvious deterioration of the power factor is observed. Interestingly, the thermal conductivity measured five months later is slightly lower due to the decreased contribution from the carriers. As a result, a slightly increased ZT value is obtained in the whole temperature region, with a peak ZT = 1.10 at 100 °C. The temperature-dependent ZT of the re-pressed Bi$_2$Te$_2$Se$_0.3$ sample reported in Ref.[18] is also shown in Figure 6(d) for comparison. The ZT value of the re-pressed Cu$_{0.01}$Bi$_2$Te$_2$Se$_0.3$ in this study is almost the same as that of the re-pressed Bi$_2$Te$_2$Se$_0.3$ at T < 125 °C. However, an enhanced ZT value is obtained in Cu$_{0.01}$Bi$_2$Te$_2$Se$_0.3$ at temperatures higher than 125 °C. At 250 °C, the ZT value of Cu$_{0.01}$Bi$_2$Te$_2$Se$_0.3$ is still 0.79, 38% higher than 0.57 for Bi$_2$Te$_2$Se$_0.3$. The higher average ZT value in the temperature range from 25 to 250 °C is useful for thermal-to-electrical conversion efficiency.

3. Conclusions

We have achieved a significant improvement on reproducibility from batch to batch processing of Bi$_2$Te$_2$Se$_0.3$ by adding a small amount of Cu to fabricate Cu$_{0.01}$Bi$_2$Te$_2$Se$_0.3$. The reason for such improvement is that Cu atoms locate at interstitial sites, suppressing the escape of Te atoms, and as a consequence,
reducing the concentration of Te vacancies. The copper atoms located at the interstitial sites between the van der Waals bound layers enhance the electrical bonding of the layers and improve the electronic transport along the direction perpendicular to the basal plane. Some parallel black and white stripes perpendicular to the <001> direction with periodicity of about 30 nm were observed in TEM images of the Cu doped Cu$_{x}$Bi$_2$Te$_{2.7}$Se$_{0.3}$, which is found to be related to the copper content fluctuation on the nanoscale and responsible for the reduced lattice thermal conductivity. As a result, an enhanced peak ZT value of 0.94 and 0.99 were obtained in as-pressed Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ samples along the parallel and perpendicular directions, respectively, higher than the value of 0.85 for Bi$_2$Te$_2$Se$_{0.3}$ with an optimized carrier concentration. The peak ZT of Cu$_{0.01}$Bi$_2$Te$_{2.7}$Se$_{0.3}$ is further increased from 0.99 for the as-pressed sample to 1.06 for the re-pressed sample, and to 1.10 for the sample after five-month aging in air at room temperature.

4. Experimental Section

Synthesis: The fabrication process is similar to that in previous reports.[7,11,18] Appropriate amounts of Cu (99.999%, Alfa Aesar), Bi (99.999%, Alfa Aesar), Te (99.999%, Alfa Aesar), and Se (99.999%, Alfa Aesar) were weighted according to the stoichiometric ratio...
Cu_0.01Bi_2Te_2.7Se_0.3 (x = 0, 0.01, 0.02, and 0.03), and loaded into the stainless steel ball-milling jar in a glove-box under argon atmosphere. The jar was then subjected to ball-milling for 20 h at 1200 rpm. The phase composition and microstructure of the ball-milled powders were studied by X-ray diffraction and transmission electron microscopy, respectively, which confirmed that the ball-milled powders are fully alloyed fine grains with grain sizes ranging 20–50 nm. The ball-milled powders were then loaded into a graphite die with an inner diameter of 12.7 mm in a glove-box. The graphite die with the loaded powder was removed from the glove-box, and immediately sintered by dc-HP at 500 °C for 2 min into a rod with a height of 12–13 mm. These dimensions allow us to carry out the thermal and electrical conductivity measurements along the same direction.

**Phase identification and microstructure characterization: X-ray diffraction**

Measurements were conducted on a PANalytical multipurpose diffractometer with an X'celerator detector (PANalytical X'Pert Pro). The lattice parameters of Bi_2Te_3 phase were calculated from Rietveld refinement, which was performed using X'pert HighScore Plus software (PANalytical, X'Pert Pro). The Cu_xBi_2Te_2.7Se_0.3 samples were cut by a diamond saw, mechanically polished, and ion-milled for TEM specimens. The microstructure was investigated using a transmission electron microscope (JSM2010F, JEOL).

**Thermoelectric transport property measurement:** The electrical resistivity (ρ) was measured by a reversed dc-current four-point method, while the Seebeck coefficient was determined by the slope of the voltage difference versus temperature-difference curve based on a static temperature difference method. The simultaneous measurement of electrical resistivity and Seebeck coefficient was conducted on a commercial system (ZEM-3, ULVAC). The thermal conductivity was calculated from the relationship κ = DCp/d, where D, Cp, and d are the thermal diffusivity, heat capacity, and volume density, respectively. The thermal diffusivity was measured by a laser flash method with a commercial system (LFA447, Netzsch). The heat capacity was determined by a differential scanning calorimeter (DSC200-F3, Netzsch). The volume density was measured by an Archimedes method. The Hall coefficient measurement of the sample was carried out on a commercial system (7600, LakeShore), with a magnetic field of 2 T and an electrical current of 30 mA.

In order to differentiate the properties along different directions, we use the hot-pressing direction as the reference: parallel direction (∥) is defined as that all the properties are measured along the hot pressing direction whereas the perpendicular direction (⊥) is defined as that all the properties are measured in the plane that is perpendicular to the hot-pressing direction.

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**Figure 6.** Comparison of the temperature-dependent thermoelectric properties of re-pressed Cu_0.01Bi_2Te_2.7Se_0.3 samples that were measured immediately after preparation with those measured again after being stored in air for 150 days, (a) electrical resistivity, (b) Seebeck coefficient, (c) thermal conductivity, and (d) ZT. The ZT of re-pressed Bi_2Te_2.7Se_0.3 from Ref. 18 was also plotted for comparison.
Supplementary References