Ultrahigh Power Factor and Electron Mobility in n-Type Bi₂Te₃–x%Cu Stabilized under Excess Te Condition

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Abstract: The thermoelectric (TE) community has mainly focused on improving the figure of merit (ZT) of materials. However, the output power of TE devices directly depends on the power factor (PF) rather than ZT. Effective strategies of enhancing PF have been elusive for Bi₂Te₃-based compounds, which are efficient thermoelectrics operating near ambient temperature. Here, we report ultrahigh carrier mobility of ∼467 cm² V⁻¹ s⁻¹ and power factor of ∼45 μW cm⁻¹ K⁻² in a new n-type Bi₂Te₃ system with nominal composition CuₓBi₂Te₃₋ₓ (x = 0.02, 0.04, and 0.06). It is obtained by reacting Bi₂Te₃ with surplus Cu and Te and subsequently pressing powder products by spark plasma sintering (SPS). The SPS discharges excess Te but stabilizes the high extent of Cu in the structure, giving unique SPS CuₓBi₂Te₃₋ₓ samples. The analyzed composition is close to “CuₓBi₂Te₃₋ₓ”. Their charge transport properties are highly unusual. Hall carrier concentration and mobility simultaneously increase with the higher mole fraction of Cu contrary to the typical carrier scattering mechanism. As a consequence, the electrical conductivity is considerably enhanced with Cu incorporation. The Seebeck coefficient is nearly unchanged by the increasing Cu content in contrast to the general understanding of inverse relationship between electrical conductivity and Seebeck coefficient. These effects synergistically lead to a record high power factor among all polycrystalline n-type Bi₂Te₃-based materials.

Keywords: thermoelectric, bismuth telluride, n-type, power factor, carrier mobility

Introduction

The global population growth and economic development require a 50% increase in the use of fossil fuels by 2040, which are being depleted rapidly.¹ Their consumption is inevitably accompanied by a large amount of CO₂ emission, causing serious environmental problems. In addition, they are main sources for generating electric energy, more than a half of which is lost as waste heat upon consumption.² Thermoelectric (TE) technology is a promising candidate to address these multiple issues because it can convert heat into electrical energy directly without releasing undesirable gaseous residues. TE devices also operate with no noise and vibration, giving high mechanical reliability. The performance of TE materials is typically expressed by a dimensionless figure of merit ZT = σS²T/κtot where σ is the electrical conductivity, S is the Seebeck coefficient, the product σS² is the power factor (PF), κtot is the total thermal conductivity, and T is the absolute temperature.³ The κtot comprises electrical (κₑ), lattice (κₗ), and bipolar thermal conductivities (κᵦ).

At present, TE materials exhibiting high ZT and PF simultaneously are scarce. Historically, improving ZT has been the main interest in this technology.⁴⁻¹⁶ Indeed, ZT has been greatly enhanced in the last two decades mainly due to the discovery of new materials and many innovative strategies that can reduce κtot. However, κtot of the representative TE systems is rapidly reaching a lower bound of the amorphous limit. In contrast, PF does not have a theoretical upper bound, but just a few strategies have been developed to improve the PF.

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With the recent progress in ZT of TE materials, fabricating TE devices and enhancing their performance have emerged as a primary task to commercialize this technology. Average ZT of TE materials determines the efficiency of the TE devices. This is important when the heat supply is unstable and limited so that TE devices have to generate power from a limited amount of heat. In contrast, the PF directly determines the output power density (\(\omega\)) of TE devices at given working boundary conditions, which include the temperature gradient \(\left(\frac{T_h - T_c}{L}\right)\) and temperature difference \(\left(T_h - T_c\right)\). It is expressed by eq 1:

\[
\omega = \frac{1}{4L} \left(\frac{T_h - T_c}{L}\right)^2 PF
\]

(1)

where \(T_h\) and \(T_c\) are the temperatures at the hot and cold sides of TE materials, respectively, and \(L\) is the dimension of TE legs, along which the temperature gradient is applied. Output power density is a pivotal specification of TE devices to advertise their capability of generating power from heat on commercial markets.\(^{19-21}\) PF is of paramount importance when heat source is either unlimited or given consistently at low cost or free.\(^{22-24}\) It is important to note that \(\kappa_{tot}\) does not affect the output power density under steady-state heat conduction.\(^{25}\) Based on these accounts, it is essential to develop strategies of enhancing the PF of TE materials.

Bi\(_2\)Te\(_3\)-based compounds serve as representative TE materials for near-ambient-temperature power generation. There are still major challenges that should be addressed for this important class of TE materials. First, few performance-enhancing strategies have been established for Bi\(_2\)Te\(_3\)-based materials. Proven dopants and substituents for both n- and p-type materials are also limited. These result in a sluggish improvement in their TE performance. This is in striking contrast to the recent advance in PbTe-based compounds operating in the intermediate temperature range. Their performance has been greatly improved by numerous innovative strategies. For example, \(\kappa_{tot}\) can be reduced substantially with minimal damage to electrical transport properties by nanostructuring\(^{26,27}\) and hierarchical architecture.\(^{28}\) A few strategies have been introduced to improve their PF, for instance, energy-filtering effect\(^{29}\) and band engineering such as band convergence\(^{30-32}\) resonant states,\(^{33,34}\) and band flattening,\(^{35}\) although it is still challenging.

Second, n-type Bi\(_2\)Te\(_3\)-based materials underperform compared with the p-type counterparts in terms of PF and ZT, resulting in a serious performance imbalance between n- and p-type materials. ZT of the latter has been raised mainly by reducing \(\kappa_{tot}\) through defect engineering\(^ {26,37}\) and mechanical processes to obtain nanoscale grains such as ball milling,\(^ {38}\) hot deformation,\(^ {37,39}\) and melt spinning.\(^ {40}\) However, some strategies that have been proved for p-type Bi\(_2\)Te\(_3\)-based materials are mostly ineffective for n-type materials, making it highly challenging to enhance their TE performance. Electrical transport properties of the latter tend to be heavily damaged by mechanical nanostructuring in contrast to the cases of the former. Furthermore, most high-performance n-type Bi\(_2\)Te\(_3\)-based materials are alloyed with Se to form Bi\(_2\)Te\(_3-x\)Se\(_x\), leading to the sacrifice of PF for reducing \(\kappa_{tot}\).\(^ {41,42}\) As a result, they typically exhibit a much lower PF than the p-type counterparts. The commercially available n-type materials are highly oriented ingots of Bi\(_2\)Te\(_3-x\)Se\(_x\), prepared by a relatively tedious process of zone melting (ZM), showing a remarkably high PF of 43 \(\mu\)W cm\(^{-1}\) K\(^{-2}\) at 300 K.\(^ {36}\) However, ZM ingots suffer from intrinsically poor mechanical stability because of the cleavage along the basal plane, making them unreliable for device fabrication.\(^ {43}\)

Enhancing the TE properties of n-type Bi\(_2\)Te\(_3\)-based materials has been relatively undeveloped. Among a few of examples, incorporating Cu atoms into Bi\(_2\)Te\(_3-x\)Se\(_x\) has been extensively studied. Cu is an amphoteric dopant to induce a p-type conduction or be inserted into interlayer and/or interstitial sites to give a n-type conduction.\(^ {44,47}\) For the latter case, high PF of \(\sim 31.5\) \(\mu\)W cm\(^{-1}\) K\(^{-2}\) and ZT of 0.99 were achieved in ball-milled and hot-pressed Cu\(_{0.02}\)Bi\(_2\)Te\(_2.7\)Se\(_0.3\) samples.\(^ {41}\) Recently, extraordinary off-stoichiometric bulk Cu\(_{0.06}\)Bi\(_2\)Te\(_3\) was stabilized by a combined process of kinetically controlled nanosynthesis and subsequent spark plasma sintering (SPS), exhibiting a very high PF of \(\sim 43\) \(\mu\)W cm\(^{-1}\) K\(^{-2}\) and ZT >1.1 at 323 K. Excess K and Te atoms in Cu\(_{0.06}\)Bi\(_2\)Te\(_3\) occupy the interlayer and interstitial voids in the Bi\(_2\)Te\(_3\) structure.\(^ {48}\)

Here, we report a new n-type polycrystalline Bi\(_2\)Te\(_3\) system with the nominal composition of Cu\(_x\)Bi\(_2\)Te\(_{3-x}\) (\(x = 0.02-0.06\)) exhibiting ultrahigh power factor and carrier mobility near room temperature. These compounds are uniquely stabilized by the reaction of Bi\(_2\)Te\(_3\) with excess Cu and Te and the subsequent consolidation by spark plasma sintering (SPS). Excess Te serves as a “catalyst” for enhancing charge transport and suppressing thermal transport properties simultaneously. It only exists in the reaction melts and plays several highly favorable roles, and is expelled by SPS under high pressure. First, excess Te present in the reaction melt suppresses the intrinsic generation of adverse Te vacancies in Bi\(_2\)Te\(_3\) and optimizes the carrier concentration. In fact, high carrier concentration is unfavorable for charge transport properties because it reduces the carrier mobility and Seebeck coefficient. Second, excess Te helps stabilize the high content of Cu up to 6 mol % in the Bi\(_2\)Te\(_3\) structure, leading to an ultrahigh carrier mobility. The Cu doping level is far above the solubility limit allowed by the phase diagram.\(^ {49}\) Third, it induces high-density edge dislocations, thereby considerably reducing \(\kappa_{tot}\).

The incorporation of high concentration of Cu atoms, enabled by excess Te in the reaction melt, induces unusual charge transport behaviors. The carrier concentration and mobility of SPS Cu\(_x\)Bi\(_2\)Te\(_{3-x}\) samples increase simultaneously with the higher extent of Cu doping, contrary to the general trend of their mutual inverse proportionality. As a result, the electrical conductivity of Cu\(_x\)Bi\(_2\)Te\(_{3-x}\) also increases with the larger amount of Cu. The synergistic effect of excess Cu and Te leads to ultrahigh mobility of \(\sim 467\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) and PF of \(\sim 45\) \(\mu\)W cm\(^{-1}\) K\(^{-2}\) for the \(x = 0.06\) sample of SPS Cu\(_{0.06}\)Bi\(_2\)Te\(_{3}\). These are record high values reported to date for the polycrystalline n-type Bi\(_2\)Te\(_3\)-based materials. In fact, poorer PF of the n-type Bi\(_2\)Te\(_3\)-based materials has been a major challenge in improving the output power of TE power generators operating near ambient temperature. The novelty of this work can be highlighted by TE properties of the control samples. The as-prepared Cu\(_{x}\)Bi\(_2\)Te\(_{3-x}\) ingots exhibit a p-type conduction. SPS processed samples with nominal composition Cu\(_{x}\)Bi\(_2\)Te\(_3\) without excess Te show a decreasing electrical conductivity with a higher mole fraction of Cu doping and underperform compared with SPS Cu\(_{0.06}\)Bi\(_2\)Te\(_{3}\).
**EXPERIMENTAL SECTION**

**Reagents.** The reagents in this work were used as received unless noted otherwise: Bi shot (99.999%, SN Plus, Canada), Te shot (99.999%, SN Plus, Canada), and Cu wire (99.99%, SN Plus, Canada).

**Synthesis.** Ingots with the nominal compositions “Cu_{0.01}Bi_{2}Te_{3.07}” (x = 0.02, 0.04, 0.06, 0.08, and 0.10) were prepared by reacting an appropriate molar ratio of the starting reagents in evacuated fused silica tubes at 973 K for 12 h, followed by quenching to water. Afterward, the nominal composition is used for the specimens. The synthesized ingots were ground into fine powders, loaded into a 13 mm diameter graphite die in an Ar-filled glovebox, and densified by spark plasma sintering (SPS) (SPS-211Lx, Fuji Electronic Industrial Co., Japan) in 823 K for 20 min under an axial pressure of 50 MPa. Although all these SPS-processed Cu_{x}Bi_{2}Te_{3−x} samples are phase pure, our discussion will concentrate on the samples with x = 0–0.06.

Data for the other samples are given in the Supporting Information. Control SPS samples with the nominal composition Cu_{0.01}Bi_{2}Te_{3.07} (x = 0.02 and 0.04) were prepared similarly. For control ingot samples with the nominal composition Cu_{0.01}Bi_{2}Te_{3.17}, the reaction mixtures of Bi_{2}Te_{3} (JCPDS 15-0863), Cu_{0.01}Bi_{2}Te_{3} (JCPDS 13-0310), and Cu_{0.02}Bi_{2}Te_{3} (JCPDS 21-1126) were prepared and heated to 823 K at a rate of 10 K min^{-1} under an Ar atmosphere.

**Charge Transport Properties.** Samples were cut and polished into parallelepipeds with dimensions of ∼3 × 3 × 11 mm^3. Electrical conductivity and Seebeck coefficient were measured simultaneously from room temperature to 473 K under a He atmosphere on an ULVAC-RIKO ZEM-3 instrument.

**Thermal Transport Properties.** Samples were cut and polished into disks with a radius of ∼8 mm and a thickness of ∼1.5 mm under a N_{2} atmosphere. The prepared disks were coated with graphite before characterization. Thermal diffusivity (D) was directly obtained by the laser flash diffusivity method using a Netzsch LFA 457 MicroFlash instrument. Thermal conductivity was calculated from the relation κ_{th} = DCρ, where C_{p} is the specific heat capacity and ρ is the mass density of the materials. The C_{p} can be derived indirectly employing a standard sample of Pyroceram. The ρ was calculated from geometrical dimensions and masses of specimens (Table S1).

**Hall Coefficient Measurement.** The Hall effect measurement with respect to temperature in a 1.5 T magnetic field was performed on a Lake Shore HMS8407 system. Carrier concentration (n_{H}) and mobility (μ_{H}) were calculated by the formula n_{H} = 1/(eR_{H}) and μ_{H} = eR_{H}, respectively.

**Transmission Electron Microscopy (TEM) Measurements.** Specimen for TEM investigations was prepared using gallium ion milling with focused ion beams (FIB, Helios 650, FEI) with a dual beam microscope. TEM analyses were performed on a JEM ARM–200F microscope (Cold FEG Type, JEOL) installed at the National Center for Inter-university Research Facilities (NCIRF) at Seoul National University.

**RESULTS AND DISCUSSION**

**Synthesis and Structural Characterization.** The title compounds of this work with the nominal composition Cu_{0.01}Bi_{2}Te_{3.17} (x = 0.02, 0.04, and 0.06) were synthesized in ingot forms by the vacuum melting method, pulverized into...
fine powders, and subsequently pressed by spark plasma sintering (SPS) into dense pellets. The resulting samples are denoted as "SPS Cu$_{x}$Bi$_2$Te$_{3.17}$" to emphasize the nominal composition. According to energy-dispersive spectroscopy (EDS) analysis, the average composition for SPS Cu$_{0.02}$Bi$_2$Te$_{3.17}$ ($x = 0.02$, 0.04, and 0.06) is Cu$_{0.00}$Bi$_2$Te$_{3.00}$, Cu$_{0.03}$Bi$_2$Te$_{3.03}$, and Cu$_{0.05}$Bi$_2$Te$_{3.05}$ respectively (Table S2). Dark gray bubbles were ejected from the resulting pellets after SPS, which were mostly Te with a trace of Cu and Te and being absent of Bi atoms, are embedded in the Bi$_2$Te$_3$ matrix. White scale bar corresponds to 50 μm.

Figure 2. (a) Typical SEM image and (b–d) EDS elemental maps for (b) Cu, (c) Bi, and (d) Te atoms on the polished surface of the SPS Cu$_{0.06}$Bi$_2$Te$_{3.17}$ sample show the homogeneous distribution of the constituent elements without phase segregation. (e) Typical SEM image of the control ingot Cu$_{0.05}$Bi$_2$Te$_{3.17}$ sample and EDS elemental maps taken at the rectangular region in (e) reveal that the line features, consisting of Cu and Te and being absent of Bi atoms, are embedded in the Bi$_2$Te$_3$ matrix. White scale bar corresponds to 50 μm.

To investigate the phase homogeneity of SPS Cu$_{x}$Bi$_2$Te$_{3.17}$ samples, we re-ground SPS specimens to fine powders and recorded their XRD patterns. Despite the presence of a high degree of Cu doping detected by EDS, all samples crystallize in the Bi$_2$Te$_3$-type structure with the space group R3mH (PDF# 15-0863) without the extra Bragg reflection peaks from impurities within the detection limit of laboratory XRD instrument (Figure 1a). We observed that the (006) reflection peak at around $\sim$15° shifts to a lower angle with a higher Cu concentration (Figure 1b). The refined unit cells reveal that the cell dimension expands significantly from 30.409(5) Å for Bi$_2$Te$_{3.17}$ to 30.471(6) Å for Cu$_{0.06}$Bi$_2$Te$_{3.17}$ along the c-axis due to the widened interlayer distance (Figure 1c). This result implies that a majority of Cu is intercalated into the van der Waals gaps between the Bi$_2$Te$_3$ layers. A slight increase from 4.373(3) to 4.383(2) Å along the a-axis for the same samples strongly suggests that the rest of Cu presumably occupies interstitial voids in the Bi$_2$Te$_3$ lattices rather than replacing Bi, given the large difference in the ionic radii of Cu$^+$ (0.91 Å) and Bi$^{3+}$ (1.17 Å) in an octahedral coordination environment and the large enough interstitial holes to accommodate small Cu$^+$ cations (Figure 1d). This model is further supported by their TE properties as described later.

The XRD patterns of the control SPS Cu$_{x}$Bi$_2$Te$_3$ samples are also indexed as the Bi$_2$Te$_3$ structure without the presence of the impurity phase. Neither the change in cell dimension nor the evolution of secondary phase is observed before and after SPS, indicating no chemical change during SPS (Figure S2a). However, control SPS Cu$_{x}$Bi$_2$Te$_3$ samples show a narrower solubility limit of Cu in the Bi$_2$Te$_3$ matrix than the SPS Cu$_{x}$Bi$_2$Te$_{3.17}$ samples so that the x = 0.06 sample of the former cannot be obtained in a pure form. This implies that excess Te in the reaction mixture of the latter helps the unusually high concentration of Cu atoms to be stabilized in the Bi$_2$Te$_3$ structure. The former has nearly the same and a slightly smaller cell dimension along the a- and c-axes, respectively, than the latter (Figure S2b,c and Table S4). For example, the respective cell parameter for the c-axis is 30.416(3) and 30.438(3) Å for the x = 0.02 and 0.04 samples.

Contrary to the phase homogeneity of SPS Cu$_{x}$Bi$_2$Te$_{3.17}$, the control as-grown Cu$_{0.06}$Bi$_2$Te$_{3.17}$ ingot without the post-SPS process shows the extra Bragg reflection peaks, which correspond to Cu$_2$Te ($\sim$13, 26, and 31°) and elemental Te ($\sim$23°) (Figure S3). We could not directly observe the position of Cu atoms in the Bi$_2$Te$_3$ structure by atomic-resolution scanning transmission electron microscopy due to the sensitivity of the samples upon extended exposure to focused ion beams and electrons. In fact, the exact location of Cu atoms in Bi$_2$Te$_3$-based materials could not be directly determined in previous reports. 

Thermogravimetric analysis (TGA) data at a rate of 10 K min$^{-1}$ under an Ar flow show that the SPS Cu$_{x}$Bi$_2$Te$_{3.17}$ samples do not lose weight up to 850 K, demonstrating their
thermal stability and phase homogeneity despite the unusually high Cu concentration in the Bi₂Te₃ structure (Figure S4). In contrast, the control Cu₀.06Bi₂Te₃.17 ingot sample without a post-SPS process loses weight above ∼670 K as elemental Te does. This observation indicates that a majority of excess Te cannot be dissolved in the Bi₂Te₃ structure by the melting reaction and decomposes out near its melting point of 720 K. The TGA results are consistent with those of the XRD.

**Microstructure.** Representative scanning electron microscope (SEM) image of the SPS Cu₀.06Bi₂Te₃.17 sample shows a highly oriented lamellar morphology (Figure S5). We examined the polished surfaces of SPS Cu₀.06Bi₂Te₃.17 and its control Cu₀.06Bi₂Te₃.17 ingot samples to understand the effect of excess Te and SPS on their quantitative composition and microstructures. The SEM and elemental mapping images of the former demonstrate a homogeneous distribution of the constituent elements with no discernible phase segregation within the detection limit of SEM (Figure 2a–d). In contrast, a typical SEM image of the control ingot sample reveals a distinct line feature embedded in the Bi₂Te₃ matrix (Figure 2e). The elemental maps taken on the rectangular region reveal that those lines consist of Cu and Te devoid of Bi atom (Figure 2f–h), which is consistent with the result of the PXRD pattern showing the presence of a CuTe secondary phase.

It is important to note that the results of PXRD, SEM, and EDS clearly demonstrate the uniqueness of the synthesis method in this work for stabilizing n-type Bi₂Te₃ compounds with high concentrations of Cu doping. Excess Cu and Te cannot be fully dissolved in the Bi₂Te₃ structure by the solid-state reaction. Post-SPS process ejects most of the excess Te from the resulting dense pellets, instead maintaining Cu atoms in the Bi₂Te₃ structure. As a result, SPS Cu₀.06Bi₂Te₃.17 behaves as a single phase, and exhibits unusual TE properties as discussed later. This finding implies that a combination of highly off-stoichiometric reaction melt and SPS can promise a rich chemistry in stabilizing unusual compositions for unpredicted physical and chemical properties, which is unavailable by conventional reaction pathways.

**Charge Transport Properties.** We compared the thermoelectric (TE) properties of the title SPS CuₓBi₂Te₃.17 (x = 0.02, 0.04, and 0.06) samples with the control samples of the as-grown CuₓBi₂Te₃.17 ingots and SPS CuₓBi₂Te₃. Note that both the SPS CuₓBi₂Te₃.17 and CuₓBi₂Te₃ samples have nearly the same analyzed composition CuₓBi₂Te₃. Because of the layered structure and the resulting highly anisotropic TE properties of Bi₂Te₃-based materials, all SPS samples were measured perpendicular to the SPS press direction. The control as-grown Cu₀.06Bi₂Te₃.17 ingot exhibits positive Seebeck coefficient (S) values over the entire temperature range, indicative of a p-type conduction possibly due to the presence of a p-type conductor CuTe as secondary phase (Figure S6a). This observation is consistent with the previous report that Bi₂Te₃ with CuTe and Te impurities shows a p-type conduction.

In striking contrast, the SPS CuₓBi₂Te₃.17 and the other control SPS CuₓBi₂Te₃ samples display negative S values in the full temperature range, showing a n-type conduction (Figure 3a). A magnitude of S(βS) for the former reaches a peak at 323 K with a maximum of ∼230 μV K⁻¹ for the x = 0.06 sample and decreases afterward, whereas that of the latter steadily declines with the increasing temperature. The diminishing |S| at high temperature is attributed to the excitation of minor carriers, known as bipolar effect, because of the inverse relationship between |S| and carrier concentration. We theoretically plot the Pisarenko relation between S and carrier concentration (nₑ) at room temperature (black line) based on a single parabolic band (SPB) model assuming acoustic...
phonon scattering mechanism (Figure 3b). The S values of SPS Cu$_{x}$Bi$_2$Te$_{3-x}$ samples fall near the theoretical Pisarenko line with an effective mass of $\sim$1.0 $m_e$ indicating that Cu doping does not affect the conduction band near the Fermi level.

Remarkably, the Hall effect measurement at room temperature shows that both Hall carrier concentration ($n_H$) and mobility ($\mu_H$) of the SPS Cu$_{x}$Bi$_2$Te$_{3-x}$ samples increase with the higher content of Cu (Figure 3c,d). This observation is contrary to the general understanding that $n_H$ and $\mu_H$ are inversely proportional to each other because of the carrier scattering mechanism. For SPS Cu$_{x}$Bi$_2$Te$_{3-x}$, $n_H$ increases from $\sim$9.35 $\times$ 10$^{18}$ to $\sim$1.20 $\times$ 10$^{19}$ cm$^{-3}$ for the $x = 0.02$ and 0.06 samples, respectively. The corresponding $\mu_H$ improves from $\sim$442 cm$^2$/V·s to $\sim$467 cm$^2$/V·s, which is the highest reported to date among all polycrystalline n-type Bi$_2$Te$_3$-based compounds. In contrast, $n_H$ for control SPS Cu$_{x}$Bi$_2$Te$_3$ samples decreases with the increasing Cu amount, indicating that Cu serves as an electron acceptor (Figure S7a). The corresponding $\mu_H$ is also considerably lower than that of the SPS Cu$_{x}$Bi$_2$Te$_{3-x}$ samples. These results clearly show that excess Te condition brings about the simultaneous enhancement in $n_H$ and $\mu_H$ (Figure S7b).

The achieved ultrahigh $\mu_H$ can arise from the simultaneous contribution from three factors. First, excess Te in the reaction mixture can reduce carrier scattering to enhance $\mu_H$ because low-melting excess Te may act as a "lubricant" so that Bi$_2$Te$_3$ lamella grains may reorient to form better aligned and packed textures along the ab-planes during SPS under high temperature and pressure, as similarly observed in the previous report. Second, excess Te in the reaction mixture can suppress the generation of adverse Te vacancies ($V_T$), thereby helping to maintain $n_H$ at the optimal level to achieve an ultrahigh $\mu_H$. Otherwise, too high $n_H$ could deteriorate $\mu_H$ due to carrier scattering and simultaneously reduce S because of the inverse proportionality between S and $n_H$. In contrast, SPS pristine Bi$_2$Te$_3$ exhibits a considerably large $n_H \sim$ 4.79 $\times$ 10$^{19}$ cm$^{-3}$ and a consequently lowered $\mu_H \sim$ 164 cm$^2$/V·s at room temperature. Third, Cu cations at van der Waals gaps between the Bi$_2$Te$_3$ layers can improve the electron transfer across the Bi$_2$Te$_3$ domains, thereby enhancing their conductivity and single-crystalline Bi$_2$Te$_3$.

We calculated $\mu_H$ for the SPS Cu$_{0.06}$Bi$_2$Te$_{3.17}$ samples with respect to $n_H$ at room temperature based on a SPB model assuming an acoustic phonon scattering (see the Supporting Information for details) (Figure 4). Experimental $\mu_H$ of poly- and single-crystalline Bi$_2$Te$_3$ and Cu$_{0.01}$Bi$_2$Te$_2$.Se$_{0.3}$ from previous reports fall near the calculated curve. In contrast, $\mu_H$ of SPS Cu$_{x}$Bi$_2$Te$_{3-x}$ is much larger than the theoretical prediction, displaying a markedly boosted $\mu_H$ in comparison with other Cu-doped Bi$_2$Te$_3$-based materials.

We performed the temperature-dependent Hall effect measurements for the SPS Cu$_{0.06}$Bi$_2$Te$_{3.17}$ sample to better understand its ultrahigh $\mu_H$ and carrier scattering mechanism (Figure 5). $n_H$ gradually increases from $\sim$1.2 $\times$ 10$^{19}$ to 3.3 $\times$ 10$^{19}$ cm$^{-3}$ in the 298–473 K temperature range. The resulting temperature-dependent Hall coefficients $R_H = 1/n_He$, where e is the electron charge, are given in Figure S8. The corresponding $\mu_H$ decreases from $\sim$468 to 180 cm$^2$/V·s$^{-1}$ (Figure 5b), consistent with their inversely proportional relationship. A temperature-dependent log($\mu_H$)−log(T) plot shows complex scattering mechanisms in SPS Cu$_{0.06}$Bi$_2$Te$_{3.17}$ (Figure 5c). From 323 to 373 K, the slopes of the curves are $\sim$1.5, indicating that scattering mechanism is dominated by acoustic phonon scattering if parabolic bands are assumed.
corresponds to electron–phonon scattering due to thermal lattice vibrations. From 398 to 473 K, the slopes increase to \( \sim -1.8 \). The slightly steeper slope at higher temperature probably results from nonparabolic bands, electron–electron scattering, and/or optical phonon scattering due to lattice vibrations with high frequency. The similar reasons could be applied to \( \mu_H \) at 298 K, which slightly deviates from the slope of \( -1.8 \).

The temperature-dependent electrical conductivity \( (\sigma) \) of the SPS \( \text{Cu}_x\text{Bi}_2\text{Te}_3_{1.17} \) samples increases significantly with the higher mole fraction of Cu doping (Figure 6a). This observation results from the concurrently raised \( n_H \) and \( \mu_H \) with the increasing concentration of Cu as well as the higher \( \mu_H \) itself than the theoretical expectation. For instance, the \( \sigma \) rises from \( \sim 665 \text{ S cm}^{-1} \) for \( \text{Cu}_{0.02}\text{Bi}_2\text{Te}_3_{1.17} \) to \( \sim 900 \text{ S cm}^{-1} \) for \( \text{Cu}_{0.06}\text{Bi}_2\text{Te}_3_{1.17} \) at room temperature, indicating that Cu serves as an electron donor. In contrast, the \( \sigma \) of the control SPS \( \text{Cu}_x\text{Bi}_2\text{Te}_3 \) samples decreases considerably with the larger extent of Cu, for example, \( \sim 950 \text{ S cm}^{-1} \) for \( \text{Cu}_{0.02}\text{Bi}_2\text{Te}_3 \) to \( \sim 235 \text{ S cm}^{-1} \) for \( \text{Cu}_{0.06}\text{Bi}_2\text{Te}_3 \). It is consistent with the Hall effect measurement results for the control SPS \( \text{Cu}_x\text{Bi}_2\text{Te}_3 \) samples that both \( n_H \) and \( \mu_H \) decrease with the increasing Cu amount (Figure S7). This observation verifies the unique role of excess Te in the reaction mixture for charge transport properties in that the analyzed EDS composition of SPS \( \text{Cu}_x\text{Bi}_2\text{Te}_3_{1.17} \) and SPS \( \text{Cu}_x\text{Bi}_2\text{Te}_3 \) is almost the same, namely, \( \text{Cu}_x\text{Bi}_2\text{Te}_3 \).

The \( x = 0.06 \) sample shows a much higher \( \sigma \) and an even slightly larger \( |S| \) than the other members in SPS \( \text{Cu}_x\text{Bi}_2\text{Te}_3_{1.17} \), contrary to the general inverse relationship between \( \sigma \) and \( |S| \). This simultaneous enhancement leads to an ultrahigh power factor (PF) for \( \text{Cu}_{0.06}\text{Bi}_2\text{Te}_3_{1.17} \), exhibiting a maximum of \( \sim 45 \mu\text{W cm}^{-1} \text{K}^{-2} \) at room temperature, which is \( \sim 1.5 \) times larger than that of \( \text{Cu}_{0.02}\text{Bi}_2\text{Te}_3_{1.17} \) (Figure 6b). The achieved PF is the highest reported to date among bulk polycrystalline n-type \( \text{Bi}_2\text{Te}_3 \)-based materials (Figure 6c).

Remarkably, polycrystalline SPS \( \text{Cu}_{0.06}\text{Bi}_2\text{Te}_3_{1.17} \) displays an even higher PF than the single-crystal \( \text{Cu}_{0.07}\text{Bi}_2\text{Te}_3 \) \( 47 \) in the previous report despite their similar actual composition. The samples with \( x = 0.08 \)
and 0.10, which do not include secondary phase, show a lower PF than that with $x = 0.06$ (Figure S9).

Since a large amount of Cu atom is introduced into the Bi$_2$Te$_3$ lattices, the chemical stability of the sample under a large current is very important for practical TE applications. Figure S10 shows a relative resistance of $R/R_0$ where $R_0$ is an initial resistance of the sample, for the SPS Cu$_{0.06}$Bi$_2$Te$_3$ sample under a current density of 12 A cm$^{-2}$ as a function of time. It is a typical stability test condition for superionic TE materials containing a large concentration of highly mobile Cu or Ag atoms. The $R/R_0$ value is nearly unchanged after about 50 000 s (14 h), demonstrating the chemical robustness of the SPS Cu$_{0.06}$Bi$_2$Te$_3$ sample under a high-current environment.

**Thermal Conductivity.** The total thermal conductivity ($\kappa_{\text{tot}}$) for both the SPS Cu$_{0.06}$Bi$_2$Te$_3$ and control SPS Cu$_{0.04}$Bi$_2$Te$_3$ samples increases with increasing temperature (Figure 7a). The former shows a lower $\kappa_{\text{tot}}$ than the latter near ambient temperature. For example, the $\kappa_{\text{tot}}$ at room temperature increases from $\sim 1.60$ W m$^{-1}$ K$^{-1}$ for SPS Cu$_{0.04}$Bi$_2$Te$_3$ to $\sim 1.85$ W m$^{-1}$ K$^{-1}$ for the control SPS Cu$_{0.04}$Bi$_2$Te$_3$. The $\kappa_{\text{tot}}$ of the SPS Cu$_{0.06}$Bi$_2$Te$_3$ samples increases with the higher concentration of Cu over the entire temperature range. Because $\kappa_{\text{tot}}$ is contributed from charge carriers ($\kappa_{\text{ele}}$), lattice phonons ($\kappa_{\text{lat}}$), and bipolar conduction ($\kappa_{\text{bip}}$), examining their portion to $\kappa_{\text{tot}}$ can reveal the effect of Cu doping and excess Te in the reaction mixture on the thermal transport of the materials. The $\kappa_{\text{tot}}$ is expressed by the formula $\kappa_{\text{tot}} = L\tau T$, where $L$ is the Lorentz number, $\tau$ is the electrical conductivity, and $T$ is the absolute temperature. The $\kappa_{\text{ele}}$ can be obtained by the Wiedermann–Franz formula, $\kappa_{\text{ele}} = \kappa_{\text{tot}} - \kappa_{\text{lat}}$ (see the Supporting Information for details). The $\kappa_{\text{lat}}$ of the SPS Cu$_{0.06}$Bi$_2$Te$_3$ samples rises with the increasing content of Cu, indicating that Cu atoms serve as electron donors. This result is consistent with the trend of $\mu_{\text{H}}$ and $\sigma$ (Figure 7b). The $\kappa_{\text{lat}}$ for the SPS Cu$_{0.06}$Bi$_2$Te$_3$ samples is comparable regardless of the Cu concentration and significantly lower than those of the control Cu$_{0.04}$Bi$_2$Te$_3$ samples up to $\sim 423$ K, implying that the excess Te condition mainly determines $\kappa_{\text{lat}}$ of the SPS Cu$_{0.06}$Bi$_2$Te$_3$ samples and differentiates it from $\kappa_{\text{lat}}$ of the control SPS Cu$_{0.04}$Bi$_2$Te$_3$ (Figure 7c). The effect of point defects by Cu doping is minor in $\kappa_{\text{tot}}$ for SPS Cu$_{0.06}$Bi$_2$Te$_3$.

To better understand this observation, we investigated the microstructures of SPS Cu$_{0.06}$Bi$_2$Te$_3$ samples using a transmission electron microscope (TEM). Figures S11a and 10b show typical low-magnification TEM images. Line features with a different contrast are embedded in the matrix, revealing the presence of a high density of dislocation arrays. The selected area electron diffraction pattern, which includes both the matrix and dislocation regions, shows a single set of spots corresponding to the Bi$_2$Te$_3$ structure along the [001] zone axis without any noticeable second phase (inset, Figure S11b). The high-resolution TEM and the corresponding inverse fast Fourier transform images clearly display edge dislocations marked by red symbols (Figure S11c,d). The average density of dislocations is estimated to be $\sim 2 \times 10^{12}$ cm$^{-2}$ from the TEM image, which is much higher than $\sim 10^7$ and $\sim 10^8$ cm$^{-2}$ observed in pristine Bi$_2$Te$_3$ and typical semiconductors, respectively. A similar observation was also previously reported that a high density of dislocations is generated via squeezing excess Te out of the Bi$_2$Te$_3$-based lattices by SPS under pressure, leading to a significant reduction in $\kappa_{\text{lat}}$. Note that dense dislocations have been established as a highly effective phonon scattering mechanism over others.

We theoretically calculated the temperature-dependent $\kappa_{\text{lat}}$ for SPS Cu$_{0.06}$Bi$_2$Te$_3$ using the Debye–Callaway model (see the Supporting Information for details). According to our TEM observation, we considered various scattering mechanisms such as intrinsic Umklapp process, grain boundaries, point defects, and dislocations based on the Matthiessen's equation. Because bipolar conduction from minor carriers is important for a narrow band gap semiconductor such as Bi$_2$Te$_3$ and PbTe, we also obtained bipolar thermal conductivity ($\kappa_{\text{bip}}$) to accurately calculate $\kappa_{\text{tot}}$ (Figure S12a). The theoretical $\kappa_{\text{bip}}$ rapidly grows with the increasing temperature, as observed in $\kappa_{\text{tot}}$ (Figure 7a), indicating that $\kappa_{\text{bip}}$ mainly contributes to $\kappa_{\text{tot}}$ at high temperature. The theoretical $\kappa_{\text{tot}}$ based on phonon scattering mechanisms of Umklapp process, grain boundary, and point defect is much higher than the experimental values (Figure S12b). Further consideration of high-density dislocations found in the TEM study greatly improves the agreement between the theoretical and experimental $\kappa_{\text{tot}}$ clearly demonstrating their major role in $\kappa_{\text{lat}}$. Overall, point defects by Cu doping and dense dislocations induced by excess Te synergistically reduce $\kappa_{\text{lat}}$. However, a degree of decrease in $\kappa_{\text{lat}}$ is not significant in comparison with other representative bulk TE materials with dense dislocations.

The enhanced PF and simultaneously reduced $\kappa_{\text{tot}}$ lead to a relatively high ZT $\sim 0.85$ for the SPS Cu$_{0.06}$Bi$_2$Te$_3$ sample (Figure 7d). There is more scope to improve the ZT of the SPS Cu$_{0.06}$Bi$_2$Te$_3$ system by developing strategies of further reducing $\kappa_{\text{tot}}$ with minimal influence on the powder factor, given its much higher $\kappa_{\text{lat}}$ than that of the state-of-the-art n-type Bi$_2$Te$_3$-based materials.

**CONCLUSIONS**

We introduced new high-performance n-type Bi$_2$Te$_3$-based thermoelectric materials with ultrahigh electron mobility and power factor. These specialize in maximizing the power factor for a high-output power thermoelectric generators operating near ambient temperature. With this new system, both the n- and p-type Bi$_2$Te$_3$-based materials eventually show a similar maximum power factor value of $\sim 45$ $\mu$W cm$^{-1}$ K$^{-2}$ around room temperature. Accordingly, the thermoelectric devices comprising their couples can promise maximized output power, although there are many other components that have to be advanced in thermoelectric device structure, for example, electrodes, metallization layers, and contact wires. Our new synthetic method widens the availability of chemical compositions to enhance the thermoelectric properties, which are otherwise strictly governed by thermodynamic phase diagrams. This synthesis concept can be widely applied to other chemical systems for various technological applications.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b10394.

Analyzed chemical compositions; Hall effect measurements, XRD, and TGA; thermoelectric properties; stability test; and TEM and calculation details for lattice and bipolar thermal conductivities (PDF).
Thermal Conductivity and Outstanding Thermoelectric Properties: Material with a Composite Crystal Structure Causing Ultralow Realizing High Figure of Merit in Heavy-Band p-Type Half-Heuslers

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The authors declare no competing financial interest.

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