



Article A Thermoelectric Performance Study of Layered Bi₂TeI Weak Topological Insulator Materials

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Abstract: Topological insulators have been considered as promising thermoelectric materials because of their high electrical transport properties and low thermal conductivity. In this work, the crystal structure, chemical composition, and thermoelectric transport properties of a weak topological insulator, Bi₂TeI, were studied. Bi₂TeI possesses the lowest lattice thermal conductivity compared with the analogously layered compounds Bi₂Te₃ and BiTeI. Cu and Zn were used as dopants with the aim of optimizing the thermoelectric performance. It was found that doping Bi₂TeI with Cu led to decreased carrier concentration and power factor. Accompanied with reduced lattice thermal conductivity, Zn-doped samples showed a largely improved dimensionless figure of merit, *ZT*. The largest *ZT* was 0.077 for Zn_{0.01}Bi₂TeI, increased by 70% as compared with the undoped Bi₂TeI.

Keywords: thermoelectric performance; weak topological insulator; electrical transport; thermal conductivity

1. Introduction

Thermoelectric (TE) technology can realize direct energy conversion between heat and electricity, having played an important role in the field of waste heat recovering, power generation, and efficient cooling [1]. The performance of a TE material is characterized by the dimensionless figure of merit $ZT = \alpha^2 \sigma T/\kappa$, where α , σ , and T are the Seebeck coefficient, electrical conductivity, and absolute temperature. κ is the thermal conductivity, which is comprised of electronic (κ_E) and lattice (κ_L) parts. High-performance TE materials should have high power factor ($\alpha^2 \sigma$) and poor thermal conduction. However, the optimization of TE performance is challenging because these transport properties are strongly interdependent, and it is necessary to synergistically regulate the electrical and thermal transport properties [2,3]. In the past decade, electronic band engineering and phonon engineering approaches have been developed for the improvement of TE properties [4–6]. Recently, magnetic nanoparticles embedded in TE materials were reported as a new strategy to optimize the electron and phonon transport [7,8]. It is thus of great interest to explore new materials in which unconventional effects would be beneficial to the TE performance.

As a kind of novel condensed matter, topological insulators (TIs) exhibit gapped states in bulk and nontrivial metallic states on the surface [9,10]. It was suggested that the unique electron transport behavior of the surface states might provide new insights into the TE community [11–14]. Theoretical calculations have shown that the TE performance of strong TIs such as Bi_2Te_3 and Bi_2Se_3 can be enhanced by the surface state hybridization with bulk states [13], or by the largely varied electron scattering rates spanning from the surface states to the bulk states [14]. These studies have provided more opportunities to explore potential TE candidates among the TI systems. As many

researchers have focused on the TE performance of the strong TIs [11–14], the weak TIs, which are distinguished from the strong ones by an even number of Dirac cones on the surface, are less studied as TE materials. Structurally, some weak TIs can be regarded as an alternate stack of quantum spin Hall (QSH) layers and normal insulator (NI) layers [10,15]. The superlattice-like stacked structure should have lower intrinsic lattice thermal conductivity [16,17]. Experimental work has showed that the weak TI Bi₁₄Rh₃I₉ manifested extremely low thermal conductivity (as low as ~0.3 W m⁻¹ K⁻¹) benefitting from low sound velocity, low Debye temperature, and large lattice anharmonicity [18]. Meanwhile, the first-principles calculations also predicted that low thermal conductivity could be found in another weak TI Bi₂TeI due to the similar stacking structure and lattice dynamics [18].

In this work, the weak TI Bi₂TeI samples were synthesized using a combination of melting, annealing, and spark plasma sintering (SPS) techniques. The microstructure and TE transport properties of Bi₂TeI were studied. The TE properties of Bi₂TeI were compared with two other important layered compounds, Bi₂Te₃ and BiTeI, since Bi₂Te₃ represents one of the most important TE candidates and is meanwhile a strong TI [13,14], while BiTeI has the same structure as the NI layers of Bi₂TeI (Figure 1a) [19,20]. It was found that Bi₂TeI possessed the lowest lattice thermal conductivity. Cu and Zn were used as dopants to further improve the TE performance of Bi₂TeI. It was revealed that doping Bi₂TeI with Zn could improve the TE properties with enhanced electrical conductivity and Seebeck coefficient and depressed thermal conductivity.

2. Experimental

A combination of melting, annealing, and SPS techniques were used to prepare Bi₂Te₃, BiTeI, and undoped and doped Bi₂TeI samples. Highly pure Bi (99.999%, powder), Te (99.999%, powder), and BiI₃ (99.99%, powder) were used as starting materials. The mixtures of these materials were weighted according to the compositions and sealed into silica tubes under vacuum. The tubes were transferred into a programmable furnace for heat treatment. For the synthesis of undoped and doped Bi₂TeI samples, the tubes were heated to 723 K and held for 8 h followed by an annealing treatment at 403 K for 48 h. The annealed products were ground into fine powders then sintered to pellets by SPS method under vacuum. The sintering temperature was 653 K and the applied pressure was 40 MPa. The synthesis process of Bi₂Te₃ and BiTeI followed the same procedures. For BiTeI, the melting and annealing treatments were carried out at 893 K for 8 h and at 403 K for 48 h, respectively. The SPS conditions were sintering temperature 653 K and a pressure of 40 MPa. For Bi₂Te₃, the melting and annealing were carried out at 893 K for 8 h and at 723 K for 48 h, respectively. The SPS conditions were sintering temperature of 40 MPa. Since iodide is volatile, excessive iodide (1 *at*%) was added in the starting materials to compensate the iodide loss during the annealing and sintering processes of Bi₂TeI and BiTeI.

Phase constituents were determined by X-ray diffraction (XRD, PANalytical X'Pert PRO, PANalytical, Almelo, The Netherlands) using Cu *K* α radiation. The microstructure and chemical compositions were analyzed by an electron probe micro-analyzer (EPMA, JXA-8230, JEOL, Tokyo, Japan). Selected area electron diffraction (SAED) and elemental mapping of Bi₂TeI were performed with transmission electron microscopy (TEM, Talos F200S, Thermo Fisher Scientific, Waltham, MA, USA) equipped with energy dispersion X-ray spectroscopy (EDX). Scanning transmission electron microscopy–energy dispersion X-ray spectroscopy (STEM-EDX) mode was used to capture the elemental distribution in the nanometre scale. The TEM sample for SAED and STEM-EDX analysis was made by a focused ion beam (FIB, Helios NanoLab G3 UC, Thermo Fisher Scientific). σ and α were measured with the standard four-probe method (ZEM-3, ULVAC Technologies, Inc., Kanagawa, Japan) in a He atmosphere. Hall effect measurements were performed on a commercial testing system (Thermoelectric and magnetic performance of multilayer film materials, NYMS-1, Shanghai, China) [7]. The measurements were performed in a He atmosphere with a maximum applied magnetic field of 1.5 T. κ was calculated using the equation $\kappa = C_p \lambda \rho_0$, where C_p is the specific heat capacity, ρ_0 is the bulk density, and λ is the thermal diffusion coefficient. λ was measured by a laser flash technique

(Netzsch LFA 457, Selb, Germany) in a flowing Ar atmosphere. ρ_0 was measured by the Archimedes method. Uncertainties for σ and κ were ± 5 –7%, and for α was ± 5 %. Since these layered compounds sintered by the SPS technique exhibited strong *c*-axis preferred orientation along the direction of pressure, the TE transport properties along the in-plane (perpendicular to the direction of pressure) and cross-plane (parallel to the direction of pressure) directions were separately measured.

3. Results and Discussion

3.1. Synthesis and TE Properties of Bi₂TeI

As shown in Figure 1a, Bi_2TeI is crystallized in a monoclinic lattice (space group C2/m) [19]. Resembling the weak TI $Bi_{14}Rh_3I_9$, Bi_2TeI has a layered structure stacked by bismuth QSH bilayers $[Bi]_2$ and BiTeI NI bilayers $[BiTeI]_2$. The formation mechanism of topological insulator states could be connected with the strong interaction between QSH and NI layers [20] and the crystal mirror symmetry [21].

Differently to Bi2Te3 and BiTeI, experimental study performed on Bi2TeI was rare since the preparation of Bi₂TeI was a challenge [22–24]. It has been reported that phase-pure Bi₂TeI could not be obtained by long-term annealing, gas phase reaction, or slow cooling [19,22–24]. As guided with the solid-state equilibria of Bi-Te-I systems [25–27], polycrystalline Bi₂TeI bulk samples were synthesized using a combination of melting, annealing, and SPS techniques in this work. This combined approach has been widely used for preparing varioustable TE materials [2,7]. Figure 1b shows the powder XRD patterns of Bi2Te3, BiTeI, and Bi2TeI. All the diffraction peaks can be indexed to the standard files of the Joint Committee on Powder Diffraction Standards (JCPDS) 89-2009 of Bi2Te3 and the JCPDS 82-0484 of BiTeI, respectively. The XRD pattern of Bi₂TeI was calculated with the reported monoclinic structure [16]. All the diffraction peaks can be indexed to the calculated pattern, indicating that the synthesized Bi₂TeI was single-phase. Figure 2a,b shows the SAED patterns taken on Bi₂TeI sample. The SAED patterns of Bi2TeI can be indexed as [103] and [010] zone axis of the monoclinic crystal structure. The layered structure can be reflected from the SAED pattern along the [010] zone axis, which shows good agreement between the experiment and simulation results. Some diffraction points that were not observed indicated the existence of intrinsic defects in the sample. Figure 2d-f shows the elemental mapping of Bi, Te, and I on Bi_2 TeI FIB sample. It can be seen that the elements were uniformly distributed in the nanometre scale, indicating the good homogeneity of Bi₂TeI samples.



Figure 1. (a) Crystal structures of Bi₂TeI, BiTeI, and Bi₂Te₃. (b) Powder XRD patterns of Bi₂TeI, BiTeI, and Bi₂Te₃ synthesized by a combination of melting, annealing, and spark plasma sintering techniques.



Figure 2. Selected area electron diffraction (SAED) patterns of Bi₂TeI along the zone axis of (**a**) [103], (**b**) [010], and (**c**) simulated SAED pattern along [010] zone axis. Elemental mapping of (**d**) Bi, (**e**) Te, and (**f**) I of Bi₂TeI measured by Scanning transmission electron microscopy–energy dispersion X-ray spectroscopy (STEM-EDX).

Figure 3 shows the temperature dependence of transport properties of Bi₂Te₃, BiTeI, and Bi₂TeI, including electrical conductivity, absolute Seebeck coefficient, and thermal conductivities measured along the in-plane and cross-plane directions. The charge transport properties at 300 K including carrier concentration and Hall mobility along the two directions are listed in Table 1. Along the two mutually perpendicular directions, the anisotropy in σ was large for Bi₂Te₃ and BiTeI but in α was small. The anisotropy in layered compounds is determined by the highly anisotropic mobility. σ of Bi₂Te₃ decreased with the increase in temperature, indicating a heavily doped semiconducting transport behavior. BiTeI and Bi₂TeI had σ increased with the increase in temperature, showing a semiconducting transport behavior. Bi₂Te₃ and BiTeI were n-type while Bi₂TeI was p-type. The absolute α of BiTeI was around 100 μ V K⁻¹ at 300 K and increased with the increase temperature from 300 to 500 K, which is consistent with the reported work [28]. Bi₂TeI had lower α values as compared with BiTeI, which might be related to the higher carrier concentration and much smaller band gap of Bi₂TeI (0.1 eV for Bi₂TeI [20] and 0.38 eV for BiTeI [29]).

Samples	$N (10^{20} \text{ cm}^{-3})$	$(cm^2 V^{-1} s^{-1})$	σ (10 ⁴ S m ⁻¹)	α (μV K ⁻¹)	$(W m^{\kappa_L} K^{-1})$
Bi ₂ Te ₃ (in-plane)	0.72	150	16.9	-111	1.10
Bi_2Te_3 (cross-plane)	0.53	92	7.75	-102	0.94
BiTeI (in-plane)	0.19	15	0.45	-106	0.86
BiTeI (cross-plane)	0.14	8.6	0.20	-102	0.58
Bi ₂ TeI (in-plane)	8.1	2.3	3.07	53.6	0.80
Bi ₂ TeI (cross-plane)	7.5	1.3	1.59	53.8	0.44

Table 1. Charge transport properties of Bi₂Te₃, BiTeI, and Bi₂TeI along the in-plane and cross-plane directions at 300 K.



Figure 3. Temperature dependence of (**a**) electrical conductivity, (**b**) Seebeck coefficient, (**c**) thermal conductivity, and (**d**) comparison of the thermal conductivity and lattice thermal conductivity of Bi₂Te₃, BiTeI, and Bi₂TeI at 300 K.

The comparison of thermal conductivity and lattice thermal conductivity of Bi₂Te₃, BiTeI, and Bi₂TeI, along the in-plane and cross-plane directions, is shown in Figure 3c,d. κ_L was obtained by subtracting κ_E from κ . κ_E was calculated by Wiedemann-Franz law $\kappa_E = L_0 T \sigma$, where the Lorenz number L_0 had a numerical value of $2.0 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$, by considering their high carrier concentration. Compared with binary Bi₂Te₃, ternary BiTeI and Bi₂TeI exhibited much lower κ and relatively weak temperature dependence of κ . At 300 K, κ_L of Bi₂TeI was about 0.44 W m⁻¹ K⁻¹ along the cross-plane direction, which was the lowest as compared with those of Bi₂Te₃ and BiTeI. The measured κ_L of Bi₂TeI was higher than those predicted by the first-principles calculations [18], which might be attributed to the fact that (1) the sound velocity and Debye temperature were overestimated in the calculations and (2) the contribution of bipolar thermal conductivity as caused by the small band gap was neglected in theoretical calculations.

3.2. TE Properties Optimization of Doped Bi₂TeI

Since Bi₂TeI possesses very low lattice thermal conductivity, it is expected to optimize the electrical properties and thus the overall TE performance. A corporation of Cu has been proven as an effective way to improve the TE performance of Bi₂Te₃ and BiTeI [28,30–32]. Here, Cu was used as a dopant to optimize the TE performance of Bi₂TeI. Meanwhile, Zn was selected as another dopant because Zn has larger electronegativity. Cu-doped and Zn-doped Bi₂TeI samples with nominal compositions Cu_xBi₂TeI and Zn_yBi₂TeI were synthesized. Figure 4 shows the powder XRD patterns of Cu-doped and Zn-doped Bi₂TeI. It can be seen that all the diffraction peaks can be indexed to the calculated diffraction patterns of Bi₂TeI, suggesting that Cu and Zn dopants were incorporated into the lattice of Bi₂TeI. Broadened diffraction peaks can be found for the (003), (205), and (020) planes. It is possible that the high concentration of dopants could bring about large lattice distortion. Figure 5 shows the elemental mapping of Cu on Cu_xBi₂TeI and Zn on Zn_yBi₂TeI samples measured by EPMA. For Cu_xBi₂TeI, the distribution of Cu was uniform with increasing the content of dopant. A slight Zn richness can be found from y = 1.5% and 2% samples. Figure 6 shows the chemical composition of a large Zn-rich area

Figure 4. XRD patterns of Cu-doped Cu_xBi₂TeI and Zn-doped Zn_yBi₂TeI.

Figure 5. Elemental mapping of (**a**–**c**) Cu on Cu_xBi₂TeI and (**d**–**f**) Zn on Zn_yBi₂TeI samples. (**a**) x = 1%, (**b**) x = 1.5%, (**c**) x = 2%, (**d**) y = 1%, (**e**) y = 1.5%, (**f**) y = 2%.

Figure 6. (a) Secondary electron image and (b) backscattered electron image of a large Zn-rich area on $Zn_{0.015}Bi_2$ TeI sample. The elemental distribution along the line marked in (a) is also presented.

Figure 7 shows the temperature dependence of in-plane electrical conductivity, Seebeck coefficient, and power factor of Cu- and Zn-doped Bi₂TeI. The in-plane charge transport properties of Cu-doped Cu_xBi₂TeI and Zn-doped Zn_yBi₂TeI at 300 K are listed in Table 2. σ of the doped samples was increased slowly while increasing the temperature, indicating a semiconducting transport behavior. Doping Bi₂TeI with 1.5% and 2% Cu led to decreased σ . With increasing the Zn content, σ of Zn_yBi₂TeI was first increased then largely decreased. The decrease in σ upon doping with large amount of Cu should be attributed to the decreased carrier concentration. After doping with Zn, the carrier concentration was greatly increased, from 8.1×10^{20} cm⁻³ for the pristine Bi₂TeI to 1.48×10^{21} cm⁻³ for Zn_{0.01}Bi₂TeI was due to the increased carrier concentration, and the decrease in σ for Zn_{0.015}Bi₂TeI and Zn_{0.02}Bi₂TeI might be related to the formation of nonconductive ZnI₂ impurity phase. Since the carrier concentration was reduced after Cu doping, it can be inferred that Cu as an intercalated dopant has entered into the interlayer space of Bi₂TeI. The electron donor behavior of the intercalated Cu has been reported in other layered compounds [29,30]. For Zn doped samples, a substitution of Zn²⁺ on Bi³⁺ sites might be accounted for the increased carrier concentration of the prive materials.

Samples	$n (10^{20} \text{ cm}^{-3})$	$(cm^2 V^{\mu_{\rm H}} s^{-1} s^{-1})$	σ (10 ⁴ S m ⁻¹)	$(\mu V K^{-1})$	$\frac{\alpha^2\sigma}{(\mathrm{mW}\mathrm{m}^{-1}\mathrm{K}^{-2})}$	$(W m^{-1} K^{-1})$	$(W m^{\kappa_L} K^{-1})$
Bi ₂ TeI	8.1	2.3	3.07	55.3	0.093	0.99	0.80
Cu _{0.005} Bi ₂ TeI	7.9	2.4	3.11	53.7	0.090	0.91	0.72
Cu _{0.01} Bi ₂ TeI	7.1	2.7	3.08	54.1	0.090	0.88	0.70
Cu _{0.015} Bi ₂ TeI	5.2	3.2	2.70	49.9	0.068	0.91	0.75
Cu _{0.02} Bi ₂ TeI	4.2	4.0	2.73	46.2	0.058	0.92	0.75
Zn _{0.005} Bi ₂ TeI	11.2	1.9	3.36	51.3	0.088	0.90	0.70
Zn _{0.01} Bi ₂ TeI	14.8	1.4	3.26	55.7	0.101	0.88	0.69
Zn _{0.015} Bi ₂ TeI	15.8	1.0	2.53	56.4	0.080	0.94	0.78
Zn _{0.02} Bi ₂ TeI	14.9	1.1	2.54	56.5	0.081	0.97	0.82

Table 2. Charge transport properties of Cu-doped Cu_xBi₂TeI and Zn-doped Zn_yBi₂TeI at 300 K.

Figure 7. Temperature dependence of in-plane (**a**) electrical conductivity, (**b**) Seebeck coefficient, and (**c**) power factor of Cu-doped $Cu_x Bi_2 TeI$ and Zn-doped $Zn_y Bi_2 TeI$.

The positive α values of Cu_xBi₂TeI and Zn_yBi₂TeI were indicative of p-type conduction behavior, which was consistent with Hall effect measurements. Doping Cu led to not only decreased σ but also decreased α , which was mainly related to the strengthened bipolar effect as the carrier concentration was decreased. Interestingly, simultaneously increased σ and α were obtained for Zn_{0.01}Bi₂TeI sample. It was highly possible that the dopant Zn introduced an additional resonant state near the Fermi level, which was beneficial for enhancing the Seebeck coefficient. However, a further theoretical calculation should be carried out to verify the electronic structure of Zn-doped Bi₂TeI.

Due to the decreased σ and α , the $\alpha^2 \sigma$ values of the Cu-doped samples decreased with increasing x in the range of 0–2%. This result originated from the strengthened bipolar effect as caused by the lowered carrier concentration. For Zn-doped samples, the $\alpha^2 \sigma$ values first increased and then decreased. The highest value reached 0.14 mW m⁻¹ K⁻² at 500 K for Zn_{0.01}Bi₂TeI sample, which showed an approximately 50% improvement as compared with that of the undoped sample. At high temperatures, all Zn doped samples showed enhanced power factors.

Theoretical predictions have suggested that the gapless surface states on the surface could bring about positive contribution to the Seebeck coefficient [13,14], which needs to adjust the Fermi level into a relatively narrow energy range [12,21]. The undoped Bi₂TeI had a high carrier concentration of 8×10^{20} cm⁻³. By inserting Cu, the carrier concentration of Bi₂TeI can be reduced to 4×10^{20} cm⁻³. However, an increase in Cu content to further lower the carrier concentration failed and finally led to the formation of impurities. Therefore, the TE properties of the undoped Bi₂TeI in this work should be contributed from the bulk states of this weak TI.

Figure 8 shows the temperature dependence of in-plane thermal conductivity, carrier thermal conductivity, and lattice thermal conductivity of Cu-doped and Zn-doped Bi₂TeI. With an increase in temperature from 300 to 500 K, κ first decreased slightly and then increased gradually. The first decrease in κ was related to the phonon–phonon scattering and the increase at higher temperatures should be mainly due to the contribution of $\kappa_{\rm E}$. The $\kappa_{\rm L}$ values for all the samples decreased with the increase in temperature, reflecting strong phonon-phonon scattering in the layered Bi2 TeI. With the increase in the doping content of Cu and Zn, the κ_L values first decreased and then increased. The first decrease in κ_L values with doping Cu might originate from the point defect scattering and disorder scattering of the intercalated Cu. The increase in κ_L values after doping more Cu should be related to the enhanced interlayer coupling between QSH and NI layers in these kinds of layered materials. It was inferred that the intercalation of dopants could lead to increased sound velocity and Debye temperature along the cross-plane directions, which leads to higher κ_L . The first decrease in κ_L values after doping with Zn should originate from the improved point defect scattering when the dopant Zn substituted for the Bi sites. The increase in κ_L values after doping more Zn should be attributed to the presence of ZnI_2 impurity. $Zn_{0.01}Bi_2$ TeI had the lowest in-plane lattice thermal conductivity with $0.69~W~m^{-1}~K^{-1}$ at 300 K and 0.58 W $m^{-1}~K^{-1}$ at 500 K.

Figure 8. Temperature dependence of in-plane (**a**) thermal conductivity, (**b**) carrier thermal conductivity, (**c**) lattice thermal conductivity, and (**d**) *ZT* of Cu-doped Cu_xBi_2TeI and Zn-doped Zn_yBi_2TeI .

Figure 8d displays the *ZT* values of the doped Bi₂TeI in the temperature range of 300–500 K. With the increase in temperature, the *ZT* values of all the samples increased gradually. With increasing the content of Cu, the *ZT* values of Cu-doped samples first slightly increased and then decreased. However, Zn_yBi_2TeI showed increased *ZT* with increasing *y* in the range of 0–1%. At high temperatures, all Zn-doped samples showed increased *ZT* values. The largest *ZT* reached 0.077 at 500 K for the $Zn_{0.01}Bi_2TeI$ sample, increased by 70% as compared with that of the undoped Bi₂TeI. The reason behind the enhancement of *ZT* was twofold: (1) lowered lattice thermal conductivity due to the substitution of Zn on Bi sites and (2) simultaneously improved electrical conductivity and Seebeck coefficient.

4. Conclusions

Single-phase Bi₂TeI was prepared by a combination of melt-annealing and SPS techniques. The TE performance of Bi₂TeI was compared with Bi₂Te₃ and BiTeI. It was found that Bi₂TeI possessed high electrical conductivity and the lowest lattice thermal conductivity. A performance optimization study was performed by doping Bi₂TeI with Cu and Zn. Structural analysis indicated that the dopants Cu and Zn were incorporated into the lattice of Bi₂TeI. The doping of Zn could improve the power factor due to the enhanced electrical conductivity and Seebeck coefficient. The maximal power factor reached 0.14 mW m⁻¹ K⁻² at 500 K for the Zn_{0.01}Bi₂TeI sample. The phonon transport of Bi₂TeI was suppressed due to the intercalation of Cu into the interlayer space and the substitution of Zn on Bi sites. The phonon scattering mechanisms included enhanced point defect scattering due to the Zn substitution and disorder scattering as a result of Cu intercalation. The largest *ZT* was 0.077 for the Zn_{0.01}Bi₂TeI sample, increased by 70% as compared with the undoped Bi₂TeI materials.

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