Article

Thermoelectric Properties of Cu$_2$Te Nanoparticle Incorporated N-Type Bi$_2$Te$_2$Se$_0.3$

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Abstract: To develop highly efficient thermoelectric materials, the generation of homogeneous heterostructures in a matrix is considered to mitigate the interdependency of the thermoelectric compartments. In this study, Cu$_2$Te nanoparticles were introduced onto Bi$_2$Te$_2$Se$_0.3$ n-type materials and their thermoelectric properties were investigated in terms of the amount of Cu$_2$Te nanoparticles. A homogeneous dispersion of Cu$_2$Te nanoparticles was obtained up to 0.4 wt.% Cu$_2$Te, whereas the Cu$_2$Te nanoparticles tended to agglomerate with each other at greater than 0.6 wt.% Cu$_2$Te. The highest power factor was obtained under the optimal dispersion conditions (0.4 wt.% Cu$_2$Te). The energy and environment division of the Korea Institute of Ceramic Engineering and Technology (KICET) Jinju 52851, Korea; rkda5615600@naver.com (M.K.); nguyenvubinh20121995@gmail.com (N.V.B.); whnam@kicet.re.kr (W.H.N.)

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1. Introduction

Thermoelectric (TE) technology enables direct solid-state conversion without any moving parts or harmful emissions between heat and electrical energy and shows great potential for applications in waste heat recovery. The conversion efficiency of TE devices depends on the performance of TE materials as represented by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa_{tot}$, where $\sigma$, $S$, $T$, and $\kappa_{tot}$ are the electrical conductivity, Seebeck coefficient, temperature, and total thermal conductivity, respectively. To realize a high $ZT$, it is desirable to have a high power factor ($S^2\sigma$) and low thermal conductivity ($\kappa_{tot}$) [1,2]. However, each parameter has a trade-off relation, which makes it difficult to achieve high TE performance for practical applications.
Bi$_2$Te$_3$-based TE materials are thought to be the only materials that can be considered for cooling or low-temperature energy-harvesting applications. In particular, low-temperature heat below 400 $^\circ$C accounts for more than 70% of industrial waste heat, which is the case for Bi$_2$Te$_3$-related material systems [3]. Extensive theoretical and experimental studies such as electronic band structure engineering [4,5], doping [6,7], nano-structuring [8,9], and nanocomposite fabrication [10,11] have been suggested to optimize TE performance. Kim et al. reported a significant reduction in lattice thermal conductivity without any deterioration of the electrical properties by introducing dense dislocation arrays into the simple composition of bulk p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ and obtained the highest ZT value of ~1.9 near room temperature [12]. Although significant progress in thermal conductivity reduction has been attained [12–14], it remains necessary to boost the electrical properties of TE materials to achieve efficient power generation and cooling devices. The carrier filtering mechanism alters the Seebeck coefficient by introducing interfaces between the TE matrix and secondary nanophases, and the band bending on the interfaces induces the filtering of low-energy carriers [15–20]. The secondary nanophases also strengthen the phonon scattering to reduce thermal conductivity, which could significantly enhance ZT. The effect of the nano-phase in TE materials has been reported on PbTe-based TE materials, where the SrTe nano-precipitate enhances ZT up to ~2.5 at high temperatures [18]. For Bi$_2$Te$_3$-based materials, the addition of TE to p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ thin films prepared by a pulsed laser deposition technique significantly enhances the Seebeck coefficient [19]. However, the nano-precipitate and vacuum deposition approaches require delicate processes that cannot be applied practically. In this study, we introduced Cu$_2$Te nanoparticles (NPs) into an n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$ (BTS) matrix to enhance TE performance. Several papers [21–23] have reported the existence of Cu$_2$Te phase when excess Cu is incorporated on Bi-Te-based TE materials. However, they do not discuss the direct effect of Cu$_2$Te incorporation. Cu$_2$Te NPs, which were synthesized by the organic-free chemical method, could be considered as efficient additives that would provide benefits such as modulating the carrier concentration and enhancing phonon scattering. In addition, the incorporation of Cu$_2$Te NPs only requires a simple process that can easily be employed to alter TE properties according to the target applications.

2. Materials and Methods

The BTS matrix was synthesized using a conventional melting-quenching process. Raw elements with stoichiometric ratios (Bi, 99.999%, 5 N Plus; Te, 99.999%, 5 N Plus; Se, 99.999%, 5 N Plus) were heated at 1000 $^\circ$C for 6 h under a vacuum in fused silica tubes, and the melts were quenched in a water vessel and finally ground into fine powders using ball milling.

The Cu$_2$Te NPs were synthesized using the chemical reduction method. Under an Ar atmosphere, 1 g Te was dissolved in 0.3 M NaBH$_4$ aqueous solution. Further, 0.2 M CuCl$_2$·H$_2$O aqueous solution was slowly poured into the above Te solution and stirred for 30 min. After remaining for an additional 30 min, the precipitates were centrifuged and washed with ethanol several times. For the Cu$_2$Te NP dispersion on the BTS matrix, the obtained Cu$_2$Te NPs were dispersed in ethanol and mixed with BTS by wet grinding. The mixture was dried in a vacuum oven, and fine powders were collected. The obtained powders were sintered by spark plasma sintering at 773 K for 3 min under a pressure of 60 MPa.

The consolidated samples were analysed by X-ray diffraction (XRD, Cu K$_\alpha$, 1.5406 Å, New D8 Advance, Bruker, Billerica, MA, USA), scanning electron microscopy (SEM, JSM-7600F, JEOL, Tokyo, Japan), electron probe microanalysis (EPMA, 30 kV, JXA-8530F PLUS, JEOL, Tokyo, Japan), and transmission electron microscopy (TEM, 200 kV, Tecnai G2-20, FEI, Hillsboro, Oregon, USA). The TE properties were measured using a ZEM-3 (ULVAC-RIKO, Methuen, MA, USA) for the electrical parts and the laser-flash method (LFA, DLF 1300, TA, New Castle, DE, USA) for the thermal parts. Hall measurements were conducted to obtain the carrier concentration (HT-Hall, ResiTest 8300, Toyo Corporation, Tokyo, Japan).
3. Results and Discussions

Figure 1a shows the XRD pattern of as-prepared Cu$_2$Te NPs obtained by the chemical reduction method. Our Cu$_2$Te NPs has a hexagonal structure with the space group of P3m1 (JCPDS # 49-1441). The XRD peaks are not strong due to the small size of Cu$_2$Te NPs. The size of as-prepared Cu$_2$Te is 20–50 nm from the SEM and TEM images (Figure 1b–c), and the high resolution TEM image shows the lattice distance of 0.36 nm, which corresponds to (006) plane of Cu$_2$Te phase. Figure 1e presents the powder XRD patterns of the BTS-x wt.% Cu$_2$Te NP (x = 0, 0.2, 0.4, 0.6, and 0.8) composite materials. All samples show typical BTS patterns (rhombohedral structure, space group of R-3m, JCPDS # 50-0594) without any additional peaks. The lattice parameters of the BTS-x wt.% Cu$_2$Te NP (x = 0, 0.2, 0.4, 0.6, and 0.8) are summarized in Table 1, and there are no significant changes in lattice parameters by Cu$_2$Te NPs incorporation. The small size and low content of Cu$_2$Te NPs in the composite powder were not detectable by XRD (Figure 1e). We analysed the Cu$_2$Te nanophases on BTS-x wt.% Cu$_2$Te NP (x = 0.2, 0.4, and 0.6) bulk samples by EPMA (Figure 1f–h), where the light parts of the Cu mapping were matched with the Cu$_2$Te nanophases. Cu$_2$Te NPs can be easily observed on the parent bulk materials, and as the amount of Cu$_2$Te NPs increases, a homogeneous distribution of Cu$_2$Te NPs can be found. However, for the BTS-0.6 wt.% Cu$_2$Te NPs sample, some Cu$_2$Te NPs exhibit agglomeration, which means that a large amount (more than 0.6 wt.% of Cu$_2$Te NPs on BTS cannot be dispersed uniformly.

![Figure 1](image.png)

Figure 1. (a) XRD pattern, (b) SEM image, (c) TEM image, and (d) high resolution TEM image of Cu$_2$Te NPs, (e) XRD patterns of BTS-x wt.% Cu$_2$Te NPs (x = 0, 0.2, 0.4, 0.6, and 0.8), Cu K mapping images of EPMA for (f) BTS-0.2 wt.% Cu$_2$Te NPs, (g) BTS-0.4 wt.% Cu$_2$Te NPs, and (h) BTS-0.6 wt.% Cu$_2$Te NPs, where the light dots correspond to elemental Cu.

| Lattice Constant for a (Å) | Lattice Constant for c (Å) |
|---------------------------|---------------------------|
| BTS                       | 4.3619                    | 30.3632 |
| BTS-0.2 wt.% Cu$_2$Te NPs | 4.3614                    | 30.3604 |
| BTS-0.4 wt.% Cu$_2$Te NPs | 4.3615                    | 30.3641 |
| BTS-0.6 wt.% Cu$_2$Te NPs | 4.3610                    | 30.3606 |
| BTS-0.8 wt.% Cu$_2$Te NPs | 4.3614                    | 30.3650 |

Table 1. The lattice parameters of BTS-x wt.% Cu$_2$Te NPs (x = 0, 0.2, 0.4, 0.6, and 0.8).

Figure 2a presents the temperature dependence of the electrical conductivity (σ) for BTS-x wt.% Cu$_2$Te NPs (x = 0, 0.2, 0.4, 0.6, and 0.8). The electrical conductivity gradually decreases over the entire temperature range studied here as the Cu$_2$Te NP incorporation increases. The electrical conductivities of BTS-x wt.% Cu$_2$Te NPs (x = 0, 0.2, 0.4, and 0.6) decrease with increasing temperature, indicating semi-metallic or metallic conduction.
behaviour. However, the sample with a high amount of Cu$_2$Te NPs (0.8 wt.%) incorporated shows semiconducting behaviour at a high temperature due to the carrier concentration decrease shown in Figure 2b. The carrier concentration obtained from the Hall measurements decreases as the amount of Cu$_2$Te NPs increases. The Cu intercalation in the van der Waals gap between Te–Te shows donor-like behaviour, while our Cu$_2$Te incorporation shows acceptor-like behaviour. The temperature dependence of the Seebeck coefficient ($S$) for the BTS-x wt.% Cu$_2$Te NP ($x = 0, 0.2, 0.4, 0.6, \text{and } 0.8$) samples is displayed in Figure 2c. All samples exhibit negative $S$ values, indicating that electrons constitute the majority of the charge carriers, which is consistent with the signs of the respective Hall measurements. The temperature at which the $S$ peaks ($T_{\text{max}}$) are shifted to lower temperatures with increasing Cu$_2$Te incorporation, and the absolute value of $S$ maximum ($S_{\text{max}}$) increases as the amount of incorporated Cu$_2$Te increases. Typically, BTS show anisotropic nature of TE properties due to Te vacancies and antisite defects [24]. It is noted that the reproducibility (collecting the results for more than 5 different batches) of electrical properties is greatly enhanced through Cu$_2$Te introduction.

Figure 2. Electrical properties of BTS-x wt.% Cu$_2$Te NPs ($x = 0, 0.2, 0.4, 0.6, \text{and } 0.8$). (a) Electrical conductivities, (b) electron carrier concentrations obtained by Hall measurement, (c) Seebeck coefficients, (d) power factors, (e) Pisarenko’s plot, and (f) band diagram of BTS and Cu$_2$Te NPs interfaces.
which is ~15% higher at room temperature than that of the pristine BTS sample. The Lorenz number is estimated by assuming a single parabolic band model using the following Equation (1):

\[
S = \frac{8\pi^2 k_B^2}{3eh^2} \left( \frac{\pi}{3n} \right)^{2/3} m_d^* T
\]

where \( h \) is the Planck constant, \( k_B \) is the Boltzmann constant, \( m_d^* \) is the DOS effective mass, \( e \) is the electronic charge, and \( n \) is the carrier concentration. As shown in Figure 2e, the pristine BTS has an \( m_d^* \) value of 0.97 \( m_e \) (\( m_e \) is the electron rest mass), whereas Cu2Te NP incorporation increases the \( m_d^* \) value of 1.16 \( m_e \) in the BTS-0.4 wt.% Cu2Te NP sample at room temperature. Therefore, the increase in \( m_d^* \) with Cu2Te incorporation can enhance \( S_{\text{max}} \), even when the bipolar conduction becomes strong. The \( n \) reduction observed with the incorporation of Cu2Te is also responsible for the increase in \( S_{\text{max}} \). The \( m_d^* \) change could be attributed to the engineered band structure interface between the BTS matrix and Cu2Te NPs. In this context, we can suggest a band diagram that describes the interfacial band bending between the BTS and Cu2Te NPs (Figure 2f). The electron energy barrier, i.e., the hetero-interface of the conduction bands between the BTS and Cu2Te NPs, filters the low-energy carriers. The electron affinity and band gap of BTS and Cu2Te were obtained from the literature [26–29]. A previous theoretical study of PbTe TE materials showed that ~1.5 nm nanoinclusion significantly enhanced the \( S \) value [15]. The electrostatic potential only affected the interface between the nanoinclusion and the matrix, and larger nanoinclusions were less effective than smaller nanoinclusions. Our synthesized Cu2Te NPs had sizes of ~50 nm, so we expected that the smaller Cu2Te NPs could have a greater effect. The BTS-0.4 wt.% Cu2Te NP sample has the highest calculated power factor (\( S^2\sigma \)), which is ~15% higher at room temperature than that of the pristine BTS sample.

The temperature dependence of the total thermal conductivity (\( \kappa_{\text{tot}} \)) of BTS-x wt.% Cu2Te NPs (\( x = 0, 0.2, 0.4, 0.6, \) and 0.8) is shown in Figure 3a. All samples display very low \( \kappa_{\text{tot}} \) values over the entire temperature range studied here and also exhibit upturns. The occurrence temperatures of the upturns in the thermal conductivity data move to lower temperatures with increasing Cu2Te incorporation amounts, which is consistent with the behaviour of \( S \) and \( \sigma \). This increase in thermal conductivity is due to the bipolar diffusion of the carriers and is still present in the BTS sample at elevated temperatures, as shown in Figure 3a. This increase in \( \kappa_{\text{tot}} \) with temperature is attributable to the thermal energy transported by electron–hole pairs, which is equal to the energy of the gap between the hot and cold sides of the sample. This bipolar diffusion phenomenon results in an increase in the heat transfer beyond what is expected from the normal carrier contribution (\( \kappa_{\text{ele}} \)) to \( \kappa \) defined by the Wiedemann-Franz law [30], \( \kappa_{\text{ele}} = L\sigma T \), where \( L \) is the Lorenz number. The Lorenz number is estimated by assuming a single parabolic band and acoustic phonon scattering using the following Equations (2)–(4):

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

\[
F_n(\xi) = \int_0^\infty \frac{x^n}{1 + e^{(x-\xi)}} dx \tag{3}
\]

\[
L = \left( \frac{k_B}{e} \right)^2 \left[ \frac{(r + 7/2)F_{r+5/2}(\xi)}{(r + 3/2)F_{r+1/2}(\xi)} - \left( \frac{(r + 5/2)F_{r+3/2}(\xi)}{(r + 3/2)F_{r+1/2}(\xi)} \right)^2 \right] \tag{4}
\]
Here, $\xi$, $F_n(\xi)$, and $r$ are the reduced Fermi energy ($(E_F - E_F)/k_B T$), Fermi integral of order $n$, and scattering parameter, respectively. We set $r = 0–1/2$ for acoustic phonon scattering. The temperature dependence of the lattice thermal conductivity ($\kappa_{lat}$) can be estimated by deducting the bipolar conduction portion ($\kappa_{bp}$) and electronic portion ($\kappa_{ele}$) of thermal transport from the total thermal conductivity; $\kappa_{lat} = \kappa_{tot} - \kappa_{bp} - \kappa_{ele}$. $\kappa_{bp}$ was calculated using the below Equation (5):

$$\kappa_{bp} = (\sum_i S_i^2 \sigma_i - S^2 \sigma) T.$$  

(5)

$S_i$, $\sigma_i$, $S$, and $\sigma$ are the Seebeck coefficient and electrical conductivity of an individual band, total Seebeck coefficient, and electrical conductivity from both the conduction and valence bands, respectively. $S$ and $\sigma$ are in turn defined as follows Equations (6) and (7):

$$\sigma = \sum_i \sigma_i$$  

(6)

$$S = \frac{\sum_i S_i \sigma_i}{\sum_i \sigma_i}$$  

(7)

Using the two-band (TB) model (an extension of the single parabolic band model), which includes one valence band and one conduction band, band parameters such as the density-of-states effective mass ($m^*_i$) and non-degenerate mobility ($\mu_0$) of each band were obtained. Specifically, the $m^*_i$ and $\mu_0$ of individual band were estimated by fitting the TB model to Hall carrier concentration ($n_H$)-dependent $S$ and $n_H$-dependent $\sigma$ measurements, respectively [31]. The band gap between the valence and conduction bands required in the TB model was adopted from the literature [32]. Once $m^*_i,j$ and $\mu_{0,j}$ ($i =$ valence and conduction bands) were estimated, corresponding $S_i$ and $\sigma_i$ ($i =$ valence and conduction bands) were obtained.
bands) were calculated. Furthermore, theoretical total $S$ and $\sigma$ (which agree well with experimental $S$ and $\sigma$) were computed with $S_i$ and $\sigma_i$ according to Equations (6) and (7). Finally, the calculated $S_i$, $\sigma_i$, $S$, and $\sigma$ were substituted back into Equation (5) to estimate $\kappa_{lp}$.

The incorporation of Cu$_2$Te NPs encourages bipolar conduction and, consequently, $\kappa_{lat}$ (shown in Figure 3b), after Cu$_2$Te NP incorporation is reduced over the entire temperature range due to enhanced phonon scattering. The reduction in $\kappa_{lat}$ occurs up to 0.4 wt.% Cu$_2$Te NPs incorporation, whereas more Cu$_2$Te NPs produce a negative phonon scattering effect by agglomeration of Cu$_2$Te NPs. Generally, it is acceptable that the introduction of secondary phases decreases $\kappa_{lat}$ by phonon scattering. However, the size of the secondary phase is an important factor for enhancing phonon scattering. Particles with sizes larger than hundreds of nanometres have a limited effect on $\kappa_{lat}$ [33]. Our $\kappa_{lat}$ results after Cu$_2$Te agglomeration (more than 0.6 wt.% Cu$_2$Te NPs) could be described similarly. The size of the Cu$_2$Te NPs was ~50 nm, and if several Cu$_2$Te NPs were agglomerated, the size was easily greater than a hundred nanometres. In addition, the previous report also shows that reduced particle size with the same volume fraction could decrease thermal conductivity more [34]. Therefore, a homogeneous dispersion of small Cu$_2$Te NPs is necessary for encouraging phonon scattering and enhancing the electrical properties.

Collecting the above effects, $ZT$ is shown as a function of temperature for BTS-x wt.% Cu$_2$Te NPs ($x = 0, 0.2, 0.4, 0.6,$ and $0.8$) in Figure 3c. The highest $ZT$ of 0.75 is observed at 374 K for the BTS-0.4 wt.% Cu$_2$Te NPs sample, which is 15% higher than that of the pristine sample. It is noteworthy that the maximum $ZT$ temperature for each sample is modulated by the introduction of Cu$_2$Te NPs, decreasing as the amount of Cu$_2$Te NPs increases. The simple incorporation of Cu$_2$Te can easily modulate the temperature dependence of n-type TE materials, and we suggest that the TE properties can be precisely controlled according to the target application, such as cooling or low-temperature energy harvesting. The average $ZT$ value ($ZT_{avg}$) in the temperature range studied here is shown in Figure 3d. $ZT_{avg}$ reaches 0.70 for the BTS-0.4 wt.% Cu$_2$Te NPs sample, representing 19% enhancement compared to the pristine BTS matrix.

4. Conclusions

In conclusion, we investigated the TE properties of n-type BTS by incorporating Cu$_2$Te NPs. The incorporation of Cu$_2$Te NPs encourages the Seebeck coefficient and power factor, and we thought that the band bending between the interface of the BTS and Cu$_2$Te NPs could filter the low-energy electron carrier. The Cu$_2$Te NPs on the BTS matrix also affect $\kappa_{lat}$ by encouraging phonon scattering. Together with modulating the electrical and thermal properties, the maximum $ZT$ value reaches 0.75 at 374 K for the BTS-0.4 wt.% Cu$_2$Te NPs sample, 15% higher than that of pristine BTS (0.65 at 425 K). In addition, the temperature dependence of $ZT$ can be controlled by the Cu$_2$Te NP dispersion just before the sintering process, which is a great advantage for target applications. Further advances could be expected by developing the synthesis of Cu$_2$Te NPs with sizes of several nanometres.

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