

Synthesis and thermoelectric properties of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$

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Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposites were prepared by $\text{Cu}(\text{OAc})_2$ acetate decomposition and their thermoelectric properties were evaluated. The electrical conductivity did not change significantly by the Cu nanoparticle dispersion because the doping effect by Cu nanoparticles did not occur effectively to increase the carrier concentration and Cu nanoparticles were too small to introduce charge carrier scattering. All specimens had a negative Seebeck coefficient, which confirmed that the electrical charge was transported mainly by electrons. The absolute Seebeck coefficient was remarkably increased by the Cu dispersion and slightly reduced with an increase in the temperature. The power factor values for Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ were maintained higher in the whole temperature range, and the maximum power factor at 323 K reached around two times higher than that of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. The thermal conductivity of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ was slightly increased with an increase in the temperature because of the electronic contribution, and the Cu dispersion could not reduce it. The thermoelectric figure of merit was enhanced remarkably over a wide temperature range of 323–523 K due to the high power factor and the maintenance of a low thermal conductivity.

Key words: Thermoelectric, Bismuth telluride, Dispersion.

Introduction

Thermoelectric materials are potential sources of electrical power from heat energy. Superior thermoelectric materials require a high Seebeck coefficient (α), a high electrical conductivity (σ) and a low thermal conductivity (κ) at the application temperature (T in Kelvin) for a high figure of merit (Z):

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} \quad (1)$$

which is related to the thermoelectric energy conversion efficiency. The quantity $\alpha^2 \sigma$ is called the power factor and is the key to achieve a high performance. The thermal conductivity has contributions from lattice vibrations and charge carrier transportations, and a low thermal conductivity is needed to maintain a temperature difference between the hot and cold junctions of thermoelectric materials.

There are two approaches to increase ZT [1]. One is to maximize the power factor by developing new classes of thermoelectric materials, optimizing existing materials through doping, and exploring nanoscale materials. The other is to minimize the thermal conductivity by developing

materials with an intrinsically low thermal conductivity, solid-solution alloying, and realizing nanostructural engineering. The phonon glass and electron crystal (PGEC) concept is considered to reduce the thermal conductivity while maintaining the high power factor by introducing a nanostructure or nanocomposite [2]. If the nanoparticles are well-dispersed and sufficiently small to intensify phonon scattering without increasing charge carrier scattering, the figure of merit can be enhanced [3, 4].

In general, however, a thermal conductivity reduction by phonon scattering is accompanied by an electrical conductivity reduction by charge carrier scattering due to an inhomogeneous distribution and agglomeration of nanoparticles [5, 6]. A conventional mixing process such as ball milling cannot provide an appropriate nanostructure to realize the PGEC effect effectively in nanocomposites. In this study, a novel and simple approach was employed to disperse nanoparticles (Cu) uniformly in the matrix ($\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$), and the thermoelectric properties were evaluated for Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposites.

Experimental Procedure

A polycrystalline $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ ingot was prepared by melting at 1073 K for 4 h with high purity (99.999%) Bi, Te and Se granules in an evacuated quartz ampoule. The ingot was crushed into powder and sieved to obtain $< 75 \mu\text{m}$ diameter particles. The $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powder was dry-mixed with $\text{Cu}(\text{OAc})_2$ powder. The

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mixture of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ and $\text{Cu}(\text{OAc})_2$ was then transferred to an alumina crucible and heated at 573 K for 3 h in a vacuum to decompose the $\text{Cu}(\text{OAc})_2$. This was converted into Cu nanoparticles, which were chemically bonded to the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powder. The Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposites were hot-pressed in a cylindrical graphite die with an internal diameter of 10 mm at 673 K under a pressure of 70 MPa for 1 h in a vacuum.

A scanning electron microscope (SEM: FEI Quanta400) equipped with an energy dispersive spectrometer (EDS) was used to observe the microstructure. Phase analysis was performed by X-ray diffraction (XRD: Bruker D8 Advance) using $\text{Cu K}\alpha$ radiation (40 kV, 40 mA). Diffraction patterns were measured in the θ - 2θ mode (10 to 90°) with a step size of 0.02° , a scan speed of $0.2^\circ/\text{min}$ and a wavelength of 0.15405 nm. Hall effect measurements were carried out in a constant magnetic field (1 T) and electric current (50 mA) with a Keithley 7065 system at room temperature to examine the carrier concentration and mobility. The Seebeck coefficient and electrical conductivity were measured using temperature differential and 4-probe methods, respectively, with Ulvac-Riko ZEM3 equipment in a helium atmosphere. The thermal conductivity was estimated from the thermal diffusivity, specific heat and density measurements using a laser flash Ulvac-Riko TC9000H system in a vacuum. The thermoelectric figure of merit was evaluated at temperatures from 323 K to 523 K.

Results and Discussion

Fig. 1 shows the XRD patterns of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ consolidated by hot pressing. Diffraction peaks were well-matched with the ICDD standard data. All samples were polycrystalline with good crystallinity and the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ phase was successfully synthesized in this process. Diffraction peaks for Cu particles were not identified because the amount of Cu was too small.

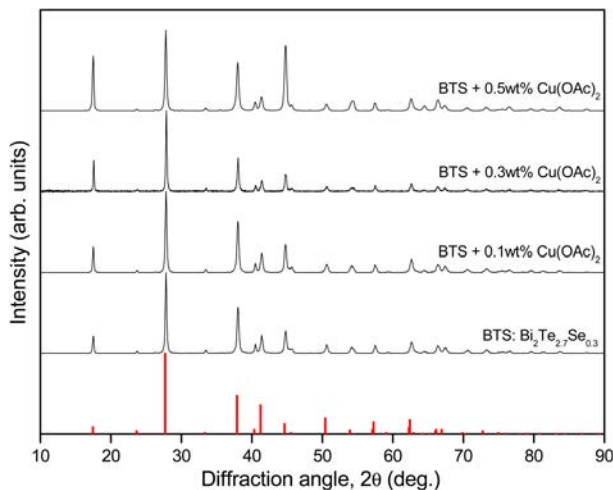


Fig. 1. X-ray diffraction patterns of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposites.

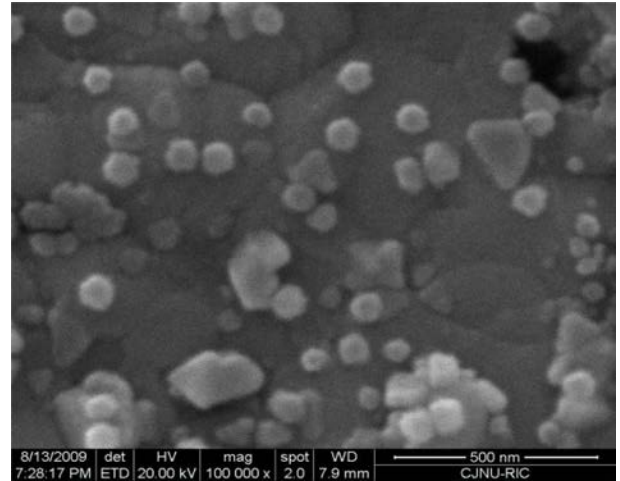


Fig. 2. Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposite prepared by $\text{Cu}(\text{OAc})_2$ decomposition.

Fig. 2 presents a SEM image of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ prepared by $\text{Cu}(\text{OAc})_2$ decomposition. It exhibits the surface of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powder after heating at 573 K for 3 h in a vacuum to decompose $\text{Cu}(\text{OAc})_2$. This heat treatment vaporized radical ions (CH_3COO^-) of the $\text{Cu}(\text{OAc})_2$ acetate, resulting in the formation of Cu nanoparticles with a spherical shape. The mean particle size of the Cu was approximately 50 nm, which is nearly the same as the $\text{Cu}(\text{OAc})_2$ powder size. Cu nanoparticles were well-dispersed and bonded to the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ powder surface.

Fig. 3 shows the electrical conductivity of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. The electrical conductivity did not change significantly by the Cu nanoparticle dispersion. It showed a high- 10^4 S/m at all temperatures examined, which means that all specimens are in a degenerate state. In order to examine the electronic transport properties, the Hall coefficient (R_H), carrier concentration (n) and mobility (μ) were measured. Table 1 lists the electronic transport properties of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ at room temperature. The sign of the Hall coefficient was

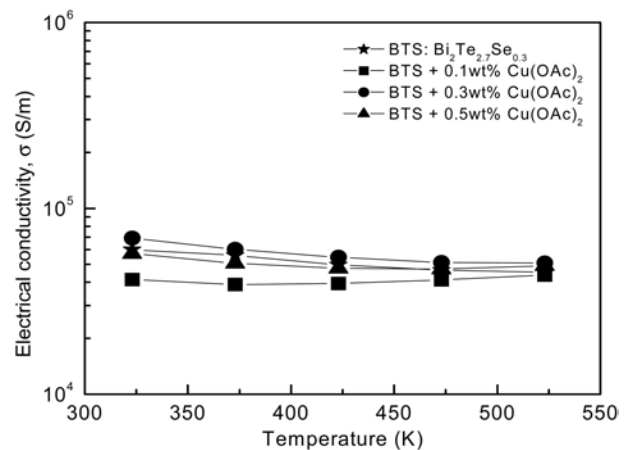
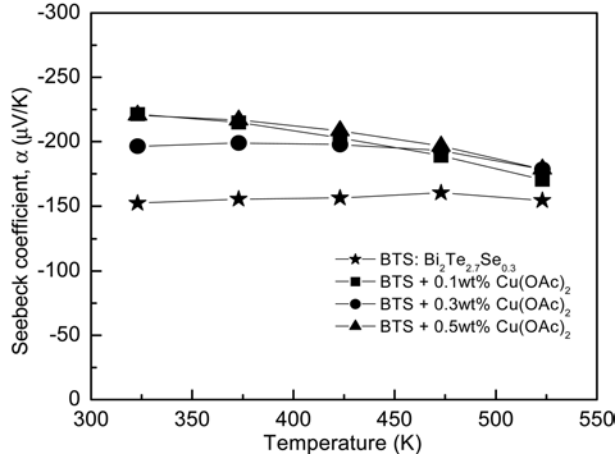


Fig. 3. Electrical conductivity of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.

Table 1. Electronic transport properties of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ at room temperature

Specimen	R_H (cm^3/C)	n (cm^{-3})	μ (cm^2/Vs)	m^* (m_0)
BTS	-0.134	4.7×10^{19}	80.4	0.091
BTS + 0.1 wt% $\text{Cu}(\text{OAc})_2$	-0.177	3.5×10^{19}	73.1	0.110
BTS + 0.3 wt% $\text{Cu}(\text{OAc})_2$	-0.145	4.3×10^{19}	99.9	0.112
BTS + 0.5 wt% $\text{Cu}(\text{OAc})_2$	-0.177	3.5×10^{19}	101.0	0.110

**Fig. 4.** Seebeck coefficient of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.

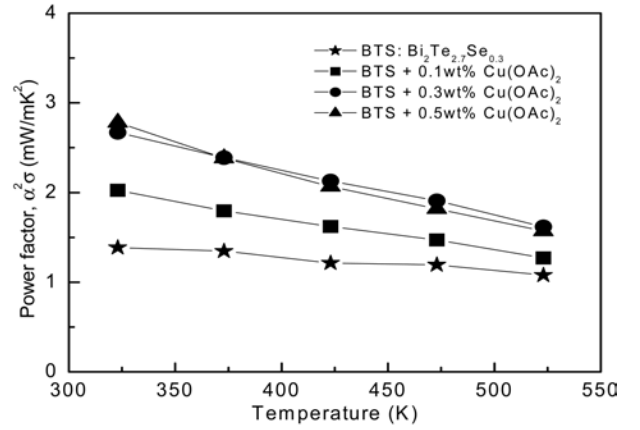
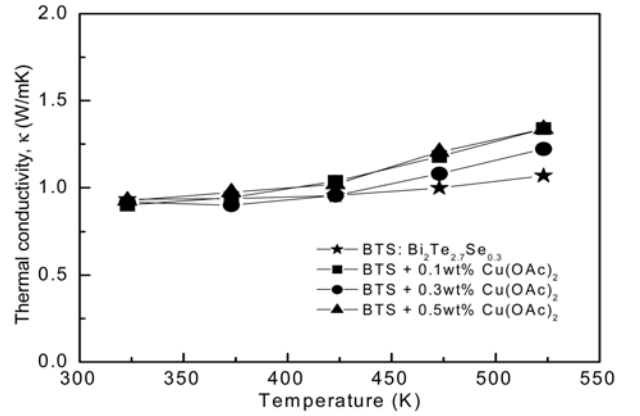
negative for all specimens and this means that the electrical charge was transported mainly by electrons. The carrier concentration and mobility did not change significantly with the Cu dispersion, which indicates that the doping effect by Cu nanoparticles did not occur effectively to increase the carrier concentration and Cu nanoparticles were too small to introduce charge carrier scattering. Consequently, the electrical conductivity did not change significantly by the Cu nanoparticle dispersion, as shown in Fig. 3.

Fig. 4 presents the Seebeck coefficient of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. All specimens had a negative Seebeck coefficient, which confirmed that the electrical charge was transported mainly by electrons as shown in Table 1. The absolute Seebeck coefficient of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ was almost constant in the temperature range 323–523 K. However, it was remarkably increased by the Cu dispersion and slightly reduced with an increase in the temperature. The sign of the Seebeck coefficient was negative, which is in good agreement with the sign of the Hall coefficient, indicating that $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ is an n-type semiconductor.

The Seebeck coefficient is affected by the carrier concentration (n) and the effective mass (m^*), and can be expressed by assuming a degenerate parabolic band semiconductor property [7]:

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} \left(\frac{\pi}{3n} \right)^{2/3} m^* T \quad (2)$$

where k_B is the Boltzmann constant, h is the Planck

**Fig. 5.** Power factor of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.**Fig. 6.** Thermal conductivity of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.

constant, and e is the electrical charge. In this study, because the carrier concentration did not change significantly, the increase in the Seebeck coefficient was due to the increase in the effective mass of a carrier, which is one of the critical factors determining the Seebeck coefficient. It is speculated that a charge-carrier energy filtering effect of the nanoparticles causes the increase in the effective mass [8]. Therefore, as shown in Fig. 5, the power factor values for Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ were maintained higher in the whole temperature range, and the maximum power factor at 323 K reached around two times higher than that of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.

Fig. 6 shows the thermal conductivity of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. It was slightly increased with an increase in the temperature because of the electronic contribution, and the Cu dispersion could not reduce it. The thermal conductivity (κ) is the sum of the lattice thermal conductivity (κ_L) by phonons and the electronic thermal conductivity (κ_E) by carriers, and it is given by Eq. (3):

$$\kappa = \kappa_L + \kappa_E = \kappa_L + L\sigma T \quad (3)$$

Both components can be separated by the Wiedemann-Franz law ($\kappa_E = L\sigma T$), where the Lorenz number is assumed to be a constant ($L = 2.0 \times 10^{-8} \text{ V}^2\text{K}^{-2}$) for the evaluation [9, 10].

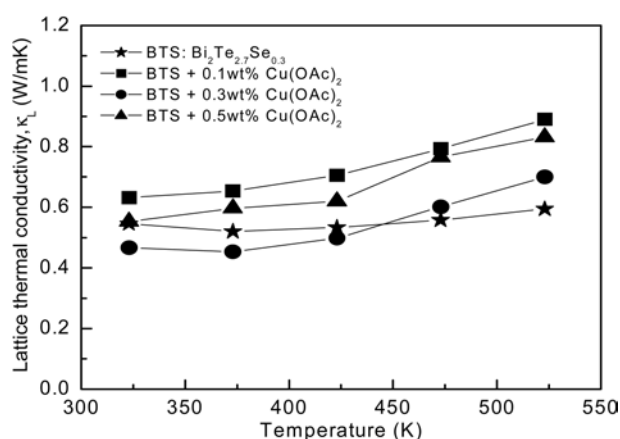


Fig. 7. Lattice thermal conductivity of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.

A lattice thermal conductivity reduction was expected by the enhancement of phonon scattering at the large density of incoherent interfaces which is created between the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ matrix and the Cu nanoparticles. However, as shown in Fig. 7, the well-controlled incoherent interfaces could not behave as effective phonon scattering centers, while several reports have suggested that coherent interfaces are essential to realize the PGEC effect effectively [3, 4]. Although the lattice thermal conductivity decreased with an increase in the amount of the Cu dispersion, it was higher than that of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ except for the specimen with 0.3 wt% $\text{Cu}(\text{OAc})_2$ below 423 K. In order to obtain the maximum phonon scattering in the metal nanoparticle dispersion systems, the following issues remain for further investigations: a size control of the metal nanoparticles, an interfacial reaction control to form coherent interfaces between the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ matrix and the metal nanoparticles, and a composition control of nano-inclusions.

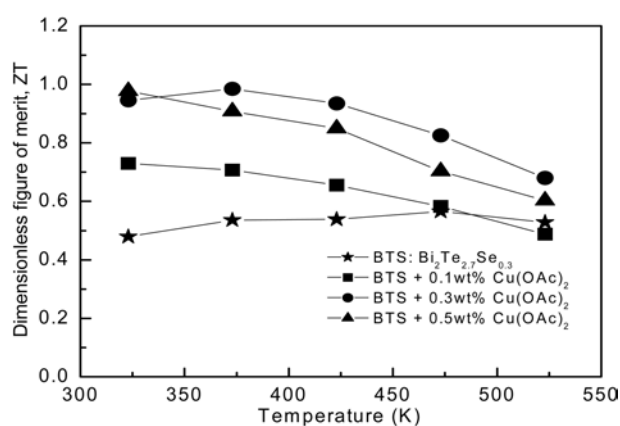


Fig. 8. Thermoelectric figure-of-merit of Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$.

Fig. 8 presents the temperature dependence of ZT for Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposites. The ZT value was enhanced dramatically by the Cu nanoparticle dispersion, which was mainly attributed to the increase in the power factor. The maximum ZT was obtained for the 0.3 wt% $\text{Cu}(\text{OAc})_2$ added $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposite. Compared to $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, the ZT value was remarkably improved by 50~200% over the wide temperature range of 323~523 K.

Conclusions

Cu-dispersed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanocomposites were prepared successfully by $\text{Cu}(\text{OAc})_2$ decomposition and hot pressing. Cu nanoparticles were well-dispersed in the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ matrix, and thereby the power factor was greatly increased due to an increase in the effective mass of a carrier. However, the Cu dispersion did not affect the carrier concentration and could not reduce the lattice thermal conductivity because Cu nanoparticles did not act as phonon scattering centers effectively. The thermoelectric figure of merit was enhanced remarkably over a wide temperature range of 323~523 K due to the high power factor. Compared to other complex nanostructuring approaches, this metal nanoparticle dispersion method is simple and cost-effective for improving the thermoelectric performance.

Acknowledgments

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