



Enhanced thermoelectric properties and their controllability in *p*-type (BiSb)₂Te₃ compounds through simultaneous adjustment of charge and thermal transports by Cu incorporation



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ABSTRACT

We report the enhanced thermoelectric properties in Cu_xBi_{0.38}Sb_{1.62}Te₃ compounds through simultaneous achievement of improved charge transport and suppressed thermal transport by Cu incorporation. Incorporated Cu acted as an acceptor rather than donor, resulting in the significant improvement of *p*-type electric conduction. Density of state effective mass was almost linearly proportional to the Cu content in the compounds, and it led to the enhancement of power factor in Cu-doped compounds regardless of the increase in hole concentration. Furthermore, reduction of bipolar and lattice thermal conductivities could also be achieved by the Cu incorporation, consequently leading to the improved thermoelectric properties of the compounds at relatively high temperatures. Effects of Cu on the thermal and charge transport properties are discussed in detail, and the controllability of the thermoelectric performance for optimum operating temperature is also reported.

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1. Introduction

Thermoelectric energy conversion has been attracted much attention due to its various applications from electronic cooling to power generation using waste heat [1,2]. The thermoelectric energy conversion efficiency is dictated by the performance of thermoelectric materials, and it is determined by the dimensionless figure of merit, ZT ($= S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity). In numerous thermoelectric materials, Bi₂Te₃ exhibits the highest ZT values near room temperature, so that Bi₂Te₃-based compounds have been the mostly commercialized thermoelectric materials [3]. Although the thermoelectric figure of merit (ZT) of *p*-type Bi₂Te₃ material was just 0.28 at room temperature when Goldsmid reported the first thermoelectric refrigeration [4], significant progresses have been successfully

achieved over decades [5–16]. Most of the recent breakthroughs to high ZT in Bi₂Te₃-based thermoelectric materials have been realized by reducing the thermal conductivity through phonon scattering in nanostructured compounds. Poudel et al. reported a strong phonon scattering at the interface in nanostructured (BiSb)₂Te₃ compounds prepared by high-energy ball-milling [9], and Kim et al. obtained the highest ZT of 1.87 at 320 K through full phonon scattering in Bi_{0.5}Sb_{1.5}Te₃ compounds with dense dislocation array produced by liquid-phase sintering [16].

Regardless of the successful enhancement of ZT by the process-dependent thermal conductivity reduction, the control of power factor ($PF = S^2\sigma$) of Bi₂Te₃-based compounds still remains as a bottleneck to further improvement because the Seebeck coefficient and the electrical conductivity of thermoelectric material are strongly interdependent to each other with a trade-off relation in terms of the charge carrier concentration. Although dopants for controlling the power factor have been well known in *n*-type Bi₂Te₃-based compounds [17], the optimization of the power factor in *p*-type compounds has been carried out mostly by Sb-alloying rather than doping from early studies [5–8,18,19]. Due to the smaller difference in electronegativity between Sb and Te than that

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between Bi and Te, the Sb-alloying in Bi_2Te_3 can facilitate the formation of Sb'_{Te} antisite defects and it leads to the increase in hole concentration, consequently resulting in the increased electrical conductivity [20–23]. However, the increased hole concentration by Sb-alloying not only lowers the Seebeck coefficient, but also increases the electronic contribution in the thermal conductivity, so that the limited enhancement of ZT could be possible by Sb-alloying only.

In this respect, the incorporation of dopants in p -type $(\text{BiSb})_2\text{Te}_3$ compounds can be a suitable way to enhance ZT due to two possibilities; (i) simultaneous control of charge transport and Seebeck coefficient for enhancing power factor through the Fermi level control and (ii) reduction of thermal conductivity through the additional alloy scattering of phonon and also through the suppression of bipolar effect [14]. Among few known p -type dopants, Cu is a quite interesting element exhibiting bipolar behavior when it is incorporated into Bi_2Te_3 -based compounds [24]. As Cu is intercalated into the van der Waals gap, it acts as an n -type donor [25–28]. On the other hand, Cu is a p -type acceptor as it occupies the Bi-site [29,30]. Cui et al. reported that thermoelectric performance in Cu-doped p -type compounds was improved due to its acceptor role of Cu [29]. We observed the acceptor behavior of Cu even in n -type Bi_2Te_3 compounds [31]. There have been a number of reports on the Cu-doped $(\text{BiSb})_2\text{Te}_3$ compounds [29,30,32–34], however, the Cu-doping effects on the thermoelectric transport properties, such as the charge transport mechanism for the electrical conductivity, the density of state effective (DOS) mass for the Seebeck coefficient, and thermal transport mechanism for the thermal conductivity, have not yet been fully understood in Cu-doped p -type $(\text{BiSb})_2\text{Te}_3$ compounds.

Herein, we report the enhancement of thermoelectric properties in $\text{Cu}_x\text{Bi}_{0.38}\text{Sb}_{1.62}\text{Te}_3$ compounds through simultaneous achievement of improved charge transport and suppressed thermal transport by Cu incorporation. Acceptor role of Cu in the compounds was observed clearly, and the charge transport was determined mainly by acoustic phonon scattering and additionally influenced by ionized impurity scattering depending on the Cu content. Regardless of the increase of hole concentration in the Cu-doped compounds, the incorporation of Cu improved the power factor of the compounds monotonically thanks to the linearly increasing DOS effective mass with Cu content. Bipolar and lattice thermal conductivities were also considerably suppressed by Cu incorporation, so that enhancement of thermoelectric properties in the $\text{Cu}_x\text{Bi}_{0.38}\text{Sb}_{1.62}\text{Te}_3$ compounds could be successfully achieved. Furthermore, it was found that the temperature for the maximum ZT could be controllable by Cu content in the compounds. It is also noted that the result was obtained only by the acceptor doping effect of Cu, indicating that it is the improvement of a property of material itself rather than the improvement by process-dependent thermal conductivity reduction. Therefore, we expect that further enhancement of the thermoelectric properties of Cu-doped $(\text{BiSb})_2\text{Te}_3$ compounds can be made based on the rapidly progressing nanotechnology for phonon scattering.

2. Experimental details

$\text{Cu}_x\text{Bi}_{0.38}\text{Sb}_{1.62}\text{Te}_3$ ($0 \leq x \leq 0.005$) compounds were synthesized by a vacuum melting method. Cu (99.999%, Alpha Aesar), Bi (99.999%, 5 N Plus), Sb (99.999%, 5 N Plus) and Te (99.999%, 5 N Plus) were used as starting materials. Mixtures of starting materials in evacuated silica tubes were melted at 663 K for 96 h, annealed at 623 K for 24 h and then quenched in water to obtain a homogeneous $(\text{BiSb})_2\text{Te}_3$ phase. The quenched ingots were pulverized by Spex-mill (8000 M mixer/mill, Spex Certiprep) for 50 min in Ar atmosphere, and then consolidated by hot pressing (WT 4000 A,

Well Tech) under a uniaxial pressure of 60 MPa at 723 K ($10^\circ\text{C}/\text{min}$) for 10 min. The relative densities of all compounds prepared by the hot pressing were higher than 98%. Phase analyses were carried out by using an X-ray diffractometer (XRD, New D8 Advance, Bruker). Microstructural characterizations were also performed by using a scanning electron microscope (SEM, JSM-6700, JEOL). Electrical conductivity and Seebeck coefficient were measured by using a four-point probe method (ZEM-3, ULVAC-RIKO), and charge transport was investigated by a Hall measurement system (ResiTest 8300, Toyo Corporation). Thermal conductivity was measured by a laser flash method (LFA-457, NETZSCH).

3. Results and discussion

Fig. 1 shows XRD patterns of the $\text{Cu}_x\text{Bi}_{0.38}\text{Sb}_{1.62}\text{Te}_3$ ($0 \leq x \leq 0.005$) compounds prepared by hot pressing of ball-milled powder, and the patterns were obtained from the specimens cut perpendicular to the pressure direction of hot pressing. All diffraction peaks could be indexed as single phase (JCPDS #49-1713), and no secondary peak of Cu-related phase was observed in all compounds. Due to the tiny amount of Cu incorporation in the compounds, the effect of Cu on the structural properties could be hardly observed by the XRD patterns. In all samples, the relative peak intensities of (006)/(015) were characterized to be ~ 0.8 , and it is quite close value to that in the powder XRD pattern (JCPDS #49-1713). This result indicates that the grains are randomly oriented in all $\text{Cu}_x\text{Bi}_{0.38}\text{Sb}_{1.62}\text{Te}_3$ compounds, and it could be seen obviously in the SEM micrographs of the compounds in Fig. 2. Randomly oriented grains were observed in all fractured surfaces of the compounds, but, any considerable difference between the compounds could not be found by the SEM characterization. With these results, it was confirmed that the structural properties of the compounds are not significantly affected by the Cu incorporation in this experimental conditions, and that the comparison of the thermoelectric properties between the compounds can be made without further consideration on the additional structural effects.

Fig. 3a shows the effect of Cu incorporation on the temperature-dependent electrical conductivities in the $\text{Cu}_x\text{Bi}_{0.38}\text{Sb}_{1.62}\text{Te}_3$ compounds. The electrical conductivity of the compound increases with the increase in the Cu content (x), while it decreases with increasing temperature regardless of the amount of Cu. In Fig. 3b, all compounds exhibit negative temperature-dependence of $\sigma \propto T^{-3/2}$ in their electrical conductivities, demonstrating the charge transport behavior is dominantly governed by hole-acoustic

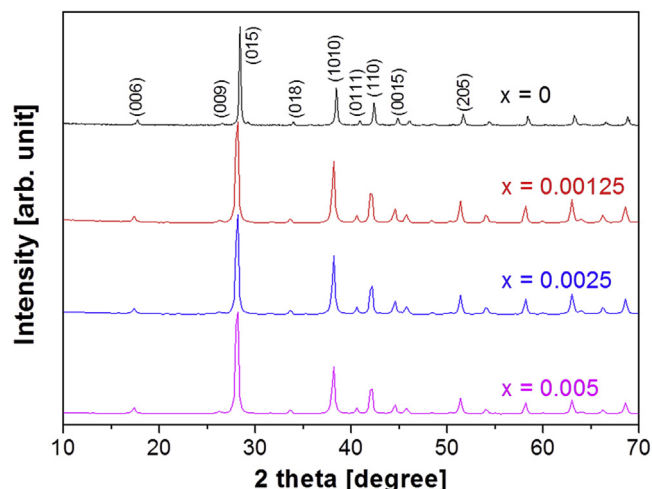


Fig. 1. XRD patterns of the $\text{Cu}_x\text{Bi}_{0.38}\text{Sb}_{1.62}\text{Te}_3$ compounds.

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