Research Article

Thermoelectric Transport Properties of Cu Nanoprecipitates Embedded $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$

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Received 20 October 2014; Revised 14 February 2015; Accepted 7 March 2015

Academic Editor: Doron Yadlovker

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We suggest a simple and scalable synthesis to prepare Cu- $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ (Cu-BTS) nanocomposites. By precipitating Cu nanoparticle (NP) in colloidal suspension of as-exfoliated BTS, homogeneous mixtures of Cu NP and BTS nanosheet were readily achieved, and then the sintered nanocomposites were fabricated by spark plasma sintering technique using the mixed powder as a raw material. The precipitated Cu NPs in the BTS matrix effectively generated nanograin (BTS) and heterointerface (Cu/BTS) structures. The maximum ZT of 0.90 at 400 K, which is 15% higher compared to that of pristine BTS, was obtained in 3 vol% Cu-BTS nanocomposite. The enhancement of ZT resulted from improved power factor by carrier filtering effect due to the Cu nanoprecipitates in the BTS matrix.

1. Introduction

Thermoelectric (TE) power generation is a key technology for clean renewable energy harvesting and reduction of greenhouse gas. Widespread use of TE power generation systems requires enhancement in performance of TE materials, evaluated in terms of a dimensionless figure merit, defined as $ZT = \sigma \cdot S^2 \cdot T / \kappa$, where σ is the electrical conductivity, S is the Seebeck coefficient, and κ is the total thermal conductivity at a given absolute temperature (T). Among TE materials, the Bi_2Te_3 -based solid solution, such as p -type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ (BST) and n -type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_{3-y}\text{Se}_y$ (BTS), is known to be the best material among those used around room temperature. Although Bi_2Te_3 -based TE materials are widely used for small-scale and high-density cooling applications, materials with higher ZT are required for the extension of application, including domestic cooling and power generation from low-grade heat. Recently, high-performance p -type Bi_2Te_3 -based bulk TE materials have been developed with the introduction

of nanotechnology, which reduce the lattice thermal conductivity ($\kappa_{\text{lat}} = \kappa - \kappa_{\text{ele}}$, where κ_{ele} is the electronic contribution) by intensified interface phonon scattering. Poudel et al. reported a significant improvement of ZT that resulted from a reduced grain size [1]. High ZT of 1.4 was obtained at 373 K owing to the reduced κ_{lat} . The key feature of the κ_{lat} reduction in this nanograined composite is the high density of the grain boundaries to scatter phonons [1, 2]. However, for the nanostructured n -type BTS, the ZT value still remains about 1.04 at 398 K even in nanograined composite [3]. Moreover, the carrier concentration (n) increased by formation of point defects (antisite defects and vacancies) generated by heavy deformation during ball milling (BM) process [4]. This uncontrollable defect in BTS is known to bring about severe reproducibility issue; thus there have been a lot of efforts to simultaneously enhance the ZT and improve the reproducibility through the composite-type materials with metallic dispersions such as Cu, In, and Cu-Te [5–8].

FIGURE 1: Schematic representation of exfoliation and reassembly processes for the mixture of Cu NP and Bi_2Te_3 nanosheet.

Recently, Liu et al. demonstrated that excess Cu could be intercalated in the interlayer space of n -type BTS, and intercalated Cu can improve the reproducibility, increase the carrier mobility (μ), and decrease the κ_{lat} [9]. On the other hand, introduction of Cu nanoprecipitates has the potential to enhance the ZT due to the enhanced S by carrier filtering effect and reduced κ_{lat} by phase boundary phonon scattering. In the present study, Cu nanoprecipitates embedded BTS bulk nanocomposites (Cu-BTS) were fabricated by combined technique of chemical reaction and spark plasma sintering in order to clarify the effect of Cu nanoprecipitates on the transport properties of BTS. We investigated their TE properties and demonstrated the origin of the enhancement of electronic and thermal transport properties.

2. Experimental

The nanocomposite powder of Cu nanoparticle (1.0, 3.0, and 5.0 vol%) and BTS nanosheet was prepared by precipitating Cu nanoparticle in colloidal suspension of as-exfoliated BTS as shown in Figure 1. The colloidal suspension of the exfoliated BTS was prepared by reaction of lithiated BTS with distilled water. Details for the formation of BTS nanosheets have been reported in our previous study [10]. For the hybridization, the colloidal suspension of the exfoliated BTS (5 wt%, 40.0 mL) was mixed with aqueous CuCl_2 solution and was refluxed with 60.0 mL of hydrazine monohydrate (98%, Junsei) for 180 min at 120°C to eliminate oxygen on the surface of the exfoliated BTS. After repeated washing, centrifugation, and drying in a vacuum, the resulting hybrid powders were loaded into a graphite die. Disk-shaped polycrystalline bulk samples (10 mm in diameter and 13 mm in thickness) were fabricated by spark plasma sintering (SPS) under 30 MPa and at 420°C for 2 min in a vacuum.

The microstructure of the sintered samples was investigated using transmission electron microscopy (TEM, JEOL JEM-4010). The measurements for S and σ were carried out in a perpendicular direction to the SPS press in order to ensure measurement of the correct TE properties. S and σ measurements from 300 K to 480 K were performed using an ULVAC ZEM-3 system. The κ values ($\kappa = \rho_s \cdot C_p \cdot \lambda$) were calculated from separated measurements: sample density (ρ_s), heat capacity (C_p), and thermal diffusivity (λ), measured in a vacuum by the laser-flash method (TC-9000, ULVAC, Japan). The densities of the sintered samples by SPS were found to range from 7.52 to 7.56 g/cm^3 (>96% of the theoretical density). Low temperature (100 K–390 K) C_p values were collected using a Quantum Design physical properties measurement system, and C_p was used at a constant value of $0.155 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ estimated from the Dulong-Petit fitting. The Hall effect measurements were carried out using a commercial system (7600 Electromagnet Series, Lake Shore Cryotronics, USA) with a magnetic field of 2 T and an electrical current of 30 mA. The μ and n values were estimated by the one-band model using $n = -1/(R_H \cdot e)$ and $\sigma = n \cdot e \cdot \mu$, where R_H and e are the Hall coefficient and electron charge.

3. Results and Discussion

Recently, a few researches about the Cu addition effects on the TE properties of Bi_2Te_3 -based alloys including single crystals [5–7] and polycrystalline bulks [8, 9] have been reported. Three different effects were demonstrated by Cu addition: First, the substitutional doping of Cu on Bi site forms an anti-site defect ($\text{Cu}_{\text{Bi}}^{2-}$) and generates a hole. Second, the occupation of the interstitial site generates a donor with Cu_i^+ . Cu is placed at the interstitial site between two quintets (intercalation) and achieves an electrical connection, resulting in an

FIGURE 2: TEM images of (a) 3.0 vol% Cu-BTS and (b) 5.0 vol% Cu-BTS nanocomposite samples.

FIGURE 3: Temperature dependence of (a) the electrical conductivity (σ) and (b) the Seebeck coefficient (S) of BTS and Cu-BTS. Inset shows the power factor ($\sigma \cdot S^2$) of BTS and Cu-BTS.

increase of the μ of carriers and a decrease in κ_{lat} [5]. Third, Cu can be precipitated as a nanoinclusion in matrix and/or grain boundary region. In this case, the heterointerface between the Cu nanoprecipitates and Bi_2Te_3 -based matrix is generated. This heterointerface might act as an energy barrier for carriers as well as phonon scattering center. In order to clarify the mechanism for ZT enhancement in this nanoinclusion-type nanocomposite, we prepared Cu nanoprecipitate embedded BTS (Cu-BTS) bulks and evaluated their TE properties.

Figure 2 shows TEM images of 3.0 vol% and 5.0 vol% Cu-BTS bulk samples. The well-dispersed Cu nanoprecipitates were clearly observed in BTS matrix, and their size remained

<40 nm, indicating that Cu-BTS bulk was successfully synthesized. The average size of Cu nanoprecipitates, which was estimated from Figure 2(b), was about 15 nm. For 3 vol% Cu-BTS, the calculated number of Cu nanoprecipitates is $\sim 1.7 \times 10^{16}$ particles/ cm^3 . Also, we calculated population of Cu nanoprecipitates from Figure 2(b). The population was $\sim 1.4 \times 10^{16}$ particles/ cm^3 . The number of Cu nanoprecipitates calculated from nominal composition is well consistent with that from TEM image.

The electronic transport properties of Cu-BTS samples and those of pristine BTS were measured to demonstrate the effect of Cu nanoprecipitates on TE properties. Figure 3

FIGURE 4: Temperature dependence of (a) the thermal conductivity (κ) and lattice thermal conductivity (κ_{lat}) and (b) dimensionless figure merit ZT of BTS and Cu-BTS.

TABLE 1: Seebeck coefficient (S), electrical conductivity (σ), Hall mobility (μ), and carrier concentration (n) for BTS and Cu-BTS at 300 K.

Samples	S ($\mu\text{V K}^{-1}$)	σ (S cm^{-1})	μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	n (10^{19}cm^{-3})
BTS	-132.9	1275	124.4	6.40
1.0 vol% Cu-BTS	-142.9	1183	121.7	6.07
3.0 vol% Cu-BTS	-153.4	1205	118.5	6.35
5.0 vol% Cu-BTS	-147.3	1030	101.6	6.33

shows the temperature dependence of σ , S and power factor values for BTS and Cu-BTS samples. The σ values slightly decreased (Figure 3(a)), while absolute values of S increased (Figure 3(b)) in the presence of Cu nanoprecipitates. To examine the behavior of σ and S , we evaluated the μ and n at 300 K and represented them in Table 1. The n values of BTS and Cu-BTS samples were almost the same ($6.07 \times 10^{19} \text{cm}^{-3}$ – $6.40 \times 10^{19} \text{cm}^{-3}$). This is considered to be related to reaction between Cu and BTS. Because substituted Cu on Bi site would be as an acceptor, small amount of Cu might be diffused into the BTS matrix. However, a greater part of Cu nanoprecipitates should remain as unreacted Cu (Figure 2), which is confirmed by the numerical analysis for the microstructure of Cu-BTS. As represented in Table 1, there is a decrease in σ of Cu-BTS mainly due to the reduction in μ . This result is another evidence for the presence of Cu nanoprecipitates, which cause electron filtering at the interface between Cu and BTS. It should be noted that S values of Cu-BTS were rather larger than that of pristine

BTS despite moderate decrease in n and exhibited peak value in 3.0 vol% Cu-BTS. This is considered to be related to the carrier filtering effect. The interface between metallic Cu and semiconducting BTS might induce an energy dependent carrier scattering effect by introducing a well and energy barrier which filter the carrier with small energy [11, 12]. The work function (Φ) of Cu is known to be 4.53 eV–5.10 eV, while the electron affinity (χ) of BTS is ~ 4.50 eV. If the energy barrier by Cu and BTS interface is generated in the BTS matrix, the electron transfer should be changed by band bending. In this heterostructured interface, Φ of Cu is higher than χ of BTS; thus a Schottky barrier is created. This barrier makes the low energy charge carrier be effectively scattered, while making the high energy charge carrier go easily through the barrier. Thus, appropriate size and density of barrier can cause an increase in the TE power factor ($\sigma \cdot S^2$) [11]. Inset of Figure 3(b) shows the temperature dependence of calculated power factor for BTS and Cu-BTS. The maximum power factor of $2.84 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ at 300 K was obtained in 3.0 vol% Cu-BTS, which is 17% up from the value of pristine BTS ($2.42 \text{ mW} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ at 300 K). This result indicates that Cu is an effective element for carrier filtering effect in BTS. Because the carrier filtering effect is strongly correlated with the interface density as well as band alignment, more detailed study using well-controlled material system such as monodispersed uniform nanoparticle embedded thin film is required to clarify the mechanism of S enhancement by a carrier filtering effect.

Figure 4(a) shows the temperature dependence of κ for BTS and Cu-BTS. We calculated κ_{lat} from the calculation of

κ_{ele} based on the Wiedemann-Franz law ($\kappa_{\text{ele}} = L \cdot \sigma \cdot T$, where L is the Lorenz number). The L values at 300 K, ranging from $1.64 \times 10^{-8} \text{ V}^2 \cdot \text{K}^{-2}$ to $1.77 \times 10^{-8} \text{ V}^2 \cdot \text{K}^{-2}$, were estimated for BTS and Cu-BTS. Details of the L calculation have been described elsewhere [13]. Low κ_{lat} values, $0.46 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ to $0.53 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 300 K, were obtained for BTS and Cu-BTS samples originated from plate-type nanograin structure [10]. Although calculated value of κ_{lat} includes the contribution from bipolar thermal conduction [14], κ_{lat} values for Cu-BTS were almost the same compared with that of BTS.

Figure 4(b) presents the temperature dependence of ZT for BTS and Cu-BTS. The peak ZT value of 3.0 vol% Cu-BTS is about 0.90 at 400 K, which is 15% higher compared to that of pristine BTS. This high ZT value is thought to be a result of synergetic effects, including power factor enhancement by carrier filtering effect and κ_{lat} reduction by intensified phonon scattering via the formation of highly dense interface between Cu and BTS. In 3.0 vol% Cu-BTS, the ZT values are enhanced over the whole measured temperature range (300 K–480 K).

4. Conclusions

Cu nanoprecipitates embedded n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ polycrystalline bulks with plate-like nanograin structure were fabricated by combined technique of chemical synthesis and spark plasma sintering. Homogeneous mixtures of nanoscale Cu and $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ were readily achieved by precipitation of Cu nanoparticles in colloidal suspension of exfoliated $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanosheets. After spark plasma sintering, the nanocomposites showed a high ZT value (0.90 at 400 K) in 3 vol% Cu nanoprecipitates embedded $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. The enhancement of ZT is due to simultaneous increase in Seebeck coefficient by carrier filtering effect and decrease in lattice thermal conductivity by intensified boundary phonon scattering in the presence of Cu nanoprecipitates and $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ nanograins.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

This work was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Trade, Industry, and Energy, Republic of Korea.

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