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Influence of powder morphology on thermoelectric anisotropy of spark-plasma-sintered Bi–Te-based thermoelectric materials

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Abstract

The influence of the starting powders' morphology on the thermoelectric anisotropy of Bi–Te-based thermoelectric materials that are fabricated by spark plasma sintering has been investigated. Starting powders with three types of morphologies are prepared through a chemical reaction method (nano-sized particles with a spherical shape), a conventional pulverization method (flake-like shape) and a gas atomizing method (spherical shape). The thermoelectric anisotropy of each sintered body is determined by measuring the electrical resistivity and thermal conductivity in both the parallel and perpendicular directions to the spark plasma sintering pressing direction. The p-type $Bi_{0.5}Sb_{1.5}Te_{3.0}$-sintered body that is composed of the spherically shaped powder has isotropic thermoelectric properties, while the same material composed of the flake-like powder shows anisotropic behavior. The n-type Bi_2Te_3 sintered body has a relatively small anisotropy when it is composed from the spherically shaped powder.

Keywords: Thermoelectric; Anisotropy; Morphology; Spark plasma sintering

1. Introduction

Bismuth–telluride-based alloys are well known as the most efficient thermoelectric (TE) materials that operate near room temperature [1,2]. Bi_2Te_3 has a rhombohedral structure with the space group $R\bar{3}m$. To visualize the structure more clearly, the layered structure is frequently studied. The hexagonal cell is composed of atomic layers that are stacked in the following order along the *c*-axis: –Te–Bi–Te–Bi–Te–. It has been shown that the Te and Bi layers are held together by strong ionic–covalent bonds, but no bonding electrons remain to connect the adjacent Te layers. The Te–Te layers are bonded by a weak van der Waals force, and the crystal has distinct cleavage planes that are perpendicular to the *c*-axis [3].

It is also well known that the structural anisotropy of the lamellar structured alloys leads to corresponding anisotropies in many of their other physical properties. The comprehensive performance of thermoelectric materials is evaluated via the dimensionless figure of merit ZT, which is a function of the resistivity, Seebeck coefficient and thermal conductivity [4,5]. Because these physical properties are related to the transport of the charge carriers, Bi–Te-based alloys have TE anisotropy due to their structural anisotropy. The anisotropy of the electrical resistivity of single-crystal Bi_2Te_3 along the crystalline axis was first reported by Delves and co-workers [6]. They found that the electrical resistivity varied by a factor of approximately 3.2 when measured parallel to the *c*-axis of the crystals in comparison with that measured perpendicular to the *c*-axis. Stordeur et al. [7] modeled the transport properties of Bi–Te-based thermoelectric materials and indicated that the resistivity in the direction perpendicular to the cleavage planes was greater than that measured in the parallel direction. These results should be considered in explanation of the anisotropic resistivity. However, there have not been any reports relating the Seebeck coefficient to

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the structural anisotropy. Many researchers have studied the anisotropy of Bi–Te-based TE materials [8–13]. According to these reports, the anisotropies of the electrical resistivity and the thermal conductivity were clearly observed along the crystalline axis while the Seebeck coefficient was nearly isotopic regardless of the crystalline axis and was only dependent on the carrier concentration. These results are consistent with experiments suggesting that the anisotropy ratios ranged from 4.3 to 6.7 for the resistivity and from 2.1 to 2.5 for the thermal conductivity. Based on the above results, we can predict that ZT will be enhanced in crystalline-oriented TE materials due to the decrease in the resistivity.

On the other hand, the structural anisotropy of the single-crystal Bi–Te-based alloys presents the disadvantage of poor mechanical integrity. These crystals are easily fractured along the cleavage planes during cutting or during operation of the modules, which causes problems in the production yield and the reliability of the modules [14–16]. Thus, investigations have been focused on polycrystalline Bi–Te-based alloys that are fabricated by powder metallurgy methods, such as pressure-less sintering [17–19], mechanical alloying [20–23], hot extrusion [24,25] and hot pressing [26–29]. Powder metallurgy techniques are broadly defined as the processes whereby powders are compacted and then sintered at elevated temperatures to form a dense body with a well-defined, coherent grain structure. These techniques are used to fabricate a variety of common thermoelectric materials. It has been reported that the thermoelectric figure of merit of hot-pressed materials is comparable to that of single crystals [30]. Recently, spark plasma sintering (SPS) was used to fabricate thermoelectric materials. SPS is a newly developed rapid sintering process that makes it possible to sinter high-quality materials. A particular advantage of SPS is its sintering speed, which allows the formation of fine crystalline materials with less grain growth. SPS reflects a recent research trend that tries to fabricate nanostructural thermoelectric materials with phonon-grain boundary scattering [31,32].

The purpose of this research was to study the influence of powder morphology on the thermoelectric anisotropy of the sintered body. SPS was applied to fabricate the thermoelectric materials. The morphologies of the starting powders were controlled by various synthesis methods: a chemical reaction method, a conventional pulverization method and a gas atomizing method. The thermoelectric properties of sintered bodies were evaluated parallel and perpendicular to the pressing direction.

2. Experimental details

2.1. Specimen preparation

To investigate the anisotropy of Bi–Te thermoelectric materials, three powder samples were prepared. The first one, which was named BTn, was synthesized by a chemical reaction method. Bismuth(III) nitrate and elemental tellurium powder were employed as precursors. Ascorbic acid and ethylenediaminetetraacetic acid were used to dissolve the bismuth source and to stabilize it in deionized water, respectively. Sodium borohydride was chosen to reduce tellurium. Bi_2Te_3 powder was obtained as a precipitate through the chemical reaction. The precipitate was filtered and rinsed with both dry ethanol and deionized water, then dried under vacuum at 60 °C overnight, which finally resulted in Bi_2Te_3 powder.

The second powder sample, which was named BSTi, was prepared by the conventional pulverization method. The metal powders (Bi, Sb and Te), which had over 99.99% purity, were weighed to a composition of $Bi_{0.5}Sb_{1.5}Te_{3.0}$ and mixed in a quartz tube. The tube was evacuated below 10^{-5} torr and sealed. The tube was heated to 1000 °C in a rocking furnace to prevent any phase segregation. After 24 h of heating, the tube was cooled to room temperature in a furnace. The obtained $Bi_{0.5}Sb_{1.5}Te_{3.0}$ ingot was crushed and sieved with a 36 μm mesh.

The last powder sample, which was named BSTs, was prepared by a gas atomization method. The Bi, Te and Sb powders, with over 99.99% purity were weighed to a composition of $Bi_{0.5}Sb_{1.5}Te_{3.0}$. After melting in a high-frequency induction furnace under an argon atmosphere in a graphite crucible, the $Bi_{0.5}Sb_{1.5}Te_{3.0}$ powder was atomized from a nozzle with compressed nitrogen gas and sieved with a 36 μm mesh.

The thermoelectric powders were sintered into cylinders that were 12 mm in height and 15 mm in diameter with a SPS machine (DR. Sinter, SPS-3, 20MK-IV) in the temperature range of 350–520 °C and under a pressure of 50 MPa in an argon atmosphere. The heating rate was 80 K min^{-1}, and the holding time at the sintering temperature was 2 min. The sintering conditions were chosen such that the sintered body had a density larger than 95% and avoided liquid phase sintering.

2.2. Characterization

The size and morphology of the powders were characterized by field emission scanning electron microscopy (Hitachi, S-4800 FE-SEM). The microstructure of the sintered body that was composed of the powder derived via the chemical reaction was observed with electron backscatter diffraction scanning microscopy (Jeol, JSM-7000F with TSL OIM EBSD), while the microstructures of the other two bodies were observed with optical microscopy (Hitachi, S-4800 FE-SEM). The Hall coefficient (R_H) was measured by the van der Pauw method at room temperature by using a Hall measurement system (Ecopia, HMS-3000). Both the carrier concentration (n) and Hall mobility (μ_H) were calculated by assuming the single carrier conduction model with the following relations: $n = -\frac{1}{R_H e}, \mu_H = \frac{1}{ne\rho}$, where e is the electronic charge and ρ is the electrical resistivity.

The electrical resistivity (ρ) and the Seebeck coefficient (α) were measured with commercial equipment (Ulvac-