Thermoelectric properties of crystal-aligned bismuth antimony tellurides prepared by pulse-current sintering under cyclic uniaxial pressure

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ABSTRACT

Pulse-current sintering under cyclic uniaxial pressure (PCS-cyclic) was applied to p-type $Bi_{2-x}Sb_xTe_3$ ($x = 1.5$, 1.6, and 1.7) to obtain sintered materials with preferred crystal orientation. PCS-cyclic was performed at 673 K for 10 min under cyclic uniaxial pressure of 100 MPa. X-ray diffraction and electron backscatter diffraction patterns showed that the texture of the PCS-cyclic samples consisted of c-plane-oriented grains. The hexagonal c-plane was aligned perpendicular to the pressing direction, which is the preferred direction for thermoelectric conversion. The carrier concentration of $Bi_{2-x}Sb_xTe_3$ ($x = 1.5$, 1.6, and 1.7) tended to increase with increasing antimony concentration. Thus, the carrier concentration was controllable in the range $(1.2-4.2) \times 10^{25}$ m^{-3}. The thermoelectric properties of the PCS-cyclic samples were compared with available data for single crystals and conventional sintered materials. The electrical resistivities of the PCS-cyclic samples were lower than those of the sintered samples, and close to those of single crystals. This behavior can be attributed to the crystal orientation. The thermal conductivities of the PCS-cyclic samples were lower than those of the single crystals and they were large value for the sintered materials. This may correspond to the grain boundaries acting as a scattering center for phonons. Consequently, the PCS-cyclic samples have single-crystal-like electrical properties with polycrystal-like thermal properties. It can be concluded that PCS-cyclic is promising for preparation of high-performance p-type Bi—Sb—Te-based thermoelectric materials with various carrier concentrations.

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1. Introduction

Bi_2Te_3-based materials are known to the best thermoelectric materials operating at close to room temperature [1] and they are widely used for many thermoelectric products. The crystal structure of these materials is a layered hexagonal (or rhombohedral) structure [2] and remarkable anisotropy exists in the physical properties. The thermoelectric figure of merit $ZT (=S^2/\rho\kappa$, where S is the Seebeck coefficient, ρ the electrical resistivity, and κ the thermal conductivity) of these materials is better in the hexagonal c-plane than the c-axis direction owing to the large anisotropy in their ρ values [3—6] because the crystal alignment is essential for improving their thermoelectric performance.

Recently, much effort has focused on preparation of sintered materials with fine structure via powder metallurgical processes to reduce the lattice thermal conductivity and enhance the mechanical strength [7—10]. Pulse-current sintering (PCS), which is known commercially as spark plasma sintering (SPS), allows ceramics and metal powders to be sintered at low temperature using short times [11,12]. These conditions are suitable for preparation of sintered materials consisting of fine crystal grains. Thus, PCS is widely used to prepare Bi_2Te_3-based materials [13—20], where the fine powder is prepared by various methods and PCS is used to prevent crystal grain growth. However, in the PCS process, the grains tend to have random orientations despite application of uniaxial pressure. This random orientation of crystal grains leads to large electrical resistivity and a small power factor.

Based on the above-mentioned background, single-crystal-like electrical properties and sintered-material-like thermal properties are desired for further development of the thermoelectric properties. This could be realized by crystal alignment of fine crystal grains. Some unique methods have been used for crystal alignment

and texture control, including hot forging [21], sintering under high magnetic field [22], and angular extrusion [23]. We previously reported PCS under cyclic uniaxial pressure (PCS-cyclic) as a simple process for preparing p-type $Bi_{0.5}Sb_{1.5}Te_3$ [24] and n-type $Bi_2Te_{2.85}Se_{0.15}$ [25] with high *c*-plane orientation. In this method, continuous cyclic uniaxial pressure is applied during the sintering process. The enhanced crystal orientation improves the power factor by decreasing of electrical resistivity. However, for p-type Bi−Sb−Te, carrier concentration control and thermal property analysis are still required.

In the present study, the PCS-cyclic process was applied to p-type $Bi_{2-x}Sb_xTe_3$ (*x* = 1.5, 1.6, and 1.7), where changing the antimony concentration was performed to attempt to control the carrier (hole) concentration. Conventional PCS, applying a constant pressure, was also performed for comparison. The texture and room-temperature thermoelectric properties were evaluated. The thermoelectric properties of PCS-cyclic samples are discussed by comparing with available data of single crystals [4] and sintered materials by the pulse-discharge sintering (MA-PDS) method [13], which is with the same as conventional PCS.

2. Experimental

The raw powder was prepared by the mechanical alloying method. Pure metallic Bi, Sb, and Te (nominal purities of 5 N) powders were weighed to give the composition $Bi_{2-x}Sb_xTe_3$ (*x* = 1.5−1.7). The mixture was placed in the zirconia vessel of a planetary ball mill with zirconia balls. The mechanical alloying was performed at a rotation speed of 300 rpm for 30 h under argon atmosphere. Completion of the alloying was confirmed by X-ray diffraction (XRD).

PCS-cyclic was performed in the same manner as that described in previous reports [24,25]. A pulse current sintering device equipped with a cyclic pressure system (PLASMAN CSP-III-1012DP, S.S. Alloy Co. Ltd., Higashi-Hiroshima, Japan) was used for this process. A carbon-dispersed WC-FeAl alloy die and punches were used because of their suitable mechanical strength and electrical resistivity for the PCS-cyclic process [26]. A schematic of the PCS-cyclic process is shown in Fig. 1(a). The prepared alloy powder was set into the die, and continuous cyclic uniaxial pressure of 100 MPa was applied through the punches. The punches moved 3 mm above the sample position when the pressure was removed. The mixture was heated to 673 K in 20 min by applying a pulse current under vacuum. After maintaining at this temperature for 10 min, the cyclic pressure was stopped and the material was allowed to cool naturally to room temperature. Fig. 1(b) shows the typical pressure cycle used. The cyclic pressure was applied for 30 min from the start of heating to the start of cooling, and the

number of cycles was approximately 450.

PCS was also performed under constant uniaxial pressure (PCS-constant) for comparison. The sintering apparatus, die and punches, and sintering conditions were the same as those described above except for the uniaxial pressure. All of the obtained materials were 10 mm in diameter, 4 and 10 mm in thickness, and had a relative density of more than 92% of the theoretical density.

The crystal orientation of the obtained samples was examined by XRD (CuKα) of the polished surface of the sintered samples. Electron backscatter diffraction (EBSD) patterns were also obtained to investigate the crystal grain orientation of the samples. The analysis was performed on polished cross-sections and surfaces of the sintered materials using a scanning electron microscope at an accelerating voltage of 15 kV. The observed area was approximately 120×60 μm^2 with a scanning step size of 0.2 μm. The crystal orientation was calculated using an automatic pattern fitting algorithm for the obtained Kikuchi patterns [27].

The Hall coefficient R_H and electrical resistivity ρ were measured at 300 K using the van der Pauw method (ResiTest 8300, Toyo Corp., Tokyo, Japan). The Seebeck coefficient S was measured at 300 K by applying a temperature difference of 1−3 K. The thermal diffusivity D was measured using the laser-flash method (LFA 457, NETZCH). The thermal conductivity κ was calculated using $\kappa = DC_pd$, where d is the density of the sample and C_p is the specific heat. The C_p value was obtained using the Dulong−Petit approximation. These measurements of the samples were conducted by applying an electrical or thermal current in the direction perpendicular to the pressing direction. That is, the samples were cut from the sintered materials of 4 and 10 mm in thickness to allow measurement of the S, ρ and D in desired directions as shown in Fig. 2.

3. Results and discussion

3.1. Crystal orientation and texture

Fig. 3(a) shows XRD patterns of PCS-cyclic samples. The measurements were performed at the top surface and middle part of the samples with a thickness of approximately 4 mm. Fig. 3(b) shows XRD patterns of PCS-constant samples at the top surface and a powder simulation pattern [28] of $Bi_{0.4}Sb_{1.6}Te_3$. All of the diffraction peaks in Fig. 3 were assigned to the Bi_2Te_3-type structure. The XRD patterns of the PCS-constant samples in Fig. 3(b) are almost the same as the simulated powder pattern, indicating that the crystal orientation is rarely enhanced by constant uniaxial pressure. In contrast, the XRD patterns of the PCS-cyclic samples have strong diffraction peaks from the hexagonal *c*-plane, such as 0 0 · 6, and 0 0 · 15, in both the top surface and middle part of all of the samples. This result means that the crystal orientation was
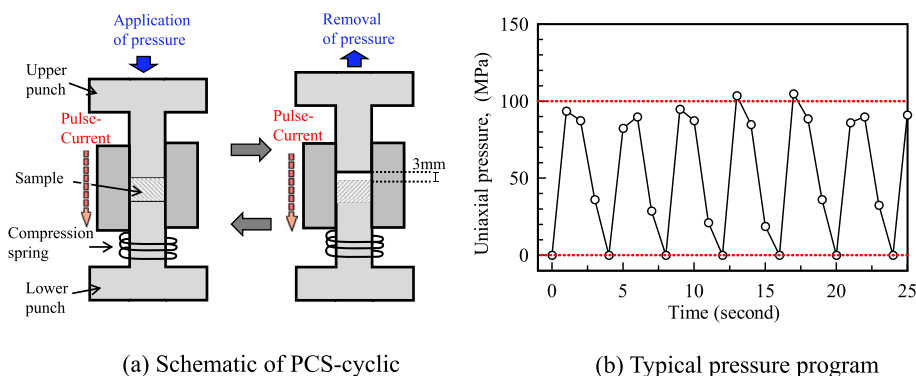

(a) Schematic of PCS-cyclic   (b) Typical pressure program

Fig. 1. (a) Schematic of PCS-cyclic and (b) the typical cyclic pressure of PCS-cyclic.