



## Evolution of thermoelectric performance for (Bi,Sb)<sub>2</sub>Te<sub>3</sub> alloys from cutting waste powders to bulks with high figure of merit



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### ABSTRACT

Bi<sub>2</sub>Te<sub>3</sub> based cutting waste powders from cutting wafers were firstly selected as raw materials to prepare p-type Bi<sub>2</sub>Te<sub>3</sub> based thermoelectric (*TE*) materials. Through washing, reducing, composition correction, smelting and resistance pressing sintering (RPS) process, p-type (Bi,Sb)<sub>2</sub>Te<sub>3</sub> alloy bulks with different nominal stoichiometries were successfully obtained. The evolution of microstructure and *TE* performance for (Bi,Sb)<sub>2</sub>Te<sub>3</sub> alloys were investigated in detail. All evidences confirmed that most of contaminants from line cutting process such as cutting fluid and oxides of Bi, Sb or Te could be removed by washing, reducing and smelting process used in this work. The carrier content and corresponding *TE* properties could be adjusted effectively by appropriate composition correction treatment. At lastly, a bulk with a nominal stoichiometry of Bi<sub>0.44</sub>Sb<sub>1.56</sub>Te<sub>3</sub> was obtained and its' dimensionless figure of merit (*ZT*) was about 1.16 at 90 °C. The *ZT* values of Bi<sub>0.36</sub>Sb<sub>1.64</sub>Te<sub>3</sub> and Bi<sub>0.4</sub>Sb<sub>1.6</sub>Te<sub>3</sub> alloy bulks could also reach 0.98 and 1.08, respectively. Different from the conventional recycling technology such as hydrometallurgy extraction methods, the separation and extraction of beneficial elements such as Bi, Sb and Te did not need to be performed and the Bi<sub>2</sub>Te<sub>3</sub> based bulks with high *TE* properties could be directly obtained from the cutting waste powders. In addition, the recycling technology introduced here was green and more suitable for practical industrial application. It can improve material utilization and lower raw material costs of manufacturers.

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### 1. Introduction

As one of the best thermoelectric (*TE*) materials for power generators and coolers near room temperature, zone-melted Bi<sub>2</sub>Te<sub>3</sub> and its solid-solution alloys have been commercialized for several decades [1–4]. However, the poor mechanical properties in all directions and actually more poor in the radial direction of an ingot limit their application scopes. They are easy to cleavage along basal plane due to weak Van der Waals bonding between Te (1)–Te (1) layers, which results in low material utilization efficiency of less than 50 wt% [5]. Industrially, various waste products are produced

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during zone melting and cutting processes such as tops and tails of single crystal bars due to high impurity concentration, cutting debris, cutting waste powders, broken irregular square particles and so on. There are more than 10 kinds of wastes if we distinguish in detail according to p-type and n-type semiconductors, which accounts for more than 50 wt% of the total raw materials. In addition, the scarce elements (such as Te and Se) are very expensive due to their low reserves and the increased use in metallurgy, petroleum chemistry and even photovoltaic industries, which result in high raw materials cost for *TE* materials manufacturers [6]. So, it is important to develop a recycle method for these waste products from zone melting and cutting processes. Generally, hydrometallurgical technology is used to extract the single element such as Te and Bi from waste products [7]. However, the average recovery is low, the process is also long and even pollutes environment. In order to overcome the pollution problems and minimize the loss of useful elements such as Bi, Sb, Te and Se, an appropriate treatment process for these wastes is very important.

In this paper,  $\text{Bi}_2\text{Te}_3$  based cutting waste powders from cutting wafers were firstly selected as raw materials to prepare p-type  $\text{Bi}_2\text{Te}_3$  based thermoelectric materials by washing, reducing, composition correction, smelting and resistance pressing sintering (RPS) process. Their compositions and  $TE$  properties were also adjusted to meet the application requirements.

## 2. Experimental

In this work, the initial cutting waste powders were obtained from Chang Shan Wangu electronic technologies Co., Ltd. (Zhejiang, China). These cutting waste powders are contaminated by linear cutting liquid and their own oxides. Firstly, the initial cutting waste powders were washed with deionized water and absolute ethyl alcohol to remove the contaminants of linear cutting liquid. The wet powders were then transferred to a vacuum drying oven to remove water at  $60\text{ }^\circ\text{C}$  [8]. And then the powders were reduced under hydrogen atmosphere at  $380\text{ }^\circ\text{C}$  for 1.5 h in a tubular resistance furnace. In order to adjust carrier concentration of  $(\text{Bi}, \text{Sb})_2\text{Te}_3$  alloys, appropriate amount of high purity ( $> 99.99\text{ wt}\%$ ) Sb and Te granules were added into the reduced particles and then sealed into a quartz tube under vacuum [9]. The raw materials with three different nominal components of  $\text{Bi}_x\text{Sb}_{2-x}\text{Te}_3$  ( $x=0.36, 0.40, 0.44$ ) were sealed in quartz tubes and then placed in a rocking furnace. The smelting temperature was fixed at  $710\text{ }^\circ\text{C}$  and the holding time was fixed for 120 min. Then, the samples were cooled to room temperature in furnace. Subsequently, the ingots were ground into powders with a size of less than  $\sim 38\text{ }\mu\text{m}$ . Finally, the grinded powders were consolidated by resistance pressing sintering (RPS) technique at  $410\text{ }^\circ\text{C}$  for 5 min under an axis pressure of 38 MPa in argon atmosphere [10,11]. The heating rate was fixed at  $50\text{ }^\circ\text{C}/\text{min}$ . For comparison, both the initial waste powders and reduced powders without adding Sb and Te were also sintered in the same condition.

The thermal gravimetric analysis (TG) was performed at a heating rate of  $5\text{ }^\circ\text{C}/\text{min}$  in argon atmosphere (Sta449 C, Netzsch). The structure, morphology and composition of the specimens were characterized by X-ray diffraction (XRD) with Cu K $\alpha$  radiation ( $\lambda=1.5418\text{ \AA}$ ) (X-Pert Philips diffractometer, D500, Siemens), field-emission scanning electron microscopy (FESEM) (FEI, Nova400 NanoSEM) and energy dispersive X-ray spectroscopy (EDS) (IE350PentaFETX-3). The bulk samples were cut into rectangular bars with an approximate dimension of  $3 \times 3 \times 15\text{ mm}^3$  for electrical transport properties. The electrical conductivity ( $\sigma$ ) were determined by four probes method [10–13]. The Seebeck coefficient ( $S$ ) were measured by applying a dynamic temperature gradient ( $\Delta T$ ) of  $5\text{--}10\text{ }^\circ\text{C}$  between both ends of the bars and measuring the output voltage ( $\Delta V$ ) between them. The  $S$  was obtained by calculating the slope of the linear regression line through the least square method [5,12,13]. The Hall coefficient ( $R_H$ ) was measured by the van der Pauw method using the Hall-effect measurement system (HMS-5500, Ekopia) under a magnetic field of 0.55 T. The carrier concentration ( $n$ ) and mobility ( $\mu$ ) were calculated according to the equations:  $n=1/R_H e$  and  $\mu=\sigma/ne$ , where  $e$  is electrical charge of electron [5,12,13]. The thermal conductivity  $\kappa$  was calculated by multiplying the measured thermal diffusivity  $\lambda$ , specific heat  $C_p$  and volume density ( $d$ ) using the relationship  $\kappa=\lambda C_p d$ . The  $\lambda$  and  $C_p$  were measured by a laser flash apparatus (LFA457, Netzsch, Germany) [10–13]. The volume densities  $d$  of the bulk samples were measured by the Archimedes method. The uncertainty in the electrical transport properties was less than  $\sim 5\%$  and in the thermal conductivity was less than 7%. In our present experiments, the electrical properties, Hall-effect and thermal properties were all measured in a direction perpendicular to the press direction during RPS process.

## 3. Results and discussion

### 3.1. The initial cutting waste powders and the corresponding as-RPSed bulks

To obtain the corresponding microstructure and composition of the initial cutting waste powders, the SEM and EDS for waste powders are performed as shown in Fig. 1(a, b). The morphology of initial cutting waste powders is flocculent and the particle size is small (Fig. 1(a)). From the EDS results, it can be found that the initial cutting waste powders contain C, O, Bi, Te and Sb elements (Fig. 1(b)). The contents of oxygen and carbon are relative high, which should come from linear cutting liquid and oxides of Bi, Sb or Te. So, the following washing and reducing process must be performed. The washing process can remove the linear cutting fluid and the reducing process can remove the element oxygen. In order to confirm the phases of the oxides in the initial cutting waste powders, the corresponding XRD pattern is shown in Fig. 1(c). It can be seen that  $(\text{Bi}_{0.5}\text{Sb}_{0.5})_2\text{Te}_3$ , Te,  $\text{Sb}_2\text{O}_3$  and  $\text{Bi}_4\text{TeO}_8$  phases are observed in the XRD patterns. For further confirm the state of these phases in the as-RPSed bulks, the SEM fractographs and EDS of the as-RPSed bulks from the initial cutting waste powders were analyzed as shown in Fig. 1(d). There are three kinds of typical morphologies for the fractographs: typical lamellar structure, agglomerated submicron-sized granules and dispersed cubic particles. The corresponding EDS results show that the smooth laminated structure is the inherent Bi–Sb–Te alloy phases, the agglomerated submicron-sized granules are the oxide of bismuth (tellurium) based alloys and the dispersed cubic particles is  $\text{Sb}_2\text{O}_3$ , respectively [14]. So, the following reducing process is important to remove the element oxygen.

### 3.2. Reducing process

At the beginning, in order to choose suitable temperature for reducing process, a small part of initial cutting waste powders are selected randomly for TG measurements as shown in Fig. 2(a). There is slight weight loss from room temperature to  $400\text{ }^\circ\text{C}$  and the weight loss is only 0.2 wt%. However, there are a large amount of volatiles when the temperature is above  $400\text{ }^\circ\text{C}$ . The volatiles obtained here can be confirmed as Te and their morphologies are tube or bar according to the SEM and corresponding EDS results (as shown in Fig. 2(b)) [15]. It is because that element Te has the highest saturated vapor pressure among elements Bi, Te and Sb (the saturated vapor pressures of Bi, Te and Sb are  $10^{-5}$ , 1 and  $10^{-3}\text{ Pa}$  at  $367\text{ }^\circ\text{C}$ , respectively) [16]. In order to remove the oxygen on the powder surface, Hong et al. also processed the gas-atomized powders at  $360\text{ }^\circ\text{C}$  under  $\text{H}_2$  atmosphere [17,18]. Lim et al. processed the pulverized powders by  $\text{H}_2$  at  $380\text{ }^\circ\text{C}$  [19].

To avoid the volatilization of element Te, the following reduced temperature is selected as  $380\text{ }^\circ\text{C}$  according to the TG results. Fig. 2(c, d) shows the SEM and EDS results of the reduced powders, respectively. Compared with the initial cutting waste powders, the slight agglomeration happens for the reduced powders. The EDS results show that the reducing process decrease obviously oxygen content from 10.08 to 3.74 wt%. The content of C also decrease from 3.85 to 2.26 wt%, suggesting that the washing and reducing process selected here are positive, but they are not enough. To confirm the phases in the reduced powders, the XRD patterns are shown in Fig. 2(e). It can be seen that there are mainly  $(\text{Bi}_{0.5}\text{Sb}_{0.5})_2\text{Te}_3$  and  $\text{Sb}_2\text{O}_3$  phases in the reduced powders. Compared with the initial cutting waste powders, the  $\text{Bi}_4\text{TeO}_8$  phase disappears but there are still  $\text{Sb}_2\text{O}_3$  in the reduced. It means that the O in  $\text{Bi}_4\text{TeO}_8$  phase can be removed but  $\text{Sb}_2\text{O}_3$  can not be reduced by  $\text{H}_2$  at  $380\text{ }^\circ\text{C}$  [20].

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