Journal of Solid State Chemistry 181 (2008) 3278–3282

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Enhanced thermoelectric properties of bismuth sulfide polycrystals prepared by mechanical alloying and spark plasma sintering

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ARTICLE INFO

Article history:
Received 12 June 2008
Received in revised form
20 July 2008
Accepted 12 August 2008
Available online 27 August 2008

Keywords:
Bismuth sulfides
Mechanical alloying
Spark plasma sintering
Thermoelectric

ABSTRACT

Bismuth sulfide powders were synthesized by mechanical alloying (MA) and then consolidated by spark plasma sintering (SPS) technique. In order to improve the electrical transport properties of bismuth sulfides, the carrier concentration was optimized by modifying chemical composition of sulfur through producing sulfur vacancies, and the carrier mobility was enhanced by a two-step SPS as a hot-forging process through increasing grain orientation. The electrical resistivity of bismuth sulfides was reduced to 10^{-4} from $10^{-2}\,\Omega$ m by optimizing sulfur content, and further lowered by hot-forging, whereby the power factor was significantly increased from 91 to 254 $\mu W/mK^2$. The hot-forged $Bi_2S_{2.90}$ sample showed the highest $ZT = 0.11$ (at 523 K), which is higher than the reported value. The present work revealed that bismuth sulfide compounds as a promising candidate of thermoelectric materials can be synthesized by a simple process.

1. Introduction

Thermoelectric (TE) power generators and refrigerators are solid-state devices without moving parts. They are silent, reliable and scalable, making them ideal for small, distributed power generation [1]. The efficiency of TE devices is determined by the dimensionless figure of merit (ZT), defined as $ZT = (\alpha^2/\rho k)T$, where α, ρ, k, and T are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively. The compounds A_2B_3 (where $A = $ Bi, Sb, Pb and $B = $ S, Se, Te) are considered to be most promising for TE applications [2]. Bi–Te-based [3] and Pb–Te-based [4,5] compounds show the best TE properties at room and middle temperatures, respectively. Although telluride-based materials usually exhibit good TE properties and hold dominant market shares in TE materials, it is necessary to develop alternative materials to replace the rare and toxic tellurium. Bismuth sulfide (Bi_2S_3) belongs to the A_2B_3 family, but little attention has been paid to Bi_2S_3 in TE development because of its high electrical resistivity due to a 1.30 eV direct band gap at room temperature [6]. It is quite encouraging that the electrical resistivity of Bi_2S_3 can be reduced by 2–3 orders of magnitude through introducing sulfur vacancies in the lattice [7]. Surprisingly, the low thermal conductivity of the sulfur-deficient Bi_2S_3 could be realized by enhancing phonon scattering on the sulfur vacancies, where the large Seebeck coefficient was maintained at same time as suggested by Chen [8]. Enhanced high electrical transport properties were achieved in the one-dismensional Bi_2S_3 films by increasing carrier mobility using its natural anisotropic [9]. Although the polycrystals of TE materials own the better mechanical properties and lower thermal conductivity, little attention has been paid to polycrystalline Bi_2S_3 materials until now probably because of their high electrical resistivity. It was found that fine-grained and textured Bi_2Te_3 TE materials which are fabricated by SPS possess high performance [10]. Therefore, we expect to enhance the electrical transport properties especially power factor by tailoring stoichiometric ratio of bismuth to sulfur and controlling grain orientation, meanwhile, to reduce the thermal conductivity by refining grain size.

In the present study, Bi_2S_3 polycrstals with substoichiometry and oriented fine grains were successfully fabricated by mechanical alloying (MA) and SPS technique. The microstructure and TE properties were investigated with special emphases on the effects of sulfur content and orientation degree. The highest ZT value known presently achieved 0.11 at 523 K in the Bi_2S_3's family.

2. Experimental procedure

Commercial high-purity powders of 99.999% Bi and 99.9% S under the same 100 mesh were used as raw materials. The

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0022-4596/$ - see front matter © 2008 Published by Elsevier Inc.
doi:10.1016/j.jssc.2008.08.022

powders with the chemical composition of Bi_2S_{3-x} ($x = 0$, 0.05, 0.10, 0.15) were MAed at 350 rpm for 15 h in a purified argon atmosphere using a planetary ball mill (QM-1SP2, Nanjing University, China). Stainless steel vessel and balls were used, and the weight ratio of ball to powder was kept at 20:1. The MAed powders were firstly SPSed at 673 K for 5 min in a Φ15 mm graphite mould under the axial compressive stress of 50 MPa in vacuum using a SPS system (Sumimoto SPS1050, Japan), resulting in a disk-shaped bulk of Φ15 mm × 6 mm. The SPSed Φ15 mm × 6 mm bulks were then charged to a Φ20 mm graphite mould and were SPSed again at 723 K for 5 min, acting as a hot-forging process. The other conditions were the same as the first SPS processing. Finally, disk-shaped samples with dimensions of Φ20 mm × 4.5 mm were obtained.

Phase structure was analyzed by X-ray diffraction (XRD, Cu$K\alpha$, Bruker D8, Germany). The morphologies of powder and fractographs of bulks were observed by scanning electron microscopy (SEM, JSM-6460, Japan). The TE properties were evaluated along the sample section perpendicular to the pressing direction of SPS. The Seebeck coefficient and electrical resistivity were measured at 323–573 K in a helium atmosphere using a Seebeck coefficient/electric resistance measuring system (ZEM-2, Ulvac-Riko, Japan). The thermal diffusivity coefficient (D) was measured using the laser flash method (NETZSCH, LFA427, Germany). The specific heat (C_p) was measured using a thermal analyzing apparatus (Dupont 1090B, USA). The density (d) of the sample was measured by the Archimedes method. The thermal conductivity (k) was calculated from the product of thermal diffusivity, specific heat (C_p) and density, $k = D\ C_p\ d$. The Hall coefficients, R_H, of the samples were measured at room temperature using a physical properties measurement system (PPMS-9T, Quantum Design Inc., USA), and a magnetic field of 2 T and electrical current of 30 mA were applied. The carrier concentration (n) was calculated by $n = 1/eR_H$, where e is the electronic charge. The carrier mobility (μ) was calculated by $\mu = R_H/\rho$, where ρ is the electrical resistivity.

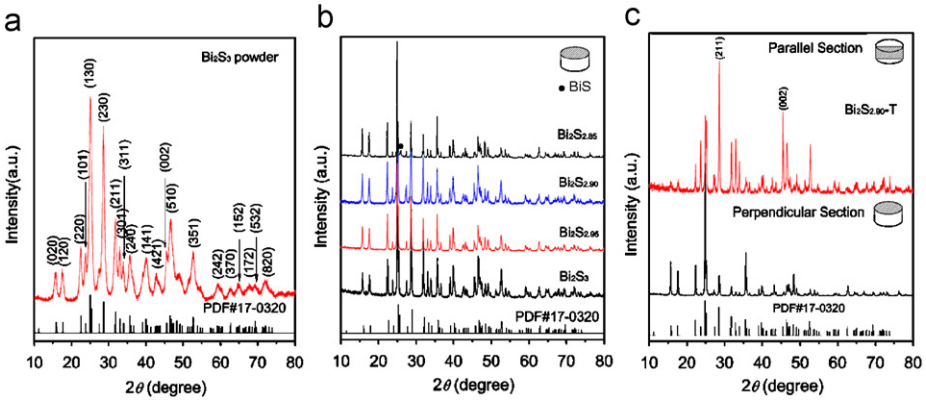

Fig. 1. XRD patterns of the MAed Bi_2S_3 powders (a), the SPSed Bi_2S_{3-x} ($x = 0.0$, 0.05, 0.10, 0.15) bulks (b), and the hot-forged $Bi_2S_{2.90}$ bulks (c) in perpendicular and parallel to the pressing direction.

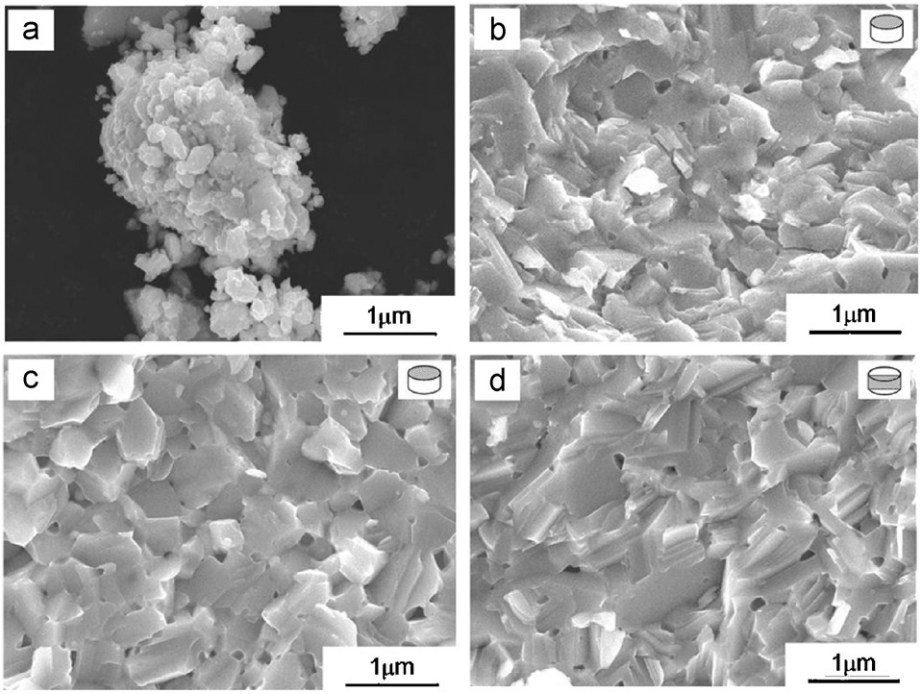

Fig. 2. SEM micrographs of the MAed Bi_2S_3 powders (a) as well as the fractured surfaces of $Bi_2S_{2.90}$ bulk before (b) and after (c, d) hot forging, in which the fractured surfaces of the later two hot-forged samples are perpendicular (c) and parallel (d) to the pressing direction, respectively.