Materials Science and Engineering B 195 (2015) 45–49

Contents lists available at ScienceDirect

Materials Science and Engineering B

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

Thermoelectric properties of Sb-doped $Mg_2(Si_{0.95}Ge_{0.05})$ synthesized by spark plasma sintering

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ARTICLE INFO

Article history:
Received 29 August 2014
Received in revised form 10 January 2015
Accepted 24 January 2015
Available online 20 February 2015

Keywords:
Magnesium silicide
Mg_2Si
Thermoelectric material
Spark plasma sintering

ABSTRACT

Magnesium silicide (Mg_2Si) has recently attracted much interest as an *n*-type thermoelectric (TE) material for converting waste heat into electric power. The objective of this work was to reveal a mechanism to increase the thermoelectric properties of Mg_2Si by Sb-doping and Ge-doping. Generally, Mg_2Si is synthesized by all-molten method. However, this synthesis method has some problems, for example, mass defects of Mg for Mg_2Si composition caused because the melting point of Mg_2Si is very close to the boiling point of Mg. In this study, we tried to synthesize high purity Mg_2Si from Mg and Si alloyed with a dopant (Sb, Ge) by spark plasma sintering (SPS). The Ge-doped samples had a higher *ZT* value than the *ZT* value of the Sb-doped sample of the same concentration without Ge because the thermal conductivity of the former was lower. The maximum *ZT* value of Sb0.23 at%-doped $Mg_2(Si_{0.995}Ge_{0.05})$ was 0.74 at 756 K.

1. Introduction

Thermoelectric (TE) power generation has recently attracted much interest for converting waste heat into electric power. The performance of TE materials is usually denoted as the dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature, and κ ($\kappa = \kappa_{el} + \kappa_{ph}$, κ_{el} is the electronic thermal conduction and κ_{ph} is the lattice thermal conduction) is the thermal conductivity. Magnesium silicide (Mg_2Si) has recently attracted much interest as an *n*-type TE material operating in the temperature range from 500 to 800 K because of its non-toxicity, environmental friendliness, lightness, and relative abundance compared with other TE materials [1–7]. However, it is known that decrease of the thermoelectric performance of Mg_2Si by generating MgO, which has high thermal conductivity caused by oxidation of Mg_2Si in the synthesis. In particular, it is known that synthesis of Mg_2Si is difficult because the boiling point of Mg is close to the melting point of Mg_2Si and Mg has a high reactivity with oxygen. It is theorized that these compounds can exhibit high *ZT* values due to their large effective masses, high mobilities, and relatively low lattice thermal conductivities [8]. Therefore, in this study, by using the spark plasma sintering (SPS) synthesis reported by Kajikawa et al. [9], we tried to fabricate a fine Mg_2Si sample in a short time and improve thermoelectric performance by adding Sb as a dopant to control carrier concentration and Ge as a dopant to decrease κ by phonon scattering. The objective of this work was to reveal a mechanism to increase the thermoelectric properties of Mg_2Si by Sb-doping and Ge-doping. The SPS process is easy and cost effective and requires no previous sintering experience. Unlike the conventional powder sintering methods, SPS makes it possible to prepare ceramics at low temperatures in less time by charging the intervals between the particles with electrical energy and applying a momentary highly energized spark electrical discharge. Moreover, it makes it possible to synthesize metal compounds, ceramics, polymers, and thermoelectric semiconductors [10,11]. Garg et al. [12] reported that the κ of Ge-doped Si decreases enough at 5 at% by first-principles study. Therefore, in this study, we fixed the proportions of the elements in the sample at $Mg_2Si_{0.95}Ge_{0.05}$. In addition, we tried to fabricate Si alloyed with Sb and Ge so that the dopant is dissolved uniformly, and take an accurate measurement of dopant concentration by XRF measurement.

2. Experiment

A sample of Si alloyed with a dopant (Ge, Sb) was fabricated using the arc melting method in a vacuum. The bulk Si was ground into a powder and sieved to a particle size of 75 μm or less in a

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http://dx.doi.org/10.1016/j.mseb.2015.01.008
0921-5107/

dry box filled with Ar gas. The Si powder and metal Mg classified with a 425 mesh sieve were mixed and placed in the same dry box. For the synthesis of Mg_2Si by SPS, SPS was carried out using a Dr. Sinter Lab 515S system (Fuji Electronic Industrial Co., Ltd., Japan). For the SPS, the mixed powder was placed in a graphite die and heat-treated up to a pre-defined temperature (923 K) at a rate of 100 K/min (to 873 K) and 10 K/min (to 923 K) at a uniaxial pressure of 20 MPa under Ar atmosphere (the program was not maintained at 873 K and 923 K). After attaining the synthesis temperature in the SPS process, the electrical power was turned off and the sintered body was cooled to room temperature in the SPS chamber. Then, the synthesized Mg_2Si bulk was polished. To increase the sintered density of the synthesized Mg_2Si by SPS, the bulk was placed in a graphite die and heat-treated up to a pre-defined temperature (1113 K) at a rate of 100 K/min (to 873 K), 50 K/min (to 1073 K), and 10 K/min (to 1113 K), after which it was maintained at 1113 K for 5 min at a uniaxial pressure of 50 MPa under vacuum. The densities of the samples were measured using the Archimedes method. The sintered body was cut and polished. The X-ray diffraction (XRD) patterns of the Mg_2Si bulk samples were measured using an Ultima IV system (Rigaku Co., Japan). The microstructures of the samples were investigated using a scanning electron microscope (JCM-5100, JEOL Ltd., Japan). The X-ray fluorescence (XRF) analysis of the bulk sample was carried out using a ZSX Primus-μ (Rigaku Co., Japan). The carrier concentrations of the samples were measured at room temperature using Hall measurement equipment (Toyo Co., Japan). The Seebeck coefficient (S) and electrical conductivity (σ) were measured by standard four-probe method (ULVAC-RIKO, ZEM-2) in a He atmosphere in a temperature range of 300 to 873 K. The thermal conductivity (κ) was measured using a laser-flash system (ULVAC-RIKO, TC-7000H).

3. Results and discussion

Fig. 1 shows the XRD patterns of JCPDS references, (a) non-doped Mg_2Si bulk after first time SPS, (A) non-doped Mg_2Si bulk after second time SPS, (B) Sb0.048 at%-doped Mg_2Si bulk, (C) Sb0.16 at%-doped Mg_2Si bulk, (D) Sb0.37 at%-doped Mg_2Si bulk, (E) Sb0.056 at%-doped $Mg_2(Si_{0.95}Ge_{0.05})$ bulk, (F) Sb0.15 at%-doped $Mg_2(Si_{0.95}Ge_{0.05})$ bulk and (G) Sb0.23 at%-doped $Mg_2(Si_{0.95}Ge_{0.05})$ bulk (bulk of (A)–(G) are sample after second time SPS). The intense diffraction peaks could be assigned to those of Mg_2Si in all XRD patterns. Intense diffraction peaks of the impurity from dopants were not observed in the any XRD patterns. Therefore, it is believed that fine Mg_2Si samples have been successfully synthesized by SPS.

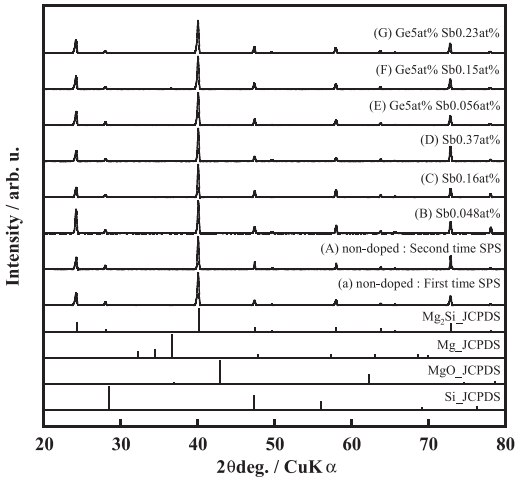

Fig. 1. XRD patterns of JCPDS Refs. [13–16] and (a) non-doped Mg_2Si bulk after first time SPS, (A) non-doped Mg_2Si bulk after second time SPS, (B) Sb0.048 at%-doped Mg_2Si bulk, (C) Sb0.16 at%-doped Mg_2Si bulk, (D) Sb0.37 at%-doped Mg_2Si bulk, (E) Sb0.056 at%-doped $Mg_2(Si_{0.95}Ge_{0.05})$ bulk, (F) Sb0.15 at%-doped $Mg_2(Si_{0.95}Ge_{0.05})$ bulk, (G) Sb0.23 at%-doped $Mg_2(Si_{0.95}Ge_{0.05})$ bulk.

Fig. 2 shows SEM images of cross section of (a) non-doped Mg_2Si bulk after first time SPS, (A) non-doped Mg_2Si bulk after second time SPS, (D) Sb0.37 at%-doped Mg_2Si bulk after second time SPS and (G) Sb0.23 at%-doped $Mg_2(Si_{0.95}Ge_{0.05})$ bulk after second time

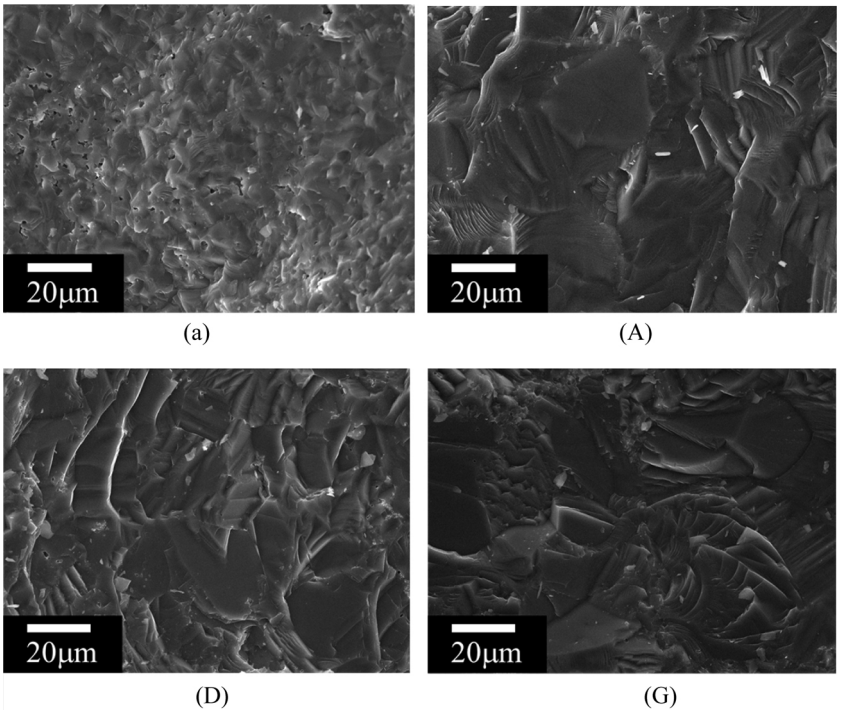

Fig. 2. SEM images of cross section of (a) non-doped Mg_2Si bulk after first time SPS, (A) non-doped Mg_2Si bulk after second time SPS, (D) Sb0.37 at%-doped Mg_2Si bulk after second time SPS, (G) Sb0.23 at%-doped $Mg_2(Si_{0.95}Ge_{0.05})$ bulk after second time SPS.