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Preparation of Mg_2Si-based thermoelectric materials using waste silicon sludge as a source material

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ABSTRACT

Sb-doped Mg_2Si was prepared using waste silicon sludge via a liquid-solid phase reaction and pulse-current sintering. Two types of Si sludge were used as a silicon source. One is an unwashed Si sludge, and the other is Si sludge washed with a water-based agent. In the samples prepared from unwashed Si sludge, Mg_2Si, Mg, and MgO phases existed. In the case of samples prepared from the washed Si sludge, the X-ray diffraction patterns showed almost a single phase, although a small MgO phase remained.

The thermoelectric properties of Mg_2Si prepared from the washed Si sludge were improved by control of weighed composition and carrier concentration. The obtained maximum figure of merit of this study was 0.66 in the samples prepared from the washed Si sludge, which is equivalent to materials prepared from reagent Si with identical carrier concentration.

1. Introduction

Mg_2Si-based compounds have semiconducting properties and are composed of environment-friendly, non-toxic, and abundantly available elements. Therefore, they have been proposed as a potential material for thermoelectric generators operating at intermediate temperature region [1–4]. In particular, n-type Mg_2Si, which can be obtained by doping with Sb [5–7], Bi [8,9], or Al [10–11], has an excellent thermoelectric figure of merit. For practical applications, development of the preparation process and the selection of raw materials are required to reduce the costs of the thermoelectric device.

The material commonly used in thermoelectric conversion is a semiconductor having a large carrier concentration (10^{25}–10^{27} m^{-3}). This means that excellent thermoelectric properties can be obtained, even if low-purity materials are selected as raw materials. For example, Laila et al. reported the preparation of $FeSi_2$-based thermoelectric materials using cast iron scrap chips [12,13]. According to their report, even when waste materials were used, a sufficient thermoelectric performance was obtained.

Si sludge is generated during the process of cutting a silicon ingot to a Si wafer. During this cutting process, approximately half of the Si ingot is discharged as sludge. This Si sludge is considered a valuable resource because most of the sludge is high-purity silicon. Recently, some studies have been conducted on the preparation of Mg_2Si using low-purity materials, including recycled waste Si sludge. Iida et al. showed that purified Si sludge was possible to be utilized as a source material for Mg_2Si, that is, the Mg_2Si prepared using purified Si sludge has good thermoelectric properties [14]. Moreover, Isoda et al. reported that the *ZT* value of Sb-doped Mg_2Si is not significantly dependent on the purity of the Si source [15]. Thus, development of a simpler process is necessary to enhance the possibility of recycling Si sludge, which may lead to a reduction in production costs for Mg_2Si-based thermoelectric modules.

In the present study, the preparation process for Mg_2Si using Si sludge was developed, where we aimed to keep the process as simple as possible. Therefore, Si sludge without complicated pretreatment was used as a Si source for the preparation of Mg_2Si, and the liquid-solid phase reaction, which does not require precise temperature control, was adopted for the preparation of Mg_2Si [16,17]. The synthesized powders were sintered by the pulse-current sintering technique. The phase constitution was investigated by X-ray diffraction, and the thermoelectric properties of the sintered materials were measured. The obtained thermoelectric properties were discussed in comparison with the available data obtained using reagent Si.

2. Experimental

2.1. Properties of Si sludge

The Si sludge used in the present study was discharged during the

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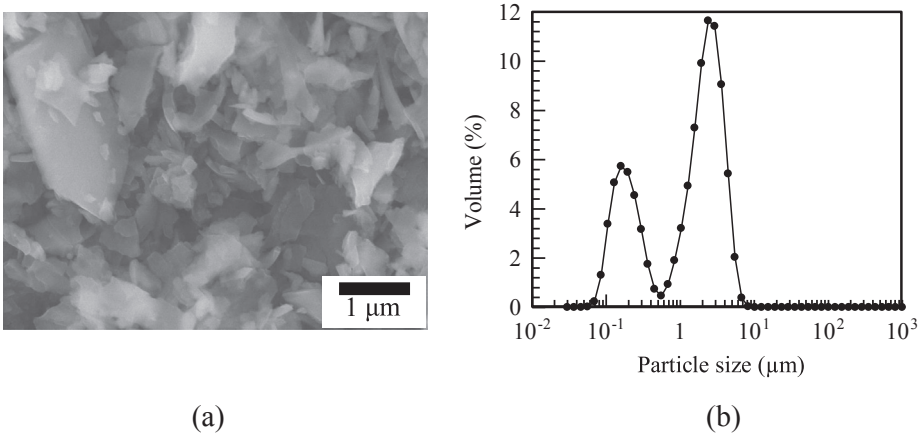


Fig. 1. (a) SEM image and (b) particle size distribution of typical dried Si sludge.

process of cutting n-type solar-grade silicon at Shinko manufacturing Co., Ltd., Tsuyama Factory (Tsuyama, Okayama, Japan). Si sludge is a mud-like substance with approximately 50 mass% moisture content. We used two types of Si sludge as a Si source for Mg_2Si, as follows.

1. The as-discharged Si sludge was dried at 100 °C for 3 h in air without any processing (unwashed Si sludge);
2. The as-discharged Si sludge was washed using water-based agent before drying at 100 °C for 3 h in air (washed Si sludge).

Before the drying process, approximately 200,000 mg/L of organic carbon was included in the unwashed Si sludge. This organic carbon was reduced to 1100 mg/L through the washing process. The main impurities in the dried unwashed powder were nickel (570 ppm), iron (250 ppm), and potassium (130 ppm). These impurities were also reduced by the washing process, to nickel (50 ppm), iron (35 ppm), and potassium (70 ppm).

Fig. 1 shows (a) an SEM image and (b) particle size distribution, obtained by laser diffraction measurement, of typical dried Si sludge. The dried Si sludge was confirmed to be a fine powder with a particle size of 0.1–10 μm.

2.2. Synthesis of Mg_2Si

Mg powder (nominal purity > 99.5%, particle size < 180 μm) and unwashed and washed Si sludge were used as starting materials, and Sb (5N, < 150 μm) was selected as a donor dopant. They were weighed to be compositions of $Mg_xSi_{0.992}Sb_{0.008}$ (x = 2–1.6) and $Mg_{1.85}Si_{1-y}Sb_y$ (y = 0.008–0.04) under an Ar atmosphere. The mixture of starting materials was set into a graphite crucible. The synthesis of Mg_2Si was performed by a liquid-solid phase reaction (LSPR) method. The graphite crucible was placed at the center of an infrared gold furnace and heated to 973 K in 5 min. After keeping this temperature for 60 min, the material was allowed to cool naturally to room temperature. The resulting powder was crushed using an agate mortar and sieved into particle sizes < 75 μm. The powder was sintered by the pulse-current sintering method at 1073 K, applying a uniaxial pressure of 60 MPa under vacuum. The sintered materials were 10 mm in diameter and 4 mm in thickness, and the density was greater than 98% of the theoretical density.

2.3. Measurements

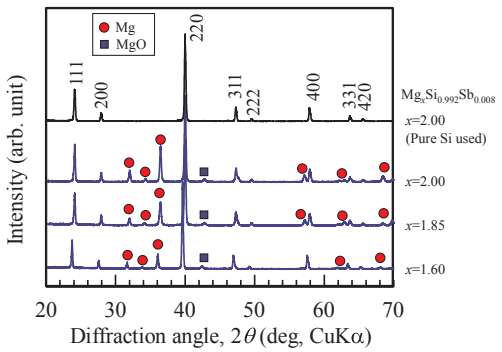
The phase constitution of LSPRed powder was identified by X-ray diffraction with CuKα radiation. The sintered samples were cut into dimensions of 7 mm × 7 mm × 1 mm for Hall coefficient measurements, 2 mm × 2 mm × 10 mm for Seebeck coefficient and electrical resistivity measurements, and 10 mmφ × 1 mm for thermal conductivity measurements. The Hall coefficient R_H was measured by the van der Pauw method (Resitest 8300, Toyo corp., Japan) at 300 K, and the carrier concentration was evaluated from the R_H as $p = 1/eR_H$, where e is the electronic charge. The electrical resistivity and Seebeck coefficient were measured using a standard four-probe method and a steady-state temperature gradient of 2–5 K, respectively, with a ZEM-3 (Advance Riko Co., Japan) at temperatures ranging from room temperature to 873 K under low-pressure He gas. The thermal diffusivity D and specific heat C_p were measured using a laser-flash method (LFA 457, NETZCH, Germany). The thermal conductivity κ was calculated using $\kappa = DC_pd$, where d is the density of the sample.

3. Result and discussion

3.1. Structures

Fig. 2 shows XRD patterns of as-LSPRed powders of $Mg_xSi_{0.992}Sb_{0.008}$ prepared from unwashed Si sludge. A strong metallic Mg phase existed, as well as a Mg_2Si phase with a nominal composition of x = 2. This Mg phase could be reduced by decreasing the Mg content from x = 2 to 1.6. However, even when the Mg composition was decreased to 1.6, it was not possible to completely eliminate the Mg phase. This result means that the single-phase preparation of Mg_2Si is difficult when unwashed Si sludge is used. In addition to the Mg phase, a weak MgO phase was also confirmed. The MgO phase was considered to originate from the SiO_2 in the Si sludge.

Fig. 3 shows XRD patterns of as-LSPRed powders of $Mg_xSi_{0.992}Sb_{0.008}$ prepared from washed Si sludge. The Mg phase was remarkably reduced with a nominal composition of x = 2. The Mg phase for x = 1.85 almost disappeared, although a small MgO phase



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