Research Article

Solid-State Synthesis and Thermoelectric Properties of Mg$_{2+x}$Si$_{0.7}$Sn$_{0.3}$Sb$_m$

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Mg$_{2+x}$Si$_{0.7}$Sn$_{0.3}$Sb$_m$ (0 ≤ x ≤ 0.2, m = 0 or 0.01) solid solutions have been successfully prepared by mechanical alloying and hot pressing as a solid-state synthesis route. All specimens were identified as phases with antifluorite structure and showed n-type conduction. The electrical conductivity of Mg-excess solid solutions was enhanced due to increased electron concentrations. The absolute values of the Seebeck coefficient varied substantially with Sb doping and excess Mg, which was attributed to the change in carrier concentration. The onset temperature of bipolar conduction was shifted higher with Sb doping and excess Mg. The lowest thermal conductivity of 1.3 W/mK was obtained for Mg$_{2.2}$Si$_{0.7}$Sn$_{0.3}$Sb$_{0.01}$. A maximum $ZT$ of 0.64 was achieved at 723 K for Mg$_{2.2}$Si$_{0.7}$Sn$_{0.3}$Sb$_{0.01}$.

1. Introduction

A thermoelectric generator that converts heat energy directly into electricity offers several benefits, including moderate efficiency, simple device structure, and no moving parts [1, 2]. Thermoelectric materials for high energy conversion efficiency should have a large figure-of-merit value ($ZT = \alpha^2\sigma T/\kappa$), that is, a large Seebeck coefficient ($\alpha$), high electrical conductivity ($\sigma$), and low thermal conductivity ($\kappa$). However, for a given material, these parameters are not independent, because they are closely related to carrier concentration and effective mass. Consequently, thermoelectric materials with a high $ZT$ value should have low lattice thermal conductivity and high carrier mobility with optimum carrier concentration [3, 4].

Magnesium compounds Mg$_2$X (X = Si, Ge, Sn) and their solid solutions have attracted increasing attention as promising thermoelectric materials at temperatures ranging from 500 to 800 K, because they are nontoxic, environmentally friendly, and abundant [5, 6]. In general, the thermal conductivity can be significantly reduced by phonon scattering of point defects as seen solid solutions, which make the low-frequency phonons decrease the thermal conductivity. Among the various solid-solution Mg$_2$X systems, it is expected that higher $ZT$ can be obtained with Mg$_2$Si$_{1-x}$Sn$_x$, because of the greater difference in atomic mass between Si and Sn [7, 8].

The content of Mg and Sb has a significant impact on the electron concentration and thermoelectric properties of n-type Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions [9, 10]. The $ZT$ values of Mg$_2$Si$_{1-x}$Sn$_x$ solid solutions can be enhanced through excess Mg and/or Sb doping. In order to reduce the changes in composition due to the volatilization and oxidation caused by Mg, Mg$_{2+x}$Si$_{0.7}$Sn$_{0.3}$Sb$_m$ solid solutions with controlled Mg contents were synthesized by mechanical alloying and hot pressing as a solid-state route.
2. Experimental Procedure

Mg$_{2+x}$Si$_{0.7}$Sn$_{0.3}$Sb$_m$ (0 ≤ x ≤ 0.2, m = 0 or 0.01) solid solutions were synthesized by mechanical alloying (MA) and consolidated by high pressing (HP). High-purity Mg (99.99%, <149 μm) with an excess of 0–10 mol%, Si (99.99%, <45 μm), Sn (99.999%, <75 μm), and Sb (99.999%, <75 μm) were weighed. The powders were mixed and loaded with hardened steel balls (5 mm in diameter) into a hardened steel vial in an argon atmosphere at a weight ratio of 1: 20. The vial was then loaded into a planetary ball mill (Fritsch, Pulversette 5) and mechanically alloyed at 300 rpm for 24 h. The synthesized powders were hot-pressed in a cylindrical graphite die with an internal diameter of 10 mm at temperatures ranging from 873 K to 1073 K under a pressure of 70 MPa for 2 h in a vacuum.

The phases and lattice constants of the synthesized solid solutions were analyzed by an X-ray diffractometer (XRD, Bruker D8 Advance) using Cu K$_\alpha$ radiation (2θ: 10–90°). The Hall coefficient measurements were performed in a constant magnetic field (1 T) and electric current (50 mA) using the van der Pauw method at room temperature. The Seebeck coefficient and electrical conductivity were measured using the temperature differential and 4-probe methods, respectively, with ZEM-3 equipment (Ulvac-Riko) in a helium atmosphere. The thermal conductivity was estimated from measurements of the thermal diffusivity, specific heat, and density, which were obtained using a laser flash TC-9000H system (Ulvac-Riko) in a vacuum. The thermoelectric figure of merit was evaluated from 323 K to 823 K.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns for solid-state synthesized Mg$_{2+x}$Si$_{0.7}$Sn$_{0.3}$Sb$_m$ solid solutions. All specimens were identified as phases with antifluorite structure. The patterns of solid solutions correspond with all the peaks located between pure Mg$_2$Si and Mg$_2$Sn, but in the equilibrium phase diagram of the Mg$_2$Si-Mg$_2$Sn pseudobinary system, the Mg$_2$Si$_{1-x}$Sn$_x$ has an immiscibility gap in the range of x = 0.4–0.6 [11] or x = 0.2–0.7 [12], and the Sn-rich phase coexists with the Si-rich phase in this composition range. In this study, the Si-rich phases were observed, but secondary phases were not found.

Table 1 lists the electronic transport properties of Mg$_{2+x}$Si$_{0.7}$Sn$_{0.3}$Sb$_m$ at room temperature. All specimens showed n-type conduction, and the carrier concentration of Mg$_2$Si$_{0.7}$Sn$_{0.3}$ was approximately $7.4 \times 10^{16}$ cm$^{-3}$, which was increased to $1.8 \times 10^{19}$ cm$^{-3}$ by excess Mg and Sb doping. The Sb successfully acted as a donor, and the excess Mg donated electrons. However, the carrier mobility was reduced by excess Mg and Sb doping, which was attributed to ionized impurity scattering.

Figure 2 shows the temperature dependence of the electrical conductivity for Mg$_{2+x}$Si$_{0.7}$Sn$_{0.3}$Sb$_m$. The electrical conductivity increased with increasing temperature, indicating nondegenerate semiconducting behavior. For the excess Mg and Sb-doped specimens, the electrical conductivity increased at specific temperature due to an increase in carrier concentration compared to Mg$_2$Si$_{0.7}$Sn$_{0.3}$, as shown in Table 1. As a result, the electrical conductivity of the Mg-excess solid solutions was enhanced.

Figure 3 presents the temperature dependence of the Seebeck coefficient for Mg$_{2+x}$Si$_{0.7}$Sn$_{0.3}$Sb$_m$. The Seebeck coefficient had a negative sign at all temperature ranges, which was in good agreement with the Hall coefficient. The absolute values of the Seebeck coefficient varied considerably with Sb doping and excess Mg, which was attributed to the changes in carrier concentration. The onset temperature of bipolar conduction was increased with Sb doping and excess Mg. According to the formula $|\alpha| = r - cm$, where $|\alpha|$ is the absolute value of the Seebeck coefficient, $r$ is the scattering parameter, $c$ is the constant, and $n$ is the carrier concentration [12], $|\alpha|$ became smaller because $n$ was increased by Sb doping and excess Mg.

Figure 4 shows the temperature dependence of the power factor (PF) for Mg$_{2+x}$Si$_{0.7}$Sn$_{0.3}$Sb$_m$. The power factor was calculated by $PF = \alpha^2 \sigma$ from the Seebeck coefficient ($\alpha$) and electrical conductivity ($\sigma$). PF increased with increasing temperature and by Sb doping and excess Mg. Compared with Mg$_2$Si$_{0.7}$Sn$_{0.3}$Sb$_{0.01}$, the PF value of specimens with excess Mg was improved by a factor of 3 to 4. The highest PF was 1.46 mW/mK$^2$ at 723 K for Mg$_{2.2}$Si$_{0.7}$Sn$_{0.3}$Sb$_{0.01}$.
Figure 2: Temperature dependence of the electrical conductivity for \( \text{Mg}_2\text{Si}_{0.7}\text{Sn}_{0.3}\text{Sb}_{0.01} \).

Figure 3: Temperature dependence of the Seebeck coefficient for \( \text{Mg}_2\text{Si}_{0.7}\text{Sn}_{0.3}\text{Sb}_{0.01} \).

Figure 4: Temperature dependence of the power factor for \( \text{Mg}_2\text{Si}_{0.7}\text{Sn}_{0.3}\text{Sb}_{0.01} \).

Figure 5: Temperature dependence of the thermal conductivity for \( \text{Mg}_2\text{Si}_{0.7}\text{Sn}_{0.3}\text{Sb}_{0.01} \).

Figure 6: Temperature dependence of the figure of merit (\( ZT \)) for \( \text{Mg}_2\text{Si}_{0.7}\text{Sn}_{0.3}\text{Sb}_{0.01} \). The \( ZT \) values of the undoped specimen were very low, with values less than 0.05 at all temperatures examined. However, the \( ZT \) was remarkably increased by Sb doping and excess Mg, mainly due to the increase in power factor. A maximum \( ZT \) of 0.64 was achieved at 723 K for \( \text{Mg}_{2.2}\text{Si}_{0.7}\text{Sn}_{0.3}\text{Sb}_{0.01} \). The \( ZT \) values of \( x = 0.1 \) and \( x = 0.2 \) were nearly the same, which makes \( x = 0.1 \) a sufficient amount of excess Mg to improve the thermoelectric properties.
4. Conclusions

Mg$_{2+x}$Si$_{0.7}$Sn$_{0.3}$Sb$_m$ ($0 \leq x \leq 0.2, m = 0$ or $0.01$) solid solutions were successfully prepared by mechanical alloying and hot pressing. All specimens showed n-type conduction, and the carrier concentration effectively increased from $7.4 \times 10^{18}$ cm$^{-3}$ to $1.8 \times 10^{19}$ cm$^{-3}$ by Sb doping and excess Mg. As a result, the electrical conductivity increased remarkably. The temperature dependencies of the Seebeck coefficient and the thermal conductivity were varied by Sb doping and excess Mg, which increased the onset temperature of bipolar conduction. A maximum $ZT$ of $0.64$ was achieved at $723$ K for Mg$_{2.2}$Si$_{0.7}$Sn$_{0.3}$Sb$_{0.01}$ with excess Mg.

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