Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2013, Article ID 815925, 4 pages
http://dx.doi.org/10.1155/2013/815925

Research Article

Solid-State Synthesis and Thermoelectric Properties of $Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$

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Received 29 May 2013; Revised 1 August 2013; Accepted 7 August 2013

Academic Editor: Hyung-Ho Park

$Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$ ($0 \leq x \leq 0.2$, $m = 0$ 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 $Mg_2Si_{0.7}Sn_{0.3}Sb_{0.01}$. 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 (α), high electrical conductivity (σ), and low thermal conductivity (κ). 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_2X ($X = Si, Ge, Sn$) 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_2X systems, it is expected that higher ZT can be obtained with $Mg_2Si_{1-x}Sn_x$, 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 $Mg_2Si_{1-x}Sn_x$ solid solutions [9, 10]. The ZT values of $Mg_2Si_{1-x}Sn_x$ 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

$Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$ ($0 \leq x \leq 0.2$, $m = 0$ or 0.01) solid solutions were synthesized by mechanical alloying (MA) and consolidated by hot 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, Pulverisette 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_α 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.

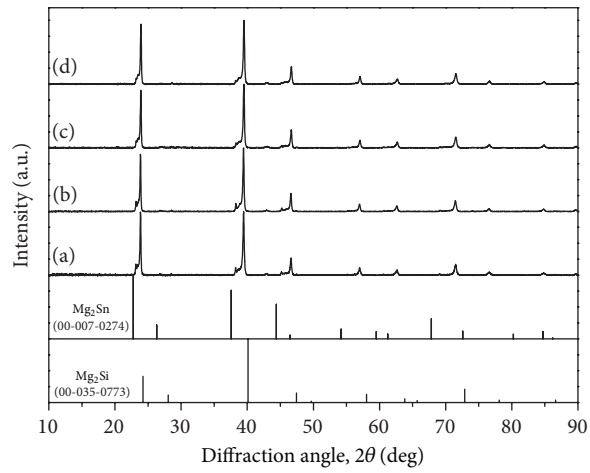

Figure 1: X-ray diffraction patterns for $Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$ solid solutions: (a) $Mg_2Si_{0.7}Sn_{0.3}$, (b) $Mg_2Si_{0.7}Sn_{0.3}Sb_{0.01}$, (c) $Mg_{2.1}Si_{0.7}Sn_{0.3}Sb_{0.01}$, and (d) $Mg_{2.2}Si_{0.7}Sn_{0.3}Sb_{0.01}$.

Table 1: Electronic transport properties of $Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$ at room temperature.

Specimen	Hall coefficient (cm^3/C)	Mobility (cm^2/Vs)	Carrier concentration (cm^{-3})
$Mg_2Si_{0.7}Sn_{0.3}$	−83.88	30.25	7.4×10^{16}
$Mg_2Si_{0.7}Sn_{0.3}Sb_{0.01}$	−4.30	9.44	1.4×10^{18}
$Mg_{2.1}Si_{0.7}Sn_{0.3}Sb_{0.01}$	−0.36	1.67×10^{-1}	1.8×10^{19}
$Mg_{2.2}Si_{0.7}Sn_{0.3}Sb_{0.01}$	−0.39	1.74×10^{-1}	1.5×10^{19}

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_2Si and Mg_2Sn, but in the equilibrium phase diagram of the Mg_2Si-Mg_2Sn pseudobinary system, the $Mg_2Si_{1-x}Sn_x$ 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 $Mg_2Si_{0.7}Sn_{0.3}$ was approximately 7.4×10^{16} cm^{-3}, which was increased to 1.8×10^{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 $Mg_2Si_{0.7}Sn_{0.3}$, 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 $|\alpha| = r - c\ln n$, 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 (α) and electrical conductivity (σ). PF increased with increasing temperature and by Sb doping and excess Mg. Compared with $Mg_2Si_{0.7}Sn_{0.3}Sb_{0.01}$, 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 $Mg_{2.2}Si_{0.7}Sn_{0.3}Sb_{0.01}$.

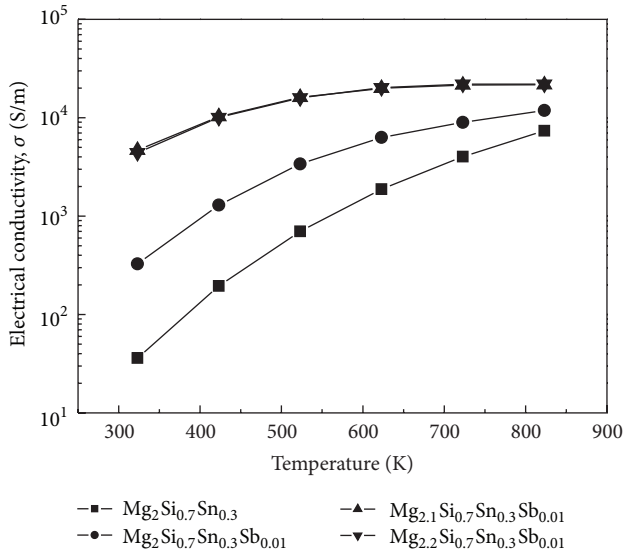

Figure 2: Temperature dependence of the electrical conductivity for $Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$.

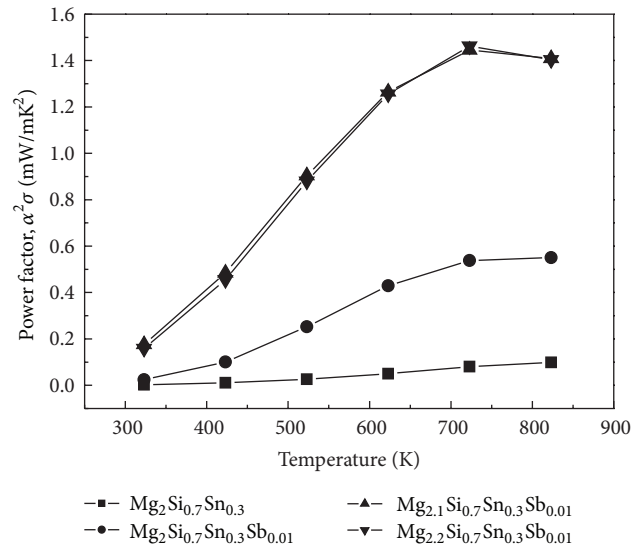

Figure 4: Temperature dependence of the power factor for $Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$.

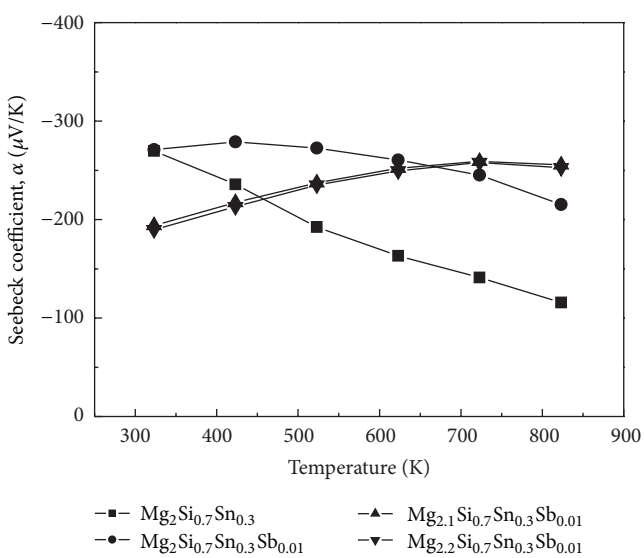

Figure 3: Temperature dependence of the Seebeck coefficient for $Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$.

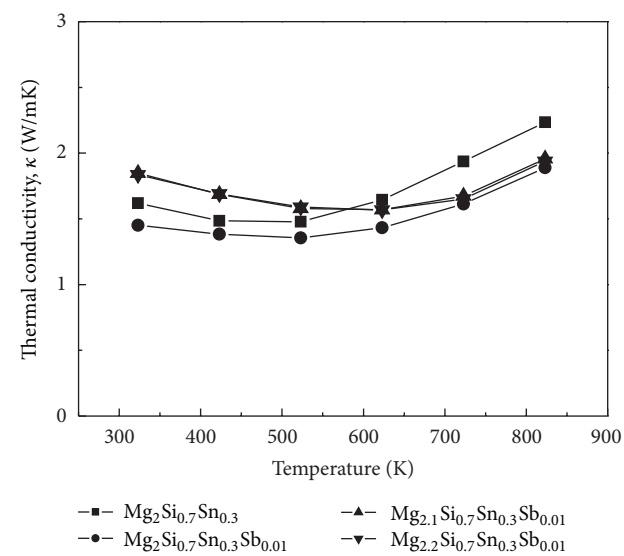

Figure 5: Temperature dependence of the thermal conductivity for $Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$.

Figure 5 presents the temperature dependence of the thermal conductivity of $Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$. The thermal conductivity was 1.3–2.2 W/mK in the temperature range of 323 K to 823 K. The thermal conductivity had a minimum value with increasing temperature. The increase in thermal conductivity at high temperatures was attributed to bipolar conduction by intrinsic excitation. Sb doping and excess Mg increased the onset temperature of bipolar conduction. $Mg_2Si_{0.7}Sn_{0.3}Sb_{0.01}$ had the lowest thermal conductivity of 1.3–1.9 W/mK at all temperatures. The lattice contribution to the thermal conductivity was dominant over the carrier contribution for $Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$ specimens because their thermal conduction behavior was inconsistent with the Wiedemann-Franz law [13].

Figure 6 shows the temperature dependence of the figure of merit (ZT) for $Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$. 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 $Mg_{2.2}Si_{0.7}Sn_{0.3}Sb_{0.01}$. 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.

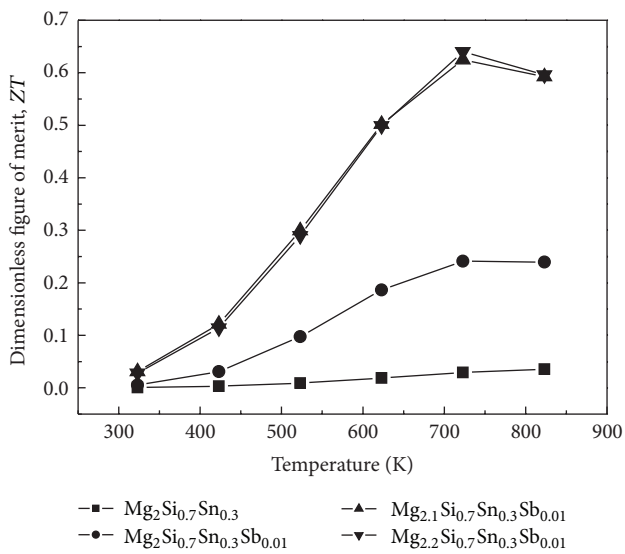

Figure 6: Dimensionless thermoelectric figure of merit for $Mg_{2+x}Si_{0.7}Sn_{0.3}Sb_m$.

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 $7.4 \times 10^{16}\,cm^{-3}$ 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.

Acknowledgments

This study was supported by the Fundamental R&D Program for Core Technology of Materials and by the Regional Innovation Center (RIC) Program, funded by the Ministry of Trade, Industry and Energy (MOTIE), Republic of Korea.

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