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Thermoelectric properties of Al-doped $Mg_2Si_{1-x}Sn_x$ ($x \leqq 0.1$)

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Abstract

The thermoelectric properties of Al-doped $Mg_2Si_{1-x}Sn_x$ ($x = 0.0$–0.1) [$Mg_2Si_{1-x}Sn_x$:Al = 1:y ($0.00 \leqq y \leqq 0.02$)] fabricated by spark plasma sintering have been characterized by Hall effect measurements at 300 K and by measurements of electrical resistivity (ρ), the Seebeck coefficient (S), and thermal conductivity (κ) between 300 and 900 K. Al-doped $Mg_2Si_{1-x}Sn_x$ samples are n-type in the measured temperature range. By Al-doping, electron concentration is controlled up to 5.3×10^{19} cm^{-3} in the composition range $0.0 \leqq x \leqq 0.1$. Al-doped $Mg_2Si_{0.9}Sn_{0.1}$ shows a maximum value of the figure of merit ZT of 0.68 at 864 K, which is 6 times larger than that of nondoped $Mg_2Si_{0.9}Sn_{0.1}$.

Keywords: Intermetallics; Thermoelectric materials; Electrical transport; Impurities in semiconductors

1. Introduction

Mg_2X (X = Si, Ge, and Sn) and their solid solutions have been considered as candidates for high-performance thermoelectric materials [1–11]. For thermoelectric materials, a large Seebeck coefficient, S, a small electrical resistivity, ρ, and a small thermal conductivity, κ, are required. These quantities determine the thermoelectric figure of merit, $Z = S^2/\rho\kappa$. A low lattice thermal conductivity and high carrier mobility are desirable for improvement of the figure of merit. Vining [12] pointed out that the factor $A' = (T/300)(m^*/m_e)^{3/2}\mu/\kappa_{ph}$, where m^* is the carrier effective mass, μ is the mobility in cm^2/(V s), and κ_{ph} is the lattice thermal conductivity in mW/(cm K), has a larger value of 3.7–14 for Mg_2X, when compared with 1.2–2.6 for SiGe and 0.05–0.8 for β-$FeSi_2$, and therefore, a Mg_2X system will achieve a higher ZT with further development. In the solid solutions of $Mg_2Si_{1-x}Ge_x$, $Mg_2Si_{1-x}Sn_x$, and $Mg_2Ge_{1-x}Sn_x$, it is pointed out that the lowest lattice thermal conductivity can be achieved in the system $Mg_2Si_{1-x}Sn_x$ due to the maximum atomic mass difference between the components [13]. Recently, Zaitsev et al. [5] reported the thermoelectric properties of Sb-doped $Mg_2Si_{1-x}Sn_x$ ($x = 0.4$ and 0.6), and the maximum value of ZT reaches 1.1, which exceeds the unity. Therefore, impurity-doped $Mg_2Si_{1-x}Sn_x$ is a promising thermoelectric material for cheap, ecologically friendly, light, and high-performance thermoelectric generators in the middle temperature range.

Kajikawa et al. [14] and Umemoto et al. [9] reported the thermoelectric properties of Mg_2Si fabricated by spark plasma sintering (SPS), which is a novel process because it is reported that the diffusion velocity becomes extremely large even at low temperatures owing to the pulse dc electric field. In the case of Mg_2Si, SPS plays two roles: (a) a solid-state reaction process between Mg and Si; (b) a densification process in a short time at relatively low temperatures, which is effective in suppressing the volatilization of Mg as well as dopants with low melting point. Al is expected to be one of the attractive dopants because of its cheap and nontoxic element. Umemoto et al. [9] reported that ZT of Al-doped Mg_2Si shows 0.57 at 856 K. However, to our knowledge, there have been no reports concerning the effect of Sn substitution on the thermoelectric properties of Al-doped Mg_2Si. A small amount of Sn substitution will affect the transport and thermoelectric properties of Al-doped Mg_2Si.

In the present study, we have fabricated Al-doped $Mg_2Si_{1-x}Sn_x$ ($x \leqq 0.1$) by the SPS method, and the transport and thermoelectric properties have been characterized by Hall effect measurements at 300 K and by measurements of electrical resistivity, the Seebeck coefficient, and thermal conductivity between 300 and 900 K.

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2. Experimental method and details of the calculations

Powders of high purity, Mg (>99.9%), Si (>99.999%), Sn (>99.9%), and Al (>99.9%), were used as starting materials. Constituent Mg, Si, Sn, and Al powders were ground together and then heated at 993–1053 K for 10 min at 20 MPa in a graphite die (15 mm in diameter) in vacuum (<4 Pa) by the SPS method with a heating rate of 30–50 K/min. The density of the annealed samples was more than 99% of the theoretical value. X-ray diffraction of the samples by Cu Kα radiation detected only the antifluorite structure. The Hall coefficient (R_H) was measured for 1.5-cm-diameter, 0.1-cm-thick samples using the Toyo Corp. Resitest 8320. Contacts between the samples and lead Au wires were formed by soldering with indium. The Hall effect was measured at 300 K using an ac magnetic method under an applied magnetic field of 0.39 T at a frequency of 200 mHz. The carrier concentration (n) of the samples was determined by the factor $1/e|R_H|$. The error for the Hall coefficient was estimated to be less than ±7%. The Seebeck coefficient (S) was measured by the standard technique using Pt electrodes in a He gas atmosphere in the temperature range of 300–900 K using an ULVAC ZEM-1S. The temperature gradient across the length of the sample was about 5 K. The error of the Seebeck coefficient measurements was estimated to be less than ±5%. The electrical resistivity (ρ) was also measured concurrently by the four-probe dc method. The error of the electrical resistivity measurements was estimated to be less than ±5%. The thermal diffusion coefficients of the samples were measured by the conventional laser flash method using a thermal constant analyzer (ULVAC TC-7000). The disk specimen was set in an electric furnace and heated to 900 K under vacuum. After the temperature was stabilized, the front surface of the specimen was irradiated by a ruby laser pulse. The temperature variation at the surface was monitored using a Pt–Pt 13% Rh thermocouple and an InSb infrared detector. The error of the thermal diffusion coefficients measurements was estimated to be less than ±5%. The density was measured by the Archimedes method. The thermal conductivity (κ) was calculated from the experimental thermal diffusivity (α), density (d), molecular weight (M_w) calculated from the chemical formula ($Mg_2Si_{1-x}Sn_x$), and a previously reported molar specific heat capacity (C_p) for nondoped Mg_2Si [15]. κ is given by the following Eq. (1):

$$\kappa = \frac{\alpha \times d \times C_p}{M_w} \quad (1)$$

To investigate the electronic and geometrical structure of Al-doped Mg_2Si, density functional theory (DFT) calculations within the pseudopotential and generalized gradient approximations (GGAs) were performed using the computer program CASTEP (Cambridge Serial Total Energy Package in Material Modeling, Accelrys) [16]. We constructed a supercell containing 48 atoms ($Mg_{32}Si_{16}$) with the space group $Fm\bar{3}m$ and replaced one of the 48 sites of the Mg or Si atoms by Al. We expanded the valence electronic wave functions in a plane-wave basis set up to an energy cutoff of 400 eV, which converges the total energy of the unit cell to better than 1 meV/atom. In the total energy calculations, integrations over the Brillouin zone were performed using a 3 × 2 × 2 Monkhorst-Pack set [17], which gives six symmetrized k points in the irreducible Brillouin zone for the 48-atom unit cell. The electron–ion interaction is described using Vanderbilt's ultrasoft pseudopotentials [18]. The lattice constant was determined through calculations for the primitive cell, using a plane-wave cutoff energy of 400 eV; the calculated value is 99.9% of the experimental value reported for Mg_2Si [19]. The positions of the atoms within the second-nearest neighbors of the impurity were allowed to relax under a constant volume condition by total energy minimization, until the residual forces for the relaxed atoms were <0.1 eV/Å.

3. Results and discussion

Table 1 lists the transport properties of Al-doped $Mg_2Si_{1-x}Sn_x$ ($x = 0.0$–0.1) at 300 K, compared with those of $Mg_2Si_{1-x}Sn_x$ without Al-doping. R_H for Al-doped $Mg_2Si_{1-x}Sn_x$ is negative, indicating that the conductivity is mainly due to electrons. The Hall mobility ($\mu_H = R_H/\rho$) at 300 K of Al-doped Mg_2Si (163 $cm^2/(V\,s)$) is lower than the value for nondoped Mg_2Si (204 $cm^2/(V\,s)$). μ_H of Al-doped or nondoped $Mg_2Si_{1-x}Sn_x$ ($x = 0.05$–0.1) shows 101–116 $cm^2/(V\,s)$, which is lower than that of Al-doped or nondoped Mg_2Si. The carrier concentration of $Mg_2Si_{1-x}Sn_x$ without Al-doping is from 4.3×10^{17} cm^{-3} for $x = 0.0$ to 3.7×10^{18} cm^{-3} for $x = 0.05$, while that of Al-doped $Mg_2Si_{1-x}Sn_x$ [$Mg_2Si_{1-x}Sn_x$:Al = 1:y ($0.005 \leqq y \leqq 0.02$)] is from 2.0×10^{19} cm^{-3} for $y = 0.0005$ to 5.3×10^{19} cm^{-3} for $y = 0.02$. The carrier concentration of Al-doped $Mg_2Si_{1-x}Sn_x$ is controlled up to 5.3×10^{19} cm^{-3} by Al-doping, but x does not affect the maximum carrier concentration.

Fig. 1 shows the temperature dependence of the electrical resistivity (ρ) of Al-doped $Mg_2Si_{1-x}Sn_x$ ($x = 0.0$–0.1), compared with those of $Mg_2Si_{1-x}Sn_x$ without Al-doping. ρ for Al-doped $Mg_2Si_{1-x}Sn_x$ ($x = 0.0$–0.1) as well as $Mg_2Si_{1-x}Sn_x$ without Al-doping increases, reaching a maximum at 470–670 K, and then decreases or shows a constant with increasing temperature. LaBotz et al. [1] and Noda et al. [4] reported that the temperature dependence of mobility in $Mg_2Si_xGe_{1-x}$ indicates that $\mu \propto T^{-3/2}$ and that acoustic lattice scattering is the predominant mechanism. Therefore, the increase in ρ at low temperatures is explained by the decrease in mobility with increasing temperature. The decrease in ρ at high temperatures is explained by the fact that intrinsic conduction occurs because of the band gap of ~0.7 eV [20–22].

Although the experimental results showing the n-type conduction of Al-doped Mg_2Si suggest that Al atoms (IIIb group) are primarily located at the Mg sites (IIa group) in Mg_2Si and that Al atoms act as donors. However, Imai et al. [23] reported that it is energetically favorable that doped Al atoms in Mg_2Si would substitute Si atoms rather than Mg atoms from first-principles

Table 1
Transport properties of Al-doped $Mg_2Si_{1-x}Sn_x$ ($x = 0.0$–0.1) [$Mg_2Si_{1-x}Sn_x$:Al = 1:y ($0.005 \leqq y \leqq 0.02$)], compared with those of $Mg_2Si_{1-x}Sn_x$ without Al-doping at 300 K

Sample number	Sn (x)	Al (y)	Carrier type	Carrier concentration (cm^{-3})	Mobility [$cm^2/(V\,s)$]	Resistivity (Ω cm)
#1	0.00	0.000	N	4.3×10^{17}	204	7.14×10^{-2}
#2	0.05	0.000	N	3.7×10^{18}	107	1.57×10^{-2}
#3	0.10	0.000	N	2.9×10^{18}	106	2.02×10^{-2}
#4	0.00	0.005	N	5.3×10^{19}	163	7.18×10^{-4}
#5	0.05	0.005	N	3.6×10^{19}	116	1.50×10^{-3}
#6	0.05	0.020	N	5.3×10^{19}	105	1.14×10^{-3}
#7	0.10	0.005	N	2.0×10^{19}	114	2.73×10^{-3}
#8	0.10	0.010	N	4.6×10^{19}	112	1.21×10^{-3}
#9	0.10	0.020	N	5.3×10^{19}	101	1.17×10^{-3}