

Synthesis and Thermoelectric Properties of *n*-Type Mg₂Si

Jae-Yong Jung and Il-Ho Kim*

Department of Materials Science and Engineering / Research Center for Sustainable Eco-devices and Materials,
Chungju National University, Chungbuk 380-702, Korea

Group B^V(Bi, Sb)- and B^{VI}(Te, Se)-doped Mg₂Si compounds were synthesized by solid state reaction and mechanical alloying. Electronic transport properties (Hall coefficient, carrier concentration and mobility) and thermoelectric properties (Seebeck coefficient, electrical conductivity, thermal conductivity and figure-of-merit) were examined. Mg₂Si powder was synthesized successfully by solid state reaction at 773 K for 6 h and doped by mechanical alloying for 24 h. Powder was fully consolidated by hot pressing at 1073 K for 1 h. All doped Mg₂Si compounds showed *n*-type conduction, indicating that the electrical conduction is due mainly to electrons. The electrical conductivity increased greatly by doping due to an increase in the carrier concentration. However, the thermal conductivity did not change significantly by doping, which was due to the much larger contribution of the lattice thermal conductivity over the electronic thermal conductivity. Group B^V(Bi, Sb) elements were much more effective at enhancing the thermoelectric properties of Mg₂Si than group B^{VI}(Te, Se) elements.

Keywords: thermoelectric, Mg₂Si, mechanical alloying, solid state reaction, hot pressing.

1. INTRODUCTION

A thermoelectric solid-state power generator that converts heat energy directly into electricity offers several benefits, including moderate efficiency, simple device structure and no moving parts.^[1] In 1961, Nikitin *et al.*^[2] showed that the compounds Mg₂B^{IV} (B^{IV} = Si, Ge and Sn) have a favorable complex of physical and chemical properties and could be a good base for the development of new efficient thermoelectrics. Since these compounds possess properties that are similar to those of the group B^{IV} elemental semiconductors^[3], they have been recognized as good candidates for thermoelectric applications.^[4] Mg₂Si with an antifluorite structure is a narrow-band-gap semiconductor with an indirect band gap of 0.77 eV; it has been recognized as a promising material for thermoelectric energy conversion at temperatures ranging from 500 to 800 K.^[5-9] Compared with other thermoelectric materials operating in the same conversion temperature range, such as PbTe and CoSb₃, important aspects of Mg₂Si include that it has been identified as an environmentally-friendly material (non-toxic), and that its constituent elements are abundant in the earth's crust.^[10-12] Vining^[13] pointed out that the material factor $A = (T/300)(m^*/m_e)^{3/2}\mu/k_L$ of Mg₂B^{IV} (3.7-14) is larger than that of SiGe (1.2-2.6) and FeSi₂ (0.05-0.8), where m^* is the carrier effective mass, μ is the mobility in cm²/Vs, k_L is the lattice thermal conductivity

in mW/cmK and T is the temperature in Kelvin. Therefore, the Mg₂B^{IV} system will attain a higher ZT (dimensionless figure of merit) with further development.

There have been some attempts to dope additives into Mg₂Si to control its semiconducting properties. The *p*-type Mg₂Si can be produced by doping with Ag and Cu, and the *n*-type by doping with Sb and Al.^[2,6,14-16] Tani and Kido^[17] suggested from the first-principle calculation that the group B^I, B^{III}, and B^V elements are expected to be primarily located at Si sites in Mg₂Si and could be used as donors for Mg₂Si. Mg₂Si and its solid solutions have been synthesized by various methods: induction melting,^[18] vertical Bridgman growth,^[19] spark plasma sintering,^[20] and mechanical alloying.^[21] However, it is very difficult to prepare Mg₂Si by a melting process due to the large difference in vapor pressures of the constituent elements and lack of solubility. Furthermore, there is a small difference between the boiling temperature of Mg (1380 K) and the melting temperature of Mg₂Si (1358 K),^[15] therefore, it is difficult to control its composition, mainly due to volatilization and oxidation of Mg. In this study, Mg₂Si was synthesized by solid state reaction and doped by mechanical alloying. The thermoelectric and electronic transport properties were examined for group B^V(Bi, Sb)- and B^{VI}(Te, Se)-doped Mg₂Si compounds.

2. EXPERIMENTAL PROCEDURE

High purity Mg powder (< 149 μ m, purity 99.99%) and Si powder (< 45 μ m, purity 99.99%) were weighed at an atomic

*Corresponding author: ihkim@cjnu.ac.kr

ratio of 2:1 and mixed homogeneously. The mixed powders were cold-pressed under a pressure of 600 MPa to make pellets, which were reacted (transformed) in solid state in an alumina crucible with a cover at 773 K for 6 h in a vacuum. The solid-state-reacted (SSRed) Mg_2Si pellets, dopant powders and hardened steel balls (diameter of 5 mm) were loaded at a weight ratio of 20 into a hardened steel vial in an argon atmosphere. The doping was done in an attempt to produce n-type $Mg_2Si:X_m$ ($m = 0$ to 0.03), where X was used as a dopant such as Bi ($< 75 \mu m$, purity 99.999%), Sb ($< 75 \mu m$, purity 99.999%), Te ($< 75 \mu m$, purity 99.999%) and Se ($< 75 \mu m$, purity 99.999%). The vial was then loaded into a planetary ball mill (Fritsch, Pulverisette 5) and mechanical alloyed (MAed) at 300 rpm for 24 h. These synthesized powders were hot-pressed (HPed) in a cylindrical graphite die with an internal diameter of 10 mm at 1073 K under a pressure of 70 MPa for 1 h in a vacuum.

The phase analysis was performed by X-ray diffraction (XRD: Bruker D8 Advance) using $Cu K\alpha$ radiation (40 kV, 40 mA). Diffraction patterns were measured in the θ -2 θ mode (10 to 90 degrees) with a step size of 0.02 degree, a scan speed of 0.2 degree/minute and a wavelength of 1.5405 Å. The HPed compact was cut into a rectangular shape with dimensions of 3 mm \times 3 mm \times 9 mm for both the Seebeck coefficient and the electrical conductivity measurements, and cut into a disc shape with dimensions of 10 mm (diameter) \times 1 mm (thickness) for the thermal conductivity and Hall effect measurements. The Hall effect measurements were carried out in a constant magnetic field (1 T) and electric current (50 mA) with a Keithley 7065 system at room temperature. The Seebeck coefficient and electrical conductivity were measured using the temperature differential and 4-probe methods, respectively, with Ulvac-Riko ZEM2-M8 equipment in a helium atmosphere. The thermal conductivity was estimated from the thermal diffusivity, specific heat and density measurements using laser flash Ulvac-Riko TC7000 system in a vacuum. The thermoelectric figure-of-merit was evaluated from 323 K to 823 K.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for the SSR-MA-HPed $Mg_2Si:X_m$ compounds. For Mg_2Si , as shown in Fig. 1(a), the diffraction peaks for Mg and Si elements were not demonstrated and only reflections for Mg_2Si compounds occurred. The SSR at 773 K for 6 h was enough to react elemental Mg with Si in order to transform those materials into Mg_2Si compound. After MA for 24 h and HP at 1073 K for 1 h, Mg_2Si phase was maintained, which means that the SSR-MA-HPed Mg_2Si compound was thermodynamically stable below 1073 K. Bi and Sb were doped so well to Mg_2Si that there were no secondary phases, but Te and Se produced MgTe and MgSe phases when the doping content (m) was

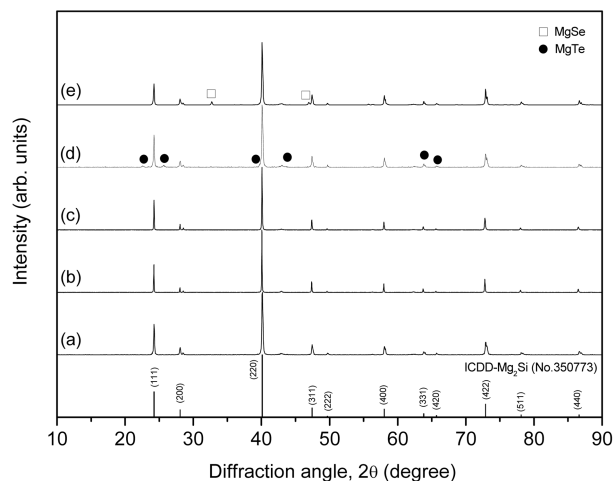


Fig. 1. X-ray diffraction patterns for solid-state-reacted, mechanically-alloyed and hot-pressed (a) Mg_2Si , (b) $Mg_2Si:Bi_{0.02}$, (c) $Mg_2Si:Sb_{0.03}$, (d) $Mg_2Si:Te_{0.03}$ and (e) $Mg_2Si:Se_{0.02}$.

larger than 0.02 and 0.01, respectively, which means that they were beyond the solubility limits.

Table 1 lists the electronic transport properties of intrinsic Mg_2Si and doped $Mg_2Si:X_m$ at room temperature. The sign of the Hall coefficient was negative, indicating that the electrical conduction was due mainly to electrons and that every dopant acted as a donor. The carrier concentration of intrinsic Mg_2Si was as low as $3.0 \times 10^{16} \text{ cm}^{-3}$ but it could be increased to 10^{17} - 10^{20} cm^{-3} by doping. The group B^V(Bi, Sb) elements were much more effective at generating the electrons in Mg_2Si than the group B^{VI}(Te, Se) elements, which was related to the solubility limits. MgTe and MgSe phases could be partially attributed to a carrier concentration increase, but that possibility is low because MgTe and MgSe have much higher band gap energy values of 3.5 eV^[22] and 4.05 eV^[23] than the 0.77 eV of Mg_2Si ^[6] at room temperature. Even though the carrier concentration of Mg_2Si increased from 10^{16} to 10^{17} - 10^{18} cm^{-3} by Se or Te doping, further increases did not materialize, possibly due to the solubility limits. The carrier mobility was reduced from around $10^2 \text{ cm}^2/\text{Vs}$ to several or several tens of cm^2/Vs by doping, and that decrease resulted from the ionized impurity scattering between carriers.

Figure 2 presents the changes in the electrical conductivity (σ) of n-type $Mg_2Si:X_m$ with temperature. The electrical conductivity of intrinsic Mg_2Si increased greatly with an increase in the temperature, which means that the compound behaves like a non-degenerate semiconductor. An increase in the electrical conductivity at high temperatures resulted from the intrinsic conduction due to the band gap of 0.77 eV.^[6,24] As compared with that of intrinsic Mg_2Si , the electrical conductivity of the group B^V(Bi, Sb)-doped Mg_2Si increased dramatically at fixed temperature, and it increased as the Bi and Sb content increased. However, the group

Table 1. Electronic transport properties of n-type Mg₂Si:X_m at room temperature

Dopant (X)	Doping content (m)	Hall coefficient (cm ³ /C)	Carrier mobility (cm ² /Vs)	Carrier concentration (cm ⁻³)
Intrinsic	0	-210.6	104.2	2.96×10 ¹⁶
Bi	0.005	-1.92	73.4	3.26×10 ¹⁸
	0.01	-0.04	2.7	1.57×10 ²⁰
	0.02	-0.026	2.8	2.40×10 ²⁰
	0.03	-0.024	3.6	2.56×10 ²⁰
Sb	0.001	-0.874	21.2	7.14×10 ¹⁸
	0.003	-0.056	3.1	1.12×10 ²⁰
	0.005	-0.052	2.6	1.20×10 ²⁰
	0.01	-0.031	3.8	2.01×10 ²⁰
	0.02	-0.026	4.2	2.37×10 ²⁰
	0.03	-0.017	4.3	3.76×10 ²⁰
Te	0.01	-92.56	26.1	6.74×10 ¹⁶
	0.02	-84.72	32.3	7.37×10 ¹⁶
	0.03	-1.95	9.6	3.20×10 ¹⁸
	0.05	-2.81	13.7	2.22×10 ¹⁸
Se	0.005	-60.01	4.1	1.04×10 ¹⁷
	0.01	-21.35	2.2	2.92×10 ¹⁷
	0.02	-39.14	2.5	1.59×10 ¹⁷
	0.03	-32.46	4.2	1.92×10 ¹⁷

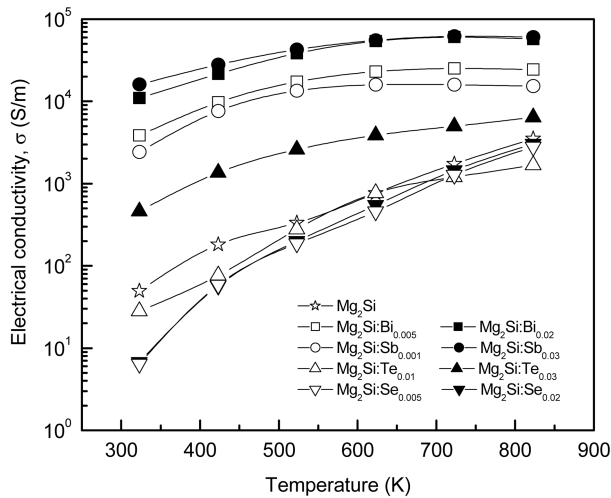


Fig. 2. Changes in the electrical conductivity of n-type Mg₂Si:X_m with temperature.

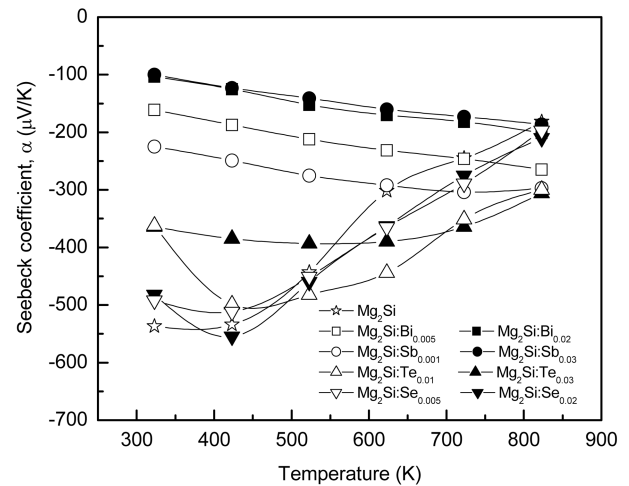


Fig. 3. Changes in the Seebeck coefficient of n-type Mg₂Si:X_m with temperature.

B^{VI}(Te, Se) dopants were less effective at increasing the electrical conductivity of Mg₂Si. A positive temperature dependence of the electrical conductivity was shown because an increase in the carrier concentration by intrinsic conduction overcame a decrease in the carrier mobility by ionized impurity scattering.

Figure 3 shows the changes in the Seebeck coefficient of n-type Mg₂Si:X_m with temperature. The Seebeck coefficient (a) of an n-type semiconductor is given by Eq. 1^[25,26]:

$$\alpha = -\frac{k}{e}(s - c \ln n) \tag{1}$$

where k is the Boltzmann constant, e is the electron charge, s is the energy-dependent scattering expression, n is the carrier concentration and c is the constant. The sign of the Seebeck coefficient was negative, which is in good agreement with the sign of the Hall coefficient, indicating an n-type semiconductor. The absolute values of the Seebeck coefficient of intrinsic

and lightly-doped (group B^{VI}-doped) Mg₂Si were reduced greatly as the temperature increased due to an increase in the carrier concentration by intrinsic conduction. However, the Seebeck coefficient of highly-doped (group B^V-doped) Mg₂Si increased with increasing temperature, and its variation with temperature was relatively low. This resulted from the electron-phonon scattering, which was predominant over an increase in the electron concentration at higher temperatures. The Seebeck coefficient is the competition result between carrier scattering and carrier concentration.

Figure 4 presents the changes in the thermal conductivity of n-type Mg₂Si:X_m with temperature. The thermal conductivity (κ) is the sum of the lattice thermal conductivity (κ_L) by phonons and the electronic thermal conductivity (κ_E) by carriers, and is given by Eq. 2:

$$\kappa = dC_p D = \kappa_L + \kappa_E = \kappa_L + L\sigma T \quad (2)$$

where d is the density, C_p is the specific heat, and D is the thermal diffusivity. Both components can be separated by the Wiedemann-Franz law ($\kappa_E = L\sigma T$), where the Lorenz number is assumed to be a constant ($L = 2.45 \times 10^{-8} \text{ V}^2\text{K}^{-2}$) for evaluation.^[27] The thermal conductivities of all specimens decreased with an increase in the temperature, and were almost constant above 650 K. By separating the lattice and the electronic components, it was found in this calculation that the lattice contribution was predominant and that > 95% of the thermal conductivity resulted from the lattice contribution at all temperatures examined. The thermal conductivity decreased by doping compared with the value for intrinsic Mg₂Si, which was attributed to the ionized impurity-phonon scattering.

Figure 5 indicates the changes in the dimensionless-figure-of-merit ($ZT = \alpha^2 \sigma T \kappa^{-1}$) of n-type Mg₂Si:X_m with tempera-

ture. The ZT value of intrinsic Mg₂Si increased with increasing temperature but it was as low as 0.04 at 823 K because of low electrical conductivity (low carrier concentration). However, this value was improved significantly by Bi or Sb doping and a maximum ZT value of 0.66 and 0.62 was obtained at 823 K for Mg₂Si:Bi_{0.02} and Mg₂Si:Sb_{0.03} specimens, respectively. This improvement is due mainly to the high power factor ($\alpha^2 \sigma$) with optimum carrier concentration. However, Te or Se doping did not effect much of an enhancement of the ZT value. Therefore, the group B^V(Bi, Sb) elements were much more effective at improving the thermoelectric properties of Mg₂Si than the group B^{VI}(Te, Se) elements were.

4. CONCLUSIONS

N-type Mg₂Si compounds were prepared by solid-state synthesis, and transport and thermoelectric properties were examined. A single phase Mg₂Si powder was obtained by solid state reaction at 773 K for 6 h and doping was performed successfully by mechanical alloying for 24 h. The synthesized powder was fully consolidated by hot pressing at 1073 K for 1 h. Intrinsic Mg₂Si and X(Bi, Sb, Te, Se)-doped Mg₂Si:X_m showed n-type conduction, and the group B^V(Bi, Sb) elements generated electrons more than the group B^{VI}(Te, Se) elements. This was related to the solubility limit. Te and Se produced MgTe and MgSe phases when the doping content (m) was larger than 0.02 and 0.01, respectively. The absolute values of the Seebeck coefficient of intrinsic and group B^{VI}-doped Mg₂Si were reduced greatly as the temperature increased, but that of group B^V-doped Mg₂Si increased with increasing temperature. The thermal conductivity decreased with an increase in the temperature, and the lattice contribution was predominant. The ZT value of intrinsic Mg₂Si was very low, but it improved remarkably

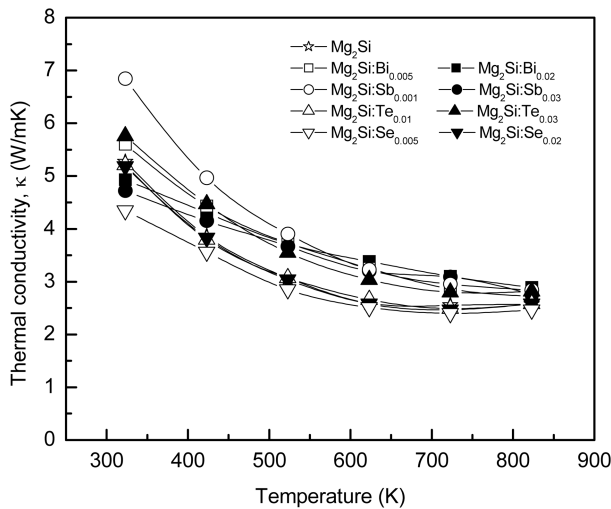


Fig. 4. Changes in the thermal conductivity of n-type Mg₂Si:X_m with temperature.

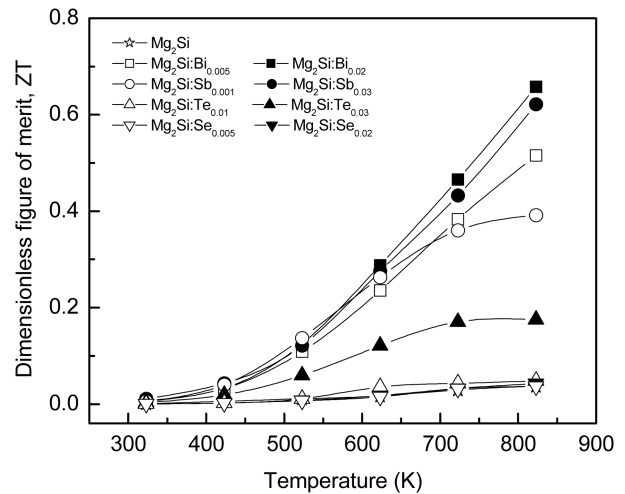


Fig. 5. Changes in the dimensionless-figure-of-merit of n-type Mg₂Si:X_m with temperature.

by doping. The group B^V(Bi, Sb) elements were much more effective at enhancing the thermoelectric properties of Mg₂Si than the group B^{VI}(Te, Se) elements were.

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