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Synthesis of thermoelectric Mg_2Si by a solid state reaction

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Mg_2Si compounds were synthesized by a solid state reaction, and the silicide transformation was analyzed using X-ray diffraction. Electronic transport properties (Hall coefficient, carrier concentration and mobility) and thermoelectric properties (Seebeck coefficient, electrical conductivity, thermal conductivity and figure-of-merit) were examined. Mg_2Si was successfully synthesized by a solid state reaction at 673-773 K for 6-12 h, and fully consolidated by hot pressing at 1073 K for 2 h. Intrinsic Mg_2Si showed n-type conduction indicating that the electrical conduction is mainly due to electrons. The absolute value of the Seebeck coefficient decreased and the electrical conductivity increased with an increase in the temperature due to intrinsic conduction at high temperatures. The thermal conductivity decreased with an increase in the temperature, and the lattice contribution was dominant. The thermoelectric figure-of-merit of intrinsic Mg_2Si was low and it should be improved by doping.

Key words: Thermoelectric, Mg_2Si, Solid state reaction, Hot pressing.

Introduction

Semiconducting alkaline-earth metal silicides have been the subject of much interest for use in thermoelectric device applications [1, 2]. The compounds of Mg_2B^{IV} (B^{IV} = Si, Ge and Sn) and their solid solutions have been considered as candidates for high-performance thermoelectric materials because they have large Seebeck coefficients, high electrical conductivities and low thermal conductivities. Magnesium silicide with an antifluorite structure is a narrow-band-gap semiconductor with an indirect band gap of 0.77 eV. Mg_2Si has been recognized as a promising material for thermoelectric energy conversion at temperatures ranging from 500 to 800 K [3-5]. Compared with other thermoelectric materials operating in the same conversion temperature range, such as PbTe and $CoSb_3$, important aspects of Mg_2Si include that it has been identified as an environmentally-friendly material (non-toxic), and its constituent elements are abundant in the earth's crust [6-8]. Based on the classical thermoelectric theory, the material factor $\beta = (m^*/m_e)^{3/2}\mu\kappa_L^{-1}$ can be recognized as the criterion for thermoelectric material selection, where m* is the density-of-states effective mass, m_e the mass of an electron, μ the carrier mobility and κ_L the lattice thermal conductivity. The β for magnesium silicides is 14, which is very high compared to 0.8 for iron silicides, 1.4 for manganese silicides and 2.6 for silicon-germanium alloys [9].

Mg_2Si and its solid solutions have been synthesized by various methods: induction melting [10], vertical Bridgman growth [11], spark plasma sintering [12], and mechanical alloying [13]. However, it is very difficult to prepare the Mg_2Si by a melting process due to large difference in vapor pressures of the constituent elements and no solubility, and furthermore a small difference between the boiling temperature of Mg (1380 K) and the melting temperature of Mg_2Si (1358 K) [14]. Therefore, it is difficult to control its composition, mainly due to volatilization and oxidation of Mg. To solve the aforementioned problems, mechanical alloying has been employed, which is an alloy formation in the solid phase by means of repeated mechanical impact during high energy ball milling, and it has been proved to be an advantageous method for the synthesis of semiconducting thermoelectric compounds or solid solutions [15-17]. However, a ductile-brittle system such as Mg-Si cannot be fully-transformed to a single phase (Mg_2Si) by mechanical alloying because Mg is so ductile as to stick to the walls of vial and balls, even though stearic acid or n-hexane is used as a process control agent. Therefore, the synthesized Mg_2Si powders have a low yield and a non-homogeneous chemical composition. In this study, a solid state reaction was attempted to synthesize the binary Mg_2Si and the thermoelectric and electronic transport properties were examined.

Experimental Procedure

Thermoelectric Mg_2Si was synthesized by a solid state reaction (SSR) and consolidated by hot pressing (HP). High purity magnesium powders (< 149 μm, purity 99.99%) and silicon powders (< 45 μm, purity 99.99%) were weighed at an atomic 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)

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in the solid state in an alumina crucible with a cover at 573-773 K for 6-12 h in a vacuum. The SSRed Mg_2Si pellets and hardened steel balls were loaded at a weight ratio of 1 : 20 into a hardened steel vial in an argon atmosphere. The vial was then loaded into a planetary ball mill (Fritsch, Pulverisette 5) and pulverized at 300 rpm for 24 h. The synthesized powders were hot-pressed in a cylindrical tungsten carbide die with an internal diameter of 10 mm at 1073 K under a pressure of 70 MPa for 2 h in a vacuum.

Scanning electron microscopy (SEM: FEI Quanta400) was used to observe the synthesized Mg_2Si powders and the microstructure of the HPed compact. The phase analysis was performed by X-ray diffraction (XRD: Bruker D8 Advance) using Cu K_α radiation (40 kV, 40 mA). Diffraction patterns were measured in the θ-2θ 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 to a rectangular shape with dimensions of $3 \times 3 \times 10\ mm^3$ for both the Seebeck coefficient and electrical conductivity measurements, and cut to a disc shape with dimensions of 10 mm (diameter) × 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 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 a laser flash Ulvac-Riko TC7000 system in a vacuum. The thermoelectric figure-of-merit was evaluated and compared with other studies.

Results and Discussion

Fig. 1(a) shows a SEM image of Mg_2Si powder synthesized by SSR at 673 K for 6 h and pulverized at 300 rpm for 24 h. A mean particle size of a few mm was obtained and the particle shape was irregular. Fig. 1(b) illustrates the microstructure of a Mg_2Si compact consolidated by HP at 1073 K for 2 h and shows nearly full density, which is close to the theoretical density (2.001 g/cm^3) of Mg_2Si.

Fig. 2 presents the XRD patterns for SSRed powders and HPed compact. They were was hardly reacted at 573 K for 12 h as shown in Fig. 2(b). However, as the SSR temperature increased, the diffraction peaks for Mg and Si elements were not seen, and reflections for only Mg_2Si compounds occurred. Furthermore, the diffraction peaks from MgO were not identified, which easily originated from oxidation during the preparation processes because magnesium is very chemically reactive, especially with oxygen and water vapor, although the SSR and HP were done in a vacuum. It was found that the SSR at 673 K for 6 h was enough to react elemental Mg with Si in order

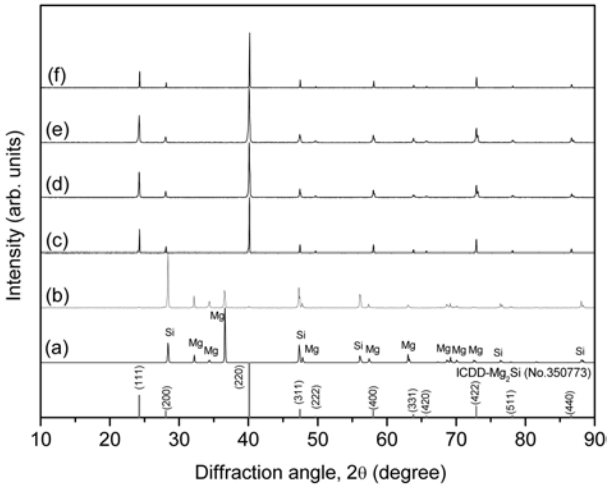

Fig. 2. X-ray diffraction patterns for solid-state reacted (SSRed) powders and hot-pressed (HPed) compact of Mg_2Si: (a) as-mixed powders, (b) SSRed at 573 K for 12 h, (c) SSRed at 673 K for 6 h, (d) SSRed at 673 K for 12 h, (e) SSRed at 773 K for 12 h, (f) HPed at 1073 K for 2 h.

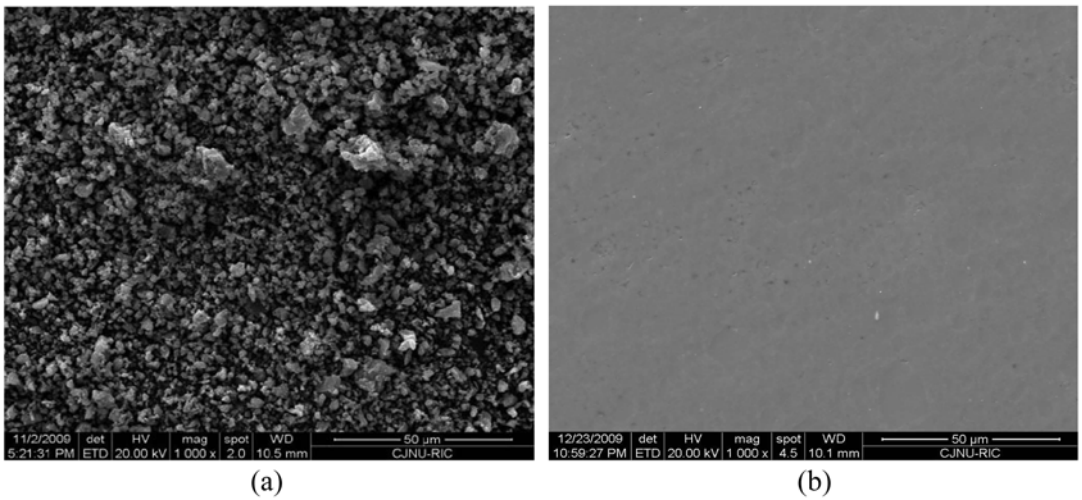

Fig. 1. Scanning electron microscopy images of Mg_2Si: (a) powders synthesized by a solid state reaction at 673 K for 6 h and pulverized at 300 rpm for 24 h, (b) compact consolidated by hot pressing at 1073 K for 2 h.

Table 1. Electronic transport properties of Mg_2Si at room temperature

Preparation method	Hall oeff. [cm^3C^{-1}]	Carrier conc. [cm^{-3}]	Hall mobility [$cm^2V^{-1}s^{-1}$]	Reference
Solid State Reaction	–210.7	3.0×10^{16}	104	this work
Mechanical Alloying	–26.3	2.4×10^{17}	48	Jung *et al*. [22]
Spark Plasma Sintering	–14.5	4.3×10^{17}	204	Tani and Kido [12]
Vertical Bridgman Growth	–7.4	8.4×10^{17}	176	Akasaka *et al.* [11]

to transform to the Mg_2Si compound, as shown in Fig. 2(c). This powder was consolidated by HP at 1073 K for 2 h, and the Mg_2Si phase could be maintained, which means that the SSR-HPed Mg_2Si compound was thermodynamically stable below 1073 K at least.

Table 1 shows the electronic transport properties of undoped (intrinsic) Mg_2Si at room temperature, and they were compared with the data from the literature [11, 12, 22]. The sign of the Hall coefficient was negative, indicating that the electrical conduction was mainly due to electrons. In this study, the carrier concentration of SSR-HPed Mg_2Si was 3.0×10^{16} cm^{-3}, and this is much lower than the values (an order of 10^{17} cm^{-3}) of other studies with samples prepared by different methods. This might result from the differences in chemical purity and particle (grain) size, and the presence of secondary phases (e.g. MgO) and partially unreacted elements. The carrier concentration of the order of 10^{16} to 10^{17} cm^{-3} is too low for thermoelectric applications because a good thermoelectric material should have a carrier concentration of the order of 10^{19} to 10^{20} cm^{-3}. Therefore, atoms should be doped into the intrinsic Mg_2Si, and this remains for further work.

Fig. 3 indicates the variation of electrical conductivity of Mg_2Si with temperature. The electrical conductivity (σ) of an n-type semiconductor is expressed as Eq. 1:

$$\sigma = en\mu = \frac{e^2 n\tau}{m^*} \tag{1}$$

where e is the electronic charge, n the electron concentration, m is the electron mobility, m* the effective mass of an electron, and τ the relaxation time of an electron. The electrical conductivity increased with an increase in the temperature, which means that intrinsic Mg_2Si 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 [3, 18]. Therefore, the 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 electron-phonon scattering. In this study, the solid-state-reacted Mg_2Si showed a similar temperature dependence to a mechanical-alloyed Mg_2Si [22], but a spark-plasma-sintered Mg_2Si [12] showed a negative temperature dependence below 500 K. This is due to the extrinsic conduction from the presence of undesirable impurities, secondary phases of MgO, non-reacted and/or decomposed Si.

Fig. 4 shows the variation of Seebeck coefficient of Mg_2Si with temperature. The Seebeck coefficient (a) of an n-type semiconductor is given by Eq. 2 [19, 20]:

$$\alpha = -\frac{k}{e}\left(\frac{5}{2} + r - \frac{E_C - E_F}{kT}\right) = -\frac{k}{e}\left(\frac{5}{2} + r + ln\frac{N_C}{n}\right) \tag{2}$$

where k is the Boltzmann constant, r the exponent of the power function in the energy-dependent relaxation time expression, E_C the bottom of the conduction band, E_F the Fermi energy, T the absolute temperature and N_C the effective

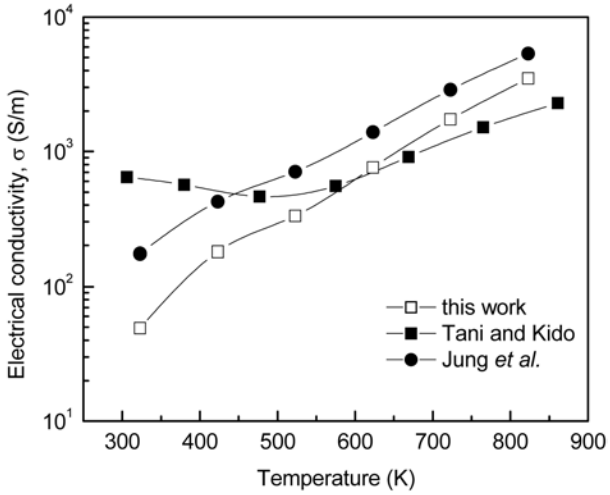

Fig. 3. Changes in the electrical conductivity of Mg_2Si with temperature.

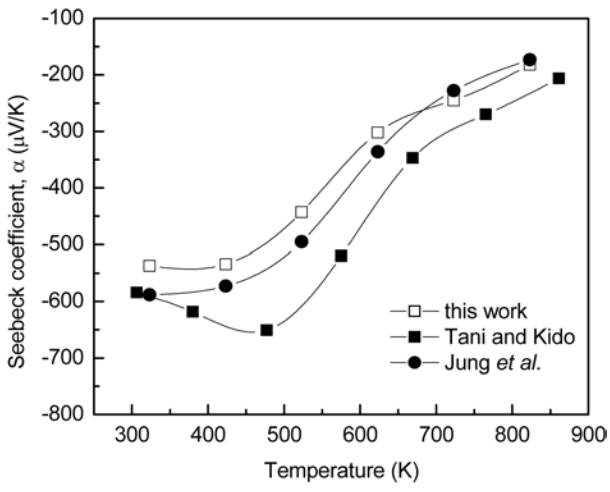

Fig. 4. Changes in the Seebeck coefficient of Mg_2Si with temperature.

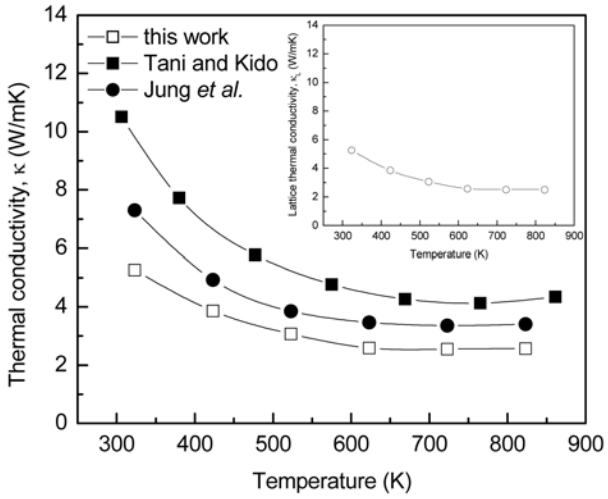

Fig. 5. Changes in the thermal conductivity of Mg_2Si with temperature.

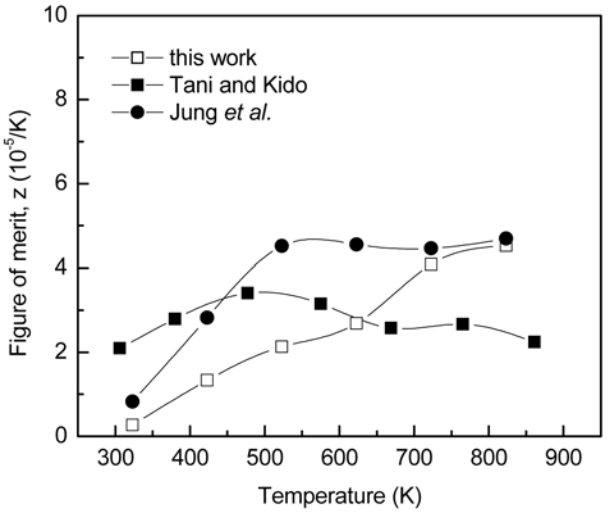

Fig. 6. Changes in the figure-of-merit of Mg_2Si with temperature.

density-of-states in the conduction band. Therefore, as shown in Fig. 4, the absolute value of the Seebeck coefficient was reduced as the temperature was increased due to an increase in the electron concentration by intrinsic conduction. The sign of the Seebeck coefficient was negative, which in good agreement with the sign of the Hall coefficient, indicating the intrinsic Mg_2Si is an n-type semiconductor.

Fig. 5 presents the variation of thermal conductivity of Mg_2Si 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 it is given by Eq. 3:

$$\kappa = dC_pD = \kappa_L + \kappa_E = \kappa_L + L\sigma T \quad (3)$$

where d is the density, C_p the specific heat, D 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 ($L = 2.45 \times 10^{-8}\ V^2K^{-2}$) for evaluation [21]. The thermal conductivity decreased with an increase in the temperature, and it was almost constant above 650 K. By separating the lattice and electronic components, it was found in this calculation that the lattice contribution was predominant for intrinsic Mg_2Si and 99% of the thermal conductivity resulted from the lattice contribution at all temperatures examined (the inset in Fig. 5). This is due to the low carrier concentration of the order of 10^{16} cm^{-3}, although the electrical conductivity increased and thereby the electronic thermal conductivity increased as the temperature increased.

The thermoelectric figure-of-merit (Z) is shown in Fig. 6 and determined by Eq. 4 [14]:

$$Z = \frac{\alpha^2\sigma}{\kappa} \sim \left(\frac{m^*}{m^e}\right)^{\frac{3}{2}} \frac{\mu}{\kappa_L} \quad (4)$$

where m_e is the mass of an electron. In this study, the Z value increased with an increase in the temperature from 300 to 650 K, and it was reduced up to 850 K. However, the Z value of intrinsic Mg_2Si was low owing to the low electrical conductivity and high thermal conductivity. It can be improved by doping to increase the carrier concentration and by introducing phonon scattering centers. The thermoelectric figure-of-merit has been used as a measure for good thermoelectric materials, and it is closely related to the material factor (β). Therefore, a superior thermoelectric material should have a large Seebeck coefficient (a large effective mass of carrier), high electrical conductivity (low carrier scattering) and low thermal conductivity (high phonon scattering), simultaneously.

Conclusions

Mg_2Si was prepared by a solid state reaction and hot pressing, and the thermoelectric and transport properties were examined. A solid state reaction was fulfilled successfully in the Mg-Si system, and fine Mg_2Si particles could be synthesized. A single phase Mg_2Si powder was obtained by a solid state reaction at 673-773 K for 6-12 h, and fully consolidated by hot pressing at 1073 K for 2 h. Intrinsic Mg_2Si showed n-type conduction and the carrier concentration was as low as the order of 10^{16} cm^{-3} at room temperature. The temperature dependence of the electrical conductivity behaved like a non-degenerate semiconductor. The absolute value of the Seebeck coefficient was reduced as the temperature increased due to an increase in the electron concentration by intrinsic conduction. The thermal conductivity decreased with an increase in the temperature, and the lattice contribution was predominant for Mg_2Si. The thermoelectric figure-of-merit of intrinsic Mg_2Si was low due to the low carrier concentration, and it should be enhanced by doping.

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