Solid State Synthesis of Ternary Thermoelectric Magnesium Alloy, Mg$_2$Si$_{1-x}$Sn$_x$

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Profound understanding and survey of magnesium base intermetallic compounds is hindered by various difficulties in their processing and fabrication. Solid-state synthesis via the bulk mechanical alloying (BMA) is free from contaminations and segregation through high reactivity of elemental constituents against crucibles or vials. Magnesium–tin system is employed to demonstrate the solid-state reactivity to Mg$_2$Sn from the elemental powder mixture. This process is characterized by the gradual solid-state reaction to Mg$_2$Sn with processing time. Since the blended mixture of magnesium and tin with the initial molar ratio of Mg$_66.7$%Sn$_33.3$%, is repeatedly strained via BMA in the controlled conditions, the solid-state reaction advances monotonically with refinement of interparticle distance between magnesium and tin. Ternary semi-conductive compounds, Mg$_2$Si$_{1-x}$Sn$_x$, for $0 \leq x \leq 1$, are also synthesized by this process. Thermoelectric properties of this ternary alloy are investigated to discuss the effect of tin content on the band-gap, the thermal conductivity, the Seebeck coefficient and the figure-of-merit. In addition, these data are compared to the previously reported results by using melt and solidified samples in order to describe the common features in the solidsolution type thermoelectric compounds. Furthermore, p–n transition behavior is also reported in this ternary alloy system.

(Received October 20, 2005; Accepted December 1, 2005; Published April 15, 2006)

Keywords: solid-state synthesis, bulk mechanical alloying, Mg$_2$Sn, Mg$_2$Si$_{1-x}$Sn$_x$, thermoelectricity

1. Introduction

Modern direction toward economic and reliable thermoelectric recovery of waste heat weighs more on the initial low cost of a generator, its service life and its autonomic operation without maintenance than maximization of the absolute figure-of-merit ZT for thermoelectric materials.\(^1\) From this point of view, the reliability of p–n modules as well as their electric power density becomes a major concern rather than the conversion efficiency. On the other hand, lead-free materialization and improvement of materials efficiency turn to be important in thermoelectric, eco-material selection toward reduction of environmental burden and CO$_2$ emission.\(^2\) Intermetallic compounds with silicon, germanium and tin and their solid solutions are high-lighted as a potentially promising thermoelectric material for power generation applications in the medium temperature range instead of TAGS and Pb–Te systems.\(^3,5\)

High chemical activity and high vaporizing pressure of magnesium at the vicinity of its melting-point becomes a main bump to hinder the synthesis of these compounds. In addition, the synthesized Mg$_2$X type binary compounds for X = Si, Ge or Sn in the liquid state easily react with quartz and alumina crucibles, so that special treatment of crucibles as well as tactical experimental procedures are necessary to prevent their chemical interaction with the magnesium melts.\(^6\) Both germanium and tin are also easy to be reacted so that the solid solution formation in the ternary system is also limited to the specified range of composition.\(^7,8\) Mechanical milling and grinding provides us a method of solid-state synthesis both for binary and ternary systems.\(^9,10\) Long processing, oxidation and various contaminations are disliked by improvement of thermoelectric properties. Furthermore, this processing fails in controlling carrier concentration, so that thermoelectric properties are deteriorated.

The bulk mechanical alloying has become a new alternative method to make solid-state synthesis of bulk, intermetallic compounds in the binary and ternary systems.\(^11–14\) A single-phase, bulk Mg$_2$Si and Mg$_2$Si$_{1-y}$Ge$_y$, for $0 < y < 1$ compounds, are yielded by intense-straining the mixture of elemental particles. Different from the conventional melting and solidification methods, this process is completely free from segregation and vaporization. Chemical composition is accurately controlled to be equivalent to the initial molar ratio.\(^14,15\) Furthermore, it is also free from contamination and long processing time, which often become an issue of nuisance in using ball milling and attritting.\(^10\)

In the present paper, this bulk mechanical alloying is applied to solid-state synthesis of Mg$_2$Sn and Mg$_2$Si$_{1-x}$Sn$_x$ for $0 < x < 1$ compounds at room temperature. A few reports of liquid-phase synthesis of Mg$_2$Sn were found in literature.\(^16–18\) Mg$_2$Sn crystals grown from melts by the modified Bridgeman procedure have unique characteristics: it becomes n-type for excess tin content and p-type for excess magnesium content. Mechanical alloying by ball milling was also used for solid-state synthesis to evaluate the thermoelectric properties of Mg$_2$Sn. With respect to the ternary solid solution, Mg$_2$Si$_{1-y}$Sn$_y$, much less groups succeeded in its synthesis and measurement of thermoelectricity.\(^19,20\) This solid solution has preferable thermoelectric parameters to be working in mid-temperature range of the thermoelectric applications. Its investigation is strictly limited by difficulties in processing. In particular, precise compilation is necessary to describe the relationship between thermoelectricity and chemical composition in the pseudo binary systems like Mg$_2$Si–Mg$_2$Sn, Mg$_2$Si–Mg$_2$Ge and Mg$_2$Sn–Mg$_2$Pb. First in this study, Mg$_2$Sn compound is successfully solid-state synthesized by BMA in single phase from a powder mixture of magnesium and tin. The characteristic feature of this solid-state reaction process is experimentally described to deduce that this process is controlled by the repeated plastic flow of ductile elements. Tin content, x, in the pseudo binary system

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Mg$_2$Si–Mg$_2$Sn or in Mg$_2$Si$_{1-x}$Sn$_x$ for $0 < x < 1$ is parametrically varied to further investigate the solid solution process. Variation of band-gap and lattice parameters with tin content is investigated with comparison of the reference data. Homogeneous solid solution formation leads to continuous decrease of band-gap with increasing the tin content. Thermoelectric properties are also measured to describe the effect of tin content on thermoelectricity. Maximum figure-of-merit is attained at $x = 0.6$, irrespective of the holding temperature. The pn-transition takes place from n-type semiconductor Mg$_2$Si to p-type one Mg$_2$Si$_{1-x}$Sn$_x$ in the range of $0 < x < 0.2$.

2. Experimental Procedure

According to the molar ratio of Mg$_2$Sn and Mg$_2$Si$_{1-x}$Sn$_x$ for various tin content, $x$, the elemental powders of Mg (99.9% in purity, 100 µm in diameter), Si (99.99% in purity, 20 µm in diameter) and Sn (99.99% in purity, 10 µm in diameter) were prepared, blended and mixed. In the present experimental study for solid-state synthesis, the bulk mechanical alloying (BMA) was utilized to synthesize the binary compounds and ternary solid solutions. The powder mixture was blended homogeneously and then subjected to bulk mechanical alloying in a flowing argon atmosphere to prevent the powder compact from oxidation. As had been stated elsewhere, the pass schedule with one forward extrusion mode and two compression modes was employed for cyclic loading in the laboratory-scaled BMA equipment. Hot pressing technique was employed for fabrication of brick-type and disc-shaped samples for measurement of thermoelectric properties. After pulverizing BMA compact and sieving by the mesh of #270, the BMA powders were sintered in a stainless steel die under an argon atmosphere. The process conditions for bulk mechanical alloying and hot pressing are summarized in Tables 1 and 2, respectively.

X-ray diffraction (XRD) analysis with the monochromatic Cu K$_\alpha$ radiation was used to describe the solid-state formation of compounds and solid solutions by BMA. The differential thermal analysis (DTA) was carried out to explore the onset temperature of solid-state reaction during BMA process with the heating rate of 20 K/min up to 1073 K in an argon atmosphere. Scanning electron microscopy (SEM) with the energy dispersive X-ray spectroscopy (EDX) was utilized to observe the microstructure and to determine composition of BMAed samples.

The samples for electrical measurement were cut out from the sintered pellets: a rectangular bar with the size of $2 \times 2 \times 8$ mm$^3$ for measurement of the Seebeck coefficient and the electrical conductivity, and, a circular disc with the diameter of 10 mm and the thickness of 2 mm for measurement of thermal conductivity. The thermoelectric properties were evaluated from room temperature up to about 700 K. The Seebeck coefficient, $\alpha$, and the electrical conductivity, $\sigma$, were simultaneously measured by the four-probe dc method in helium atmosphere, using the computer-controlled equipment. The thermal diffusivity, $D$, and the specific heat capacity, $C_p$, were measured by the laser flash method, using a thermal constant analyzer (ULVAC TC-7000) in vacuum. The thermal conductivity, $\kappa$, was calculated from the measured thermal diffusivity, specific heat capacity and bulk density, $d$: $\kappa = DC_p/d$. The bulk density of the hot pressed samples was measured by the Archimedes method.

3. Experimental Results

3.1 Solid-state reaction process via BMA

Magnesium–tin system, was employed to describe the solid-state reaction process via the bulk mechanical alloying (BMA). Figure 1 depicted the variation of XRD profiles for the BMA samples with increasing the number of cycles, $N$. When $N = 0$, triplet peaks for magnesium and characteristic peaks to tin were detected. These peak intensities significantly decreased in the early stage of BMA. Even when $N = 100$, magnesium peaks were detected in the trace level. Since no change was distinguished in the XRD profiles for $N > 300$, the single phase of Mg$_2$Sn was successfully synthesized at $N = 600$. The above solid-state reactivity reflects on the DTA diagram. As shown in Fig. 2, two endothermic peaks as well as one exothermic peak were seen when $N = 0$. The former endothermic peak corresponds to the melting of tin and the latter, to the melting of Mg$_2$Sn. The exothermic peak denotes for the eutectic reaction in Mg–Sn system to form Mg$_2$Sn. From this peak, its formation enthalpy $\Delta H^0_f$ was measured: $\Delta H^0_f = 74$ J/mol. This is in good agreement with the reference data, $\Delta H^0_f = 81$ J/mol.

These former endothermic and exothermic peak intensities significantly reduced and broadened with increasing $N$. In particular, the onset temperature of eutectic reaction shifted itself to the lower temperature side. When $N = 600$, no peaks except for the latter endothermic peak were seen in DTA diagram. This proves that the single phase of Mg$_2$Sn is synthesized in solid via BMA. After precise analysis of this type of solid-state synthesis, this solid-state reactivity is driven by refinement of Mg and Sn particle size and mechanical alloying between two constituents. Repeated plastic flow of Mg and Sn particles leads to refinement of the layered microstructure with Mg–Sn–Mg–..., so that the
solid-state reaction advances gradually as shown in Figs. 1 and 2. During BMA, the relative density of BMA sample is held constant, 80% T.D. (true density). Different from the mechanical alloying via ball milling, attriting or grinding, the synthesized materials are shaped as a cylindrical billet with the relative density of 80% T.D. as shown in Fig. 3.

### 3.2 Solid-state reactivity of $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$

The similar experimental procedure was applied to solid-state synthesis of $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$. The tin content, $x$, is parametrically controlled by the initial molar ratio of elemental constituents. Being also discussed in Ref. 14), this initial molar ratio is equivalent to the final chemical composition of the synthesized compound within its deviation less than 0.5 at%. When increasing the number of cycles up to $N = 600$, no peaks except for the synthesized compounds were seen in XRD profiles and no peaks were also detected in DTA except for the endothermic peak corresponding to the melting of compound in the similar manner as shown in Figs. 1 and 2. Figure 4 compares the XRD profiles of the solid-state synthesized $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ for various tin content, $x$.

![Fig. 1 Variation of XRD profiles with increasing the number of cycles in BMA.](image1)

![Fig. 2 Variation of DTA diagrams with increasing the number of cycles in BMA.](image2)

![Fig. 3 Solid-state synthesized billet via BMA with the relative density of 80% T.D.](image3)

![Fig. 4 XRD profiles of the solid-state synthesized $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ for various tin content, $x$.](image4)

![Fig. 5 Variation of the lattice constant for $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ with increasing the tin content, $x$.](image5)
Solid State Synthesis of Ternary Thermoelectric Magnesium Alloy, Mg$_2$Si$_{1-x}$Sn$_x$

$x \leq 1.0$ was calculated to describe the solid solution formation. The calculated lattice parameter for each $x$ was depicted in Fig. 5 together with the reference data. The solid line denotes for the theoretical estimate by Vegard’s law. The present results are in fairly good agreement with reference data. This proves that homogeneous solid solution formation takes place irrespective of the tin content. Every thermoelectric property is thought to vary in continuous manner with the tin content. Figure 6 depicted the microstructure of Mg$_2$Si$_{0.4}$Sn$_{0.6}$ before and after hot pressing.

3.3 Thermoelectricity of Mg$_2$Si$_{1-x}$Sn$_x$

The temperature dependence of the electrical conductivity for Mg$_2$Si$_{1-x}$Sn$_x$ samples was shown in Fig. 7. In all the samples, the electrical conductivity increases monotonically with temperature, $T$, in the range of 300 K $< T < 700$ K. Different from Mg–Si–Ge system in Ref. 14), Mg$_2$Sn has the highest electrical conductivity and it decreases with increasing the silicon content, irrespective of $T$. In particular, significant decrease of electrical conductivity was seen in the range of 0.0 $< x < 0.2$. This is just corresponding to the reference data.\(^{19}\)

The band-gap ($E_g$) is one of the most important parameters for design of thermoelectric, semi-conductive materials. $E_g$ is estimated by the slope when logarithmically plotting the above electrical resistivity ($\rho$) against the reciprocal temperature:\(^{24}\)

$$\ln \rho = \frac{E_g}{(2K_B T)} + A, \quad (1)$$

where $K_B$ is the Bolzmann constant, and, $A$, the material constant. Figure 8 shows the variation of estimated band-gap by eq. (1) for Mg$_2$Si$_{1-x}$Sn$_x$ in the function of tin content, $x$. After Ref. 25), $E_g$ for Mg$_2$Si = 0.7 eV and $E_g$ for Mg$_2$Sn = 0.36 eV. The present results are in fairly good agreement with these reference data: $E_g$ (for Mg$_2$Si) = 0.71 eV and $E_g$ (for Mg$_2$Sn) = 0.36 eV.

Variation of thermal conductivity with temperature was depicted in Fig. 9. Corresponding to monotonic increase of electrical conductivity with $T$ in Fig. 7, the thermal conductivity decreases monotonically with $T$ irrespective of the tin content in Mg$_2$Si$_{1-x}$Sn$_x$. Figure 10 shows the sensitivity of this thermal conductivity, $\kappa$, to the tin content for various temperatures. Irrespective of $T$, $\kappa$ becomes minimum in the

Fig. 6 Microstructure of the sold-state synthesized ternary compound, Mg$_2$Si$_{0.4}$Sn$_{0.6}$: a) before hot pressing, and, b) after hot pressing.

Fig. 7 Variation of the electrical conductivity versus the temperature for Mg$_2$Si$_{1-x}$Sn$_x$.

Fig. 8 Variation of the measured band gap with increasing the tin content, $x$ in Mg$_2$Si$_{1-x}$Sn$_x$.

Fig. 9 Variation of thermal conductivity with temperature.

Fig. 10 Variation of the sensitivity of thermal conductivity, $\kappa$, to the tin content for various temperatures.
range of $0.4 < x < 0.8$. References 17, 18) reported the variation of $\kappa$ with the tin content at room temperature; $\kappa$ becomes minimum for $0.4 < x < 0.6$. In these reference data, the minimum thermal conductivity at room temperature ($\kappa_{\text{minimum}}$) becomes $2.4 \text{ Wm}^{-1}\text{K}^{-1}$ at $x = 0.5$ while $\kappa_{\text{minimum}}$ at $T = 323 \text{ K}$ is $4.5 \text{ Wm}^{-1}\text{K}^{-1}$ at $x = 0.6$ in the present results.

Variation of the Seebeck coefficient, $\alpha$, with $T$ was also depicted in Fig. 11 for Mg$_2$Si$_{1-x}$Sn$_x$ samples. Its absolute value $|\alpha|$ monotonically decreases with $T$ irrespective of the tin content, $x$, since the number of carriers increases by thermal activation. The highest Seebeck coefficient is attained at room temperature for n-type semiconductor, Mg$_2$Si and p-type Mg$_2$Si$_0.2$Sn$_{0.8}$: e.g. $\alpha = -750 \mu\text{VK}^{-1}$ for Mg$_2$Si, and, $\alpha = +330 \mu\text{VK}^{-1}$ for Mg$_2$Si$_0.2$Sn$_{0.8}$. In particular, extraordinary variation of Seebeck coefficient with $T$ was seen when $x = 0.2$. Mg$_2$Si$_{0.8}$Sn$_{0.2}$ is p-type for $T < 500$ K while it turns to be n-type for $T > 500$ K. This behavior is also seen at the vicinity of critical germanium content in Mg–Si–Ge system.\(^{14}\)

Figure 12 depicts the variation of figure-of-merit, $Z$, with temperature for Mg$_2$Si$_{1-x}$Sn$_x$ ($0 < x < 1$). Relatively high figure-of-merit is obtained for $0.6 < x < 0.8$. This is partially because the solid solutions in this range of tin content have higher electrical conductivity and Seebeck coefficient.

4. Discussion

4.1 Solid-state reactivity via BMA

The solid-state reactivity is enhanced by the repeated plastic flow and intense straining during the bulk mechanical alloying. After Ref. 22), the solid-state reactivity in the binary system of Mg–Sn and the ternary system of Mg–Si–Sn is thought to be driven by the ductile deformation and straining of magnesium and tin particles. Mg–Sn system was employed to measure the average interparticle distances, $D_M$ and $D_S$, between adjacent deforming magnesium particles and tin particles in the refined microstructure by SEM and
EDX analyses, respectively. Figure 13 depicted the variation of $D_{Mg}$ and $D_{Sn}$ with the processing time, $t$, in BMA. In the early stage, only magnesium particles with larger initial size plastically deformed during BMA. After this early refinement of magnesium particles, both particles plastically deformed together with nearly the same strain rate in refinement down to sub-micrometer size. In order to investigate the relationship between this simultaneous refinement and solid-state reactivity, the current formation enthalpy, $\Delta H_f$, was measured for each BMA sample together with $D_{Mg}$ and $D_{Sn}$. Two parameters are defined: $D_N = D_{Sn}/D_{Sn}^{0}$ for the initial tin particle size, $D_{Sn}^{0}$, and $\chi = \Delta H_f/\Delta H_f^{0}$ for the initial formation enthalpy, $\Delta H_f^{0}$ in Mg–Sn system. Figure 14 showed the decrease of the non-dimensional formation enthalpy ratio, $\chi$, with the non-dimensional particle size, $D_N$. Simultaneous, monotonic reduction of $\chi$ with $D_N$ from $\chi = 1$ at $D_N = 1$ to $\chi = 0$ when $D_N$ approaches to 0, proves that the solid-state reactivity is governed by repeated plastic flow of ductile elements. This mechanically induced solid-state reactivity is true to solid solution formation in Mg–Sn system. Although the conventional processing is often limited to yield the solid solution semi-conductors, the present solid-state synthesis is free from the tin contents since the solid-state reactivity is mechanically induced.

### 4.2 Thermoelectricity of solid-state synthesized Mg$_2$Sn

After Refs. 18–20, thermoelectric data were measured and reported for a single crystal of Mg$_2$X (X = Si, Ge or Sn). Thermal conductivity ($\kappa_{RT}$) for Mg$_2$Si at room temperature is 7.8 to 9.4 Wm$^{-1}$K$^{-1}$ while $\kappa_{RT}$ for Mg$_2$Sn is 6.0 to 7.1 Wm$^{-1}$K$^{-1}$. As shown in Fig. 9, the present hot-pressed samples have much lower thermal conductivity: e.g. $\kappa_{RT}$ for Mg$_2$Si = 4.9 Wm$^{-1}$K$^{-1}$ and $\kappa_{RT}$ for Mg$_2$Sn, 4.6 Wm$^{-1}$K$^{-1}$. BMA samples have fine grain size even after hot-pressing as shown in Fig. 6(b). The above decrease of thermal conductivity is attributed to phonon scattering by grain boundaries in nano-structured polycrystalline materials. In Refs. 18, 26, 27, it was also reported that Mg$_2$Si is an n-type semiconductor, the Seebeck coefficient ($\alpha$) of which decreases monotonically with temperature for $T > 323$K, and, that Mg$_2$Sn is almost p-type, the $\alpha$ of which abruptly reduces itself for $T > 323$K. With respect to Mg$_2$Si, monotonic decrease of $\alpha$ with $T$ in Fig. 11 is corresponding to the reported behavior: e.g. $\alpha$ at 323 K is ~500 to ~600 $\mu$VK$^{-1}$ in Ref. 18) while $\alpha$ at 323 K in Fig. 11, ~740 $\mu$VK$^{-1}$. On the other hand, gradual decrease of $\alpha$ with $T$ is observed in Fig. 11 for Mg$_2$Sn, while $\alpha$ becomes nearly zero or small negative for $Z > 400$ K in Refs. 18, 26, 27). When $T = 323$ K, both results are in good agreement: e.g. $\alpha$ at 323 K is about +50 $\mu$VK$^{-1}$ in Ref. 18), and, it is 60 $\mu$VK$^{-1}$ in the present results.

### 4.3 Thermoelectricity of solid-state synthesized Mg$_2$Si$_{1-x}$Sn$_x$

After Refs. 16, 17, 19), the band-gap for Mg$_2$Si$_{1-x}$Sn$_x$ decreases with the tin content, $x$, and it has a kink-point at the vicinity of $x = 0.7$ as shown as a broken line with solid circles in Fig. 8. On the other hand, corresponding to the monotonic increase of lattice parameters with the tin content in Fig. 5, the measured band-gap continuously decreases from 0.71 eV for Mg$_2$Si to 0.36 eV for Mg$_2$Sn in Fig. 8. This difference might come from the processing route. In Refs. 16, 17), the samples were prepared at the temperature, 50 K higher than the liquids temperature using direct melting and mixing in the crucibles and placed in the argon-filled ampoules. After homogenizing annealing for 100–500h at temperature, 200 K lower than solids temperature, the solidified ingots were obtained not to have second-phase impurities or inclusions in the microscopic level. Since every compound is in equilibrium phase, Mg$_2$Si$_{1-x}$Sn$_x$ must be separated into two phases of Mg$_2$Si + Mg$_2$Sn in the region of 0.3 < $x$ < 0.7, where kink point was observed in the band-gap, as suggested in the pseudo-binary diagram between Mg$_2$Si and Mg$_2$Sn. On the other hand, the present approach stands on the solid-state synthesis to accurately control the chemical composition for Mg$_2$Si$_{1-x}$Sn$_x$ with less contaminants in microscopic level and to yield non-equilibrium phase compounds. Homogeneous solid solution formation is thought to take place, being free from the above two-phase region. In fact, the thermal conductivities in Refs. 16, 17, 19) were much lower than the present data for Mg$_2$Si$_{1-x}$Sn$_x$ in $0.2 < x < 0.8$. This might be because phonon scattering is enhanced by fine microstructure with two phases of Mg$_2$Si + Mg$_2$Sn. In case of homogenous solid solution, the thermal conductivity is not so sensitive to tin content even for 0.4 < $x$ < 0.6.
Table 3 Comparison of figure-of-merits at room temperature for various tin contents in Mg$_2$Si$_{1-x}$Sn$_x$ with the reference data.

<table>
<thead>
<tr>
<th>x</th>
<th>Mg$_2$Si</th>
<th>x = 0.2</th>
<th>x = 0.4</th>
<th>x = 0.6</th>
<th>x = 0.8</th>
<th>x = 1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z/K</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Nikitin et al.</td>
<td>0.1</td>
<td>0.37</td>
<td>0.17</td>
<td>0.12</td>
<td>0.05</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Figure-of-merit: Z/K$^{-1}$ Present

0.005 0.035 0.065 0.085 0.075 0.04

Fig. 15 Variation of the Seebeck coefficient at 550 K with the tin content, x in Mg$_2$Si$_{1-x}$Sn$_x$.

Nikitin et al.\(^{28}\) first reported the figure-of-merit at the room temperature for this ternary compound of Mg$_2$Si$_{1-x}$Sn$_x$. Table 3 compares the variation of figure-of-merit at room temperature ($Z_{RT}$) in the function of the tin content, x, with the above reference data. $Z_{RT}$ becomes higher for 0.2 $< x < 0.4$ and gradually decreases with increasing x; e.g. $Z_{RT} = 0.065 \times 10^{-3}$ K$^{-1}$, and, $Z_{RT}$ (for Ref. 28) $= 0.17 \times 10^{-3}$ K$^{-1}$ at $x = 0.4$. This difference comes from the difference of thermal conductivity between two.

Effect of doping on $Z_{RT}$ was also discussed in Refs. 29, 30). Higher $Z_{RT}$ was obtained by Sb-doping at $x = 0.0$ or for Mg$_2$Si in Ref. 29); e.g. $Z_{RT} = 0.89 \times 10^{-3}$ K$^{-1}$. For Mg$_2$Si$_{1-x}$Sn$_x$, effect of Sb-doping on Z was reported in Ref. 30): e.g. $Z_{RT} = 0.7 \times 10^{-3}$ K$^{-1}$ for Mg$_2$Si$_{0.7}$Sn$_{0.3}$ and $Z_{RT} = 0.11 \times 10^{-3}$ K$^{-1}$ for Mg$_2$Si$_{0.55}$Sn$_{0.45}$. These data imply that Sb-doping is effective to improve the figure-of-merit in the lower tin content. This doping effect has close relationship with p–n transition in Mg$_2$Si$_{1-x}$Sn$_x$.

Figure 15 depicted the variation of the Seebeck coefficient at 550 K with the tin content, x in Mg$_2$Si$_{1-x}$Sn$_x$. Here to be interested is that pn-transition takes place between $x = 0.0$ and $x = 0.2$. That is, $\alpha$ is negative when $x = 0.0$ or for Mg$_2$Si, and, $\alpha$ turns to be positive for $x > 0.2$ in Mg$_2$Si$_{1-x}$Sn$_x$. Variation of Seebeck coefficient with tin alloying level is related to the change in the electric structure near the Fermi energy. The Boltzmann theory\(^{31}\) suggests that the Seebeck coefficient is optimized for the material which has rapid variation on electronic conductivity within a few $k_B T$ of the Fermi energy. Hence, unusual band structure or steep band edge near the Fermi energy is favorable for improvement of Seebeck coefficient. The complicated change in Seebeck coefficient with the tin content in Fig. 11, indicates that the solid solution formation gives rise to complex band structure in the ternary Mg–Si–Sn system in the similar manner to Mg–Si–Ge system.\(^{14}\) The critical content of the third element or germanium for pn-transition is 0.35 in Mg–Si–Ge system while it is 0.2 in Mg–Si–Sn. In both systems, the Seebeck coefficient changes its sign with increasing the temperature. The complex band structure at the vicinity of critical tin content is sensitive to doping. Sb-doping at $x = 0$ and $x = 0.3$ in Refs. 29, 30) implies that antimony works as a dopant both for n-type and p-type semi-conductors by selective Sb-doping to Mg$_2$Si$_{1-x}$Sn$_x$ with $x < 0.2$ and $x > 0.2$, respectively. Mg$_2$Si always shows n-type semi-conductivity, independent of magnesium composition. As first reported in Ref. 16), Mg$_2$Sn has a stoichiometric effect. Mg$_2$Sn becomes p-type by enrichment of magnesium while it is n-type when including excess amount of tin. Bulk mechanical alloying provides accurate chemical composition both to Mg$_2$X for X = Si and Sn and Mg$_2$Si$_{1-x}$Sn$_x$ while the conventional processing is strongly affected by this stoichiometric effect. As had been discussed in Ref. 14), the alloyed perform by BMA can be thought to have point defects or Mg/Sn vacancies which were insufficiently annealed during hot pressing. It is possible that the remaining defects might have an influence on the transport properties related p–n transition.

5. Conclusion

Bulk mechanical alloying was successfully applied to solid-state synthesis of Mg$_2$Si$_{1-x}$Sn$_x$ for $0 \leq x \leq 1$ from elemental powder mixture at the room temperature in a relatively short duration. This successful solid-state synthesis is driven by repeated plastic flow of ductile elements like magnesium and gradual reactivity of tin and silicon with magnesium matrix. Using the dense single-phase samples, the thermoelectric properties were measured for various tin contents in Mg$_2$Si$_{1-x}$Sn$_x$. Owing to homogeneous solid solution formation to Mg$_2$Si$_{1-x}$Sn$_x$ with accurate control of chemical composition, the band-gap decreases monotonically from 0.71 eV for Mg$_2$Si to 0.36 eV for Mg$_2$Sn with increasing the tin content in accordance with the monotonic increase of lattice parameter with x. This monotonic decrease of band-gap without kink might be attributed to homogenous, single-phase solid solution even in the range of $0.4 \leq x \leq 0.6$. Highest figure of merit can be attained for 450 K < $T < 650$ K for Mg$_2$Si$_{1-x}$Sn$_x$ with $0.6 < x < 0.8$ due to relatively high Seebeck coefficient and electrical conductivity: e.g. $Z = 0.15$ to $0.17 \times 10^{-3}$ K$^{-1}$ or $ZT = 0.13$ for Mg$_2$Si$_{0.4}$Sn$_{0.6}$ in this temperature range even without doping. At the vicinity of $x = 0.2$, pn-transition takes place; n-type semi-conductivity abruptly changes to p-type one. In the p-type semi-conductive materials Mg$_2$Si$_{1-x}$Sn$_x$ for $x > 0.4$ except for Mg$_2$Sn, the band structure is fixed as well as Mg$_2$Si since the temperature dependency of Seebeck coefficient is insensitive to tin content in the range of $x > 0.4$. Variation of Seebeck coefficient with temperature is complex at the vicinity of $x = 0.2$. This reveals that band structure also becomes much complex in this pn-transition range. In fact, effective antimony doping was reported for $x \leq 0.3$. That is,
n-type doping can be designed for $x < 0.2$ while p-type doping becomes effective for $x > 0.2$.

Acknowledgements

Authors would like to express their gratitude to Mr. A. Mitsuo, Tokyo Metropolitan Industrial Research Institute for his help in experiments. This study is financially supported in part by the national projects on the barrier-free processing and the environmental benign manufacturing.

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