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Fabrication and thermoelectric properties of eco-friendly silicides for thermoelectric power generation using waste heat†

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KEY WORDS: (Eco-friendly) (Higher manganese silicide) (Magnesium silicide) (Synthesis) (Mechanical grinding) (Pulse discharge sintering) (Liquid-solid phase reaction) (Thermoelectric properties)

1. Introduction

Development of alternative energy sources like the recycled energy sources is required for resolution of energy security and environmental problems. Thermoelectric power generation (TEG) is a prospective means using the waste heat discharged from many kinds of energy systems, and it is expected to contribute to the resolution of these issues. The low-cost thermoelectric materials are required for the practical use of TEG and the materials with low-environmental load are preferred. P-type higher manganese silicide (HMS) [1-3] and n-type dimagnesium silicide (Mg_2Si) [4-6] are candidates for low-cost and eco-friendly thermoelectric materials. In this research, the HMS compounds were synthesized and consolidated by pulse discharge sintering (PDS) combined with mechanical grinding (MG). Influence of Si content on the microstructure and the thermoelectric properties were investigated. The Mg_2Si compounds were synthesized by liquid-solid phase reaction (LSPR), and consolidated by PDS. Influences of Al dopant on the lattice parameter and the thermoelectric properties were also investigated.

2. Experimental Procedures

For fabricating HMS compounds, pure Mn powder (purity >99.9 %, particle size <75 μm) and Si powder (>99.9 %, <75 μm) were used as the raw powders. Each of Mn and Si powders were mechanically ground using planetary ball milling equipment at 400 rpm for 3 h. The ground Mn and Si powders, passing through a sieve of 44 μm opening, were individually collected. The sieved Mn and Si powders were weighed with non-stoichiometry of $MnSi_x$ (x=1.73, 1.80, 1.84 and 1.90), and mixed by using a rotary blender at 60 rpm for 1 h. The HMS compounds were synthesized from the powder mixtures and simultaneously consolidated by PDS at 1173K for 15 min under 60 MPa in a vacuum atmosphere. Influences of Si content on the microstructure and the thermoelectric properties were investigated.

For fabricating Al-doped Mg_2Si compounds, Mg powder (> 99.9 %, < 180 μm), Si powder (> 99.9 %, < 75 μm) and Al powder (> 99.9 %, 106-180 μm) were used as the raw powders. The powders were weighed with non-stoichiometry of $Mg_{66-y}Al_ySi_{33.3}$, and mixed in an argon atmosphere. The powder mixtures with different amounts of Al (y=0, 0.05, 0.10, 0.15, and 0.20 at.%) were prepared. The powder mixture was put into an alumina crucible, and $Mg_{66-y}Al_ySi_{34}$ compound was synthesized from the mixture through the LSPR process at 953 K for 1 h in an argon atmosphere using an infrared lamp heating furnace. The synthesized powder was consolidated by PDS at 1003 K for 30 min under the pressure of 60 MPa. Influences of Al dopant on the lattice parameter and the thermoelectric properties were investigated.

3. Results and Discussion

The fabricated $MnSi_x$ (x=1.73, 1.80, 1.84 and 1.90) samples had the relative density of 93, 92, 91 and 92 %, respectively. In the x-ray diffraction (XRD) analysis, HMS phase and MnSi phase were detected in the $MnSi_{1.73}$ and $MnSi_{1.8}$ samples. The relative diffraction intensity of MnSi phase of the $MnSi_{1.73}$ sample was larger than that of the $MnSi_{1.8}$ sample. On the other hand, only HMS phase was detected in the $MnSi_{1.84}$ and $MnSi_{1.9}$ samples. **Figure 1** shows the scanning electron microscope (SEM) images of the samples. In the $MnSi_{1.73}$ and $MnSi_{1.8}$ samples, MnSi phase coexisted with HMS phase, and in the $MnSi_{1.84}$ and $MnSi_{1.9}$ samples, free Si particles were dispersed in the HMS matrix. The microstructures were changed with Si content.

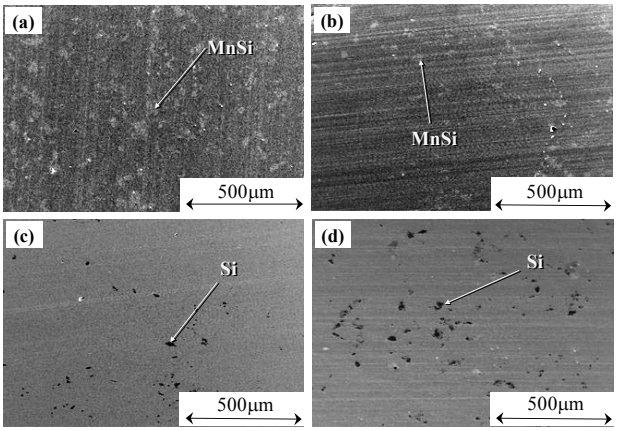

Fig. 1 SEM images of four $MnSi_x$ samples; (a) x=1.73, (b) x=1.8, (c) x=1.84, and (d) x=1.9.

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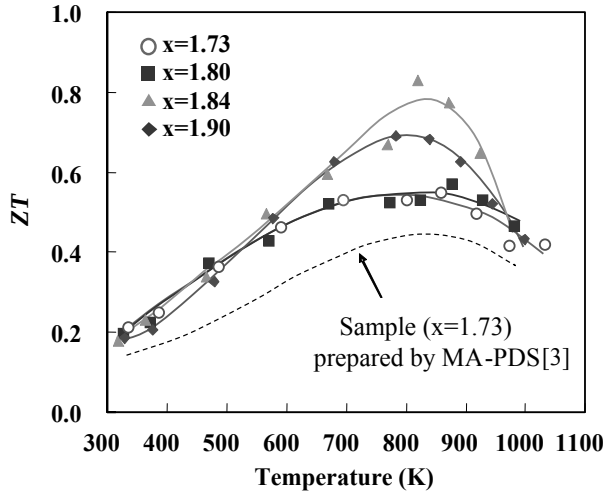

Fig. 2 Temperature dependence of the dimensionless figure of merit, *ZT* of four $MnSi_x$ samples (x=1.73, 1.8, 1.84 and 1.9) and of $MnSi_{1.73}$ sample prepared by MA-PDS [3].

The optimum Si content that makes a nearly single HMS phase will exist between x=1.8 and 1.84.

The electric resistivity of $MnSi_x$ samples increased with increase of Si content. This would be caused by the amount of MnSi phase having a lower electrical resistivity than HMS phase and by the amount of free Si having a larger electrical resistivity than HMS phase. The maximum Seebeck coefficient was achieved in the $MnSi_{1.84}$ sample having a small amount of free Si, because both MnSi phase and free Si have lower Seebeck coefficients than the HMS phase. All of the $MnSi_x$ samples had similar levels of thermal conductivity. From these thermoelectric properties, the dimensionless figure of merit, *ZT* was calculated. **Figure 2** shows the temperature dependences of *ZT* for the four $MnSi_x$ samples together with the result of the $MnSi_{1.73}$ sample prepared by PDS combined with mechanical alloying (MA) [3]. In the $MnSi_{1.84}$ sample, the best thermoelectric performance was obtained and the maximum *ZT* of 0.83 was achieved at 818K.

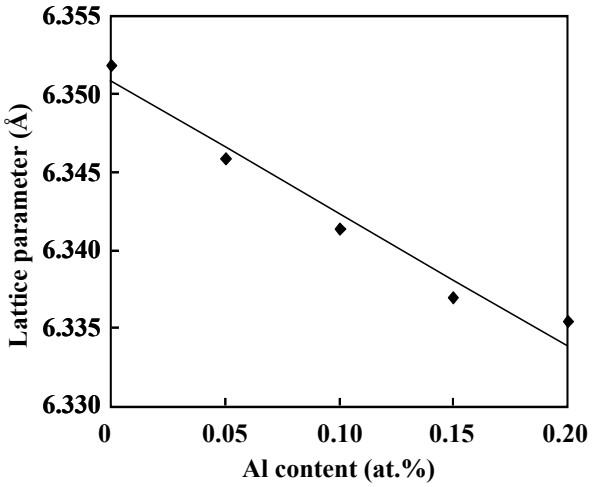

Fig. 3 Relation between Al content and lattice parameter of $Mg_{66-y}Al_ySi_{34}$ samples.

The relative density of all $Mg_{66-y}Al_ySi_{34}$ samples obtained by LSPR-PDS was more than 95%. In the XRD analysis, only Mg_2Si phase was detected in all samples. It indicates that $Mg_{66-y}Al_ySi_{34}$ compounds were successfully synthesized regardless of Al content. It is also found out that the diffraction peak positions shift slightly toward the larger diffraction angle with an increase of Al content, indicating that the lattice parameter of $Mg_{66-y}Al_ySi_{34}$ becomes smaller with increase of Al content. The relation between the Al content and the lattice parameter estimated from the XRD data is shown in **Fig. 3**. It linearly decreases with increasing Al content, obeying the Vegard's law. This result supports the view that Al atoms successfully substituted into a part of Mg sites in Mg_2Si and the lattice parameter decreased with substituting Al atoms having smaller atomic radius than Mg atoms.

The electrical resistivities of the $Mg_{66-y}Al_ySi_{34}$ samples (y=0.15 and 0.20 at.%) were one sixth or less than that of the non-doped sample (y=0 at.%) all over the temperature range. The absolute value of the Seebeck coefficient was remarkably decreased by Al doping, but the Seebeck coefficients of the $Mg_{66-y}Al_ySi_{34}$ samples (y=0.15 and 0.20 at.%) were varied similarly with temperature. The thermal conductivities of all samples increased with increase of Al content all over the temperature range. The temperature dependences of the dimensionless figure of merit, *ZT* are shown in **Fig. 4**. The maximum *ZT* was 0.27 at 789 K for the non-doped sample, 0.61 at 883 K for the 0.15 at.%Al-doped one, and 0.47 at 833 K for the 0.20 at.%Al-doped one, respectively. The 0.15 at.%Al-doped sample had the best thermoelectric performance.

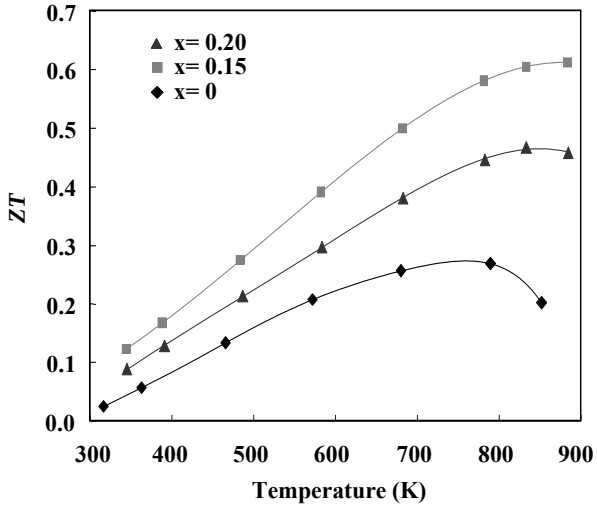

Fig. 4 Temperature dependence of the dimensionless figure of merit, *ZT* of three $Mg_{66-x}Al_xSi_{34}$ samples (x=0, 0.15 and 0.20).

4. Conclusions

The $MnSi_x$ compounds were synthesized by MG-PDS. The MnSi phase or free Si existed in the matrix of HMS depending on Si content. The maximum *ZT* of 0.83 was achieved at 818K by optimizing Si content (x=1.84) in $MnSi_x$. The $Mg_{66-y}Al_ySi_{34}$ compounds were synthesized by LSPR, and consolidated by PDS. The Al atoms were

substituted into parts of Mg sites in Mg_2Si. The maximum *ZT* of 0.61 was achieved at 883K by optimizing Al content (y=0.15 at.%) in Mg_2Si.

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