Thermoelectric Performance of p-Type Mg$_2$Si$_{0.25}$Sn$_{0.75}$ with Li and Ag Double Doping

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The single-phase of p-type Mg$_2$Si$_{0.25}$Sn$_{0.75}$ with Li and Ag double doping were prepared by the liquid-solid reaction and hot-pressing methods. All samples thus obtained were identified by XRD as single-phase solid solutions with an anti-fluorite structure. The effects of Li and Ag double doping on thermoelectric performance were investigated at temperature differences ($\Delta T$) of 0 to 500 K. The thermoelectromotive force ($E$) of the Li-25000 ppm single-doped sample was determined to be 88 mV at $\Delta T = 500$ K. For the Li-20000 ppm and Ag-5000 ppm double-doped sample, the $E$ value became larger (92 mV) after Ag substitution. A maximum $E$ value of 97 mV was obtained for the Ag-25000 ppm single-doped sample and the Li-5000 ppm and Ag-20000 ppm double-doped sample. Mean resistivity ($\rho_m$) at $\Delta T = 500$ K decreased by double doping and showed a minimum value of 2.94 x 10$^{-5}$ $\Omega$m for the Li-5000 ppm and Ag-20000 ppm double-doped sample. The maximum effective power ($P = E^2/\rho_m$) increased with $\Delta T$. The $P$ values of single-doped samples at $\Delta T = 500$ K were 38 Wm$^{-1}$ for Li single-doped and 72 Wm$^{-1}$ for Ag single-doped samples. $P$ for the Li-20000 ppm and Ag-5000 ppm double-doped sample was 64 Wm$^{-1}$, which was an improvement of about 90% compared with the Li single-doped sample. The maximum value of $P$ at $\Delta T = 500$ K was 80 Wm$^{-1}$ for the Li-5000 ppm and Ag-20000 ppm double-doped sample, which was an improvement of about 10% compared with the Ag single-doped sample.

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1. Introduction

The Mg$_2$(SiSn)-system solid solutions have been proposed as promising materials for high-performance thermoelectric generators in the temperature range of 500 to 800 K. The constituent elements of the Mg$_2$(SiSn)-system solid solutions are environmentally friendly, non-toxic, and abundantly available. Therefore, they are known as ecofriendly thermoelectric semiconductors. In our previous study, a single-phase of n-type Mg$_2$Si$_{0.25}$Sn$_{0.75}$ doped with Sb or Bi was successfully obtained using the liquid-solid reaction and hot-pressing methods. And a dimensionless figure of merit ($ZT$) of over 1.0 reached. However, the $ZT$ values of p-type samples of size suitable for measurement were cut by a diamond disk from the sintered compacts of Mg$_2$Si$_{0.25}$Sn$_{0.75}$ sintered compacts double doped with Li and Ag were more than 99% of the theoretical values.

In this paper, the single-phase of p-type Mg$_2$Si$_{0.25}$Sn$_{0.75}$ with Li and Ag double doping, prepared by the liquid-solid reaction and hot-pressing methods, and the effects of Li and Ag double doping on the thermoelectric performance are investigated with temperature differences ($\Delta T$) ranging from 0 to 500 K.

2. Experimental Procedures

Mg granules (nominal purity 3N), Sn granules (5N), Si powder (6N), Ag powder (4N) and lithium acetate (CH$_3$COOLi) were used as starting materials. Lithium acetate converted to lithium (Li), water (H$_2$O) and carbon dioxide (CO$_2$) by thermal decomposition above 525 K. Mg$_2$Si$_{0.25}$Sn$_{0.75}$ with Li and Ag double doping was synthesized in graphite crucibles by the liquid-solid reaction method. The total doping was limited to 25000 ppm. The following samples were prepared: single-doped with 25000 ppm Li (Sample L25), single-doped with 25000 ppm Ag (Sample A25), double-doped with 20000 ppm Li and 5000 ppm Ag (Sample L2A5), and double-doped with 5000 ppm Li and 20000 ppm Ag (Sample A2L5). The ingots obtained by this process were crushed in an alumina mortar, and sifted out to 38 to 75 μm. The powders were hot-pressed under a pressure of 50 MPa at 933 K for 1 h. The relative densities of the Mg$_2$Si$_{0.25}$Sn$_{0.75}$ sintered compacts double doped with Li and Ag were more than 99% of the theoretical values.

The phase structures of the sintered compacts were analyzed by the X-ray powder diffraction (XRD) using Cu K$_\alpha$ radiation. Prior to the thermoelectric measurements, samples of size suitable for measurement were cut by a diamond disk from the sintered compacts of Mg$_2$Si$_{0.25}$Sn$_{0.75}$ double doped with Li and Ag. In addition, the surfaces of samples were polished to a dimensional accuracy of better than 0.2% with a sheet of #600 emery paper. The resistivity and Hall coefficient at room temperature were measured by a standard 4-terminal method with a dc current of 10 mA. The Seebeck coefficient at room temperature was determined by measuring the temperature and the thermoelectromotive forces with two pairs of thermocouples attached to the tops and bottoms of the longitudinal specimens, with an accuracy of better than 3%. The mean resistivity ($\rho_m$) values were calculated from the measured sample sizes and $\rho_m$ values. The maximum effective power ($P = E^2/\rho_m$) was calculated from the previously determined values of $E$ and $\rho_m$. 
3. Results and Discussion

The XRD patterns of the sintered compacts of Samples L25, A25, A2L5 and L2A5 are shown in Fig. 1. The X-ray diffraction peaks of all sintered samples were located between the diffraction peaks of Mg$_2$Si and Mg$_2$Sn, and were single-pinnacle peaks. The peaks associated with metallic Mg, Si and Sn phases are not indicated. Also, all the sintered samples clearly showed only the Bragg peaks associated with an anti-fluorite structure (space group, Fm3m). For this reason, all samples obtained by hot-pressing were identified as single-phase solid solutions with the anti-fluorite structure.

The amount of doping, the carrier concentration and thermoelectric properties at room temperature for all samples are listed in Table 1. The measured Hall and Seebeck coefficients showed p-type conduction, which implies that holes were the principal conduction carriers. The carrier concentrations of single-doped samples were $1.74 \times 10^{25}$ m$^{-3}$ in the Li-25000 ppm single-doped sample (L25); and $3.70 \times 10^{25}$ m$^{-3}$ in the Ag-25000 ppm single-doped sample (A25). The carrier concentrations were increased by double doping, and the values obtained were $3.82 \times 10^{25}$ m$^{-3}$ in the Li-20000 ppm and Ag-5000 ppm double-doped sample (L2A5), and $4.12 \times 10^{25}$ m$^{-3}$ in the Ag-20000 ppm and Li-5000 ppm double-doped sample (A2L5). It is evident from these results that double doping by Ag and Li is effective in increasing the carrier concentration.

Seebeck coefficients of single-doped samples at room temperature were measured as 183.6 $\mu$VK$^{-1}$ for the L25 sample and 150.4 $\mu$VK$^{-1}$ for the A25 sample. When the samples were doped with Ag and Li, the Seebeck coefficient decreased. For the L2A5 and the A2L5 samples, the smallest values of the Seebeck coefficient were 137.1 $\mu$VK$^{-1}$ and 134.0 $\mu$VK$^{-1}$, respectively. The resistivity at room temperature was the highest for the L25 sample, a value of $3.836 \times 10^{-5}$ $\Omega$m. The resistivity of the A25 sample was smaller compared with L25; it was $2.776 \times 10^{-5}$ $\Omega$m. The resistivities of the double-doped samples were slightly lower compared with the single-doped samples, and were $2.461 \times 10^{-5}$ $\Omega$m for L2A5 and $2.460 \times 10^{-5}$ $\Omega$m for A2L5. These results suggest that the decreases in Seebeck coefficient and resistivity are due to increased carrier concentration. The L25 sample had the largest thermal conductivity (2.65 WK$^{-1}$m$^{-1}$), and the A25 and the A2L5 samples had the smallest (2.40 WK$^{-1}$m$^{-1}$). The thermal conductivities of the L2A5 double-doped samples were 2.48 WK$^{-1}$m$^{-1}$. These values can be attributed to the fact that the atomic radius of Ag is larger than that of Li and the atomic mass is also larger. This result proved that the Ag-atom is effective in reducing thermal conductivity.

The temperature dependence of the Seebeck coefficient is shown in Fig. 2. Seebeck coefficient increased up to the maximum values of 256 $\mu$VK$^{-1}$ at 492 K for L25, 221 $\mu$VK$^{-1}$ at 527 K for A25, 208 $\mu$VK$^{-1}$ at 532 K for L2A5 and 219 $\mu$VK$^{-1}$ at 537 K for A2L5. Above these temperatures, Seebeck coefficients decreased with increasing temperature; that is attributed to a mixed conduction carrier in the intrinsic

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**Table 1 Carrier concentration and thermoelectric properties at room temperature.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of doping, ppm</th>
<th>Carrier concentration, n/m$^{-3}$</th>
<th>Seebeck coefficient, $\alpha$/mVK$^{-1}$</th>
<th>Resistivity, $\rho$/$\Omega$m</th>
<th>Thermal conductivity, $\kappa$/WK$^{-1}$m$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L25</td>
<td>25000</td>
<td>0</td>
<td>1.74 $\times 10^{25}$</td>
<td>183.6</td>
<td>3.836 $\times 10^{-5}$</td>
</tr>
<tr>
<td>A25</td>
<td>0</td>
<td>25000</td>
<td>3.70 $\times 10^{25}$</td>
<td>148.5</td>
<td>2.724 $\times 10^{-5}$</td>
</tr>
<tr>
<td>L2A5</td>
<td>20000</td>
<td>5000</td>
<td>3.82 $\times 10^{25}$</td>
<td>143.7</td>
<td>2.461 $\times 10^{-5}$</td>
</tr>
<tr>
<td>A2L5</td>
<td>5000</td>
<td>20000</td>
<td>4.12 $\times 10^{25}$</td>
<td>140.9</td>
<td>2.460 $\times 10^{-5}$</td>
</tr>
</tbody>
</table>
region. For the Li-25000 ppm single-doped sample, the Seebeck coefficient in the intrinsic region showed a rapid decrease.

The temperature dependence of electrical resistivity is shown in Fig. 3. The electrical resistivity exhibit the same behavior as that of a metal: it increase monotonously with temperature. And in the intrinsic region, it decreases linearly above 500 K. The electrical resistivity of the Li25 sample was larger than that of other samples in the measured temperature range.

The temperature dependence of thermal conductivity is shown in Fig. 4. The thermal conductivity decreases linearly with increasing temperature and reaches a minimum near the intrinsic region, and then increases rapidly because of intrinsic conduction. In the temperature region below about 500 K, the thermal conductivity showed the $T^{-1}$ relationship, which is predominantly affected by the phonon components.

Because electrons as well as holes exist in the intrinsic region, the contribution of the bipolar component to thermal conductivity should be taken into consideration.9) Figure 5 shows thermoelectromotive force ($E$) as a function of the temperature difference ($\Delta T$). $E$ increased monotonously with increasing temperature difference. The $E$ values obtained at $\Delta T = 500$ K were 88 mV for L25, 92 mV for L2A5 and 97 mV for A2L5 and A25. There was hardly any identifiable difference between the single doped (A25) and the double-doped (A2L5) samples, as regards the temperature difference dependence of $E$. Therefore, this proved that addition of silver is effective in enhancing the thermoelectromotive force.

Figure 6 shows the mean resistivity ($\rho_m$) as a function of the temperature difference ($\Delta T$). The value of $\rho_m$ increased slightly with increase in the temperature difference. The $\rho_m$
of the L25 sample was the largest, which increased from 3.84 × 10⁻⁵ Ωm at ΔT = 0 K to 5.28 × 10⁻⁵ Ωm at ΔT = 500 K. And the smallest ρm was for the A2L5 sample which increased from 2.46 × 10⁻⁵ Ωm at ΔT = 0 K to 3.25 × 10⁻⁵ Ωm at ΔT = 500 K. The ρm of the A25 sample at ΔT = 500 K was 3.50 × 10⁻⁵ Ωm. The ρm of the L2A5 sample at ΔT = 500 K was 3.48 × 10⁻⁵ Ωm. The temperature dependence of ρm was similar to that of resistivity. Double doping was effective to decrease of the mean resistivity.

The maximum effective power \(P = E^2/4r_m\) was estimated by using the measured thermoelectromotive force \(E\) and the mean resistivity \(ρ_m\). Figure 7 shows \(P\) as a function of temperature difference \(ΔT\); \(P\) increases monotonously with temperature difference. The \(P\) values of single-doped samples at ΔT = 500 K were 38 Wm⁻¹ for L25 and 72 Wm⁻¹ for A25. The \(P\) value of the L2A5 sample increased to 64 Wm⁻¹, which is a much higher increase than that obtained for the Li single-doped sample. The maximum \(P\) at ΔT = 500 K was 80 Wm⁻¹ for the Li-5000 ppm and Ag-20000 ppm double-doped sample (A2L5), which was an improvement of about 10% when compared with the Ag single-doped sample. The addition of Ag was effective in improving the performance of Mg₂Sn₇.5Si₅.5 with compared with Li single-doping.

4. Conclusions

The single-phase of p-type Mg₂Sn₇.5Si₅.5 with Li and Ag double doping were prepared by the liquid-solid reaction and hot-pressing methods. The effects of Li and Ag double doping on thermoelectric performance were investigated at temperature differences \(ΔT\) of 0 to 500 K. All the samples obtained by hot-pressing were identified by XRD as single-phase solid solutions with an anti-fluorite structure. The Hall and Seebeck coefficients were positive, which indicated p-type conduction with holes as the principal conduction carriers. Double doping increased the carrier concentration to more than double of that achieved by Li-doping. We thus established the validity of double doping for increasing carrier concentration. The thermoelectromotive force \(E\) of the Li-25000 ppm single-doped sample was determined to be 88.4 mV at ΔT = 500 K. The addition of Ag caused the Li-20000 ppm and Ag-5000 ppm double-doped sample to achieve \(E\) values higher than 91.5 mV. The maximum \(E\) values of 97.1 mV were attained for the Ag-25000 ppm single-doped sample and the Li-5000 ppm and Ag-20000 ppm double-doped sample. The maximum effective power \(P = E^2/4r_m\) increased with ΔT. The \(P\) values of single-doped samples at ΔT = 500 K were 38 Wm⁻¹ and 72 Wm⁻¹ for the Li single-doped and the Ag single-doped samples, respectively. The \(P\) value for the Li-20000 ppm and Ag-5000 ppm double-doped sample was 64 Wm⁻¹, which was an improvement of about 90% compared with the Li single-doped sample. The maximum \(P\) value of 80 Wm⁻¹ at ΔT = 500 K was obtained for the Li-5000 ppm and Ag-20000 ppm double-doped sample, which was an improvement of about 10% compared with the Ag single-doped sample.

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