

Development of $\text{Mg}_2(\text{SiSn})$ Thermoelectric Material for Automobile

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ABSTRACT

As an appropriate material for automotive thermoelectric generators, which directly convert waste heat of exhaust gas into electricity, we have developed $\text{Mg}_2(\text{Si}_{1-x}\text{Sn}_x)$ thermoelectric materials with high thermoelectric performance. The performance is evaluated with the dimensionless figure of merit (ZT), and the ZT has been improved through the development of the fabrication process and the investigation of the optimum composition and dopant element. A novel liquid-solid reaction synthesis method incorporating hotpressing for the sample fabrication was effective in reducing the thermal conductivity. The n-type $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ doped with Sb attained a high ZT of 1.1 at 620 K. The p-type $\text{Mg}_2(\text{Si}_{0.25}\text{Sn}_{0.75})$ doped with Li and Ag simultaneously achieved a ZT of 0.3 at 600 K. The effective maximum power of n-type thermoelectric element and that of p-type were calculated with the thermoelectromotive force and the mean resistivity. The calculated power generation showed the possibility of improving fuel consumption in automobiles.

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INTRODUCTION

The Increase of greenhouse gas emissions including carbon dioxide (CO_2) is one of the big problems in the world. Automobiles, which emit the most of greenhouse gas in the transportation field, are required to improve fuel consumption by decreasing CO_2 in emissions. An approach to the improvement is the waste heat recovery from the exhaust gas [1, 2, 3, 4, 5]. A thermoelectric generator (TEG) directly converts waste heat into electricity. The electricity generated from the TEG is charged in a battery through a DC-DC converter [6]. It is used in lights, navigation systems and audio systems of electrical devices. The electricity not generated from the TEG in an automobile is generated from the alternator using the energy of the engine. Since the TEG added in an automobile can reduce the load on the alternator in the running engine, much of the energy from the engine is used for running. In this way, automobiles equipped with a TEG can improve the fuel consumption. However, TEGs have not been mass-produced yet. There are only a few practical thermoelectric materials such as bismuth telluride (BiTe), lead telluride (PbTe) and silicon germanium (SiGe) [7]. BiTe , the most popular thermoelectric material, has a high thermoelectric performance in the low temperature range. It is installed in thermoelectric watches utilizing body heat. PbTe has a high thermoelectric performance in the middle temperature range. A high temperature material SiGe was installed in NASA's Voyager as a radioisotope thermoelectric generator. Most of these materials contain toxic, scarce and expensive elements. The development of materials not containing such elements is expected in recent years.

The advantages of $\text{Mg}_2(\text{SiSn})$ are environmentally friendly, nontoxic, lightweight and inexpensive. Moreover, this material has high thermoelectric performance in the temperature range from 400 to 800 K. $\text{Mg}_2(\text{SiSn})$ is promising as alternative material for PbTe in the middle temperature range. The thermoelectric properties of $\text{Mg}_2(\text{SiSn})$ was revealed by Nikitin et al in 1960s [8,9]. However, $\text{Mg}_2(\text{SiSn})$ was not developed for the improvement of the thermoelectric performance until the study by Fedorov in the 2000s [10,11]. One of the reasons was the difficulty in making samples by melting. In the process, there is a risk of explosion caused by the proximity to the melting temperature of Mg_2Si (1358 K) and evaporating temperature of Mg (1363 K) [12]. Due to the melting process, Mg composition of the synthetic composites is different from the nominal composition. The mechanical alloying method has also problems of explosion of Mg powder. $\text{Mg}_2(\text{SiSn})$ showed another problem that the samples in the region of $0.4 < x < 0.6$ for $\text{Mg}_2(\text{Si}_{1-x}\text{Sn}_x)$ are multi-phase [13]. According to the report by Zaitsev [14], the thermal conductivity around $x = 0.5$ for $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ is the lowest in the composition. The thermal conductivity of $\text{Mg}_2(\text{SiSn})$ solid solutions is lower than that of Mg_2Si due to the alloy effect which causes more phonon scattering by disorder of atomic weights of Si and Sn.

In this study, we developed a fabrication process using a novel liquid-solid reaction synthesis method incorporating hot-pressing. Then, we improved the thermoelectric performance for $\text{Mg}_2(\text{SiSn})$ of n-type and p-type conduction. The thermoelectric performance is evaluated by the dimensionless figure of merit ZT , defined by $ZT = \alpha^2 T / \rho \kappa$, where α is the Seebeck coefficient, T is the absolute temperature, ρ is the resistivity, and κ is the thermal conductivity.

Finally, the effective maximum power for $\text{Mg}_2(\text{SiSn})$ was measured and the power generation for the $\text{Mg}_2(\text{SiSn})$ module was calculated using the effective maximum power measured.

FABRICATION PROCESS

As already mentioned above, we developed a fabrication process of a novel liquid-solid reaction synthesis method incorporating hotpressing. The features of the process are safety, low input energy and reproducibility. For the purpose of making single phase $\text{Mg}_2(\text{SiSn})$ samples, the effects of sintering temperature and time on them were investigated.

The starting materials were Mg granules (nominal purity 99.9%), Sn granules (99.999%) and Si powder (99.9999%). Undoped Mg_2Si and Mg_2Sn were fabricated using a liquid-solid solution reaction method. The sintered compacts of undoped $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ and $\text{Mg}_2(\text{Si}_{0.55}\text{Sn}_{0.45})$ were made from the mixed powder of Mg_2Si and Mg_2Sn using a hot-pressing method in Ar atmosphere. The sintering conditions, i.e., temperature and time were varied to make singlephase $\text{Mg}_2(\text{SiSn})$ sample. The sintering temperatures for $\text{Mg}_2(\text{Si}_{0.55}\text{Sn}_{0.45})$ were 973 K, 1023 K and 1073 K under a pressure of 50 MPa for 0.5 h. The sintering times for $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ were 0.5 h, 5 h and 20 h under a pressure of 80 MPa and at 1053 K. The phases of the sintered compacts were analyzed by using XRD. Figure 1 shows XRD patterns for $\text{Mg}_2(\text{Si}_{0.55}\text{Sn}_{0.45})$ samples sintered under different temperatures. For all the samples, the peaks in the range from 20 to 90 degrees in 2θ existed between those of Mg_2Si and Mg_2Sn and all the peaks shown were those derived from an antiferroite structure. The XRD patterns were estimated whether the samples were multi-phase or single-phase. The samples sintered at 973 K and 1023 K were multi-phase. However, the pattern of the latter was similar to that of single-phase samples. The pattern of the sample sintered at the highest temperature of 1073 K was single phase with a narrow full width half maximum. Figure 2 shows XRD patterns for $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ samples sintered under different lengths of time. The XRD peaks of all the samples existed between Mg_2Si and Mg_2Sn with an anti-fluorite structure, and all the peaks shown were those derived from the structure. The sample of sintering time of 0.5 h was multi-phase with a Mg_2Si pattern and some $\text{Mg}_2(\text{Si}_{1-x}\text{Sn}_x)$ patterns. The sample of sintering time of 5 h was also multiphase with similar patterns to those of Mg_2Sn and Mg_2Si . However, the latter was closer to single phase than the former. The sample of sintering time of 20 h was single-phase with sharp peaks located in the middle of Mg_2Sn and Mg_2Si peaks. As these results show, the sintering temperature under which the single-phase samples of $\text{Mg}_2(\text{SiSn})$ were obtained was 1073 K, and the sintering time 20 h. The hot-pressing method using the mixed powder required a long sintering time to obtain single phase samples. The novel liquid-solid reaction synthesis method where the starting materials put in the graphite crucible are synthesized made it possible to reduce the time of hot-pressing. Figure 3 shows XRD patterns of $\text{Mg}_2(\text{Si}_{0.5}\text{Sn}_{0.5})$ using the mixed powder and that using solid-liquid reaction synthesis method. The single phase sample for $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ using solid-liquid reaction method was obtained by sintering for 5 hours while it took 20 hours when using mixed powder.

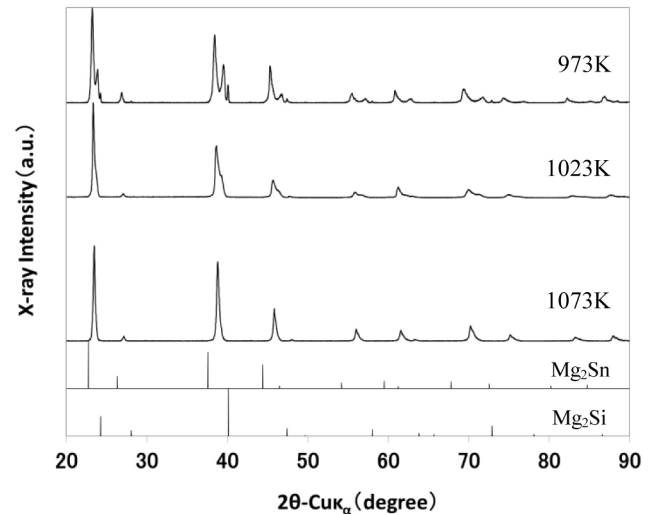


Figure 1. XRD patterns for undoped $\text{Mg}_2(\text{Si}_{0.55}\text{Sn}_{0.45})$ depending on sintering temperature

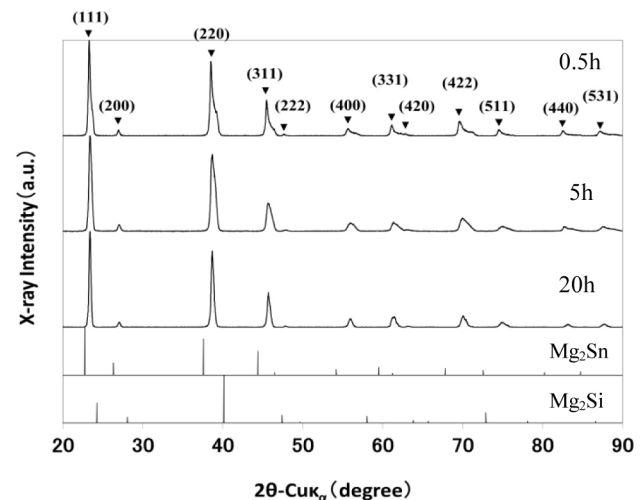


Figure 2. XRD patterns for undoped $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ depending on sintering time

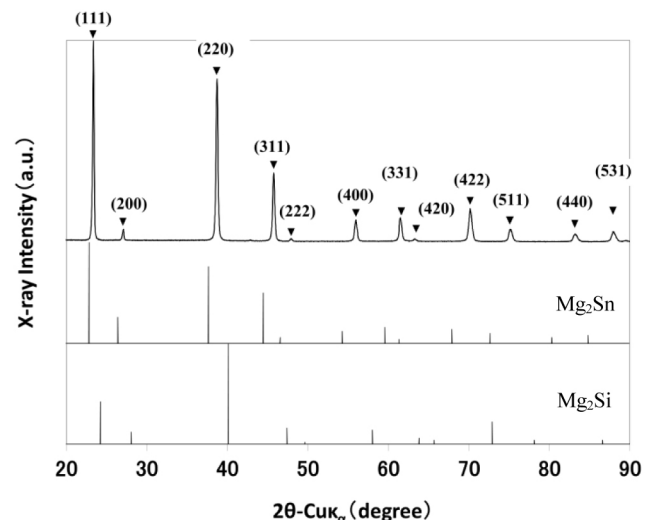


Figure 3. XRD patterns for undoped $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ under 1043 K, 5 h and 80 MPa

N-TYPE $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$

To improve the ZT , the carrier concentration of $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ required to be controlled by doping the dopant [15,16]. Sb of n-type dopant was doped in $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$. The samples of $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ doped with Sb were fabricated using a liquid-solid reaction incorporating hot-pressing. The starting materials within the graphite crucible were synthesized under Ar +3 % H_2 reactive atmosphere in electrical furnace. The obtained ingots were ground and sieved in a size from over 38 up to 75 μm . The powder was sintered under 80 MPa at 1043 K for 5 hours. The doping amounts of Sb are 0, 5000 and 7500 ppm. The X-ray diffraction peaks of all the sintered samples existed between Mg_2Si and Mg_2Sn with an antifluorite structure (space group: $\text{Fm}\bar{3}\text{m}$), and all the peaks shown were those derived from the structure. The peaks of oxides, Mg_2Si and Mg_2Sn were not observed. These results confirmed that all the samples were single phase.

The carrier concentration of the samples increased with the increase of Sb amount, i.e., $3.40 \times 10^{-4} \text{ m}^{-3}$ for 0 ppm, 2.25×10^{-5} for 5,000 ppm and 1.59×10^{-6} for 7500 ppm. Moreover, all the samples exhibited the negative conduction. Therefore, it was demonstrated that the carrier concentration of the sample was controlled by Sb doping. Figure 4 shows the temperature dependence of the resistivity ρ for $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ doped with Sb between 80 K and 800 K. The samples with 0 and 5000 ppm Sb behave like a semiconductor, i.e., the resistivity decreased with the increase in temperature up to 182 and 267 K, respectively, and decreased rapidly in the intrinsic region where the same number of electrons and holes came from thermal excitation, in particular above 516 and 630 K, respectively. On the other hand, the sample with 7500 ppm Sb behaves like a metal. The resistivity increased with the increase in temperature between 80 and 299 K and increased rapidly in the intrinsic region, i.e., above 299 K. Therefore, it revealed that the samples with 0 and 5000 ppm Sb were in the non-degenerate state and the sample with 7500 ppm Sb is in the degenerate state.

Figure 5 shows the temperature dependence of the Seebeck coefficient α for the $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ doped with Sb between 300 and 800 K. The absolute value of the Seebeck coefficient α is expressed as $|\alpha|$. The temperature dependence of $|\alpha|$ is similar in the samples with 0 and 5000 ppm Sb. The $|\alpha|$ increased with the increase in temperature, but decreased above the temperature of maximum $|\alpha|$, because the range was the intrinsic region. The samples with 0 and 5000 ppm Sb showed the maximum value of $|\alpha|$ at 435 and 590 K, respectively. The sample with 7500 ppm Sb increased monotonously in the whole range of measured temperature. As the Sb amount increased, the maximum value of $|\alpha|$ got lower and the temperature for the maximum value of $|\alpha|$ increased.

Figure 6 shows the temperature dependence of the thermal conductivity κ between 300 and 800 K. All samples had a similar tendency in the dependence. The thermal conductivity increased with the increase in the Sb amount. In addition to phonon and carrier components, bipolar component in which the electron and the hole interact with each other contributed to the thermal conductivity in the intrinsic region, above 570 K. Therefore, the thermal conductivity increased rapidly in the temperature range.

Figure 7 shows the temperature dependence of ZT . The ZT for the sample with 7500 ppm Sb was higher than that of the sample with 5000 ppm Sb. Since the resistivity of the former was lower than that

of the latter, it can be said that the resistivity was greatly influenced by the increase of ZT . The ZT of the $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ sample doped with 7500 ppm Sb reached 1.1 at 620 K.

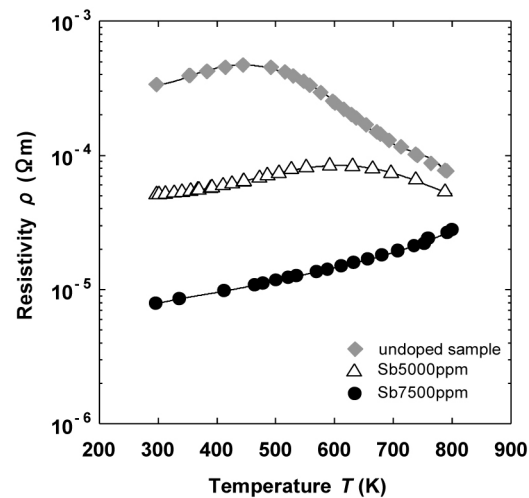


Figure 4. Temperature dependence of resistivity for n-type $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ depending on amount of Sb

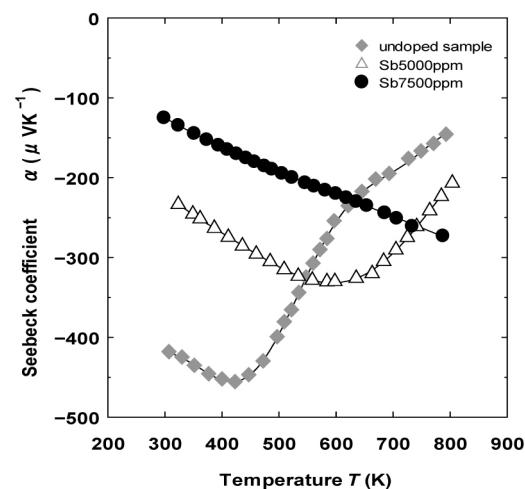


Figure 5. Temperature dependence of Seebeck coefficient for n-type $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ depending on amount of Sb

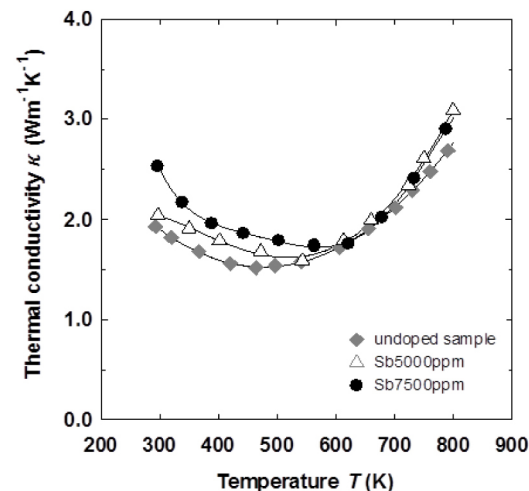


Figure 6. Temperature dependence of thermal conductivity for n-type $\text{Mg}_2(\text{Si}_{0.50}\text{Sn}_{0.50})$ depending on amount of Sb