

Doping Effects on Thermoelectric Properties in the Mg₂Sn System

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A weak point of Mg₂X thermoelectrics is the absence of a *p*-type composition, which motivates research into the Mg₂Sn system. Mg₂Sn thermoelectrics were fabricated by a vacuum melting method and a spark plasma sintering process. As a result, Mg₂Sn single phases were acquired in a wide range of Mg-to-Sn atomic ratios (67:33 to 71:29), showing slightly different thermoelectric characteristics. However, the thermoelectric properties of the undoped system were not sufficient for application in commercial production. To maximize the *p*-type characteristics, many atoms [Ni (VIII A), Cu (IB), Ag (IB), Zn (IIB), and In (IIIB)] were doped into the Mg₂Sn phase. Among them, the power factor values increased only in the Ag-doped case. Ag-doping resulted in a power factor that was more than 10 times larger than the value in the undoped case. This result could be important for developing *p*-type polycrystalline thermoelectrics in the Mg₂X (X = Si, Sn) system. However, other atoms [Ni (VIII A), Cu (IB), Zn (IIB), and In (IIIB)] were not determined to act as acceptor atoms. The maximum *ZT* value for the Ag-doped Mg₂Sn thermoelectric was more than 0.18, which is comparable to the value for the *n*-type Mg₂Si system.

Key words: Thermoelectric, Mg₂Sn, spark plasma sintering (SPS), polycrystalline

INTRODUCTION

Thermoelectric materials with sufficient performance levels at high temperatures are a key factor in the realization of a TE generator.¹ Mg₂X (X = Si, Sn) compounds are semiconductors that crystallize in the cubic fluorite structure in space group *Fm3m*.² They are promising thermoelectric materials for power generation. The Mg₂X (X = Si, Sn) systems have received special attention because their constituent elements are abundant in the Earth's crust and their processing by-products are nontoxic. In addition, ecofriendly Mg₂X provides for

safe handling and operation of devices for practical applications.³ For such reasons, many researchers have reported numerous papers regarding the fundamental electrical properties of Mg₂X since the end of the 1950s. For many reasons, research related to Mg₂Sn thermoelectrics is essential for developing a thermoelectric module in these Mg₂X fluorite systems. Most reports about doped Mg₂X systems are limited to the *n*-type characteristic, but research related to doped Mg₂Sn thermoelectrics can address the lack of the *p*-type characteristic in the Mg₂X fluorite systems.

In this study, undoped Mg₂Sn thermoelectrics were fabricated by a vacuum melting method and the spark plasma sintering (SPS) process in a wide range of ratios between Mg and Sn atoms. To

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control impurity contamination from the atmosphere, the powder was sealed in a quartz ampoule under vacuum. The Mg_2Sn specimens were densified by means of SPS. In the case of SPS, the diffusion velocity of a material was reported to become extremely large at low temperature owing to the pulsed DC electric field.⁴ SPS plays an important role in the sintering process of Mg_2Sn , providing a densification process in a short time at relatively low temperature, which is very effective for suppressing volatilization of Mg and Sn, and of dopants with low melting points.⁵

In addition, to maximize the p -type thermoelectric properties of the Mg_2Sn system, many atoms can be doped into the Mg_2Sn phase. Thus far, many metals have been reported as effective acceptor ions in the Mg_2Sn system;^{6–9} however, most studies have reported single-crystal cases, whereas few results for polycrystalline material have been reported. Therefore, in this study we investigated the effect of many dopants on the p -type thermoelectric properties in the Mg_2Sn polycrystalline system.

EXPERIMENTAL PROCEDURES

Mg_2Sn samples were prepared by a vacuum melting method. Mg (>99.8%, powder) and Sn (99.999%, granular) were used as the starting materials. Obtaining a Mg_2Sn single phase is difficult due to the high vapor pressure and chemical reactivity of Mg and low melting temperature of Sn. To synthesize a Mg_2Sn single phase, Mg powders and granular Sn were homogeneously and stoichiometrically mixed into five compositions with Mg-to-Sn molar ratios ranging from 67:33 to 71:29. The weighted mixture of Mg powder and granular Sn was put into an alumina crucible and then sealed in an evacuated quartz ampoule. The encapsulated crucible was then placed in an electrical furnace, and melting was carried out for 30 min at about 1083 K, which is 30 K higher than the melting temperature of Mg_2Sn . The ingot was then annealed *in situ* at 673 K for 5 h. The polycrystalline ingot was ground in an alumina mortar and sieved with a 45- μm sieve. The sieved powders were sintered by a SPS method at 800 K under 40 MPa of pressure for 10 min in a vacuum. The prepared samples were sliced with a low-speed diamond saw and then polished to measure the thermoelectric properties.

To maximize the p -type thermoelectric property, high-purity Ni (VIII, 99.99%, grain), Cu (IB, 99.99%, powder), Ag (IB, 99.99%, powder), Zn (IIB, 99.99%, shot), and In (IIIB, 99.99%, powder) atoms were doped into Mg_2Sn specimens at various doping amounts. The same process was applied to synthesize these doped specimens. The phase analyses were performed using x-ray diffraction (XRD) on a Rigaku D/MAX-2500/PC diffractometer using Cu radiation. The thermoelectric properties, the electrical conductivity, and the Seebeck coefficient were measured by using a thermoelectric property measurement

system (model RZ2001i; Ozawa Science), and the thermal conductivity was measured using a laser flash technique (LFA 457; NETZSCH) from room temperature to 750 K. Carrier concentration values were measured by a Hall measurement system (ResiTest 8340; Toyo) at room temperature.

RESULTS AND DISCUSSION

As mentioned in the “Introduction” section, the main theme of this study is to improve the p -type thermoelectric properties of the Mg_2Sn system by means of doping with foreign atoms [Ni (VIII), Cu (IB), Ag (IB), Zn (IIB), and In (IIIB)]. For this purpose, first we had to optimize the process of synthesizing the Mg_2Sn stoichiometric single phase. We manufactured five compositions (Mg:Sn = 67:33 to 71:29) by means of a vacuum melting process as mentioned in the “Experimental Procedures” section to optimize the manufacturing process of the Mg_2Sn stoichiometric single phase (Mg:Sn = 66.6:33.3). We investigated various compositions because we needed to consider the vaporization problem associated with Mg and Sn. Although we employed a vacuum melting process, the vaporization problem or the possibility of Mg and Sn reacting with the quartz ampoule could still occur when seeking to create a stoichiometric ingot. As a result of the five compositions with a ratio range between Mg and Sn atoms of 67:33 to 71:29, we acquired Mg_2Sn single phases with the vacuum melting process.

However, the thermoelectric characteristics of these compositions were different. This difference was considered to be due to nonstoichiometry problems in these Mg_2Sn samples, as shown in Fig. 1. Although all compositions showed p -type characteristic at room temperature, an Mg-excess composition (Mg:Sn = 71:29) became n -type at temperature higher than about 400 K. In contrast, a Sn-excess composition (Mg:Sn = 67:33) retained the p -type characteristic even at higher temperature, as high as 500 K. It then changed to n -type characteristic when the temperature exceeded 500 K. The reason for this different carrier type appearing for different compositions is not yet clear. However, it should be noted here that the defect chemistry for the two types of nonstoichiometric compositions (Mg excess and Sn excess) can differ due to Mg evaporation and the reaction between the Mg vapor and the quartz ampoule.⁶ Specifically in the case of Sn-excess compositions (Mg:Sn = 67:33), a Mg-deficient, nonstoichiometric $\text{Mg}_{2-\delta}\text{Sn}$ phase could be synthesized owing to Mg evaporation. In general, if a charged point defect is formed in a stoichiometric ionic crystal (for example, a metal oxide), a complementary point defect with an opposite effective charge must be formed to conserve the electrical neutrality of the stoichiometric crystal.¹⁰ Kroger and Vink list six basic types of defect structures (internal atomic disorder) which are possible in a

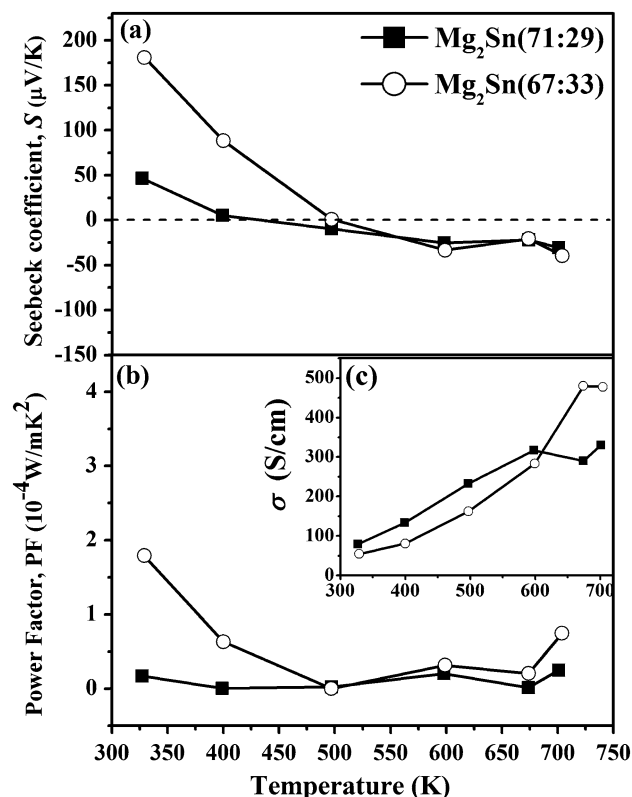


Fig. 1. Temperature dependence of (a) the Seebeck coefficient, (b) the power factor, and (c) the electrical conductivity of undoped Mg₂Sn samples (Mg:Sn = 67:33 and 71:29).

stoichiometric compound. Schottky disorders and Frenkel disorders are included among these six types of defect structures.¹⁰ For our case, Mg₂Sn can also be seen as a predominantly ionic material with partial covalent bonding, as Grosch et al. reported.¹¹ Thus, the indispensable Mg²⁺ vacancy (V_{Mg}^{2-}) in the Sn-excess compositions (Mg:Sn = 67:33) could behave as an acceptor ion in this Mg_{2- δ} Sn semiconductor, resulting in movement of the acceptor level slightly above the top of the valence band of this semiconductor. As a result, the Mg_{2- δ} Sn semiconductor showed *p*-type characteristic at temperature lower than 500 K, then a transition to intrinsic *n*-type conduction at temperatures higher than 500 K, in agreement with previous reports on undoped Mg₂Sn.^{7,9,12} This transition from a *p*- to an *n*-type conduction characteristic may have resulted from the narrow band gap of this Mg₂Sn semiconductor of about 0.3 eV.⁸ Chen and Savvides also reported a *p*-type characteristic in Sn-excess (Mg-deficient) compositions.⁹ In contrast, in the case of an Mg-excess composition (Mg:Sn = 71:29), the probability of creating the Mg-deficient Mg_{2- δ} Sn phase was low owing to the excess Mg atoms. Therefore, although it showed a *p*-type characteristic at room temperature, the characteristic could easily become an intrinsic *n*-type characteristic with a small elevation of temperature, even at a lower temperature (400 K) than the case

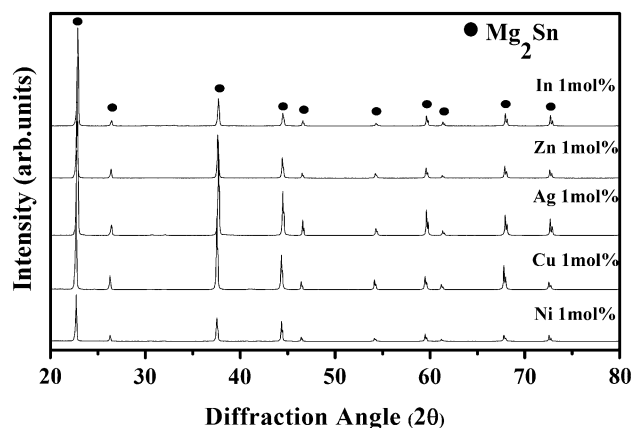


Fig. 2. X-ray diffraction patterns of doped Mg₂Sn (67:33) samples with 1 mol.% of various foreign atoms (Ni, Cu, Ag, Zn, and In) synthesized by a vacuum melting method.

noted with Sn-excess compositions (500 K). More detailed studies of this defect chemistry will be done as follow-up studies. In addition, why the Sn-excess composition (Mg:Sn = 67:33) showed stronger temperature dependence of the Seebeck coefficient compared with the Mg-excess composition (Mg:Sn = 71:29), as shown in Fig. 1a, remains unclear thus far.

As we expected, the power factor values for these undoped Mg₂Sn compositions were not very high, as shown in Fig. 1b. Therefore, to maximize the *p*-type thermoelectric power factor, it was necessary to dope foreign atoms into the Mg₂Sn system. The efficiency of a thermoelectric material is determined by its dimensionless thermoelectric figure of merit, $ZT = S^2\sigma T\kappa^{-1}$, where S , σ , κ , and T are the Seebeck coefficient, electrical conductivity, total thermal conductivity, and absolute temperature, respectively. According to this equation, good thermoelectric materials should possess large power factor ($\text{PF} = S^2\sigma$) and low thermal conductivity. We sought to improve the *p*-type properties by doping five acceptor atoms [Ni (VIII A), Cu (IB), Ag (IB), Zn (IIB), and In (IIIB)] into Sn (IVB) sites. Because the main objective of this study is to develop a *p*-type characteristic, as mentioned above, the Sn-excess composition (Mg:Sn = 67:33) was selected as the Mg₂Sn matrix to be doped with foreign atoms. Figure 2 shows the phase analysis results for Mg₂Sn samples doped with the same amount (1 mol.%) of various foreign atoms [Ni (VIII A), Cu (IB), Ag (IB), Zn (IIB), and In (IIIB)]. For each of the five different dopant systems, the XRD analysis results showed no secondary phase related to the foreign atoms even with a large amount as high as 1 mol.%. Therefore, we measured the thermoelectric properties for the five different dopant compositions, expecting an increase in the *p*-type thermoelectric property.

Although the five compositions showed *p*-type characteristics at room temperature, when the

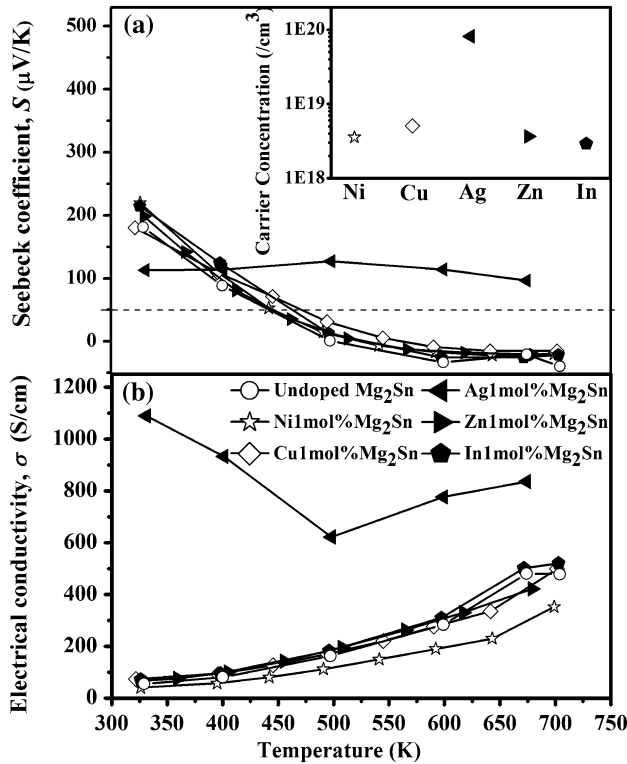


Fig. 3. Temperature dependence of (a) the Seebeck coefficient and carrier concentration at room temperature, and (b) the electrical conductivity of the Mg_2Sn (67:33) samples (undoped, Ni, Cu, Ag, Zn, and In).

measuring temperature was increased, the Seebeck coefficients of all specimens except for the Ag-doped case denoted n -type characteristic at temperature of nearly 400 K, similar to the undoped specimen, as shown in Fig. 3a. Only for the Ag-doped case did the Seebeck coefficient show p -type characteristics throughout the measured temperature range, even at temperature higher than 700 K, unlike the undoped specimen as shown in Fig. 3a. This result shows that only Ag atoms act as an acceptor when doped into a Mg_2Sn ($\text{Mg}:\text{Sn} = 67:33$) specimen. As shown in the inset to Fig. 3a, the exclusive effect of the Ag-dopant as an acceptor was reconfirmed by measurements of carrier concentration. Most dopants except for Ag did not increase the carrier concentration in this Mg_2Sn system. They (Ni, Cu, Zn, and In) even brought about lower carrier concentration values than in undoped Mg_2Sn .⁸ As a result, only in the Ag-doped case was the electrical conductivity much higher than that of the undoped case, unlike the cases of the other dopants, as shown in Fig. 3b. Why the other four atoms did not act as an acceptor remains unclear; however, we can assume the possibility that they remained at grain boundaries and did not react with the Mg_2Sn matrix. A second assumption is the possibility of the synthesis of M_xSn_y ($M = \text{Ni}, \text{Cu}, \text{Zn}, \text{and In}$) phase at trace levels. In this case, these four atoms (Ni, Cu, Zn, and In) would not be substituted at Sn sites

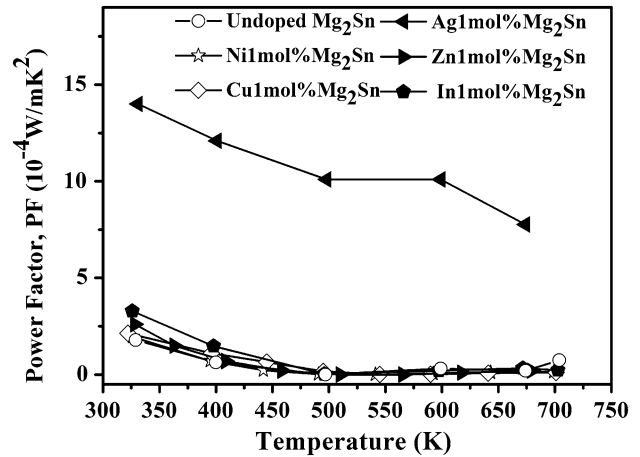


Fig. 4. Temperature dependence of the power factor of an undoped Mg_2Sn (67:33) sample and doped Mg_2Sn (67:33) samples with 1 mol.% of various foreign atoms (Ni, Cu, Ag, Zn, and In).

but would react with Sn atoms, forming M_xSn_y phase. Moreover, the formation of this new second phase may have disturbed the formation of the p -type $\text{Mg}_{2-\delta}\text{Sn}$ phase. This may also explain why there is no improvement in the p -type characteristics of the systems doped with these four atoms (Ni, Cu, Zn, and In). In contrast, there is also the possibility of the formation of Mg_xX_y ($M = \text{Ni}, \text{Cu}, \text{Zn}, \text{and In}$) phase in this system at trace levels. However, if the dopants atoms react with Mg, the formation of the p -type $\text{Mg}_{2-\delta}\text{Sn}$ phase would be promoted. This hypothesis is inconsistent with the result showing no change in the p -type characteristics. As a result, most dopant systems except for Ag did not show an improvement in their p -type characteristic or in the power factor value of the $\text{Mg}_{2-\delta}\text{Sn}$ system. Only the Ag dopant was effective in improving the p -type characteristic and increasing the value of the power factor, as shown in Fig. 4. Therefore, more detailed research aimed at optimizing the doping level was performed to maximize the p -type characteristics in the Ag-doped system.

Figure 5 shows the phase analysis results for various Ag-doping amounts. Every Ag-doped phase, even with a large amount up to 3 mol.%, showed no secondary phase related to Ag atoms. Only for the 3 mol.% Ag-doped case could we detect the MgAg phase at a trace level, as Chen et al. reported.⁷ As intended, the Seebeck coefficient for the Ag-doped specimen, even with a small amount (0.5 mol.%), showed p -type characteristics throughout the measured temperature range as shown in Fig. 6a, unlike the undoped specimen. This result also can be explained in terms of an acceptor effect of Ag atoms doped into the Mg_2Sn ($\text{Mg}:\text{Sn} = 67:33$) specimen; specifically, hole concentrations could increase owing to the acceptor doping effect, as shown in the inset of Fig. 3a. These increases of the p -type carrier concentration could be confirmed by the lower values of the Seebeck coefficients of the

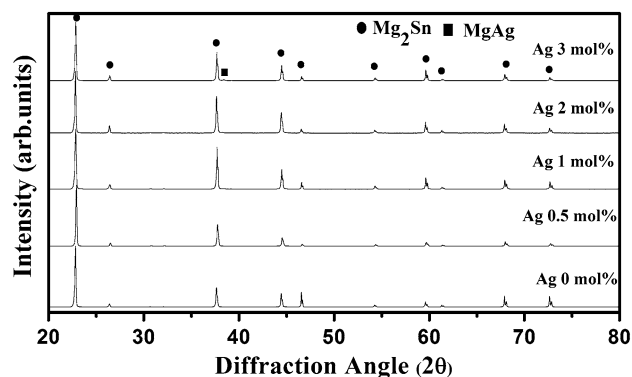


Fig. 5. X-ray diffraction patterns for Ag (0 mol.%, 0.5 mol.%, 1 mol.%, 2 mol.%, and 3 mol.%) -doped Mg₂Sn (67:33) samples synthesized by a vacuum melting method.

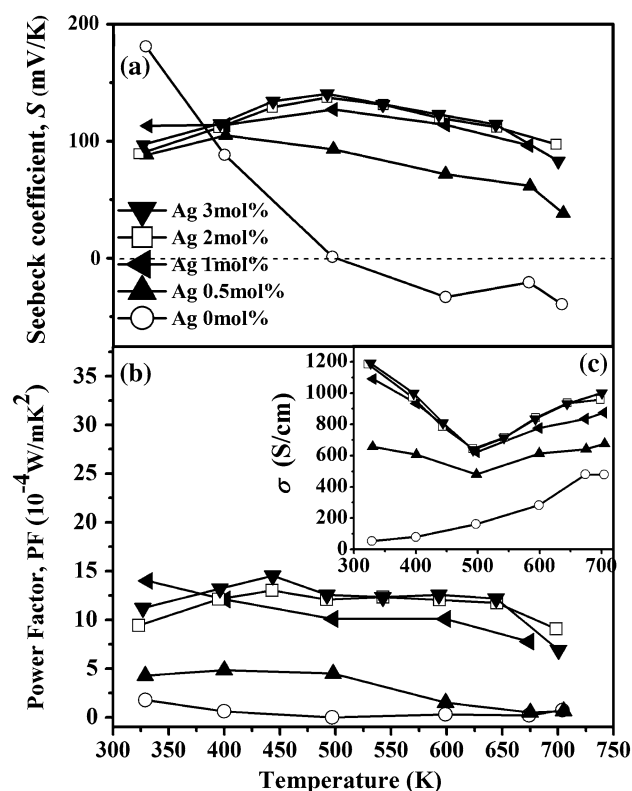


Fig. 6. Temperature dependence of (a) the Seebeck coefficient, (b) the power factor, and (c) the electrical conductivity of Ag (0 mol.%, 0.5 mol.%, 1 mol.%, 2 mol.%, and 3 mol.%) -doped Mg₂Sn (67:33) samples.

Ag-doped specimens compared with the undoped specimen at room temperature. In general, the Seebeck coefficient and the carrier concentration are inversely proportional; hence, the smaller Seebeck coefficients of the Ag-doped system compared with the undoped sample at room temperature can serve as evidence of an increase in hole concentration.

Moreover, the heavily doped (3 mol.%) specimen maintained a *p*-type Seebeck coefficient at temperature even higher than 700 K, while low-doped

(0.5 mol.%) specimens showed a tendency to be nearly *n*-type at 700 K. These improved *p*-type characteristics can also be explained by the increase of hole concentration owing to the acceptor doping effect. Despite the narrow band gap of pure Mg₂Sn, the *p*-type characteristic of the heavily Ag-doped systems even at high temperature can be explained by the fact that an increase in the hole concentration may help to maintain the *p*-type characteristic at higher temperatures. For the same reason, the Seebeck coefficients decreased in inverse proportion to the Ag-doping amount, as shown in Fig. 6a. In general, the Seebeck coefficient and the carrier concentration are inversely proportional, as mentioned above. In addition, the *p*- or *n*-type conduction characteristic can be determined not only by the carrier concentration but also by other factors, for example, the electronic structure or the carrier mobility.¹³ Thus, more detailed studies of this mobility change should be done in the future. As can be expected by the decrease of the Seebeck coefficient, the electronic conductivity values for heavily Ag-doped specimens were higher than the value of the low-doped specimen, as shown in Fig. 6b, owing to increasing hole concentration, as mentioned above. As a result, the *p*-type power factor values for the Ag-doped specimens increased by a maximum of 10 times compared with the value of the undoped composition (Mg:Sn = 67:33), as shown in Fig. 6b. This result could be important for developing *p*-type thermoelectric polycrystalline materials in the Mg₂X (X = Si, Sn) system. Thus, the slight difference in the electrical conductivity among the 1 mol.%, 2 mol.%, and 3 mol.% Ag-doped systems remains unclear. However, the possibility of overdoping above the solubility limit of Ag atoms in this Mg₂Sn system and the possibility of segregation of the MgAg phase⁷ should be noted here, as mentioned above for Fig. 5. In this case, MgAg phases segregated at the grain boundary should not decrease the electrical conductivity owing to their sufficiently high electrical conductivity.

The temperature dependences of the thermal conductivities for this Mg₂Sn system are plotted in Fig. 7a. The observed κ values decreased monotonically with increase in the measurement temperature to less than 600 K, indicating an increase in phonon scattering. They then increased with an increase in the measurement temperature above 600 K, indicating bipolar transport properties.¹⁴ In general, the thermal conductivity and electrical conductivity are proportional and simultaneously depend on the porosity and the carrier concentration. However, in this work the highest electrical conductivity for the 2 mol.% and 3 mol.% Ag-doped specimen led to the lowest thermal conductivity. The reason for the lower conductivity of the 2 mol.% and 3 mol.% specimens is not yet clear. It should be also noted here, however, that there is a possibility for the segregation of the MgAg phase to increase the phonon scattering at the grain boundaries. If

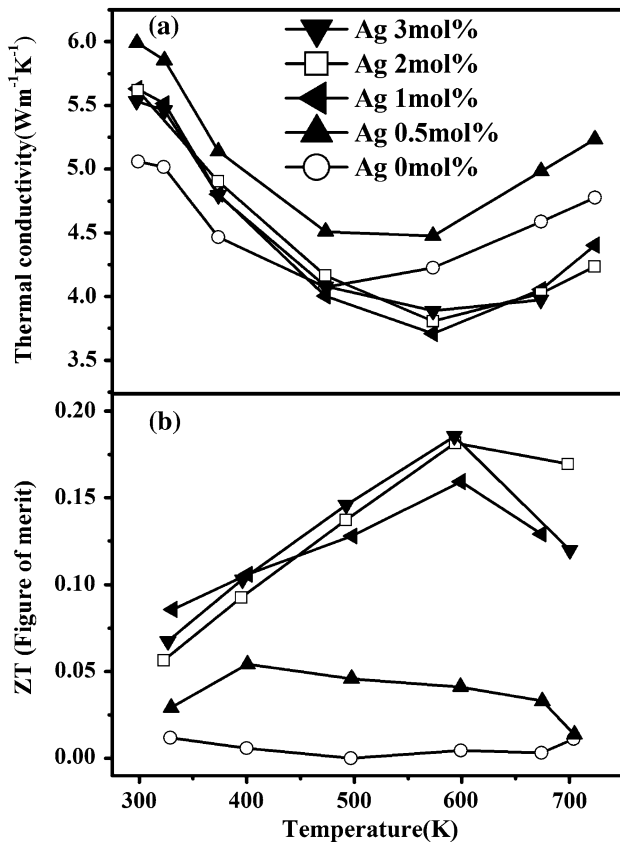


Fig. 7. Temperature dependence of (a) the thermal conductivity and (b) ZT (figure of merit) of Ag (0 mol.%, 0.5 mol.%, 1 mol.%, 2 mol.%, and 3 mol.%) -doped Mg_2Sn (67:33) samples.

this is true, the lower thermal conductivity levels for the 2 mol.%- and 3 mol.%-doped cases are feasible. The dimensionless figure of merit, ZT , was calculated at temperatures ranging from room temperature to 700 K, as shown in Fig. 7b. The ZT value for the Ag-doped samples increased as the temperature increased to less than 600 K, mainly because the thermal conductivity decreased with temperature. The maximum ZT value was 0.18 at 600 K for the case of the Ag 3 mol.%-doped Mg_2Sn sample; this value is 40 times larger than the value of the undoped sample.

CONCLUSIONS

Various compositions in the Mg_2Sn system were synthesized through the vacuum melting process. Then, the Mg_2Sn single phase was acquired at five compositions with a ratio between Mg and Sn atoms ranging from 67:33 to 71:29. The Mg-excess compositions showed n -type characteristic at temperatures higher than about 400 K. In contrast, Sn-excess compositions showed p -type characteristic at temperatures higher than 500 K, after which they displayed the n -type characteristic.

To maximize the p -type thermoelectric properties, we doped five acceptor atoms [Ni (VIII), Cu (IB), Ag (IB), Zn (IIB), and In (IIIB)] at Sn (IVB) sites. As a result, most dopant systems apart from Ag did not show an improved p -type characteristic of the $Mg_{2-\delta}Sn$ system. Only the Ag dopant was effective in improving the p -type characteristic. The Seebeck coefficient for the Ag-doped specimen showed p -type characteristic throughout the measured temperature range (room temperature to ~ 700 K), unlike the undoped specimen. The p -type power factor values for the Ag-doped specimens also increased by as much as 10 times compared with the value noted for the undoped composition.

The ZT value for the Ag-doped samples increased as the temperature increased at less than 600 K, mainly because the thermal conductivity decreased with temperature. The maximum ZT value was 0.18 at 600 K for the case of the Ag 3 mol.%-doped Mg_2Sn sample; this value is 40 times larger than the value of the undoped sample, being comparable to the value for the n -type Mg_2Si system.^{3,15} This result could be important for developing p -type thermoelectric polycrystalline materials in the Mg_2X ($X = Si, Sn$) system.

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