Thermoelectric Properties of Ge-doped Higher Manganese Silicides $\text{MnSi}_{1.72-1.73}\text{:Ge}_m$

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Abstract: Ge-doped higher manganese silicides (HMSs) $\text{MnSi}_{1.72-1.73}\text{:Ge}_m$ ($m = 0.01-0.04$) were prepared and their thermoelectric properties were studied. HMS powders were synthesized by solid-state reaction of raw material powders (Mn, Si, and Ge) at 1273 K for 6 h in vacuum, and hot-pressed at 1173 K for 2 h under 70 MPa. $\text{Mn}_{11}\text{Si}_{19}$ or $\text{Mn}_{15}\text{Si}_{26}$ was the main HMS phase; only a small quantity of Si remained. The intermetallic compound MnSi was not produced. The lattice constants increased with the substitution of Ge at Si sites. With the increase in the Ge doping concentration, the electrical conductivity increased, while the Seebeck coefficient decreased. The power factor was significantly increased by the Ge doping, owing to the increase in the electrical conductivity. The Ge doping led to phonon scattering owing to the difference in mass between Ge and Si, leading to a reduced thermal conductivity. Therefore, the dimensionless figure of merit (ZT) was remarkably enhanced by the Ge doping. For $\text{MnSi}_{1.72}\text{:Ge}_m$, the maximum ZT of 0.44 was obtained at 823 K for $\text{MnSi}_{1.72}\text{:Ge}_{0.01}$, while for $\text{MnSi}_{1.73}\text{:Ge}_m$, the maximum ZT of 0.37 was achieved at 823 K for $\text{MnSi}_{1.73}\text{:Ge}_{0.03}$.

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1. INTRODUCTION

Higher manganese silicide (HMS) is a promising thermoelectric material for thermoelectric generations at intermediate temperatures, as it is eco-friendly, non-toxic, and has abundant constituents [1]. The HMS has several phases with a Nowotny chimney-ladder (NCL) structure, including $\text{Mn}_{11}\text{Si}_{19}$ ($\text{MnSi}_{1.72}$), $\text{Mn}_{15}\text{Si}_{26}$ ($\text{MnSi}_{1.73}$), $\text{Mn}_{27}\text{Si}_{47}$ ($\text{MnSi}_{1.74}$), and Mn_4Si_7 ($\text{MnSi}_{1.75}$) [2-4]. This NCL structure belonging to the tetragonal system is composed of a ladder-shaped sub-lattice of Mn and helical-chimney-shaped sub-lattice of Si. Among the doping elements of HMS, V, Cr, and Mo substitute Mn sites, while Al and Ge are doped at Si sites. Among these dopants, Ge is reported as one of the most effective ways to control the transport properties of HMS [1,5,6]. Ge doping improves the power factor (PF) by increasing the charge carrier concentration and induces point defects by changing the electronic structure, thereby reducing the lattice thermal conductivity through enhanced phonon

scatterings [7-10]. Lee *et al.* [1] reported a high dimensionless figure of merit (ZT) of 0.64 at 773 K for $\text{MnSi}_{1.75}\text{:Ge}_{0.028}$ prepared by solid-state reaction (SSR) and spark plasma sintering (SPS).

However, the thermal conductivity can be increased owing to the secondary phases (MnSi and Si) and self-defects (Si vacancies), usually generated in the synthesis of the doped HMS [9]. In order to achieve high ZT values, secondary phases and self-defects should be suppressed. The distribution of the plate-like MnSi was confirmed when molten HMS was solidified during quenching [10]. Therefore, in order to inhibit the formation of the MnSi phase, solid-state synthesis processes have been employed, such as mechanical alloying (MA) [11,12] and SSR [1,10,13]. In our previous studies [14,15], the formation of secondary phases could be suppressed by SSR; Al- and Cr-doped HMSs were successfully synthesized by SSR. In this study, Ge-doped HMS powders ($\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$) were synthesized by SSR and consolidated by hot pressing (HP), and their thermoelectric properties were studied.

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2. EXPERIMENTAL METHODS

Elemental powders of Mn (purity: 99.9%), Si (purity: 99.99%), and Ge (purity: 99.99%) were weighed to the desired stoichiometries of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$ ($m = 0.01\text{--}0.04$), followed by ball milling for 30 min to achieve uniform mixtures. The mixed powder was then placed into an alumina crucible and subjected to SSR at 1273 K for 6 h in vacuum. The synthesized powder was crushed to fine powder with particle sizes smaller than 75 μm and then charged into a graphite mold with an inner diameter of 10 mm and subjected to HP at 1173 K for 2 h under 70 MPa.

An X-ray diffraction (XRD, Bruker D8-Advance) analysis was performed using Cu- K_α radiation (40 kV, 30 mA, $\lambda = 0.15405$ nm) in the θ - 2θ mode at a scan step of 0.02° and scan speed of $3^\circ/\text{min}$. XRD patterns were obtained from powders synthesized by SSR and sintered bodies formed by HP. The lattice constants were calculated by the Rietveld refinement method (Bruker, TOPAS). Elemental mapping was performed to observe the microstructures of the sintered specimens and verify the distributions of constituent elements in the specimens using a scanning electron microscope (SEM, FEI Quanta400) equipped with an energy-dispersive spectrometer (EDS, Bruker, Quantax200).

Thermoelectric properties were measured and analyzed in the temperature range of 323 K to 823 K. The Seebeck coefficient (α) and electrical conductivity (σ) were measured by the temperature differential and DC four-probe method (Ulvac-Riko, ZEM-3) in a He atmosphere:

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{\frac{2}{3}} \quad (1)$$

$$\sigma = ne\mu \quad (2)$$

where k_B is the Boltzmann constant, e is the electron charge, h is the Planck constant, m^* is the effective carrier mass, T is the absolute temperature, n is the carrier concentration, and μ is the mobility. The thermal conductivity (κ) was evaluated using Eq. 3 by measuring the thermal diffusivity (D), specific heat (c_p), and density (d) by the laser flash method (Ulvac-Riko, TC-9000H):

$$\kappa = Dc_p d \quad (3)$$

The PF and ZT were evaluated from the measured thermoelectric parameters using Eqs. 4 and 5:

$$PF = \alpha^2 \sigma \quad (4)$$

$$ZT = \frac{\alpha^2 \sigma}{\kappa} T \quad (5)$$

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$ powders synthesized by SSR. All the diffraction peaks of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$ were well matched with standard data of $\text{Mn}_{11}\text{Si}_{19}$ (PDF #01-089-2629) and $\text{Mn}_{15}\text{Si}_{26}$ (PDF #01-089-2413), respectively. Therefore, Ge-doped HMS phases were successfully synthesized. MnSi was not observed in this study, but a small amount of Si remained, possibly due to the substitution of Ge for Si and Si vacancies as self-defects [9].

Figure 2 presents the XRD patterns of the $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$ specimens sintered by HP. Phase transformations were not observed after the HP. The diffraction peaks shifted to lower angles with the increase in the Ge substitution concentration. For example, as shown in Figs. 2(b) and 2(c), the diffraction peaks corresponding to the planes (21 $\times$ 11) and (2115) shifted to lower angles with the increase in the Ge content, which implies that the HMS lattice with the NCL structure was expanded by the Ge substitution. The calculated lattice constants of $\text{MnSi}_{1.72}\text{:Ge}_m$

Fig. 1. XRD patterns of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$ powders synthesized using SSR.

Fig. 2. (a) XRD patterns of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{Ge}_m$ specimens sintered using HP, and (b) and (c) enlarged XRD peaks showing the peak shifts due to Ge doping.

Table 1. Lattice constants of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$

Specimen	a [nm]	c [nm]	Remark
$\text{MnSi}_{1.72}$	0.5500	4.7881	Ref. 17
$\text{MnSi}_{1.72}\text{:Ge}_{0.01}$	0.5526	4.8041	
$\text{MnSi}_{1.72}\text{:Ge}_{0.02}$	0.5526	4.8045	
$\text{MnSi}_{1.72}\text{:Ge}_{0.03}$	0.5527	4.8060	
$\text{MnSi}_{1.72}\text{:Ge}_{0.04}$	0.5527	4.8061	
$\text{MnSi}_{1.73}$	0.5502	6.5284	Ref. 18
$\text{MnSi}_{1.73}\text{:Ge}_{0.01}$	0.5526	6.5524	
$\text{MnSi}_{1.73}\text{:Ge}_{0.02}$	0.5526	6.5527	
$\text{MnSi}_{1.73}\text{:Ge}_{0.03}$	0.5526	6.5528	
$\text{MnSi}_{1.73}\text{:Ge}_{0.04}$	0.5527	6.5545	

and $\text{MnSi}_{1.73}\text{Ge}_m$ are shown in Table 1. The lattice constants increased with the Ge content owing to the difference in covalent radius between Ge (0.122 nm) and Si (0.117 nm) [6]; the increase along the c -axis was larger than that along the a -axis. Therefore, the SSR-HP processes are suitable to fabricate the Ge-doped HMSs, as reconfirmed in this study.

Figure 3 shows SEM images and EDS elemental mappings of the HP specimens. Fractured surfaces of $\text{MnSi}_{1.72}\text{:Ge}_{0.01}$ and $\text{MnSi}_{1.73}\text{:Ge}_{0.03}$ are illustrated as typical examples. The specimens had dense and compact sintered bodies, where the Mn, Si, and Ge elements were homogeneously distributed.

Figure 4 presents the temperature dependence of the electrical conductivities of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$. The electrical conductivity decreased with the increase in the

Fig. 3. SEM images and EDS elemental mappings of $\text{MnSi}_{1.72}\text{:Ge}_{0.01}$ and $\text{MnSi}_{1.73}\text{:Ge}_{0.03}$.

Fig. 4. Temperature dependence of the electrical conductivities of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$.

temperature, i.e., a negative temperature dependence was observed, corresponding to a metallic or degenerate-semiconductor behavior. At all analyzed temperatures, Ge doping significantly enhanced the electrical conductivities of $\text{MnSi}_{1.72}$ and $\text{MnSi}_{1.73}$, which increased with the Ge content. Al acts as a p-type dopant in the HMS system owing to its smaller valence than that of Si, providing additional holes by substituting Al for Si; therefore, the electrical conductivity of HMS can be increased by Al doping [16]. However, although Ge and Si have equal valences, the electrical conductivity is increased by the Ge doping. This is attributed to the changes in the Si–Si bonding affected by the Ge substitution; consequently, the Si lattice distorted by the Ge substitution helps the charge carriers (holes) enhance the electrical conductivity [7–10]. $\text{MnSi}_{1.73}\text{:Ge}_{0.03}$ exhibited the highest electrical conductivities of $4.5 \times 10^4 \text{ Sm}^{-1}$ at 323 K and $2.5 \times 10^4 \text{ Sm}^{-1}$ at 823 K.

Figure 5 shows the temperature dependence of the Seebeck coefficients of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$. The Seebeck coefficients had positive values in the whole measured temperature range, which implies that major charge carriers were holes (p-type conduction). The Ge-doped HMSs had slightly lower Seebeck coefficient values than the undoped $\text{MnSi}_{1.72}$ and $\text{MnSi}_{1.73}$. As shown in Eqs. 1 and 2, the Seebeck coefficient was also affected by the carrier concentration and mobility (i.e., effective mass). Therefore, the Ge doping increased the electrical conductivity and decreased the Seebeck coefficient. The Seebeck coefficient increased with

Fig. 5. Temperature dependence of the Seebeck coefficients of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$.

Fig. 6. Temperature dependence of the PFs of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$.

the temperature; the temperature dependence weakened at high temperatures as the Seebeck coefficient was proportional to the temperature but inversely proportional to the carrier concentration. The significant increase in the carrier concentration, attributed to intrinsic transitions at high temperatures, decreased the Seebeck coefficient, $228 \mu\text{VK}^{-1}$ for $\text{MnSi}_{1.72}\text{:Ge}_{0.01}$ and $224 \mu\text{VK}^{-1}$ for $\text{MnSi}_{1.73}\text{:Ge}_{0.03}$ at 823 K.

Figure 6 presents the temperature dependence of the PFs of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$. The PF increased with the temperature with peak values at certain temperatures owing to the “trade-off” relationship between the electrical conductivity and Seebeck coefficient, as shown in Eq. 4. This

Fig. 7. Temperature dependence of the thermal conductivities of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$.

was attributed to the degenerate-semiconductor behavior of the electrical conductivity and effect of intrinsic transitions on the Seebeck coefficient. The PF was remarkably increased by the Ge doping owing to the significant increase in the electrical conductivity and slight decrease in the Seebeck coefficient. Maximum PF values were obtained at 823 K, $1.26 \text{ mWm}^{-1}\text{K}^{-2}$ for $\text{MnSi}_{1.72}\text{:Ge}_{0.02}$ and $1.23 \text{ mWm}^{-1}\text{K}^{-2}$ for $\text{MnSi}_{1.73}\text{:Ge}_{0.03}$.

Figure 7 shows the temperature dependence of the thermal conductivities of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$. The thermal conductivity (κ) is a sum of the electronic thermal conductivity (κ_e), lattice thermal conductivity (κ_l), and bipolar thermal conductivity (κ_{bi}), attributed to the effects of carrier concentration, phonon scattering, and bipolar conduction, respectively. The difference in atomic mass (Si: 28.08, Ge: 72.59) can lead to phonon scattering; therefore, the lattice thermal conductivity can be decreased by the Ge substitution. In the case of $\text{MnSi}_{1.72}\text{:Ge}_m$, the Ge substitution was not very effective to the thermal conductivity. However, the thermal conductivity of $\text{MnSi}_{1.73}\text{:Ge}_m$ increased with the Ge doping as the increase in the electronic thermal conductivity owing to the increased carrier concentration was larger than the decrease in the lattice thermal conductivity owing to the enhanced phonon scattering. The total thermal conductivity decreased with the increase in the temperature with minimum values at temperatures between 623 K and 723 K owing to bipolar conduction. The lowest thermal conductivity of $\kappa =$

Fig. 8. ZT values of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$.

$2.07 \text{ Wm}^{-1}\text{K}^{-1}$ was achieved at 623 K for $\text{MnSi}_{1.72}\text{:Ge}_{0.01}$.

Figure 8 presents the ZT values of $\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$. In our previous studies, the maximum ZT values of undoped $\text{MnSi}_{1.72}$ and $\text{MnSi}_{1.73}$ were 0.29 [13] and 0.33 [13] at 823 K, respectively, while the maximum ZT values of doped $\text{MnSi}_{1.73}\text{:Al}_{0.005}$ and $\text{MnSi}_{1.73}\text{:Cr}_{0.01}$ were 0.41 [14] and 0.36 [15] at 823 K, respectively. In this study, the PF was enhanced with the increase in the temperature, while the thermal conductivity maintained low values at high temperatures; therefore, the ZT values were significantly increased with the temperature. In addition, the enhanced PF by the Ge doping could further improve the ZT values. In the $\text{MnSi}_{1.72}\text{:Ge}_m$ systems, $\text{MnSi}_{1.72}\text{:Ge}_{0.01}$ exhibited the maximum ZT of 0.44 at 823 K, while in the $\text{MnSi}_{1.73}\text{:Ge}_m$ systems, $\text{MnSi}_{1.73}\text{:Ge}_{0.03}$ exhibited the maximum ZT of 0.37 at 823 K.

4. CONCLUSION

Ge-doped HMSs ($\text{MnSi}_{1.72}\text{:Ge}_m$ and $\text{MnSi}_{1.73}\text{:Ge}_m$) were prepared by SSR and HP, and their thermoelectric properties were evaluated. The XRD analysis showed that Ge was successfully substituted for Si. The MnSi phase was not identified. The electrical conductivity and PF increased with the Ge content owing to the increased charge carrier concentration. However, the Ge doping slightly decreased the Seebeck coefficient. In the case of $\text{MnSi}_{1.73}\text{:Ge}_m$, the Ge substitution increased the thermal conductivity, while in the

case of $\text{MnSi}_{1.72}\text{:Ge}_m$, it did not significantly affect the thermal conductivity. The Ge doping improved the ZT, yielding values of 0.44 for $\text{MnSi}_{1.72}\text{:Ge}_{0.01}$ and 0.37 for $\text{MnSi}_{1.73}\text{:Ge}_{0.03}$ at 823 K.

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