

Microstructures and thermoelectric properties of $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ alloys prepared by rapid solidification and hot pressing

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Iron disilicide based thermoelectric materials $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) were prepared by rapid solidification (melt spinning) and hot uniaxial pressing at 1248 K with 50 MPa for 30 min, followed by annealing at 1073 K for 20 h. X-ray diffraction and scanning electron microscopy showed excess silicon phase for samples with $x \geq 2.1$, and both the configurations and the amounts of secondary silicon particles varied with an increase in x . Hall measurements carried out at room temperature showed that the carrier concentrations for $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) were between 2.6×10^{18} and $5.6 \times 10^{18} \text{ cm}^{-3}$. The Seebeck coefficient, electrical conductivity and thermal conductivity were measured from room temperature to 973 K. It was found that a little excess silicon in the sample, $x = 2.1$, enhanced the Seebeck coefficient weakly, but was effective for decreasing the thermal conductivity. A maximum figure of merit, $ZT = 0.17$, was obtained for $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_{2.0}$ at 973 K.

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I. INTRODUCTION

Thermoelectric materials, which can be used to convert energy between heat and electricity directly, are of interest for application as heat pumps and power generators. Semiconductor thermoelectric materials based devices are rugged, durable, solid-state energy converters, and have long been the choice for providing power for deep-space demission, such as for Voyagers I and II and the Cassini mission to Saturn. They are also well suited to certain remote, extreme environments, as well as to small-scale cooling for defense and aerospace applications.^{1,2} Semiconducting iron disilicide ($\beta\text{-FeSi}_2$) is a potential thermoelectric candidate for use in the high temperature range up to 1200 K due to its high Seebeck coefficient, low cost of raw materials, high oxidation resistance, and nontoxicity.³ Since iron disilicide has a direct band gap, it also has potential as an important candidate for silicon-compatible devices in optoelectronic technology.^{4,5}

By doping with different elements, the conduction type and properties of $\beta\text{-FeSi}_2$ can be modified and improved. Manganese, chromium, zirconium, or aluminum doped FeSi_2 shows p -type conduction^{6–10} whereas cobalt or boron doped FeSi_2 shows n -type conduction.^{6,11} Research on solid solution formation,¹² fine particle dispersion,¹³ and grain refinement^{14,15} have been carried out to improve the figure of merit, $Z = \alpha^2 \sigma / \kappa$, of $\beta\text{-FeSi}_2$ based materials, where α is the Seebeck coefficient, and σ and κ are the electrical and thermal conductivity, respectively. Heavily doped $\beta\text{-FeSi}_2$ thermoelectric materials have a Seebeck coefficient α well above 200 $\mu\text{V/K}$, as high as that of the best-known thermoelectric materials such as Bi_2Te_3 , PbTe , SiGe , etc.^{16,17} So the deci-

sive factor in improving its figure of merit is to improve the ratio of the electrical conductivity to the thermal conductivity (σ/κ) of $\beta\text{-FeSi}_2$, which is only 2000 V^{-2}K for p -type $\beta\text{-FeSi}_2$ doped with manganese, and much lower than that of Bi_2Te_3 based thermoelectric materials ($>60\,000 \text{ V}^{-2}\text{K}$).

It has been shown that rapid solidification is very effective for producing a fine crystalline microstructure: it enhances the phonon scattering on grain boundaries and improves the thermoelectric properties.^{18–20} Hot pressing is a convenient method by which to compact powders to high densities within a shorter time and at a lower temperature than pressureless sintering processes.

Studies on bulk and thin-film $\beta\text{-FeSi}_2$ based thermoelectric materials to investigate the influence of different Si/Fe ratios of thermoelectric properties have also been carried out,^{21–24} and they have shown some common features but also large differences due to different preparation techniques and the different purity of the source materials.

In the present work, a constructive combination of rapid solidification and hot pressing was applied to $\beta\text{-FeSi}_2$ based thermoelectric materials with different Si/Fe ratios. $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) compounds were chosen for this study. Except for investigations of the microstructures and thermoelectric properties, Hall measurements were also carried out at room temperature.

II. EXPERIMENTAL PROCEDURE

Nonstoichiometric mixtures of commercial pure iron (purity $>99.3\%$), semiconductor grade silicon (purity $>99.999\%$), and commercial pure manganese (purity $>99.5\%$) with the desired composition of $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) were comelted by levitation melting (LM) in a high-frequency induction furnace. The ingots obtained were remelted in an arc furnace, then rapidly

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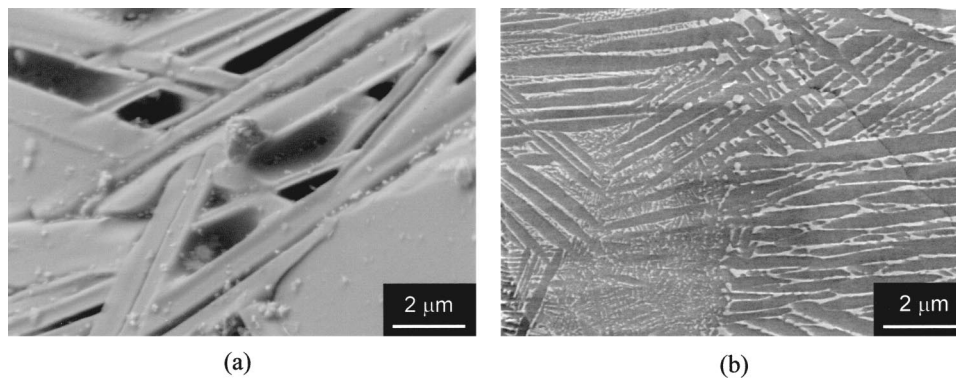


FIG. 1. SEM micrographs of rapidly solidified powders: (a) surface structure and (b) internal structure.

solidified (RS) by sputtering the melt onto the edge of a chilled rolling molybdenum wheel with a linear speed of about 27.5 m s^{-1} at the edge. Both LM and RS were carried out under high purity argon atmosphere.

The rapidly solidified thin ribbons were then milled in a carmelian mortar to sizes smaller than 150 μm . Subsequently, the powders were hot uniaxially pressed (HUP) at 1248 K with 50 MPa for 30 min under vacuum of about 10^{-3} Pa using a graphite die with a diameter of 16 mm . The hot pressed samples were then vacuum annealed at 1073 K for 20 h .

The densities of the samples were measured using the Archimedes method. The crystalline structure of the annealed samples was investigated by x-ray diffraction (XRD) with a D-5000 diffractometer using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ Å}$) at the Institute of Materials Research at the German Aerospace Center (DLR). The microstructures were characterized by a S-570 scanning electron microscope (SEM), with the specimen etched for 2 min with a solution of HNO_3 (65%–68%): HF (>40%): HCl (36%–38%): H_2O = 6:2:3:9. The Hall effect was measured at 300 K on rectangular, 1 mm thick samples with the Bio-Rad HL5500, using a dc magnetic method under applied magnetic field of 0.324 T . An In–Sn alloy was soldered to act as a contact between the samples and the lead metal wires. Seebeck coefficient α and electrical conductivity σ were simultaneously measured in vacuum of about 10^{-1} Pa from room temperature to 973 K using computer-controlled equipment, which was rebuilt from a self-installed device described elsewhere.^{3,18} Each sample was measured at least three times, and the average value was chosen as the final result. The measuring errors were less than 8%. Thermal diffusion a and specific heat C_p were measured at the DLR with a Netzsch LFA-427 laser flash apparatus and a Netzsch DSC 404 differential scanning calorimeter, respectively. Thermal

conductivity κ was calculated from $\kappa = \rho C_p a$ where ρ is the density of the specimen.

III. RESULTS AND DISCUSSION

Typical rapidly solidified powders in the present experiment are thin ribbons with thickness less than 0.1 mm . Figure 1 shows micrographs SEM of the surface and internal structure. There are even finer grain structures with characteristic size of about 100 nm in a ribbon as one can see in Fig. 1(a). Figure 1(b) shows a fine eutectic structure consisting of $\alpha\text{-FeSi}_2$ and $\epsilon\text{-FeSi}$ phases, typical of rapidly solidified powders, with the dark matrix being α phase and the white stripes ϵ phase.

Table I gives a comparison of the densities of the hot pressed $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) samples. All these samples have relative density above 90% of the theoretical density calculated according to the components.

Figure 2 shows the microstructures of $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($2.0 \leq x \leq 2.5$). The $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_{2.0}$ sample, Fig. 2(a), shows a homogeneous structure with average grain size of about 2 μm . For $x \geq 2.1$, the dispersed particles shown in Figs. 2(b)–2(d) are excess silicon particles, which were confirmed by energy dispersive x-ray (EDX) analysis and XRD. The contrast between these particles may be caused by the different degree of etching. Min and Lee²² reported that the particle sizes of dispersed excess silicon in $\beta\text{-FeSi}_2$ materials prepared by mechanical alloying and sintering grew gradually with an increase of sintering temperature, and were not affected by compositional variation. But in our experiment for $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($2.0 \leq x \leq 2.5$), both the amount and the size of coarse silicon particles increased significantly with an increase of x . For the sample with $x = 2.1$ shown in Fig. 2(b), silicon particles dispersed in the β phase matrix had particle size of several hundred nanometers. In

TABLE I. Bulk density and relative density of hot pressed $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ samples.

Density	Spanner Specimen $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$)					Nondoped FeSi_2
	$x = 1.9$	$x = 2.0$	$x = 2.1$	$x = 2.3$	$x = 2.5$	
Bulk density (g cm^{-3})	4.71	4.62	4.34	4.30	4.19	4.77
Theoretical density (g cm^{-3})	4.92	4.79	4.67	4.46	4.29	4.93
Relative density (%)	95.6	96.5	92.8	96.3	97.8	96.8

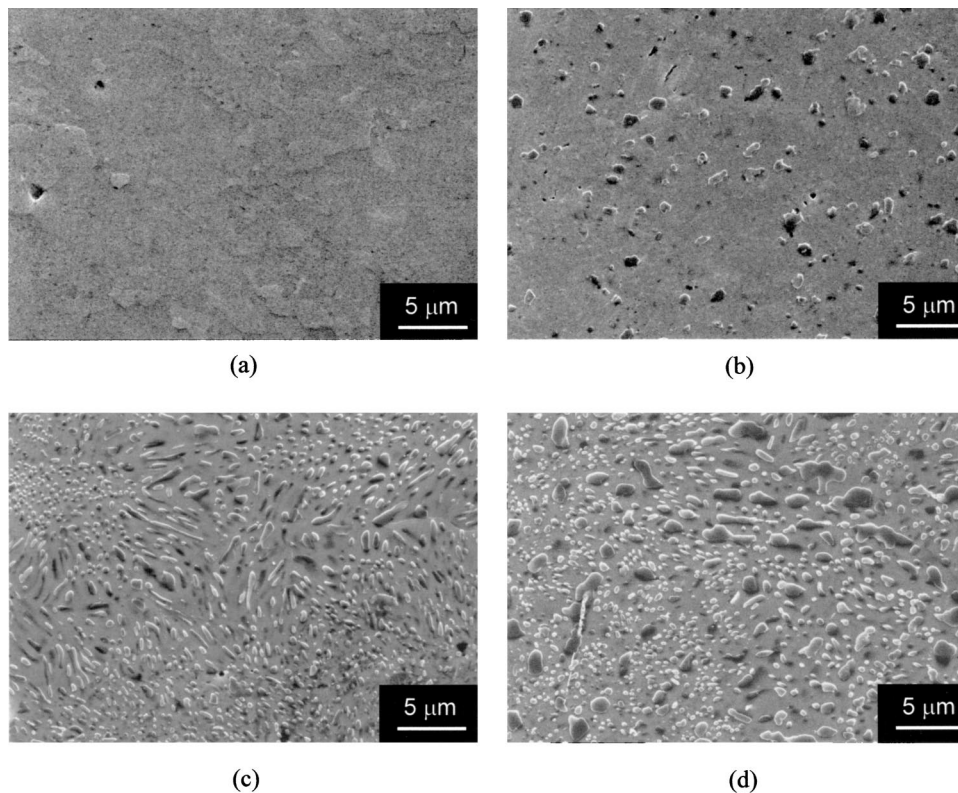


FIG. 2. SEM micrographs of hot pressed $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($2.0 \leq x \leq 2.5$) samples with x =(a) 2.0, (b) 2.1, (c) 2.3, and (d) 2.5.

the sample with $x=2.3$ in Fig. 2(c) the silicon phase has a morphology with rods with diameters of about 200 nm and length of more than a few micrometers. The silicon particles are quite coarse and show an irregular configuration in the sample with $x=2.5$ in Fig. 2(d).

The formation of β phase as well as excess silicon phase was confirmed by the XRD results given in Fig. 3. Only β phase was observed for both nondoped $\beta\text{-FeSi}_2$ and sample

$x=2.0$ as shown in the patterns in Figs. 3(a) and 3(c). The pattern in Fig. 3(b) shows a very weak peak of ϵ phase in the sample with $x=1.9$, due to the silicon content being lower than the stoichiometric concentration of $\beta\text{-FeSi}_2$. And for $x=2.1, 2.3$, and 2.5 , the silicon peaks apparently become sharper with an increase of x . The weight percentages of excess silicon in the samples were obtained from the XRD measurements, and were about 1% and 6% for $x=2.1$ and 2.3 , respectively. These are lower than the theoretical weight percentages of 2.44% and 6.98%, respectively, for $x=2.1$ and 2.3 , possibly due to loss of silicon during the preparation process.

Figure 4 gives the temperature dependence of the See-

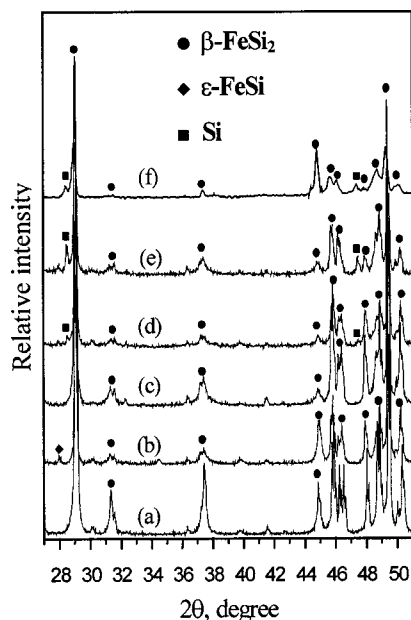


FIG. 3. XRD patterns of hot pressed $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) samples: (a) nondoped FeSi_2 samples and samples with x =(b) 1.9, (c) 2.0, (d) 2.1, (e) 2.3, and (f) 2.5.

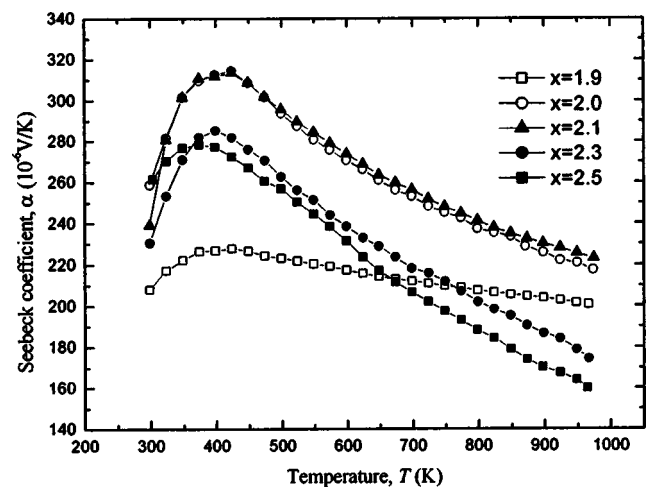


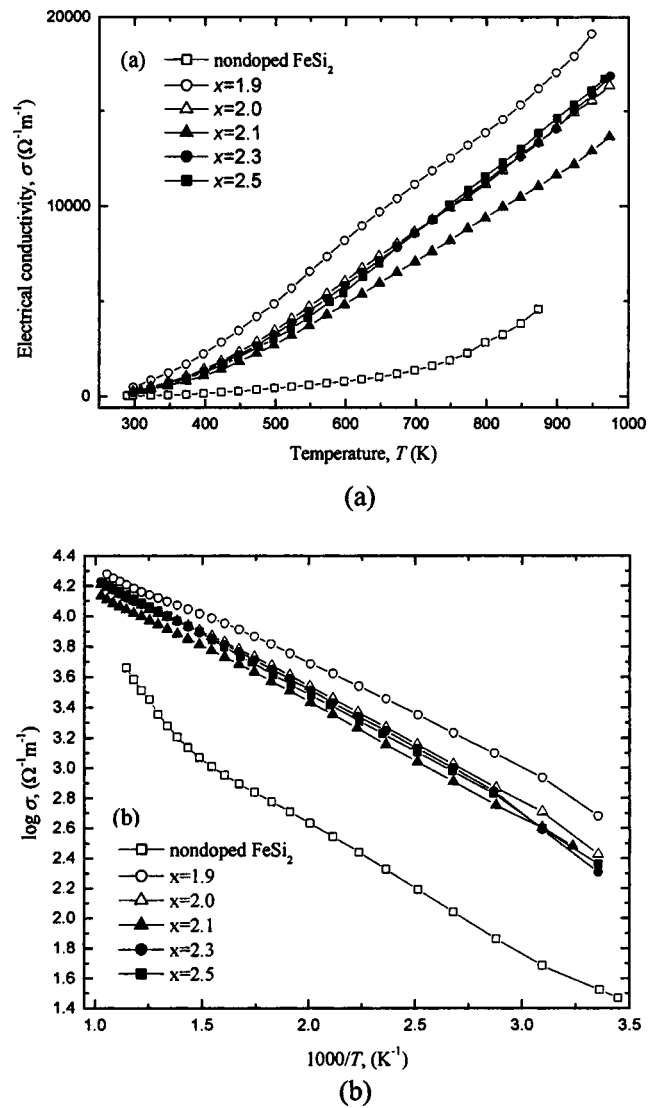
FIG. 4. Temperature dependence of the Seebeck coefficient for various hot pressed $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) samples.

TABLE II. Electrical properties of hot pressed $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ samples at 300 K.

x	Hall coefficient ($\text{cm}^3 \text{C}^{-1}$)	Carrier concentration (cm^{-3})	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Electrical conductivity ($\Omega^{-1} \text{m}^{-1}$)
1.9	1.4	4.4×10^{18}	6.3	441
2.0	1.1	5.6×10^{18}	1.7	155
2.1	1.5	4.3×10^{18}	3.0	208
2.3	2.4	2.6×10^{18}	3.6	151
2.5	1.2	5.0×10^{18}	1.4	114

beck coefficients (α) of $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) between 290 and 980 K. It is seen that the Seebeck coefficient of the sample with $x=1.9$ is much lower than that of other samples below 700 K, due to metallic ϵ phase in the former. In the lower temperature region of 290–430 K, the Seebeck coefficients of all the samples increase with an increase in temperatures up to a maximum value of $315 \mu\text{V K}^{-1}$ for $x=2.0$ at 423 K, due to more acute lattice scattering with the increase in temperature, then decrease with an increase in temperature above 425 K. The decrease in Seebeck coefficient above 425 K could be due to a rapid increase in carrier concentration with an increase in temperature. The Seebeck coefficient for $x=2.1$ is a little lower than that of $x=2.0$ below 425 K, and becomes the highest one among all the samples in the higher temperature range. This result indicates that a small amount of excess silicon increases the Seebeck coefficient, because the dispersed silicon particles contribute as the center for both phonon and carrier scattering. Rather surprisingly, as shown in Fig. 4, the excess silicon for the samples with $x=2.3$ and 2.5 deteriorates the Seebeck coefficients apparently, especially at higher temperatures above 650 K. The origin of this is the impurities in the raw materials, especially sulfur (about 0.0056 at. %) and phosphorus (about 0.0024 at. %), in the commercial pure iron used in the present work. Since sulfur and phosphorus may diffuse into silicon as n -type dopants in silicon, samples with excess silicon can be considered a composite with n -type silicon particles in a p -type β - FeSi_2 matrix. It can easily be recognized that the existence of n -type silicon would decrease the Seebeck coefficient of p -type β - FeSi_2 , since the thermoelectric potentials of both phases are opposite each other.

Table II shows the results of the Hall effect and electrical conductivity measurements at 300 K for the manganese doped samples. The Hall coefficients are not much different from those of the $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ samples. The carrier concentrations are 2.6 – $5.6 \times 10^{18} \text{ cm}^{-3}$, which are comparable to the concentration of $5.08 \times 10^{18} \text{ cm}^{-3}$ for $\text{Fe}_{0.94}\text{Mn}_{0.06}\text{Si}_2$ at room temperature reported by Nishida,⁷ but much lower than the manganese atom concentration ($2.1 \times 10^{21} \text{ cm}^{-3}$) doped in the samples. Since the values of electrical conductivity in Table I obtained by Hall measurement agree well with the results of the electrical conductivity measurements given in Fig. 5, some reason other than serious measuring error must be taken into account for the low carrier concentration compared with the amount of doping. The possible mechanism is suggested to be the formation of manganese silicides such as MnSi and $\text{MnSi}_{1.75}$. It is also possible that

FIG. 5. Temperature dependence of the electrical conductivity for hot pressed $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$): (a) σ - T plots and (b) $\log \sigma$ - $1/T$ plots.

the solubility of manganese in β - FeSi_2 would be limited at a value much lower than the doping amount, since there is no disilicide of manganese. In comparing the data in Table I with the work of Nishida,⁷ it is suggested that the carrier concentration in manganese doped β - FeSi_2 could be increased by an increase in the amount of manganese doping, and would be limited at about $5 \times 10^{18} \text{ cm}^{-3}$. According to Umemoto,²⁵ the optimal carrier concentration for a β - FeSi_2 based thermoelectric material is about $5 \times 10^{19} \text{ cm}^{-3}$, so other doping methods such as double doping with manganese and aluminum should be used to improve the thermoelectric properties of iron disilicide based materials.

Figure 5(a) shows that the electrical conductivities of all the samples increase exponentially with an increase in temperature, which indicates semiconducting behavior. Compared to the nondoped FeSi_2 , the electrical conductivities of p -type $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ are greatly enhanced. Over the whole temperature range, $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_{1.9}$ showed the highest elec-

trical conductivity of all the samples, a result of the secondary metallic ϵ phase in the β -FeSi₂ matrix. The electrical conductivities in the composition range of $2.0 \leq x \leq 2.5$ are not much different, except that of $x=2.1$ which shows the lowest value. The $\log \sigma-1/T$ plots shown in Fig. 5(b) for Fe_{0.92}Mn_{0.08}Si_x exhibit straight lines with different slopes in the low and high temperature range, which is considered to correspond to an impurity conductive region and an intrinsic conductive region, respectively. Conductive energy E can be calculated from the $\log \sigma-1/T$ slopes using $\sigma = \sigma_0 \exp(-E/k_0T)$,⁶ where σ_0 is a pre-exponential factor, E is the conductive energy, k_0 is the Boltzmann constant, and T is the absolute value. The $\log \sigma-1/T$ slope of the nondoped FeSi₂ is about 0.87 eV in the intrinsic range of 523–700 K, and 1.7 eV in the higher temperature range (above 700 K). It is believed that the 0.87 eV obtained is the energy gap, E_g , and that 1.7 eV results from double activation of the carriers, that is, the energy needed for activating two carriers. E_g of the doped samples is about 0.64, 0.71, 0.70, 0.72 and 0.73 eV for $x=1.9, 2.0, 2.1, 2.3$, and 2.5 , respectively. Strictly speaking, we cannot equal E_g to the $\log \sigma-1/T$ slope for either $x=1.9$ or ≥ 2.1 , because these samples contain secondary ϵ -FeSi phase or silicon phase. Since ϵ -FeSi and silicon can affect the structural properties of β -FeSi₂,²³ the E_g calculated in this study shows only the total band properties of the samples. The higher E_g for $x=2.3$ and 2.5 somewhat confirmed the existence of n -type silicon, since silicon has a much higher band gap (about 1.12 eV) than β -FeSi₂. It was reported earlier,^{10,26,27} that the E_g value decreased when a p -type dopant such as Zr, Mn, or Nb was doped, because the doping of these impurities expanded the width of the valence band. The E_g values for Fe_{0.92}Mn_{0.08}Si_x in this study also agree with these reports. The slopes of the $\log \sigma-1/T$ plots in the impurity conductive range give the conductive activation energies E_a of the samples. E_a of the nondoped FeSi₂ was calculated to be 0.83 eV, a little lower than the E_g of 0.87 eV, indicating weak unexpected doping in this sample. Fe_{0.92}Mn_{0.08}Si₂ shows the highest E_a value, 0.78 eV, among the manganese doped samples. E_a increased from 0.72 eV for $x=2.1$ to 0.75 and 0.77 eV for $x=2.3$ and 2.5 , respectively. This means that the acceptor levels of Fe_{0.92}Mn_{0.08}Si_x become further from the valence band with an increase in silicon content.

The temperature dependence of thermal conductivity κ of Fe_{0.92}Mn_{0.08}Si_x ($1.9 \leq x \leq 2.5$) is shown in Fig. 6. The κ of all the samples decreases sharply with an increase in temperature below 973 K, followed by a slight increase above 973 K due to intrinsic conduction. The thermal conductivity κ of a material can be written as $\kappa = \kappa_c + \kappa_l$, where κ_c is the carrier contribution and κ_l is the lattice contribution.²⁸ Carrier contribution κ_c can be estimated by Wiedemann–Franz law, $\kappa_c = L\sigma T$, where σ is the electrical conductivity and L is the Lorenz number, which is theoretically equal to about $2.45 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ in a metal or approximately $1.5 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ in a nondegenerate semiconductor. For the heavily doped β -FeSi₂ based samples in the present work, κ_c is estimated using the Lorenz number of a metal. The resulting κ_c increases with the temperature and has a maximum that varies from $0.33 \text{ W m}^{-1} \text{ K}^{-1}$ for the sample with

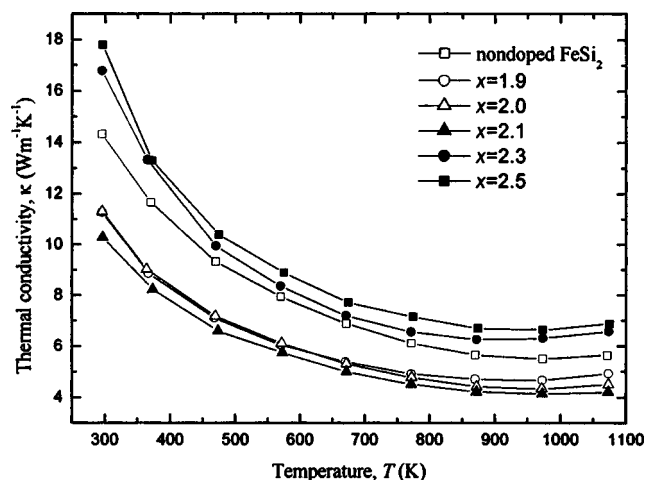


FIG. 6. Temperature dependence of thermal conductivities for hot pressed Fe_{0.92}Mn_{0.08}Si_x ($1.9 \leq x \leq 2.5$) samples.

$x=2.1$ to $0.44 \text{ W m}^{-1} \text{ K}^{-1}$ for $x=1.9$. Compared with the data in Fig. 6, one can see that the carrier contribution to the total thermal conductivity is less than 10% for all samples in the present work. This means that the rapid decrease of κ with an increase in temperature below 970 K in this study is caused by the decrease of κ_l , due to the enhancement of phonon scattering. The thermal conductivities of samples with $x=1.9, 2.0$, and 2.1 are even lower than that of nondoped FeSi₂, although the electrical conductivity of the manganese doped samples is much higher than that of the nondoped sample. The sample with $x=2.1$ has the lowest thermal conductivity in the whole temperature range with a minimum value of about $4.1 \text{ W m}^{-1} \text{ K}^{-1}$ at about 973 K, which is about 95% compared to that of the sample with $x=2.0$, and 75% of the nondoped β -FeSi₂. This means that doping elements as well as a small amount of finely dispersed excess silicon particles could act as phonon scattering centers and are effective for decreasing the thermal conductivity. The thermal conductivity of samples with a large amount of excess silicon, $x=2.3$ and 2.5 , is remarkably higher than that with $x \leq 2.1$. This is mainly due to the high thermal conductivity of silicon, which is about $140 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, much higher than that of β -FeSi₂, about $15 \text{ W m}^{-1} \text{ K}^{-1}$, at room temperature. In the case of $x \geq 2.3$, the volume influence of high thermally conductive silicon phase exceeds the effect of phonon scattering on the phase boundaries, thus the thermal conductivity is contrarily increased.

Figure 7 summarizes the temperature dependence of the dimensionless figures of merit ZT calculated with $ZT = (\alpha^2 \sigma / \kappa) T$. The figure of merit for Fe_{0.92}Mn_{0.08}Si_x is much higher than that of the nondoped FeSi₂, and increases monotonously with an increase in temperature. The figure of merit for $x \geq 2.0$ decreases with an increase in x , especially for $x=2.3$ and 2.5 , which results from the reduction in Seebeck coefficient and the increment in thermal conductivity. The maximum figure of merit, $ZT=0.17$, was obtained for the sample with $x=2.0$ at 973 K in this work, and is comparable to the best results ever reported for manganese doped β -FeSi₂ materials. The figure of merit for $x=2.1$ is very

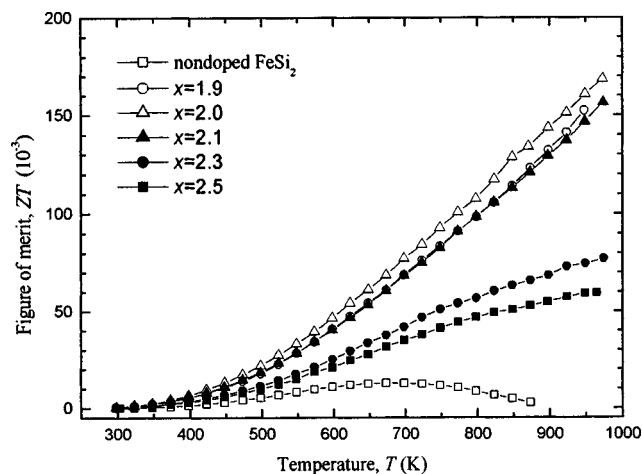


FIG. 7. Temperature dependence of the thermal conductivity for various hot pressed $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) samples.

close to that for $x=1.9$, and only a little smaller than that for $x=2.0$. This indicates that a smaller offset of x other than 2.0, i.e., $x=1.9$ –2.1, is better for thermoelectric properties than a larger offset ($x \geq 2.3$).

As reported by others,^{29,30} the figure of merit for their respective Co- and Mn-doped n -type and p -type thermoelectric materials are significantly reduced in the high temperature range, which is caused both by a steep decrease in Seebeck coefficient and by an increase in thermal conductivity. But in this work for the $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) samples, the ZT values increase with an increase in temperature even at high temperatures due to the continuous decrease in thermal conductivity for all samples. This may be exciting news for practical use of β - FeSi_2 , which is required for high thermoelectric performance at high temperatures.

IV. CONCLUSIONS

From the above experimental results and discussion on β - FeSi_2 based thermoelectric materials $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) prepared by rapid solidification and hot uniaxial pressing, the following conclusions can be drawn.

- (1) Rapidly solidified powders obtained by melt spinning are thin ribbons with nanosize $\alpha + \epsilon$ eutectic structures which grow to about 2 μm during hot pressing. The morphology of the excess silicon changes from nanosized polyhedrons to micrometer long rods and further to micrometer-sized irregular particles with an increase in the amount of excess silicon.
- (2) Some excess silicon in the sample with $x=2.1$ enhances the Seebeck coefficient slightly and is very effective in decreasing the thermal conductivity.
- (3) Hall measurements carried out at room temperature showed that the carrier concentrations for $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$) are between 2.6×10^{18} and $5.6 \times 10^{18} \text{ cm}^{-3}$, much lower than the amount of doping of manganese. This is suggested to be due to the limit of solubility of manganese in β - FeSi_2 .

- (4) The maximum figure of merit of $ZT=0.17$ at 973 K was obtained for the sample with $x=2.0$. An offset of x from 2.0 to smaller than 0.1 has no significant influence on ZT . However a large amount of excess silicon deteriorates the thermoelectric properties of the materials due to the high thermal conductivity of silicon and the possible n -type doping of silicon from impurities such as sulfur and phosphorus in raw material iron.
- (5) The increase of the figure of merit is still ongoing towards higher temperature above 1000 K for $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Si}_x$ ($1.9 \leq x \leq 2.5$).

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