



## Regular article

## Effect of Si content on the thermoelectric transport properties of Ge-doped higher manganese silicides

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## ABSTRACT

Polycrystalline bulks of Si-content tuned Ge-doped higher manganese silicides (HMSs) were fabricated to elucidate the effects of Si content on the phase formation behavior and thermoelectric properties. The phase formation and electronic transport characteristics of HMSs were significantly dependent on Si content. Improved power factor was obtained at higher Si contents because of an enhanced Seebeck coefficient due to the increase in density of states effective mass, maintaining electrical conductivity. Furthermore, the lattice thermal conductivity was reduced through Si-content tuning, which suppressed the formation of secondary phases. Thus, a maximum  $ZT$  of 0.61 at 823 K was obtained in  $\text{MnSi}_{1.77}\text{Ge}_{0.027}$ .

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## 1. Introduction

Thermoelectric power generation (TEG) is one of the most promising technologies for renewable energy generation owing to the direct conversion of heat to electrical energy. Recently, applications involving a TEG system have been focused on recovering waste heat from automobiles and industries because of the increasing societal need for high-efficiency energy use. The energy conversion efficiency of a TEG system is directly determined by the temperature difference and the dimensionless figure of merit  $ZT$  ( $= \sigma S^2 T / \kappa$ , where  $\sigma$  is the electrical conductivity,  $S$  is the Seebeck coefficient,  $\kappa$  is the total thermal conductivity, and  $T$  is the absolute temperature) of TE materials. Several TE materials including skutterudite-, [1,2] half-Heusler-, [3] and Si-based alloys [4,5] have been considered as promising candidates for mid-to-high temperature power generation applications owing to their high  $ZT$  and good chemical stability. Si-based alloys are more favorable for a TEG system owing to their earth-abundant and non-toxic constituents (Mg, Mn, and Si); however, it is necessary to obtain excellent TE performance, which implies a high  $ZT$ , particularly in  $p$ -type materials to ensure economic feasibility.

Transition metal silicides such as Fe-Si, Cr-Si, and Mn-Si have been intensively investigated as  $p$ -type Si-based TE materials owing to their low and anisotropic thermal conduction behavior and good chemical stability even at higher temperatures [6–8]. Among these materials, higher manganese silicides (HMSs) with a crystal structure known as the Nowotny chimney ladder (NCL) have high flexibility in terms of composition (Mn to Si ratio) owing to the different periodicity of the Si atoms and their modulation [9]. HMSs consist of a Mn sublattice and an interpenetrating helical Si sublattice and form four distinct phases, namely,  $\text{Mn}_4\text{Si}_7$ ,  $\text{Mn}_{11}\text{Si}_{19}$ ,  $\text{Mn}_{15}\text{Si}_{26}$ , and  $\text{Mn}_{27}\text{Si}_{47}$ . In HMSs, the substitutional doping approach has proven to be one of the effective ways to improve  $ZT$  as this approach can either improve the power factor ( $\sigma S^2$ ), due to the modification of electronic structure, or reduce the lattice thermal conductivity ( $\kappa_{\text{lat}}$ ), due to intensified point-defect phonon scattering [10–17]. For example, Ge has been reported as the most effective doping element to induce point defects on Si substrates for simultaneous enhancement of carrier transport and phonon scattering [10–12]. On the other hand, controlling the phase formation behavior of HMSs is another key issue for obtaining high  $ZT$ , since the presence of secondary phases (MnSi and Si) and self-defects (Si vacancy) have effects on the electronic and thermal transport properties of HMSs. A previous study [13] reported that the formation of nano-scale (100–200 nm) metallic MnSi platelets gives rise to enhanced electronic transport properties of HMSs, originating from an increased electrical conductivity due to the increase in carrier concentration without a reduction in the carrier mobility. However, little is known about the

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effects of Si content on the phase formation behavior, related with TE properties.

In the present study, we fabricated Ge-doped HMS polycrystalline bulks with controlled Si content expecting that it could manipulate the carrier and phonon transport properties of HMSs. An enhanced thermoelectric power generation (TEG) ( $\sim 1.77 \text{ mW m}^{-1} \text{ K}^{-2}$  at 823 K) and a reduced  $\kappa_{\text{lat}}$  ( $\sim 1.75 \text{ W m}^{-1} \text{ K}^{-1}$  at 823 K) resulting from the compositional tuning effect were simultaneously obtained by the optimization of Si content, and a maximum  $ZT$  of 0.61 at 823 K was achieved in  $\text{MnSi}_{1.77}\text{Ge}_{0.027}$ .

## 2. Experiment

Ge-doped HMS polycrystalline bulks (Ge-HMSs) with compositions  $\text{MnSi}_{1.70+x}\text{Ge}_{0.027}$  ( $x = 0, 0.03, 0.05, 0.07, \text{ and } 0.1$ ) were synthesized by combining a conventional solid-state reaction (SSR) and spark plasma sintering (SPS) using high purity elemental Mn (99.95%, Alfa Aesar), Si (99.9%, Alfa Aesar), and Ge (99.999%, Sigma Aldrich). The amount of Ge was kept constant at a value of 0.027, which was calculated based on 1 at% of the entire composition [10–12]. Pristine (undoped)  $\text{MnSi}_{1.727}$  (or  $\text{Mn}_{11}\text{Si}_{19}$ ) was synthesized by the same process. The stoichiometric materials mixed in an agate mortar were placed in a tube-type furnace; they were heat-treated at 1273 K for 24 h under dynamic vacuum and cooled to room temperature. The samples thus obtained were ground into a powder by conventional ball milling and sieved under  $53 \mu\text{m}$  in mesh size. Then, bulk samples with a 10 mm diameter and thickness were prepared by SPS under 60 MPa, at 1193 K for 5 min under vacuum.

Phase analysis of the bulk samples prepared by SPS was carried out using powder X-ray diffraction (PXRD, Ultima IV/ME 200DX, Rigaku, Japan) with  $\text{CuK}\alpha$  radiation. Structural factors obtained from the XRD data were calculated using Rietveld refinement. To measure  $\sigma$ ,  $S$ , and  $\kappa$  in the same direction, square-shaped samples ( $6 \text{ mm} \times 6 \text{ mm} \times 1.2 \text{ mm}$ ) for thermal diffusivity measurements and bar-shaped samples ( $2 \text{ mm} \times 2 \text{ mm} \times 8 \text{ mm}$ ) for  $\sigma$  and  $S$  measurements were cut on a plane parallel and perpendicular to the SPS press direction, respectively. The  $\sigma$  and  $S$  values from 300 K to 873 K were measured using a TE property measurement system (ZEM-3, ULVAC, Japan) in a He atmosphere. Hall effect measurements were performed in the van der Pauw configuration under a constant magnetic field (1 T). Owing to the high Hall carrier concentration ( $p_{\text{H}}$ ) of the Ge-HMSs, the Hall mobility ( $\mu_{\text{H}}$ ) was calculated using a single parabolic band (SPB) model without considering the minority carriers. The  $\kappa$  values were calculated using the equation  $\kappa = DC_p\rho$ , where  $\rho$  is the bulk density of the sample,  $D$  is the thermal diffusivity measured by using a laser flash method (Netzsch LFA-457, Germany), and  $C_p$  is the specific heat measured by using differential scanning calorimetry (DSC 8000, Perkin Elmer, USA).

## 3. Results and discussion

According to the stacking period difference, four distinct HMSs ( $\text{Mn}_4\text{Si}_7$ ,  $\text{Mn}_{11}\text{Si}_{19}$ ,  $\text{Mn}_{15}\text{Si}_{26}$ , and  $\text{Mn}_{27}\text{Si}_{47}$ ) are formed, indicating that the ratio of Mn/Si is a critical factor influencing the crystal structure. Fig. 1 shows the XRD patterns for the bulks of pristine  $\text{MnSi}_{1.727}$  and Ge-doped  $\text{MnSi}_{1.70+x}$  (Ge-HMSs) obtained by SPS. All major peaks are indexed to  $\text{MnSi}_{1.727}$ , while MnSi and Si are detected as secondary phases in all compounds. To clarify the phase formation behavior with varying Si content, we calculated the actual wt% of secondary phases using Rietveld refinement, as given in Table 1. Interestingly, the amounts of MnSi are significantly decreased with increasing Si content, suggesting that the additional Si is effective in suppressing the generation of MnSi by the acceleration of following reaction:  $\text{MnSi} + x\text{Si} \rightarrow \text{MnSi}_{1.727}$ . However, at a higher Si content ( $\text{MnSi}_{1.80}\text{Ge}_{0.027}$ ), the wt% of Si ( $\sim 1.22 \text{ wt\%}$ ) increases owing to the limit of occupancy on the Si site. These results suggest that the phase formation behavior of the HMSs could be controlled by adjusting the Si content of the starting

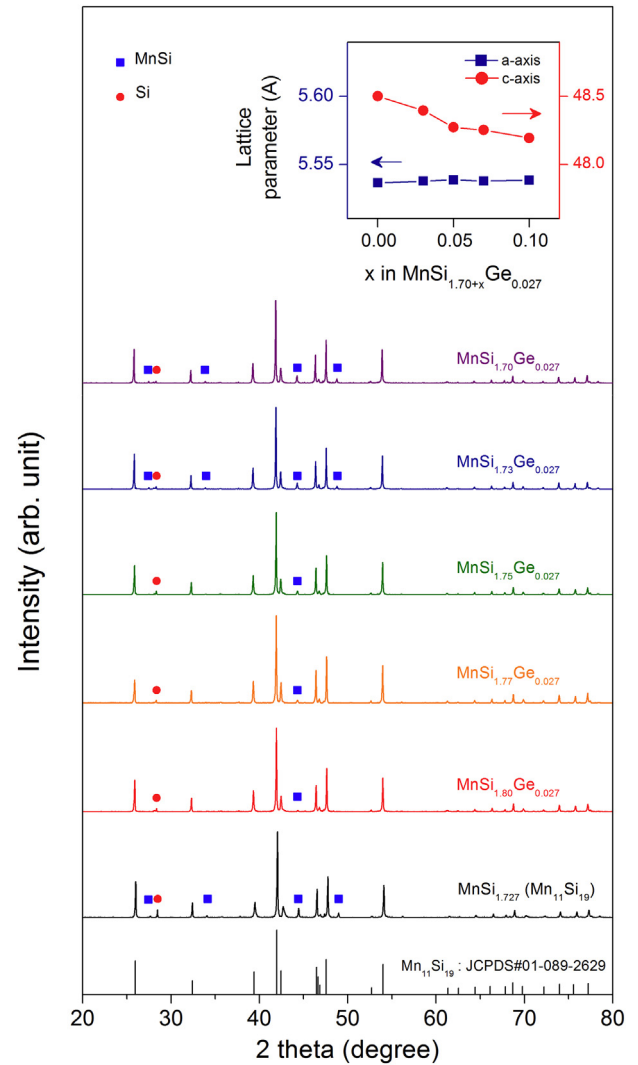


Fig. 1. Powder XRD patterns of SPSed HMS samples (Ge-HMSs and pristine  $\text{MnSi}_{1.727}$ ) and the variation of lattice parameters ( $a$  and  $c$ ) with Si content (inset).

materials. To further explain this phenomenon, we calculated the variation of lattice parameters ( $a$  and  $c$ ) with Si content (inset of Fig. 1). It is noted that the values of lattice parameter  $a$  are almost the same for all Ge-HMSs, while the values of  $c$  monotonously decrease with increasing Si content. The formation of Si-content tuned HMSs with different Si-site occupancies is further confirmed from the fact that the lattice parameter for the [Si]-sublattice along the  $c$ -axis tends to decrease from 2.537 Å ( $\text{Mn}_{11}\text{Si}_{19}$ ) to 2.495 Å ( $\text{Mn}_4\text{Si}_7$ ) when the Mn to Si ratio increases [9].

To clarify the effects of Ge-doping and Si content on the electronic transport properties of HMSs, we measured the temperature dependences of  $\sigma$  and  $S$  (Fig. 2(a)) and  $p_{\text{H}}$  and  $\mu_{\text{H}}$  values at 300 K (Table 2). All Ge-HMSs exhibit a  $\sigma$  value higher than that of pristine  $\text{MnSi}_{1.727}$

Table 1

Amounts of calculated secondary phases (MnSi, Si) and densities for  $\text{MnSi}_{1.70+x}\text{Ge}_{0.027}$ .

| Samples    | Secondary phases |          |             | Density<br>( $\text{g}/\text{cm}^3$ ) |
|------------|------------------|----------|-------------|---------------------------------------|
|            | MnSi (wt%)       | Si (wt%) | Total (wt%) |                                       |
| $x = 0.0$  | 5.13             | 0.35     | 5.48        | 5.06                                  |
| $x = 0.03$ | 4.16             | 0.78     | 4.94        | 4.98                                  |
| $x = 0.05$ | 1.67             | 0.85     | 2.52        | 4.91                                  |
| $x = 0.07$ | 1.13             | 0.81     | 1.93        | 4.87                                  |
| $x = 0.10$ | 0.25             | 1.22     | 1.47        | 4.82                                  |

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