Thermoelectric Properties of Si$_2$Ti-Type Al-Mn-Si Alloys

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By using the first principle band calculations, we identified that Si$_2$Ti-type Al-Mn-Si CS4-phase possesses an electronic structure suitable for the thermoelectric materials. The formation range of the Al-Mn-Si CS4-phase was determined by preparing samples at a number of different compositions, and the samples solely consisting of the CS4-phase were successfully obtained around Al$_{55}$Mn$_{30}$Si$_{15}$. The carrier concentration of the Al-Mn-Si CS4-phase was controlled by the partial substitution of the constituent elements, and behaviors in electrical properties characteristic to n-type and p-type thermoelectric materials were alternatively observed for the samples of a larger electron concentration and a smaller electron concentration, respectively. The absolute value of the Seebeck coefficient |S| was found to exceed 300$\mu$V/K for both n-type and p-type samples. [doi:10.2320/matertrans.M2010022]

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1. Introduction

Thermoelectric materials have attracted considerable interest because those materials are used as one of the main components in both thermoelectric generators and Peltier coolers. The former application is especially important for the construction of sustainable society, because it is capable of recovering the wasted heat into the useful electricity, and hence, the consumption of fossil fuels and amount of the global-warming-gas-emission could be effectively reduced. However, the low efficiency of energy conversion in the practical thermoelectric generators and their expensive cost have limited their practical applications.

The efficiency of energy conversion in thermoelectric generator increases with increasing magnitude of the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$ where $S$, $\sigma$, and $\kappa$ indicate Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively. Since thermal conductivity consists of the electron contribution and the lattice contribution as $\kappa = \kappa_{el} + \kappa_{lat}$, the dimensionless figure of merit $ZT$ is simply transformed into the product of two factors; $A = S^2\sigma T/\kappa_{el}$ and $B = 1/(1 + \kappa_{lat}/\kappa_{el})$. The factor $A$ is determined solely by the electron spectral conductivity $\sigma(\varepsilon, T)$, while the factor $B$ is by the ratio between $\kappa_{lat}$ and $\kappa_{el}$. The magnitude of $B$ is always kept below unity because of the positive value both of $\kappa_{lat}$ and $\kappa_{el}$. Therefore, the factor $A$ represents the maximum value of $ZT$ obtainable from a given spectral conductivity, while the factor $B$ always reduces the value of $ZT$ from the value of $A$.1)

We should also mention here that the factor $A$ is less sensitive about the scattering process, because the scattering process generally produces less obvious energy dependence in the narrow energy range where the electrons contribute to electrical conduction and such factors in the spectral conductivity are vanished from the equation representing the factor $A$.1) It is also understood from the equation representing $ZT$ that the larger magnitude of $\kappa_{el}$ is preferable for the increase of factor $B$, and that this condition is definitely contrary to the usually used, over-simplified argument of the smaller $\kappa$ leading to a large magnitude of $ZT$.

By taking the considerations described above into account, one may naturally realize a simple strategy to develop new thermoelectric materials of high performance. As the first step, one should find the materials possessing a large magnitude of $ZT$. In this model, the band edge, the step structure, and the Fermi level must be located in the narrow energy range of a few $k_B T$, where $k_B$ represents the Boltzmann constant and $T$ is the absolute temperature. This condition could be realized for some semiconducting alloys containing transition metal elements as one of the main components, because the widely extended $s,p$-bands in such alloys are able to overlap with some $d$-bands of a narrow energy width.

Recently, we realized that the Al$_3$Ru alloy, which was recently reported to possess a large magnitude of power factor $PF = S^2\sigma$2-4) has an electronic structure possessing the above mentioned characteristics leading to a large magnitude of factor $A$. The observed large value of power factor $PF$ must be caused by the characteristic electronic structure of Al$_3$Ru, because the power factor $PF$ is directly related to the factor $A$. Despite its good thermoelectric properties, Al$_3$Ru is not still practical because Ru is one of the most expensive noble metal elements and its Clarke number is very small ($< 5 \times 10^{-7}$%). However, the charac-
teristics of the electronic structure observed for Al$_2$Ru let us realize a strategy of finding new thermoelectric materials desirably consisting of cheap, environment-friendly elements.

We tried, in this study, to find the inter-metallic compounds possessing an electronic structure similar to that of Al$_2$Ru by using the first-principle band calculation. As the result of the calculations and experiments, we succeeded in finding a compound capable of possessing a large magnitude of factor $A$ in Al-Mn-Si alloy system. Its characteristic electronic structure and the relation with the thermoelectric properties will be discussed in detail.

2. Calculations and Experiments

To obtain information about the electronic structure of the objective phases, we performed the first-principles band calculations using the Vienna *Ab initio* Simulation Package (VASP) as implemented with the plane-wave projector augmented-wave (PAW) method. The lattice constants (VASP) as implemented with the plane-wave projector augmented-wave (PAW) method. The lattice constants and ionic positions were fully relaxed to find the optimized structure before calculating the detailed electronic structure.

The mother ingots of the samples were prepared by the induction melting in a pressurized argon atmosphere, followed by annealing at 800°C for 24 h in a vacuum atmosphere. We also used the liquid quenching technique (LQ) for some mother ingots using a single-role Cu wheel rotating at 3000 rpm to reduce the size of grains in the samples. The quenched sample in ribbon shape was ground to 15 mm, sintered at 1073 K for 15 min under a pressure of 50 MPa in vacuum by the spark plasma sintering (SPS) technique.

The phases involved in the samples were identified by the conventional powder X-ray diffraction measurements with Cu-Kα radiation source and a Bragg-Brentano-type diffractometer set in RIGAKU RINT2000. The spatial distribution of the grains of both the objective phase and the impurity phase(s) were observed using scanning electron microscope (SEM). The composition of each grain was determined by the energy dispersive X-ray spectroscopy (EDC) equipped in the SEM apparatus.

The electrical conductivity, Seebeck coefficient, and thermal conductivity at low temperatures below 300 K for the rectangular bulk-samples cut in a size of $\sim 1 \text{mm} \times 1 \text{mm} \times 15 \text{mm}$ were measured using the Physical Properties Measurement System with the Thermal Transport Option developed by Quantum Design, Inc. The Seebeck coefficient of the samples at the temperature range of 90 K $< T < 600$ K was also measured using the Seebeck Measurement System of MMR Technologies, Inc. We also measured the high temperature electrical resistivity at 300 K $< T < 600$ K in the vacuum furnace using the probes assembled by ourselves.

3. Results

3.1 Electronic structure

Since the electronic structure of solids is directly related to their crystalline structure, we selected materials that possess the same crystalline structure with that of Al$_2$Ru. The structure of Al$_2$Ru is known as the orthorhombic Si$_2$Ti-type structure (C54-phase, Pearson Symbol: oF24, Space group: Fddd) in which the two-dimensional, close packed, hexagonal Si$_2$Ti layers are stacked along $c$-axis with four different positions so as the Ti atoms to construct a spiral structure. Its structure is schematically drawn in Figs. 1(a) and (b). Note here that the C54-phase is known as the prototype of a large family of Nowotny chimney-ladder compounds, which are considered as one of the promising candidates for the practical thermoelectric materials.

The C54-phase was reported to stabilize in a number of different alloy systems. For example, Al$_2$Ru, AlGeCr, Al$_7$Ge$_3$Mo$_{10}$, Al$_{13}$Si$_3$Mn$_{10}$, Al$_2$Si$_3$Nd$_3$, Si$_6$Cr$_3$Ti$_{12}$, Ga$_7$Ge$_3$Mo$_5$, Ga$_2$Os, Ga$_2$Ru, Ge$_2$Ti, Si$_6$Re$_3$Ti$_{31}$, Si$_2$Ti, and Sn$_2$Zr are listed in the Pearson’s handbook. We realized that the compounds listed above are roughly classified into two groups in terms of the number of valence electrons per transition metal element, which is sometimes called as the “Valence Electron Concentration (VEC)”.

The materials in the first group, such as Al$_2$Ru, possess a value of VEC equal or nearly equal to 14, while those in the second group involving Si$_2$Ti have VEC $\sim 12$. This difference in number of electrons definitely results in different positions of the Fermi level: therefore, we excluded the materials in the second group, to which Si$_2$Ti belongs, from the candidates of the thermoelectric material possessing the similar electronic structure with that of Al$_2$Ru.

Among the compounds in the first group, we selected Al$_{13}$Si$_3$Mn$_{10}$ as one of the best compounds, because every constituent of Al$_{13}$Si$_3$Mn$_{10}$ possesses a large Clarke number and is harmless both to human and environment. In order to calculate the electronic structure of Al$_{13}$Si$_3$Mn$_{10}$ C54-phase in which the chemical disordering between aluminum and silicon was reported, we constructed a hypothetical model free from disordering. In this model, the aluminum atoms are located in the first and third hexagonal close packed layers, while the silicon atoms in the second and fourth layers. The composition of this model is expressed as Al$_3$Mn$_8$Si$_4$, and the structure is schematically drawn in Fig. 1(c). Here we used the chemical formula of Al$_3$Mn$_8$Si$_4$ rather than AlMnSi because C54-phase contains 24 atoms in the unit cell.

Figures 2(a) and (b) show the electronic density of states calculated for Al$_3$Mn$_8$Si$_4$ and Al$_{16}$Ru$_8$ (which represents Al$_2$Ru), respectively. The electronic structure of Al$_3$Ti$_8$ was also calculated as a representative of the materials in the second group and its electronic density of states is shown in Fig. 2(c). Obviously an energy gap is observable both for Al$_{16}$Ru$_8$ an Al$_3$Mn$_8$Si$_4$ at the Fermi level, while it is vanished to be metallic in the Si$_6$Cr$_3$Ti$_{12}$ phase because its smaller VEC significantly reduces the Fermi energy. Although the step structure near the band edge observable in the valence band of Al$_{16}$Ru$_8$ is obscured in Al$_3$Mn$_8$Si$_4$, the large density of states just below/above the band gap of the Al$_3$Mn$_8$Si$_4$ C54-phase could result in a large Seebeck coefficient with positive or negative sign at slightly different electron concentrations. It is also argued that partial substitutions for the constituent elements, which will be used to increase or decrease the number of carriers, could recover the step structure, because the energy-width and the relative energy of the $sp$-bands and $d$-bands, that contribute to produce a step structure near $\varepsilon_F$, are affected by the atomic substitutions especially of
elements possessing different atomic radii. The presence of the step structure in Al\textsubscript{16}Ru\textsubscript{8} and its absence in Al\textsubscript{8}Mn\textsubscript{8}Si\textsubscript{8} suggest that the partial substitution of Ru for Mn in Al\textsubscript{8}Mn\textsubscript{8}Si\textsubscript{8} is one of the best candidates for recovering the step structure.

3.2 The formation range of C\textsubscript{54}-phase in Al-Mn-Si system

We prepared the first sample at the composition of Al\textsubscript{43}:Si\textsubscript{23}:Mn\textsubscript{33}, which corresponds to Al\textsubscript{13}Si\textsubscript{7}Mn\textsubscript{10}. Although the C\textsubscript{54}-phase was reported to stabilize at this composition\textsuperscript{12,13}, we did not succeed to obtain the single C\textsubscript{54}-phase. This fact is clearly understood from the XRD pattern of the sample shown in Fig. 3(a). Although the C\textsubscript{54}-phase persisted in the Al\textsubscript{43}:Si\textsubscript{23}:Mn\textsubscript{33} sample, its amount was very small to be presumably less than 20%. The main phases of the sample was identified as Al\textsubscript{10}Mn\textsubscript{3}type ternary phase that was reported to stabilize in a wide composition range centered at Al\textsubscript{66}Mn\textsubscript{24}Si\textsubscript{10}.\textsuperscript{14} Since the composition of the Al\textsubscript{10}Mn\textsubscript{3}-type ternary phase contains a larger amount of aluminum than that in the first sample, we expected that the Al-Mn-Si C\textsubscript{54}-phase is stabilized at a composition range containing a smaller amount of aluminum than that in Al\textsubscript{43}:Si\textsubscript{23}:Mn\textsubscript{33}. After preparing the first sample, we realized that the Al-Mn-Si C\textsubscript{54}-phase was reported to stabilize at Al\textsubscript{34}Mn\textsubscript{34}Si\textsubscript{32} in a recently published paper,\textsuperscript{14} and this composition definitely contains a smaller amount of aluminum than Al\textsubscript{43}:Si\textsubscript{23}:Mn\textsubscript{33} of the first sample.

As the second step of investigation, therefore, we made samples in the vicinity of Al\textsubscript{34}Mn\textsubscript{34}Si\textsubscript{32} and revealed the
thermodynamically stable phase(s) obtainable at each composition. After preparing a number of samples at different compositions, we succeeded in obtaining a sample consisting solely of the $\text{C}_{54}$-phase at the nominal composition of $\text{Al}_{32}\text{Mn}_{34}\text{Si}_{34}$. This composition is not exactly the same with $\text{Al}_{34}\text{Mn}_{34}\text{Si}_{32}$ reported by Raghavan, but obviously very close to it. The XRD patterns of the prepared samples are shown in Fig. 3, and the formation-range of the $\text{C}_{54}$-phase thus determined is indicated in Fig. 4.

The $\text{C}_{54}$-phase in the Al-Mn-Si system was reported to possess the chemical disordering between aluminum and silicon. The presence of disordering between aluminum and silicon let us speculate that the formation range of the $\text{C}_{54}$-phase would be distributed widely along a constant manganese line, and therefore that the carrier concentration could be controlled by the ratio of aluminum to silicon as we did for the $\text{Al}_{102-x}\text{Mn}_{3x}\text{Si}_{x}$ and $\text{Al}_{102-y}\text{Re}_{24}\text{Si}_{x}$ ($7 < x < 12$) cP138 inter-metallic compounds. However, by preparing the samples with a number of different nominal compositions, we realized that the sample consisting solely of $\text{Al}_{32}\text{Mn}_{34}\text{Si}_{34}$ where the single $\text{C}_{54}$-phase was successfully prepared.

![Fig. 3](image-url)  
(a) The powder XRD pattern of $\text{Al}_{32}\text{Mn}_{34}\text{Si}_{34}$ and $\text{Al}_{34}\text{Mn}_{34}\text{Si}_{32}$. The calculated patterns of $\text{C}_{54}$-phase and $\text{Al}_{10}\text{Mn}_{3}$-type structure are shown at the bottom. At $\text{Al}_{32}\text{Mn}_{34}\text{Si}_{34}$, we obtained the sample consisting solely of the $\text{C}_{54}$-phase, while the mixture of the $\text{C}_{54}$-phase and the ternary phase of $\text{Al}_{10}\text{Mn}_{3}$-type structure at $\text{Al}_{34}\text{Mn}_{34}\text{Si}_{32}$. (b) The XRD patterns of samples prepared in the vicinity of $\text{Al}_{32}\text{Mn}_{34}\text{Si}_{34}$ where the single $\text{C}_{54}$-phase was successfully prepared.

<table>
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<tr>
<th>Composition</th>
<th>Intensity</th>
<th>Diffraction Angle, $2\theta$ (degree)</th>
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<td>20 - 80</td>
</tr>
<tr>
<td>$\text{Al}<em>{32}\text{Mn}</em>{34}\text{Si}_{33.5}$</td>
<td>(2)</td>
<td>20 - 80</td>
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<td>$\text{Al}<em>{32.5}\text{Mn}</em>{34}\text{Si}_{33}$</td>
<td>(3)</td>
<td>20 - 80</td>
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<tr>
<td>$\text{Al}<em>{32.5}\text{Mn}</em>{33.5}\text{Si}_{34}$</td>
<td>(4)</td>
<td>20 - 80</td>
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<td>(5)</td>
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<td>(7)</td>
<td>20 - 80</td>
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<tr>
<td>$\text{Al}<em>{33.5}\text{Mn}</em>{34.5}\text{Si}_{33}$</td>
<td>(8)</td>
<td>20 - 80</td>
</tr>
<tr>
<td>$\text{Al}<em>{34}\text{Mn}</em>{34}\text{Si}_{33}$</td>
<td>(9)</td>
<td>20 - 80</td>
</tr>
</tbody>
</table>
association with these elements would persist in the unit structure (basis). This speculation, however, was clearly denied from the behaviors of electrical resistivity, which will be shown in the next subsection. Another possible scenario is that some mechanisms, such as the Hume-Rothery stabilization mechanism,\textsuperscript{18} restrict the ratio of aluminum to silicon, and for the nearly single-phased sample at Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{34}\). Although an impurity phase, FeSi-type MnSi phase (Pearson symbol: cP8, Space group: P2\(_{1}\)3), was precipitated in the latter, the very small intensity of the XRD peaks indicates that the secondary phase was distributed over the sample as the negligibly small particles persisting at the boundaries of the grains of the main phase. Therefore its contribution to the thermoelectric properties is supposed to be safely ignored.

Figures 5(a)–(c) show the Seebeck coefficient, electrical resistivity, and thermal conductivity of the Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{34}\) and Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{33}\) samples, respectively. The magnitude of Seebeck coefficient \(|S|\) of both samples linearly increases with increasing temperature, and it eventually exceeds 300\(\mu\)V/K at about 400–500 K. The maximum magnitude of \(|S|\) observed for Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{34}\) and Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{33}\) is 330\(\mu\)V/K at \(T_{peak} = 490\) K and 320\(\mu\)V/K at \(T_{peak} = 400\) K, respectively. After becoming maximal at \(T_{peak}\), \(|S|\) turns out to decrease with increasing temperature. Notably, the Seebeck coefficient of Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{34}\) is kept negative over the whole temperature range of the present measurement, while Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{33}\) always possesses the positive Seebeck coefficient. The large magnitude of Seebeck coefficient and the alternatively observed positive- and negative-signs let us strongly believe that the Al-Mn-Si C54-phase can be utilized as a practical thermoelectric material.

From the different sign of Seebeck coefficient between Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{34}\) and Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{33}\), we considered that the C54-phase in the Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{34}\) sample has a slightly different composition from that of the Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{33}\). The carrier concentration in these samples, therefore, must be slightly different from each other, despite the fact that the lattice constant of the C54-phase in these two compounds are nearly identical (\(a = 0.776(1)\) nm, \(b = 0.450(1)\) nm, and \(c = 0.842(1)\) nm). The negligibly small variation of lattice constants would be caused by the very small difference of composition less than 1 at% and the similar atomic radii of aluminum and silicon.

The electrical resistivity both of the Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{34}\) and Al
\(_{32}\)Mn
\(_{34}\)Si
\(_{33}\) is characterized by the large magnitude of residual resistivity exceeding 5 m\(\Omega\)cm. It moderately increases with increasing temperature and turns out to decrease after becoming maximal at around 450 K. The positive temperature coefficient of electrical resistivity (TCR) at low temperature together with the negative value at high temperature indicates that both samples are alternatively classified into the group of degenerate semiconductor possessing a narrow energy gap or that of metals characterized by the narrow pseudogap near \(\varepsilon_F\). The small value of positive TCR at low temperature together with the large residual resistivity suggests that the both compounds possess considerable disordereding in the unit structure (basis). Note here that if the compounds had less obvious disordereding, the residual resistivity would become smaller and the TCR would become larger. The reduction of the electrical resistivity observable at high temperature would be closely related to the reduction of \(|S|\) at high temperature. The origin of these behaviors will be explained in terms of electronic structure in Discussion.

The thermal conductivity of the both samples was not very small but rather large reaching 10 W/m K at room temperature, which is one order larger than that of typical, practical thermoelectric materials. The contribution of electron is negligibly small due to the relatively large electrical resistivity as shown in Fig. 5(d), and therefore the observed thermal conductivity is unambiguously dominated by the
contribution of lattice. Because of the large magnitude of lattice thermal conductivity, the dimensionless figure of merit shown in Fig. 5(f) did not exceed 0.1 over the whole temperature range of the measurement.

3.4 The effects of liquid quenching and spark plasma sintering on thermal conductivity

Although the ZT-value obtainable for the present samples possesses a much smaller magnitude than that of the practical thermoelectric materials, the Al-Mn-Si C54-phase is still considered as one of the promising candidates for the practical thermoelectric materials, because these samples were prepared solely with the induction melting and subsequent heat-treatment and, therefore, the magnitude of ZT is presumably increased by the reduction of lattice thermal conductivity using the sample preparation techniques, such as the sintering of ball-milled powders or rapidly quenched ribbons.

In order to confirm the validity of this consideration, we tried to prepare the samples possessing a small mean grain size using the liquid quenching and the spark plasma sintering (LQ+SPS) techniques at the composition of Al$_{32}$Mn$_{34}$Si$_{34}$ where the n-type behavior was observed. The SEM image of the original sample and the LQ+SPS sample was shown in Figs. 6(a) and (b), respectively. The size of grains was indeed reduced from 50$\mu$m to less than 15$\mu$m by the LQ+SPS process.

The powder XRD pattern of the LQ+SPS sample suggests that the volume fraction of the impurity phase, which was identified as the FeSi-type MnSi phase containing small amount of aluminum, slightly increased as shown in Fig. 6(c). Composition change of the samples during the LQ+SPS process would increase the amount of the impurity phase in the sample. Comprehensive investigations using various conditions of LQ+SPS process and various sample compositions are required to remove the impurity phase or to quantitatively reveal the effects of this impurity phase on the thermoelectric properties. We decided to leave this point unsolved in the present papers, but will be investigated in detail in our future work.

The Seebeck coefficient, electrical resistivity, thermal conductivity, and dimensionless figure of merit of the sample prepared by the LQ+SPS method were shown in Figs. 7(a)–(d). Unfortunately the value of Seebeck coefficient was slightly decreased presumably due to the composition change during the LQ+SPS process. The electrical resistivity was roughly calculated using the Wiedemann-Franz law, (e) power factor, and (f) dimensionless figure of merit, of the Al-Mn-Si C54-phases are plotted as a function of temperature. Those of the n-type Al$_{32}$Mn$_{34}$Si$_{34}$ and the p-type Al$_{33}$Mn$_{34}$Si$_{33}$ are shown with the solid circles and the open circles, respectively.
also reduced by the LQ+SPS method. This reduction in electrical resistivity would be caused by the small but finite precipitation of the secondary phase together with the composition shift of the sample during the LQ+SPS process. Notably, the LQ+SPS process indeed reduced the magnitude of \( \kappa \) to nearly a half value. Since an increase of electron thermal conductivity is suggested from the reduction in the electrical resistivity, the reduction in the thermal conductiv-

![Fig. 6](image1.png)  
Fig. 6  Scanning electron microscope images taken for (a) the original sample and (b) the sample prepared with the LQ+SPS process. The XRD pattern of the LQ+SPS sample is shown in (c). The grain size in the original sample is distributed over 20\( \sim \)150\( \mu \)m, while that in the LQ+SPS sample is reduced to less than 15\( \mu \)m. This reduction in grain size must be responsible for the large reduction of lattice thermal conductivity. Small, light gray areas indicate the presence of the impurity phase, AlMn, and the black are represents the micro voids. After the LQ+SPS process, the size both of the micro voids and impurity phase was reduced significantly as well as that of the main phase.

![Fig. 7](image2.png)  
Fig. 7  (a) Seebeck coefficient, (b) electrical resistivity, (c) thermal conductivity, and (d) dimensionless figure of merit of the Al\( \text{Si}_2\)Mn\( \text{Si}_3\) samples prepared by the LQ+SPS process. The slightly small magnitude of Seebeck coefficient than that of the samples without the LQ+SPS process would be caused by the composition change during the LQ+SPS process. The large reduction in lattice thermal conductivity and absence of the large enhancement of the electrical resistivity strongly indicates that the Al-Mn-Si C54-phase possessing a large value of dimensionless figure of merit could be prepared with appropriate selection of the nominal composition.
ity must be caused by the reduction of the lattice thermal conductivity in association with the fine grain size in the LQ+SPS process.

Although the lattice thermal conductivity was effectively reduced by the LQ+SPS process, the reduction of Seebeck coefficient due to the composition shift in the present sample prevented us from obtaining a large enhancement in dimensionless figure of merit; it increased less than 20% from that of the sample without the LQ+SPS process. Nevertheless, we stress here that if the composition were appropriately controlled in the LQ+SPS process, the reduction of lattice thermal conductivity must lead to the increase of $ZT$ twice as large as that of the sample without the LQ+SPS method.

4. Discussion

In this section, we discuss the mechanism leading to the characteristic behaviors of thermoelectric properties of the Al-Mn-Si C54-phase in terms of electronic structure. The potential of the Al-Mn-Si C54-phase as a practical thermoelectric material is also discussed in detail with proposing the strategies to make it practical.

The presence of a peak in the temperature dependence both of Seebeck coefficient and electrical resistivity definitely indicates the presence of a narrow energy gap or a narrow pseudogap in the vicinity of the Fermi level. Generally speaking, the number of electrons excited from the valence band to the conduction band exponentially increases with increasing temperature. At low temperatures the number of excited electrons would be negligibly small, and therefore the electron scattering dominates the temperature dependence of electrical resistivity so as to increase with increasing temperature. In such a case, Seebeck coefficient also increases with increasing temperature as it is suggested by the well-known Mott formula. At high temperatures, the thermal broadening in the Fermi-Dirac distribution function, becomes equivalent to the energy width of the gap, and hence the electron excitation across the band gap becomes obvious. In such a condition, the electrical resistivity and the absolute value of Seebeck coefficient start to decrease with increasing temperature due to the increased number of both holes and electrons.

The sign reversal of Seebeck coefficient caused by the variation in composition (variation in carrier concentration) lends a great support to the scenario of a narrow gap or a narrow pseudogap persisting at the Fermi level. The negative sign of Seebeck coefficient of the $\text{Al}_{132}\text{Mn}_{34}\text{Si}_{34}$ (VEC $\sim 13.82$) would be caused in association with the Fermi level located in the conduction band at the energy just above the gap. In the $\text{Al}_{133}\text{Mn}_{34}\text{Si}_{33}$ sample, on the other hand, has slightly small electron concentration (VEC $\sim 13.79$), and hence the Fermi level is presumably moved into the valence band at the energy just below the gap. This condition provides us with the positive sign of Seebeck coefficient. The small magnitude of electronic density of states near the band edge would be responsible for the significant variation of the Fermi level with the very small variation of VEC.

Some of the readers may feel strange by knowing that $n$-type behavior is observed at VEC $\sim 13.82$ in $\text{Al}_{132}\text{Mn}_{34}\text{Si}_{34}$, because the $n$-type behavior should be realized at the VEC larger than 14 if the C54-phase has a real gap. We speculate that the $n$-type behavior with VEC $\sim 13.82$ calculated from the nominal composition might be caused by a small but finite composition shift during the sample preparation, or by the presence of a pseudogap rather than a real gap. Presence of excess atoms in the unit cell could be another candidate leading to this behavior, because the band filling is not directly determined by the number of electron per transition metal elements but by the number of electrons in the unit cell so as each band to be fully filled by two electrons per unit cell.

By using the Wiedemann-Frantz law, $\kappa_{el} = L_0\sigma T$, together with the maximum magnitude of Seebeck coefficient, we roughly estimate the maximum value of factor $A = S^2\sigma T/\kappa_{el} \sim S^2/L_0$ to be 4.46 and 4.20 for the $n$-type $\text{Al}_{132}\text{Mn}_{34}\text{Si}_{34}$ and $p$-type $\text{Al}_{133}\text{Mn}_{34}\text{Si}_{33}$, respectively. Notably, the estimated values of factor $A$ are comparable with or even larger than that of the practical thermoelectric materials. If we could obtain the small lattice thermal conductivity $\kappa_{lat}$ less than 3.2$\kappa_{el}$ for the present samples, the magnitude of factor $B = 1/(1 + \kappa_{lat}/\kappa_{el})$ became larger than 1/4.2 and, hence, the magnitude of $ZT = A \cdot B$ would exceed unity. Unfortunately, however, the lattice thermal conductivity was so large to reach 10 W/m K and the electron thermal conductivity was so small to be limited less than 1 W/m K. The factor $B$, therefore, provides us with a very small magnitude less than 0.01 at 300 K, and hence the magnitude of $ZT = A \cdot B$ of the present samples was consequently kept much smaller than unity even with the large magnitude of factor $A$ exceeding 4.

In order to increase the magnitude of $ZT$, therefore, we have to increase the factor $B$ by increasing $\kappa_{el}$ or decreasing $\kappa_{lat}$ without affecting the value of factor $A$. Once the crystal structure is determined, the increase of $\kappa_{el}$ without affecting the Seebeck coefficient and electrical resistivity is hardly achieved because all these transport properties are closely related with each other via the spectral conductivity $\sigma(\epsilon, T)$ which is directly related to the electronic structure and, therefore, to the crystal structure. The reduction solely of $\kappa_{lat}$, on the other hand, might be managed by use of some scatterers that do not strongly enhance the scattering probability of electrons but that of phonons. Indeed, we definitely proved in this study that the grain boundaries additionally introduced by the LQ+SPS process play the role of such a special scatterer for the present samples.

The additionally introduced grain boundaries always reduce the magnitude of $\kappa_{lat}$ by reducing the mean free path of phonons. However, such grain boundaries do not always increase the factor $B = 1/(1 + \kappa_{lat}/\kappa_{el})$ but sometimes provide us with no significant effect on it, because the grain boundaries scatter not only the phonons but also the electrons and, hence, the ratio of $\kappa_{lat}$ to $\kappa_{el}$ could be kept almost unchanged. Nevertheless we succeed in reducing $\kappa_{lat}$ of the present samples without greatly altering the value of $\kappa_{el}$ by using the LQ+SPS method. The mechanism leading to this experimental fact is accounted for with the difference in mean free path between phonons and electrons in the samples prepared without the LQ+SPS process. The small temperature coefficient of electrical resistivity and the large
magnitude of residual resistivity of the present samples indicate that the mean free path of the conduction electrons is extremely small even at low temperature most likely due to the disordering in the unit cell and, therefore, is hardly shortened by the additionally introduced grain boundary. The mean free path of phonons, on the other hand, is presumably long enough to be effectively reduced by the additionally introduced grain boundary. These conditions allowed the additionally introduced grain boundary to effectively reduce $k_{\text{lat}}$ without greatly altering $k_{\text{el}}$ of the present samples. It is, therefore, argued that the reduction of grain size caused by the LQ+SPS process effectively increases the value of $ZT$ by increasing the magnitude of factor $B$ only when the mean free path of electrons is already shortened while that of phonon is long enough to be shortened by the additionally introduced grain boundaries.

We propose the use of superstructures as another method to effectively reduce $k_{\text{lat}}$ without greatly affecting $k_{\text{el}}$ nor the factor $A$. If we produce some superstructure, the folding of Brillouin zone takes place. Consequently the number of acoustic phonons is effectively reduced and the umklapp process, which is responsible for the thermal resistance, occurs even at low temperatures.$^{17}$ The lattice thermal conductivity $k_{\text{lat}}$, therefore, must be greatly reduced by the superstructure. The electron transport properties, on the other hand, would be less affected by the folding of Brillouin zone because the electron bands typically distributed over a few eV while the energy-window where the electron transport takes places is limited less than a few hundred meV even at high temperatures.$^{17}$ The superstructure, therefore, hardly affects the electron transport properties unless the newly produced zone boundary coincides with the Fermi wave vector. Note, however, that this argument is still in controversial, and therefore some experimental evidences are required to draw a conclusion. We are now in progress on the comprehensive investigation about the effect of LQ+SPS process and superstructure on the lattice thermal conductivity and will be reported in another paper.

Before finishing discussions, we comment on the usefulness of the first-principles band calculations as one of the most effective tools to develop functional materials. Recently, many package programs of first-principles calculation are distributed, and even without knowing the detailed information about the involved program codes, one can obtain information about the electronic structure that can be used to understand the unusual properties observed for some materials.$^{15–17}$ We have to remind, however, that there still remain the weak points of the package programs. For example, the reliable information about the electronic structure is obtainable only when the crystal structure is well investigated. The disordering in the structure is not easily taken into account in the first principle band calculation, despite the fact that the chemical disordering caused by the substitution of the constituent elements is often used to control the carrier concentration in the materials. The electronic structure in the excited states is also difficult to investigate precisely by the widely distributed band calculation package programs. This is easily understood by knowing that the energy gap of semiconductors predicted by the first principle calculation is generally smaller than that determined at finite temperatures by a variety of experimental values. Taking such limitations or accuracy of results properly into consideration, we maximize opportunity to utilize the first-principle calculations not only for obtaining information about electronic structure but also for constructing the guiding principle to control the electron transport properties to develop the functional materials including the thermoelectric materials.

5. Conclusion

By making the full use of information about the electronic structure obtained by the first principle band calculation, we identified that Al-Mn-Si C54-phase capable of possessing the thermoelectric properties suitable for the practical thermoelectric materials. The prepared samples indeed possess a large magnitude of Seebeck coefficient exceeding $|S| > 300 \mu \text{V/K}$ with positive and negative sign alternatively at different compositions. Unfortunately, the dimensionless figure of merit $ZT$ is kept below 0.1 over the whole temperature range of the present measurement, because of the large magnitude of lattice thermal conductivity. Since there still remain the technical methods leading to the reduction of lattice thermal conductivity, we conclude that the newly developed Al-Mn-Si C54-phase is one of the promising candidates for the practical, environmental friendly thermoelectric materials.

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