Metal silicide-based thermoelectric (TE) materials have attracted attention in the past two decades, because they are less toxic, with low production cost and high chemical stability. Here, we study the TE properties of ytterbium silicide YbSi2 with a specific layered structure and the mixed valence state of Yb2+ and Yb3+. YbSi2 exhibits large Seebeck coefficient, S, accompanied by high electrical conductivity, σ, leading to high power factor, S2σ, of 2.2 mW m–1 K–2 at room temperature, which is comparable to those of state-of-the-art TE materials such as Bi2Te3 and PbTe. Moreover, YbSi2 exhibits high Grüneisen parameter of 1.57, which leads to relatively low lattice thermal conductivity, κlat, of 3.0 W m–1 K–1 at room temperature. The present study reveals that YbSi2 can be a good candidate of TE materials working near room temperature.

Thermoelectric (TE) devices can convert heat to electricity and vice versa; thus, they have attracted interest as power generators or refrigerators. The efficiency of a TE device is determined by the temperature gradient across the device as well as the properties of the TE material characterized by a dimensionless figure of merit ZT = S2σTκ–1, where S is the Seebeck coefficient, T is the absolute temperature, σ is the electrical conductivity, and κ is the total thermal conductivity (κ = κlat + κel), where, κlat and κel are the lattice and electronic contributions, respectively.[1–3] In general, both high efficiency and high power output are required for TE power generation. S2σ is referred as a power factor that determines the power generation performance of a TE material. Essentially, a material with high ZT as well as high S2σ needs to be developed.

So far considerable efforts have been made toward enhancing the figure of merit values in several existing thermoelectric material classes, including silicides,[4] half-Heuslers,[5,6] and tellurides (e.g., of Bi,[7] Pb,[8,9] and Ge[10,11]). Bi2Te3 and PbTe are conventional TE materials showing high ZT values around unity in the low (300–400 K) and mid (500–600 K) temperature regions, respectively.[12–16] Very recently, SnSe has been developed as an excellent TE material with an ultrahigh power factor (≥4.0 mW m–1 K–2 at 300 K[17]) and ZT (≥2.6 at 923 K[18]). However, these materials contain highly toxic and rare elements; this restricts the range of consumer applications of TE generators. Therefore, high performance TE materials composed of non-toxic and abundant elements need to be developed. Si[19–22] and metal silicides[23–27] could be good candidates of such advanced TE materials.

Recently, various metal silicide-based TE materials have been developed because of their low toxicity, high chemical stability, and low production costs. Among these, Mg2Si-based alloys are the most well-known TE materials with ZT values close to unity around 600–800 K.[23,24] Other popular metal silicides used as TE materials are β-FeSi2, Ru3Sn1, and higher manganese silicide (HMS) which also show good ZT values.[25–27] However, these materials show good TE properties at only medium (≥600 K for Mg2Si) or high (≥800 K or higher for β-FeSi2, Ru3Sn1, and HMS) temperatures. In other words, metal silicides with a maximum ZT near room temperature have not been developed so far.

On the contrary, certain Yb compounds have attracted interest for application in TE devices because they exhibit large S values accompanied by high σ values which lead to an exceptionally high power factor.[28–34] Yb compounds can exhibit two electron configurations: divalent Yb2+ (4f14) and trivalent Yb3+ (4f13).[15] In intermediate valence compounds, interaction between the 4f electrons and the conduction electrons can occur, resulting in a sharp feature of D(E) near the Fermi level, also referred as the Kondo resonance.[36–38] The well-known TE metallic compound...
YbAl13, which presents an unusually large S although it exhibits high σ like metals, shows the Kondo resonance.28,29 Such enhancement of S can be explained by the Mott formula shown below30:

\[
S = \frac{\pi^2}{3} \left( \frac{k_B^2 T}{q} \right) \left\{ \frac{d[\ln(\sigma(E))]}{dE} \right\}_{E=E_F}
\]

\[
S = \frac{\pi^2}{3} \left( \frac{k_B^2 T}{q} \right) \left\{ \frac{1}{n} \frac{d\ln(E)}{dE} + \frac{1}{\mu} \frac{d\mu(E)}{dE} \right\}_{E=E_F}
\]  

(1)

where \(k_B\) is the Boltzmann constant, \(q\) is the electronic charge, \(\sigma(E)\) is the differential conductivity, \(n(E)\) is the energy derivative of the carrier concentration, and \(\mu(E)\) is the carrier mobility. \(n(E)\) can be defined as

\[
n(E) = D(E)f(E)
\]  

(2)

where \(D(E)\) is the density of state and \(f(E)\) is the Fermi–Dirac distribution. Thus, Eq. (1) can be rewritten in terms of \(D(E)\) and \(f(E)\) as follows:

\[
S = \frac{\pi^2}{3} \left( \frac{k_B^2 T}{q} \right) \left\{ \frac{1}{n} \left( D(E) \frac{df(E)}{dE} + f(E) \frac{dD(E)}{dE} \right) + \frac{1}{\mu} \frac{d\mu(E)}{dE} \right\}_{E=E_F}
\]  

(3)

As shown in Eq. (3), S increases when the energy derivative of the density of state \(dD(E)/dE\) increases at the Fermi level. In other words, S can increase when the feature of \(D(E)\) near the Fermi level is sharp. This behavior has been predicted theoretically40,41 and observed experimentally in materials such as Bi nanowires42 and Ti-doped PbTe.12

The YbSi system has been reported to show intermediate valence fluctuation behavior.33 Yb in the Yb-Si system can exhibit two electron configurations: a non-magnetic \(\text{Yb}^{2+}\) ion with fully occupied \(4f^14\) and a magnetic \(\text{Yb}^{3+}\) ion \(4f^13\). Landelli et al.33 reported that \(\text{Yb}^{2+}\) is the major ionic component at low temperature, and the amount of \(\text{Yb}^{3+}\) increases with increasing temperature. In other words, \(\text{Yb}^{3+}\) ions act as magnetic impurities in the non-magnetic metal, at low temperatures.

Here, we focus on YbSi2, because Yb in YbSi2 exhibits temperature-dependent \(\text{Yb}^{2+/3+}\) fluctuations35 and the \(\sigma\) value is relatively high near room temperature.43,44 Moreover, YbSi2 has a specific layered crystal structure.15,45 In this article, we report on the synthesis, physical properties, and TE properties (near room temperature) of polycrystalline bulk samples of YbSi2.

Figure 1 presents the crystal structure of YbSi2. YbSi2 crystallizes in the hexagonal C32 structure (P6/mmm, No. 191), also referred as the AlB2-type structure. As shown, YbSi2 has a specific layered structure, in which hexagonal graphene-like sheets of Si are located between the Yb planes.15,45 The layered structure of YbSi2 would result in anisotropy of transport properties. For example, the anisotropy of SnSe which has a similar layered structure with that of YbSi2 has been deeply investigated by characterizing high quality single crystalline samples.18 However, since our samples are polycrystalline bulks, they do not show anisotropic transport properties but isotropic ones.

Figure 2 shows the powder XRD patterns of the YbSi2 samples. For all samples, it was confirmed that the peaks corresponding to YbSi246 were obtained as the major phase. The measured densities of the samples and the lattice parameters (\(a\) and \(c\) for the hexagonal system) of YbSi2 calculated from the observed XRD peaks are summarized in Table 1. The values of the relative density varied between 94 and 95% from sample to sample, while most of the samples exhibited slightly smaller \(a\) and \(c\) values than those of the literature values \((a = 0.3771\ \text{nm} \quad \text{and} \quad c = 0.4098\ \text{nm})\).45 Although all the samples exhibited the unavoidable impurity phases of Yb2O346 and Yb3Si5,46 nearly single-phase bulk samples of YbSi2 with a sufficiently high relative density were successfully obtained. The Yb2O3 and Yb3Si5 impurities would have various influences on the TE properties of the samples. Since Yb2O3 indicates very low \(\sigma\) in the range of \(10^{-7} \Omega^{-1}\ \text{m}^{-1}\) as well as the \(p\)-type characteristic,47 the existing of the Yb2O3 impurities would reduce both \(\sigma\) and the absolute \(S\) of the samples. On the other hand, there are no available data on the \(\kappa\) of Yb2O3, so that the effect of Yb2O3 on the \(\kappa\) of the samples is hard to evaluate. Furthermore, since there are no available data on the \(\sigma\), \(S\), and \(\kappa\) of YbSi2, effect of YbSi2 on these properties of the samples is hard to evaluate too.

Figure 3 shows the surface image of sample No. 1. Quantitative EDS analysis revealed that the average composition of the sample is 33 at.% Yb, 64 at.% Si, and 3 at.% O, i.e., the Yb/Si atomic ratio = 1:1.94. The average composition was determined by performing the quantitative EDS point analysis.
at least five times for each sample. The standard deviation of the average composition is \( \approx 2\% \). The resolution of our EDX detector is \( \approx 138 \text{ eV} \). In the present study, the arc melting chamber was evacuated to a pressure below \( 5 \times 10^{-3} \text{ MPa} \) and high-purity Ar gas (\( > 99.999\% \)) was filled at 0.04 MPa. A piece of zirconium was used to eliminate any remaining oxygen in the chamber. However, the powder XRD pattern of the arc-melted ingots indicated small peaks corresponding to Yb\(_2\)O\(_3\). Thus, we conclude that a small amount of oxygen possibly remained in the arc melting chamber. The SEM image shows that the sample surface is smooth with no remarkable cracks or pores. However, a few small particles are observed as indicated by arrows. The elemental mapping images for Yb and Si revealed that Si and Yb are distributed homogeneously. On the other hand, in the elemental mapping image for oxygen, an oxygen rich region was confirmed, corresponding to the small particles shown in the SEM image. From the results of both XRD and EDS analyses, the chemical composition of the small particles observed in the SEM image could be Yb\(_2\)O\(_3\).

The main objective of the present study is to investigate the TE and physical properties of YbSi\(_2\) around room temperature. However, to understand the mechanism of the transport
Table 1. The measured density \(d\), relative density % T.D., lattice parameters \((a\) and \(c)\), Hall carrier concentration \(n_H\), and Hall mobility \(\mu_H\) of the samples. All parameters were obtained at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(d) (g cm(^{-3}))</th>
<th>% T.D.</th>
<th>(a) (nm)</th>
<th>(c) (nm)</th>
<th>(n_H) (10(^{21}) cm(^{-3}))</th>
<th>(\mu_H) (cm(^2) V(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>7.15</td>
<td>94.8</td>
<td>0.3761</td>
<td>0.4091</td>
<td>3.65 ± 0.18</td>
<td>12.5 ± 0.6</td>
</tr>
<tr>
<td>No. 2</td>
<td>7.19</td>
<td>95.3</td>
<td>0.3764</td>
<td>0.4089</td>
<td>2.89 ± 0.14</td>
<td>17.1 ± 0.9</td>
</tr>
<tr>
<td>No. 3</td>
<td>7.18</td>
<td>95.2</td>
<td>0.3773</td>
<td>0.4096</td>
<td>4.44 ± 0.22</td>
<td>11.0 ± 0.6</td>
</tr>
<tr>
<td>No. 4</td>
<td>7.12</td>
<td>94.4</td>
<td>0.3768</td>
<td>0.4091</td>
<td>4.18 ± 0.22</td>
<td>11.7 ± 0.6</td>
</tr>
<tr>
<td>No. 5</td>
<td>7.14</td>
<td>94.7</td>
<td>0.3761</td>
<td>0.4092</td>
<td>6.54 ± 0.33</td>
<td>7.1 ± 0.4</td>
</tr>
</tbody>
</table>

properties, the temperature dependence of the TE properties was also investigated. Temperature dependences of \(S\), \(\sigma\), \(S\sigma\), \(\kappa\), \(\kappa_{\text{lat}}\), and \(ZT\) for each sample are shown in Figure 4(a)–(f), respectively. The TE properties of a Bi\(_2\)Te\(_3\)-based alloy, which is utilized in Peltier modules for TE refrigeration near room temperature, are shown for comparison.\(^{[16]}\) The \(S\) values of YbSi\(_2\) are negative in the entire temperature range, implying that electrons are the majority carriers. \(S\) and \(\sigma\) decreased linearly with increasing temperature. The trend in the \(\sigma\) values observed in the present study is in good agreement with the literature data.\(^{[43,44]}\) The average values of the absolute \(S\) and \(\sigma\) at room temperature are 53 \(\mu\)V K\(^{-1}\) and 7.5 \(\times\) 10\(^{5}\) \(\Omega\) m \(^{-1}\) \(\text{cm}^{-1}\), respectively, leading to the power factor \((S^2\sigma)\) value of 2.2 mW m\(^{-1}\) K\(^{-2}\). This value is comparable to those of Bi\(_2\)Te\(_3\)-based alloys. As summarized in Table 1, YbSi\(_2\) shows the Hall carrier concentration \((n_H)\) of the order of 10\(^{21}\) cm\(^{-3}\), while the average Hall mobility \((\mu_H)\) value for all the samples is around 12 cm\(^2\) V\(^{-1}\) s\(^{-1}\). Unlike most intermetallic compounds, YbSi\(_2\) exhibits uncommonly large absolute \(S\) values, even though the \(\sigma\) values are very high. According to Eq. (3), there are two possible reasons for the large \(S\) of YbSi\(_2\): one is the Kondo resonance described above and the other is the relatively small \(n_H\) compared to those of most metals.

As shown in Figure 4(d) and (e), with increasing temperature, \(\kappa\) of all YbSi\(_2\) samples increased, while \(\kappa_{\text{lat}}\) decreased slightly. At room temperature, the average values of \(\kappa\) and \(\kappa_{\text{lat}}\) for the YbSi\(_2\) samples are 8.6 and 3.0 W m\(^{-1}\) K\(^{-1}\), respectively. The temperature dependence of \(\kappa_{\text{lat}}\) does not follow the \(T^{-3}\) relationship, implying that scattering due to impurities occurs in addition to the Umklapp scattering. In the present case, both the oxide phase and non-stoichiometric defects are impurities, which could result in considerably decreased \(\kappa_{\text{lat}}\). Similar behavior has been observed in case of other materials such as SiGe alloys.\(^{[48]}\)

Note that, in this case, not only \(\kappa_{\text{lat}}\) but also \(\sigma\) is lowered by the impurities. The \(\kappa_{\text{lat}}\) values of YbSi\(_2\) are slightly higher than those of the Bi\(_2\)Te\(_3\)-based alloys. Moreover, the \(\kappa_{\text{lat}}\) values of YbSi\(_2\) are relatively low compared to those of Mg\(_2\)Si (\(\approx\) 6.0 W m\(^{-1}\) K\(^{-1}\) at room temperature\(^{[49]}\)). One possible reason for this low \(\kappa_{\text{lat}}\) is the high anharmonicity of YbSi\(_2\), which is related to the Grüneisen parameter \((\gamma)\).

From the results of the dilatometer measurements, the average value of the linear thermal expansion coefficient \((\alpha)\) of YbSi\(_2\) was evaluated to be 11.4 \(\times\) 10\(^{-6}\) K\(^{-1}\) in the temperature range of room temperature to 1073 K. For an isotropic medium, the bulk modulus \((B)\) and Debye temperature \((\theta_D)\) can be expressed in terms of the longitudinal \((V_L)\) and shear sound velocities \((V_S)\) as follows\(^{[50]}\):

\[
B = \left( \frac{V_L^2}{3} - \frac{4}{3} \frac{V_S^2}{3} \right) \rho 
\]

\[
\theta_D = \left( \frac{h}{k_B} \right) \left( \frac{3nN_A d}{4\pi M} \right)^{1/3} V_L
\]

where \(h\) is the Planck constant, \(k_B\) is the Boltzmann constant, \(n\) is the number of atoms per molecule, \(N_A\) is Avogadro’s number, \(M\) is

Figure 3. Surface image of sample No. 1: (a) SEM image and (b)–(d) EDS mapping images of Yb, Si, and O, respectively. The scale bars represent 10 \(\mu\)m. The arrows in (a) point at the oxidized particles.
is the molar weight, and $V_A$ is the average sound velocity expressed as follows:

$$V_A = \left( \frac{1}{V_S^3} \left( \frac{1}{V_L^3} \right) \right)^{-1/3}. \quad (6)$$

$B$ and $\theta_D$ values evaluated in the present study are summarized in Table 2. Further, the Grüneisen parameter ($\gamma$) can be expressed as follows:

$$\gamma = \frac{3\alpha_1 B v_m}{C_V} \quad (7)$$

where $v_m$ is the molar volume and $C_V$ is the heat capacity estimated as 74.83 J mol$^{-1}$ K$^{-1}$ using the Dulong–Petit model. As listed in Table 2, the $\gamma$ value of YbSi$_2$ was estimated to be 1.57, while that of Mg$_2$Si is 1.13.\textsuperscript{51,52} The high $\gamma$ value of YbSi$_2$ indicates the high anharmonicity of the material, which leads to
Table 2. Physical properties of YbSi2. Data are derived from the sound velocity and thermal expansion measurements performed on sample No. 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value (at temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear thermal expansion coefficient, $a_1$ (K$^{-1}$)</td>
<td>$11.4 \times 10^{-5}$ (300–1073 K)</td>
</tr>
<tr>
<td>Longitudinal sound velocity, $V_L$ (ms$^{-1}$)</td>
<td>5374 ± 269</td>
</tr>
<tr>
<td>Shear sound velocity, $V_S$ (ms$^{-1}$)</td>
<td>3228 ± 161</td>
</tr>
<tr>
<td>Average sound velocity, $V_A$ (ms$^{-1}$)</td>
<td>3570 ± 179</td>
</tr>
<tr>
<td>Bulk modulus, $B$ (GPa)</td>
<td>106 ± 11</td>
</tr>
<tr>
<td>Debye temperature, $\theta_D$ (K)</td>
<td>406 ± 20</td>
</tr>
<tr>
<td>Grüneisen parameter, $\gamma$</td>
<td>1.57 ± 0.16</td>
</tr>
</tbody>
</table>

In the present study, we measured the sound velocity and thermal expansion coefficient for sample No. 1. Therefore, the $\gamma$ value of 1.57 is not representative of pure YbSi2 but of the polycrystalline YbSi2 sample (No. 1) containing small amounts of impurities and pores.

In summary, polycrystalline samples of YbSi2 were prepared and their physical properties as well as TE properties were investigated. Around the room temperature, YbSi2 simultaneously exhibited large $\kappa$ and high $\sigma$, leading to a high power factor $S^2\sigma$ of 2.2 mW m$^{-1}$ K$^{-2}$, which is attributed to the temperature-dependent valence fluctuation of Yb. Furthermore, the $\kappa_{lat}$ values of YbSi2 are relatively low (3.0 W m$^{-1}$ K$^{-1}$ at room temperature), mainly due to the specific layered structure as well as the high anharmonicity confirmed by its high $\gamma$ of 1.57. As shown in Figure 4(f), a maximum $ZT$ value of 0.08 is obtained at room temperature. The present study reveals that YbSi2 can be a good TE material functioning in the low temperature region.

Experimental Section

Using high purity chunks of Si (11N) and Yb (99.9%, under spindle oil), YbSi2 ingots were prepared by arc melting under an Ar atmosphere. The resulting ingots were ground to fine powders, and then placed in a graphite die for spark plasma sintering (SPS). The SPS was performed at 1373 K for 3 min under an axial pressure of 100 MPa in an Ar atmosphere. The arc melting and SPS processes were carried out several times under the same conditions, using fresh starting materials each time. We randomly selected five bulk samples after SPS, denoted as Nos. 1–5. Before the phase and composition were determined at room temperature by powder X-ray diffraction (XRD; Ultima IV, Rigaku Co.) using Cu Ka radiation and scanning electron microscopy (SEM) performed on an electron microscope (SEM, JSM-6500F, JEOL) equipped with an energy dispersive spectrometer (EDS), $S$ and $\sigma$ were measured simultaneously in the range of room temperature to 525 K using a commercial apparatus (Ulvac ZEM-3) under a He atmosphere. $\sigma$ was measured by the four-point probe method, where the current was applied through electrodes attached to the top and bottom of the sample, and two thermocouples were used to measure the voltage between two points at the side of the sample (distance ≈0.6 mm). The Hall coefficient ($R_H$) was measured by the Van der Pauw technique with a Hall measurement system (Toyo Resitest8300) at room temperature in vacuum under an applied magnetic field of 0.5 T. $n_{14}$ and $\mu_{14}$ were calculated from $R_H$ assuming a single-band model and a Hall factor of 1; i.e., $n_{14} = 1/\varepsilon R_H$ and $\mu_{14} = \sigma R_H$, where $\varepsilon$ is the elementary electric charge. $\kappa$ was calculated using the relationship, $\kappa = a d C_P$, where $a$, $d$, and $C_P$ are the thermal diffusivity, density, and heat capacity of the material, respectively. $d$ was measured at temperatures ranging from room temperature to 525 K using a flash diffusivity apparatus (Netzsch LFA-457). A $C_P$ value of 326 J kg$^{-1}$ K$^{-1}$ was estimated from the Dulong–Petit model, $C_P = 3nR$, where $n$ and $R$ are the number of atoms per formula unit and the gas constant, respectively. For metals, it is known that the $C_P$ values estimated from the Dulong–Petit law deviate significantly at low temperatures. However, in the present study, it is suggested that the use of the Dulong–Petit law would be acceptable because most of the temperature range studied here is higher than the Debye temperature $\theta_D$ of YbSi2 (406 K). $d$ was calculated from the measured weight and dimensions, as presented in Table 1. $\kappa_{lat}$ was calculated by subtracting $\kappa_{el}$ from $\kappa$; $\kappa_{el}$ was estimated by the Wiedemann–Franz law using the relationship, $\kappa_{el} = LT\sigma(L$ is the Lorenz number: $2.44 \times 10^{-8}$ W K$^{-2}$). The TE property of each sample was measured repeatedly at each measurement temperature; approximately 10% deviation for $ZT$ was evaluated from 2, 3, and 3% deviations for $S$, $\sigma$, and $\kappa$, respectively. The thermal expansion was measured using a dilatometer in an Ar atmosphere and the linear thermal expansion coefficient in the temperature range of room temperature to 1073 K was evaluated. The longitudinal and shear sound velocities were measured by an ultrasonic pulse-echo method in air at room temperature, using 5 MHz sound wave echogenic transducers. From the sound velocities, the bulk modulus and Debye temperature were evaluated.

Acknowledgment

This work was supported in part by JST, PRESTO Grant Number JPMJPR15R1.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

electrical resistivity, Seebeck coefficient, thermal conductivity, thermoelectric materials, YbSi2

Received: October 26, 2017
Revised: November 27, 2017
Published online: December 12, 2017
