The low and high temperature thermoelectric properties of Yb$_3$Si$_5$

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Abstract

Silicides have been of great interest for thermoelectric applications due to their abundant elements as well as thermal and chemical stability. In this paper, we examined the thermoelectric properties of Yb$_3$Si$_5$ polycrystalline samples in a wide temperature range from 10 to 800 K. The temperature dependence of the Seebeck coefficient was successfully analyzed by assuming a narrow 4f quasi-particle band, indicating the intermediate valence state of Yb$^{2+}$, Yb$^{3+}$ is responsible for the high power factor. A very large maximum power factor of $\sim 4.70 \text{ mW m}^{-1}\text{K}^{-2}$ was observed at 72 K and room temperature value $\sim 1.56 \text{ mW m}^{-1}\text{K}^{-2}$ for Yb$_3$Si$_5$. These results show that Yb-Si compounds have large potential to be used as low temperature TE applications in the future. We also studied the Co-doping effect in Yb$_3$Si$_5$, namely, Yb$_3$Co$_x$Si$_{5-x}$ where $x = 0, 0.1, 0.15, 0.20$ and investigated their thermoelectric properties. While powder X-ray diffraction analysis confirmed all main peaks indexed to Yb$_3$Si$_5$ phase, SEM and EDX analyses revealed that Co is precipitated as metal particles, forming a composite material with Yb$_3$Si$_5$ phase. Thermoelectric properties of the Co-doped samples are also reported.

Introduction

Thermoelectric (TE) materials convert waste heat into electricity utilizing Seebeck effect [1, 2]. TE materials can play a major role in overcoming the challenges for sustainable future in energy [3–7]. TE energy conversion technology offers multiple advantages, i.e. Long term stability, less noise pollution, small size as well as no harmful gases being produced during operation, etc. [8–13]. Hence the demand for efficient TE materials is gaining more and more attention. Usually figure of merit (ZT) equation is used to gauge the efficiency of a TE material. $ZT = S^2T/\rho\kappa$, where $S$ is Seebeck coefficient, $\rho$ is electrical resistivity, $\kappa$ is thermal conductivity and $T$ is absolute temperature. From equation, to achieve high ZT, Seebeck coefficient values should be large while resistivity and thermal conductivity needs to be minimized simultaneously. Optimizing these parameters presents a major challenge as they are interrelated and enhancing one of these parameters affects the other negatively [14–17]. Well known thermoelectric materials used in TE devices are bismuth telluride Bi$_2$Te$_3$, Silicon germanium alloys SiGe, and lead telluride PbTe [8, 9, 14, 18, 19]. These materials possess good thermoelectric properties but are limited to be used in non-oxidizing environment and thermal stabilities are the concerns that still need to be resolved.

Silicides have been considered promising thermoelectric materials since many decades due to their high chemical and thermal stabilities [20, 21]. Use of abundant elements like Si, Mg can be cost effective and support economically viable TE devices. Hence many silicide materials were extensively studied i.e. CoSi$_2$, Ru$_3$Si$_5$, FeSi$_2$, MnSi$_3$, CrSi$_2$, Mg$_2$X based solid solutions (X = Ge, Si, Sn) etc. [22–31]. Notable silicide materials among these with high ZT values includes Mg$_5$Si$_{5.5}$Sn$_{0.5}$ with a maximum ZT of 1.39 at 663 K [32] Mn$_x$Si$_3$ (ZT $\sim 0.9$) [33].
behavior of Yb sintered samples. Seebeck and electrical resistivity were measured simultaneously using ULVAC ZEM-2 under microscope (Akishima, Tokyo, Japan). Furnace temperature was slowly raised to 973 K and kept for 4 days. Later samples were cooled rapidly to room temperature. Samples were then crushed with mortar in Ar atmosphere. Powder X-ray diffraction using Cu Kα radiation was performed at 1073 K for 9 min under an axial pressure of 50 MPa in an Ar atmosphere. These pellets were then cut and used for thermoelectric measurements. In this paper we synthesized Yb3Si5 polycrystalline samples by Spark Plasma sintering technique and carried out thermoelectric property measurements. Yb3Si5 exhibit high Seebeck values and resistivity values are quite low, leading to high power factor. A very large peak value of power factor (~ 2.2 mWm⁻¹K⁻¹) at room temperature [42]. These results motivated us to study thermoelectric properties of another phase of Yb-Si compound, Yb3Si5. Yb3Si5 crystalizes in hexagonal structure with space group P-62m No. 189. Schematic structure is shown in figure 1. Si occupies two sites Si2 and Si3 with two and three Si neighbors connected in similar to benzene ring. Seebeck coefficient of Yb3Si5 at low temperature was reported previously [38], while the property in the whole temperature range has not been studied so far.

In this paper we synthesized Yb3Si5 polycrystalline samples by Spark Plasma sintering technique and carried out thermoelectric property measurements. Yb3Si5 exhibit high Seebeck values and resistivity values are quite low, leading to high power factor. A very large peak value of power factor (~ 4.70 mWm⁻¹K⁻¹) observed at 72 K and at room temperature ~ 1.56 mWm⁻¹K⁻¹ for the non-doped sample. These results show that Yb-Si compounds have large potential to be used as low temperature TE applications. Temperature dependence of the Seebeck coefficient was well analyzed by a phenomenological Fermi-liquid model with a Lorentzian-type quasi particle band. This suggests that the Yb3Si5 behaves like a nonmagnetic metal with narrow 4f bands through hybridization between 4f and conduction electrons.

From our previous research, magnetic ion doping and/or inducing magnetic ordered states by doping can help to further increase the thermoelectric properties [43, 44]. We thus examined the possibility of magnetic ion doping to Yb3Si5 to add magnetic character to the system. We chose Co as a dopant, since some transition metals such as Cr, Fe and Co are known to be incorporated into YbSi2 with a related tetragonal structure [44]. We synthesized Yb3CoxSi5−x where x = 0, 0.1, 0.15, 0.20 by the same method, and characterized the structures and thermoelectric properties.

**Materials and methods**

Polycrystalline samples of Yb3CoxSi5−x where x = 0, 0.1, 0.15, 0.20 were prepared by direct reaction method followed by ball milling and spark plasma sintering (SPS). Yb (99.9 %) and Si (10 N) chunks were crushed and mixed with Co (99.9%) powder in boron nitride crucibles. Crucibles were then inserted in quartz tubes which were evacuated and small amount of Ar gas was inserted. Quartz tubes were then sealed and placed in furnace. Furnace temperature was slowly raised to 973 K and kept for 4 days. Later samples were cooled rapidly to room temperature. Samples were then crushed with mortar in Ar-filled glove box. All samples were ball milled for 1 h at 300 RPM under Ar atmosphere. Powder specimens were then pressed into pellets using SPS. The SPS was performed at 1073 K for 9 min under an axial pressure of 50 MPa in an Ar atmosphere. These pellets were then cut and used for thermoelectric measurements. Powder X-ray diffraction using Cu Kα radiation (Rigaku Co., Akishima, Tokyo, Japan) was used for phase analysis. Samples were further characterized by a Scanning electron microscope (JSM-7001F, JEOL Co.) and the energy dispersive spectroscopy (EDS) on polished surfaces of the sintered samples. Seebeck and electrical resistivity were measured simultaneously using ULVAC ZEM-2 under...
inert atmosphere in the range 323–823 K. TE measurements below room temperature were carried out using Quantum Design Physical Property Measurement System (PPMS). The experimental error in the measurement of resistivity, Seebeck coefficient and thermal conductivity are usually around 5% in each category \cite{45, 46}. The total error in the ZT measurement follows by the summation of the individual relative uncertainties is smaller than 20%.

Results and discussion

Figure 1 shows schematic structure of Yb$_3$Si$_5$ shown along c-axis. Figure 2 shows powder X-ray patterns for Yb$_3$Co$_x$Si$_{5-x}$ where $x = 0, 0.1, 0.15, 0.20$. All main diffraction peaks observed in X-ray patterns were matched with those of the Yb$_3$Si$_5$ structure. Symbols ◆ and ♦ represents peaks observed for Si and Yb respectively. ICSD Reference card (PDF # 01–070–5701) 2θ positions are shown in the bottom of the graph with bar symbol.

Figure 2. XRD patterns of Yb$_3$Co$_x$Si$_{5-x}$ where $x = 0, 0.1, 0.15, 0.20$. All main diffraction peaks observed in X-ray patterns were matched with those of the Yb$_3$Si$_5$ structure. Symbols ◆ and ♦ represents peaks observed for Si and Yb respectively. ICSD Reference card (PDF # 01–070–5701) 2θ positions are shown in the bottom of the graph with bar symbol.

In figure 3(a), back scattered electron (BSE) image obtained by a scanning electron microscope (SEM) for Yb$_3$Si$_5$ sintered sample is shown. Figures 3(b) and (c) display the elemental mapping image for Yb and Si, respectively. These results show that the sample has almost uniform distribution of Yb and Si over the scanned area, with a minor precipitation of Si. The averaged chemical composition of the surface by EDS analysis was 37.1 and 62.9 atomic % for Yb and Si, respectively. It is also found that the sample consists of large grains up to about 10 micro meters and small grains with submicron sizes. The existence of this small grain size is expected to be beneficial for lowering thermal conductivity.

In figure 4, the SEM results for Yb$_3$Si$_{5-x}$Co$_x$ with $x = 0.2$ are presented. The BSE image clearly shows that there are two chemically-different regions, and the elemental mapping images reveal that those are Yb$_3$Si$_5$-like and Co-like phases. The EDS analysis for the former phase indicates that the chemical composition is 38.5 and 61.5 atomic % for Yb and Si, respectively. Notably, Co was not detected by EDS in the main matrix phase. Instead, the Co-rich regions shown in figure 3(d) were turned out to be Co, Co$_2$Si, and CoSi. This indicates that Co is not incorporated in Yb$_3$Si$_5$ phase. Therefore, enhancement in the thermoelectric properties due to magnetic origin is not expected for Yb$_3$Si$_{5-x}$Co$_x$ samples. Nevertheless, improvement in thermoelectric properties may occur in such composite materials with small impurity phases through the reduced thermal conductivities \cite{50}. We thus measured the thermoelectric properties of the Co-doped samples and compared with those of the pristine sample.

Electrical transport properties for all nominal compositions are presented in figure 5. It is seen that values measured below room temperature are in good agreement with high temperature values. Figure 5(a) shows temperature dependence of electrical resistivity $\rho$ of Yb$_3$Co$_x$Si$_{5-x}$ where $x = 0, 0.1, 0.15, 0.20$. Electrical
resistivity increases with the increase of temperature for all samples. This indicates metallic type behavior. With increase in Co doping percentage \(x\), at first electrical resistivity showed slightly higher values of \(\rho\) for \(\text{Yb}_3\text{Co}_{0.1}\text{Si}_{4.9}\). However, with further increase in Co doping concentration \(\rho\) values decreased for \(\text{Yb}_3\text{Co}_{0.15}\text{Si}_{4.85}\). As seen in the plots there was no systematic change in resistivity observed and the difference in the magnitude was also very small.

Figure 5(b) shows plots of Seebeck coefficient verses temperature for \(\text{Yb}_3\text{Co}_x\text{Si}_{5-x}\), where \(x = 0, 0.1, 0.15, 0.20\). Seebeck coefficient values are negative for all samples. This shows n-type conduction. Below room temperature, Seebeck coefficient increases negatively up to 118 K. Highest absolute value of 66.5 \(\mu\)V/K was measured for pristine sample at 118 K. Absolute values of Seebeck coefficient starts to decrease with further increase in temperature. The behavior of the Seebeck coefficients is typical for Yb-based intermediate valent or Kondo-lattice compounds [38, 51, 52] Theoretical studies based on the Kondo theory roughly explain the temperature dependence of Seebeck coefficient, where the broad maximum occurs around the characteristic temperature for the Kondo effect [53, 54]. Variation in Co doping did not bring any significant change in the Seebeck coefficient values above 300 K. Below room temperature, Co doped samples showed slightly lower values of Seebeck coefficient as compared to pristine sample. Plots of power factor \((S^2/\rho)\) versus temperature calculated for \(\text{Yb}_3\text{Co}_x\text{Si}_{5-x}\), where \(x = 0, 0.1, 0.15, 0.20\) are presented in figure 5(c). Highest power factor of \(\sim 4.70\) mWm\(^{-1}\)K\(^{-2}\) was observed at 72 K. At room temperature, a still high value of \(\sim 1.56\) mWm\(^{-1}\)K\(^{-2}\) was recorded for the pristine sample. These power factors are relatively large, especially the peak value of \(\sim 4.70\) mWm\(^{-1}\)K\(^{-2}\) at low temperature, and can be considered to be a result of the relatively large Seebeck coefficient.

Figure 3. SEM back scattered electron (BSE) image of Yb\text{Si}_{5} (a), and the mapping image for Yb (b), and for Si (c).
Figure 4. SEM back scattered electron (BSE) image of Yb$_{3}$Si$_{4.8}$Co$_{0.2}$ (a), and the elemental mapping image for Yb (b), Si (c), and for Co (d).

Figure 5. Temperature dependent plots of (a) Electrical resistivity ($\rho$) (b) Seebeck coefficient (c) Power factor for Yb$_{3}$Co$_{x}$Si$_{5-x}$ where $x = 0, 0.1, 0.15, 0.20$. 
originating from the Yb valence fluctuation, as demonstrated above, despite the high electrical conductivity. Recently enhanced thermoelectric power factors have been demonstrated via paramagnon drag \[43, 50, 55, 56\] or spin fluctuating \[44\] and the utilization of such magnetic based effects for further enhancement remains an interesting research topic.

It should be noted that Yb$_3$Si$_5$ has been characterized in terms of intermediate valence systems between nonmagnetic Yb$^{2+}$ and magnetic Yb$^{3+}$ ions by the low temperature magnetic susceptibility and the electrical resistivity \[57\]. The large Seebeck coefficient in Yb$_3$Si$_5$ also is likely to be attributed to the intermediate valence behavior. The temperature dependence of Seebeck coefficient of Yb intermetallic compounds can also be described on the basis of simple phenomenological approach described in Hirst Model \[58\]. In this model it was assumed that conduction electrons are scattered by a 4f quasi particle band of a Lorentzian form. The modified form of Mott equation then takes the form \[59\]

\[
S(T) = \frac{AT}{T^2 + B^2}
\]  

Where

\[
A = \frac{2\Delta}{|\epsilon|}
\]

And

\[
B^2 = \frac{3\Delta^2 + \Gamma^2}{\pi^2k_B^2}
\]

The parameter $\Delta = \epsilon_0 - \epsilon_f$ represents measure of the position of the DOS peak in respect of the Fermi level and $\Gamma$ is the width of the 4f band. In figure 6 fits of the Experimental data with the modified Mott’s equation is presented (solid red line indicates theoretical values based on equation (1)). The experimental data for Yb$_3$Si$_5$
and model based calculations give satisfactory resemblance as seen in figure 6. Slight deviation from experimental values might be attributed to the presence of additional scattering mechanisms. Values of parameters $A$, $B^2$ and $\Delta$ obtained from fitting are $-0.1795 \times 10^{-5} \text{mV}$, $0.1619 \times 10^{-5} \text{K}^2$ and $-8.9 \text{meV}$ respectively. These fitted values give the 4f band width of $\Gamma = 17.8 \text{meV}$. This energy corresponds to the temperature scale $\Gamma/k_B = 207 \text{K}$, which is comparable to the characteristic temperature of $T_{sf} = 177 \text{K}$, obtained by the fitting of magnetic susceptibility of Yb$_3$Si$_5$ based on the intermediate valence model [57]. This agreement suggests that a narrow 4f band is formed through the valence fluctuation of Yb$^{2+}$ and Yb$^{3+}$, and is the origin of the large Seebeck coefficient and the high power factor in Yb$_3$Si$_5$. In addition, these values are of the order of similar magnitude as reported for such intermediate valence compounds [59, 60].

Figure 7. Temperature dependent Plots of (a) Total Thermal conductivity (b) Electronic Thermal conductivity (c) Lattice Thermal conductivity for Yb$_3$Co$_{x}$Si$_{5-x}$ where $x = 0, 0.1, 0.15, 0.20$. 
Plots of total thermal conductivity as function of temperature $\kappa_{\text{tot}}(T)$ for all nominal samples are presented in figure 7(a). It is seen that thermal conductivity increased with the increase of temperature for all samples. Contribution to total thermal conductivity can be separated by the relation $\kappa_{\text{tot}} = \kappa_e + \kappa_{\text{Latt}}$. Where $\kappa_e$ is electronic contribution and $\kappa_{\text{Latt}}$ is contribution from lattice vibrations. $\kappa_e$ can be calculated using Wiedemann Franz Law $\kappa_e = L T / \rho$, where $L$ is the Lorenz number, and we used the value for degenerate limit (2.44E-08) to estimate the $\kappa_e$ [61]. Figures 7(b) and (c) shows plots of electronic and lattice contribution to total thermal conductivity respectively. Clearly the major portion of total thermal conductivity is that of electronic thermal conductivity. Electronic thermal conductivity increases with the increase in temperature as expected for degenerate semiconductors. Figure 7(b) also shows a non-monotonic increase in the electronic thermal conductivity with respect to doping level especially at higher temperatures but this is probably within the error limit.

Figure 8 shows figure of merit ($ZT$) with respect to temperature for Yb$_3$Co$_x$Si$_{5-x}$ where $x = 0, 0.1, 0.15, 0.20$. Maximum value of 0.10 was observed for non-doped sample at 132 K. At room temperature $ZT$ value of 0.07 was measured for the pristine sample. It is seen that $ZT$ value was not improved with Co doping. Although $ZT$ value is small for an ideal thermoelectric material, it can be improved by reducing thermal conductivity. Optimizing charge carriers’ concentration is also needed to further enhance the $ZT$ value, because of the large contribution of electronic thermal conductivity. In spite of that, our results show Yb$_3$Si$_5$ has large potential for TE applications especially at low temperature due to its large power factor, 4.70 mWm$^{-1}$K$^{-2}$. This was probably originated to the strong correlation between carriers and valence-fluctuating Yb ions. Further study for the origin of the high power factor in Yb$_3$Si$_5$ will give us a hint to provide highly efficient TE materials.

Summary

In summary we synthesized Yb$_3$Co$_x$Si$_{5-x}$, where $x = 0, 0.1, 0.15, 0.20$ by solid state reaction followed by SPS method. We measured thermoelectric properties for all nominal samples. Electrical resistivity, Seebeck and power factor were measured for the low and high temperature (10–815 K). Thermal conductivity and $ZT$ values were measured up to 325 K. Although the $ZT$ value is considerably low at present due to high thermal conductivity, Yb$_3$Si$_5$ exhibited high Seebeck coefficient with considerably low electrical resistivity thereby power factor is high. We found that highest power factor of $\sim 4.70$ mWm$^{-1}$K$^{-2}$ observed at 72 K and at room temperature $\sim 1.56$ mWm$^{-1}$K$^{-2}$ for pristine sample. $ZT$ peak value of 0.10 was observed for non-doped sample at 132 K. At room temperature $ZT$ value of 0.07 was measured for the pristine sample. These results show the merit of utilizing valence fluctuating ions to enhance power factor. If the carrier concentration can be reduced by appropriate doping, Yb$_3$Si$_5$ has a large potential for a highly efficient TE material at low temperature.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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