Solubility study of Yb in n-type skutterudites Yb_xCo_4Sb_12 and their enhanced thermoelectric properties


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The solubility of Yb in Yb_xCo_4Sb_12 was reported to be 0.19 in bulk skutterudites made by melting and slow cooling method. Surprisingly we increased x close to 0.5 by a special sample preparation method: ball mill and hot press. We show that a higher Yb concentration not only increases the power factor due to a higher electron concentration but also reduces the thermal conductivity k because of stronger phonon scattering. In this way, we have achieved a dimensionless thermoelectric figure of merit ZT of about 1.2 at 550 °C in Yb_0.35Co_4Sb_12.

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I. INTRODUCTION

Co_4Sb_12-based skutterudites have been widely studied for their promising thermoelectric properties1–3 and are regarded as potential candidates for next-generation thermoelectric materials for electrical power generation using either a solar source or waste heat. One of the remarkable features of this material is that the cage-like open structure can be filled with foreign atoms acting as phonon rattlers. The “rattling” of the filled atoms scatters phonons strongly and drastically reduces the thermal conductivity of the skutterudite compounds.1–3 Various kinds of atoms [Ce, La, Ca, Ba, and Yb (Refs. 8–10)] have been used to fill the cages, thereby resulting in an improved dimensionless thermoelectric figure of merit (ZT). Yb is one of the ideal filler or rattler species. Nolas et al. reported Yb-filled n-type Yb_0.19Co_4Sb_12 with a peak ZT close to 1 at 373 °C,8 and Geng et al. reported Yb_0.15Co_4Sb_12 with ZT of about 0.7 at 400 °C.9 In the literature for bulk samples, the Yb concentration was limited to 0.19, the so-called bulk solubility, in samples prepared by melting and slow cooling.3 However, there is one void per each Co_4Sb_12 formula. So it should be possible to have Yb more than 0.19. Whether a higher Yb concentration can be achieved to further reduce the thermal conductivity is scientifically interesting and technologically important. Recently, a bulk solubility of 0.29 was reported in samples made by melting and fast spin cooling with higher ZT,10 demonstrating that the bulk solubility issue is not settled in Yb-filled skutterudites and clearly depends on the sample preparation method. Therefore, there is an opportunity to increase Yb into the cage if a suitable sample preparation method could be found. In this paper, we report our success on increasing the bulk solubility close to 0.5 and the good thermoelectric properties obtained by making bulk n-type skutterudites with small grains using a ball milling and direct-current-induced hot press (dc hot press) process11–15 where we chose x=0.3, 0.35, 0.4, 0.5, and 1.0 in Yb_xCo_4Sb_12 to optimize the Yb concentration for maximizing the ZT value. We found that with our process we could increase x up to 0.5 without formation of impurity phases, much higher than the literature bulk solubility value.8,16 However, when x reaches 1, there is clearly a second phase identified by x-ray diffraction (XRD), which reduces the thermoelectric performance.

II. EXPERIMENT

Pure elements of Co (99.8%, Alfa Aesar), Sb (99.999%, Chengdu Chemphys Chemical Industry, China), and Yb (99.9%, Alfa Aesar) were mixed according to the stoichiometry Yb_xCo_4Sb_12 and loaded into a stainless steel jar with stainless steel balls and the material was then ball milled. This process is much simpler than the traditional melting and slow crystal growth plus ball milling and hot press3,8–10. The as-milled nanopowder was pressed into pellets by the dc hot press method in a graphite die. After cooling down to room temperature, each dc hot pressed pellet was ejected out of the graphite die and was cut into disks and bars and polished for thermoelectric property characterization.

X-ray diffraction (D8, Bruker) analysis with a wavelength of 0.154 nm was performed on both the ball milled powder and the pressed pellets to determine the constituent phases. The freshly fractured surface of the Yb_xCo_4Sb_12 bulk samples was investigated by scanning electron microscope (SEM) (JEOL 6340F) to determine the grain size. A cross-sectional sample was prepared to check the grain size and the crystallinity using a high-resolution transmission electron microscope (TEM) (JEOL 2010). The four-probe electrical conductivity (σ) and the Seebeck coefficient (S) were measured in a commercial system (ZEM-3, ULVAC-RIKO). The thermal conductivity (k) was measured using a laser flash system (LFA 457, Netzsch).

III. RESULTS AND DISCUSSION

XRD spectra of the ball milled nanopowders (not shown in the paper) indicated that the majority of the powders were not alloyed after ball milling. After the dc hot press, however, the powder was completely transformed into a single

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skutterudite phase for \( x \) up to 0.5. When \( x = 1 \), an unknown second phase showed up. XRD spectra for all the hot pressed samples of Yb\(_x\)Co\(_4\)Sb\(_{12}\) \((x = 0.3, 0.35, 0.4, 0.5, \) and 1.0\) are shown in Fig. 1. The unknown second phase in the case of \( x = 1 \) is clearly marked.

It is worth pointing out that we started with a composition for \( x = 0.2 \) following the literature, but could only rarely obtain unbroken samples after ejection from the graphite die. Those unbroken \( x = 0.2 \) samples also showed much inferior properties to the ones with \( x \geq 0.3 \). Here, we show thermoelectric property results on all the compositions with \( x > 0.2 \).

Figure 2 shows the SEM images at low [Fig. 2(a)] and high [Fig. 2(b)] magnification of the dc hot pressed skutterudite Yb\(_{0.35}\)Co\(_4\)Sb\(_{12}\) samples that demonstrated the highest ZT among all the compositions studied. The average grain size is about 200–500 nm. There are some big grains as large as about 1 \( \mu m \), which is probably due to the grain growth from the alloyed portion of the powders during the hot press process. The grain growth from less than 50 to 200–500 nm is significant. With such large grain sizes, we do not expect a strong phonon scattering due to fewer interfaces. The clear facets show that the grains are well crystallized. The SEM image also shows that the crystallized grains are closely packed, implying a high volume mass density, consistent with the Archimedean volumetric mass density measurement of around 7.6 g cm\(^{-3}\), which is close to the full theoretical density.

Table I shows the compositions studied and their properties at about 25 °C. Those marked with an asterisk are from Nolas et al. The lattice thermal conductivity is derived by extracting the electronic thermal conductivity \( k_e \) from \( k \). Here, \( k_e \) was computed by the Weidemann-Franz law \( k_e = L_\sigma T \), where \( \sigma \) is the electrical conductivity, \( T \) is the absolute temperature, and the Lorenz number is estimated to be \( 1.8 \times 10^{-8} \) V\(^2\) K\(^{-2}\) for all samples, with uncertainties from factors including the
The temperature-dependent thermoelectric properties of YbCo4Sb12 are plotted in Fig. 4. In order not to decrease the readability of the multiple curves in Fig. 4, we intentionally did not show the measurement error bars of each property. For our measurement set up, we have a less than 5% error on the electrical conductivity, 7% on the Seebeck coefficient, and 5% on the thermal conductivity. Figure 4(a) shows that the electrical conductivity \( \sigma \) of all samples decreases with an increase in temperature \( T \). Also \( \sigma \) increases with increased Yb content. The negative Seebeck coefficients [Fig. 4(b)] indicate that electrons are the dominant carriers. Samples with different Yb content show a similar \( T \) dependence trend for the Seebeck coefficient from room temperature to 550 °C, with the maximum Seebeck coefficient occurring at 550 °C [Fig. 4(b)]. The absolute value of the Seebeck coefficient decreases with increasing \( x \) at the same temperature, consistent with the electrical conductivity increase with increasing \( x \). This behavior may be due to the increase in the electron concentration.

The thermal conductivity of the samples is shown in Fig. 4(c). For the samples with \( x = 0.3 \) and 0.35, the thermal conductivity values decrease with increasing \( T \) and reach a minimum at 200 °C and then \( k \) increases rapidly with increasing \( T \) due to bipolar effect. For the samples with \( x = 0.4 \) and 0.5, the thermal conductivity keeps rising all the way from room temperature to 550 °C, which can be attributed to the significant increase in \( k_e \) at elevated temperatures. Although higher Yb concentrations increase the electron contribution to the total thermal conductivity, it can significantly decrease the lattice contribution by either the mass fluctuation effect or the rattling effect, so that the total thermal conductivity is much lower than that of the samples without Yb. At the moment, we do not know whether the mass fluctuation effect or the rattling effect is dominant in our samples. However, we do know that the lattice thermal conductivity in the case of YbCo4Sb12 is indeed higher than that of Yb0.35Co4Sb12, which means that the mass fluctuation is a significant factor in YbCo4Sb12 system. Therefore, Yb0.35Co4Sb12 has an optimized lowest thermal conductivity with a minimum of 2.7 W m\(^{-1}\) K\(^{-1}\), which leads to the highest observed ZT value among all the samples studied in this work.

Figure 4(d) shows the temperature-dependent ZT from room temperature to 550 °C. ZT increases with temperature and reaches a maximum at around 550 °C. The highest ZT is observed for the Yb0.35Co4Sb12 sample with its maximum value of about 1.2 occurring at 550 °C. This is a high ZT value and comparable to those reported for \( n \)-type filled skutterudites made by first ingot formation followed by grinding and hot pressing.

From the commercialization point of view, the combination of ball milling and dc hot pressing probably offers some advantages over the current methods. Therefore, the commercialization of YbCo4Sb12 is indeed higher than that of Yb0.35Co4Sb12, which means that the mass fluctuation is a significant factor in YbCo4Sb12 system. Therefore, Yb0.35Co4Sb12 has an optimized lowest thermal conductivity with a minimum of 2.7 W m\(^{-1}\) K\(^{-1}\), which leads to the highest observed ZT value among all the samples studied in this work.
advantages in the sense that large quantities of powders could be ball milled and large quantities of bulk samples could be pressed in a short time. From the research point of view of studying other rattlers, the combination of ball milling and dc hot press is better in the sense that it is very fast to switch from one rattler to another and from one composition to another, since the traditional procedure of melting and slow crystal growth takes a lot of effort and a long time.

Further investigation is needed into decreasing the thermal conductivity by preserving the grain size of the original powders, which is smaller than 50 nm. We note that the grain size of 200–500 nm is relatively large, which is why the thermal conductivity is still high. If the grain size can be reduced to 10–50 nm, then phonon scattering will be much stronger by the increased interfaces so a much lower thermal conductivity can probably be expected. With a much lower thermal conductivity, a much higher ZT should be achievable in this system.

IV. CONCLUSION

In summary, we have discovered that the bulk solubility of Yb in Yb$_x$Co$_4$Sb$_{12}$ depends on sample preparation method. A ball milling and dc hot press process could increase $x$ beyond 0.3 and close to 0.5 in bulk samples of $n$-type skutterudite Yb$_x$Co$_4$Sb$_{12}$. The increased Yb concentration in our samples not only enhanced the power factor due to a better electron doping effect but also decreased the thermal conductivity due to a stronger rattling effect. In addition, the increased grain boundary density per unit volume due to the small grains in our bulk skutterudite materials may have also helped to enhance the phonon scattering and thus to reduce the thermal conductivity in some extent, but the grain size is not yet small enough to get a much lower thermal conductivity. The composition Yb$_{0.35}$Co$_4$Sb$_{12}$ was found to be optimal for achieving a peak ZT value of about 1.2 at 550 °C even though single skutterudite phase was obtained for $x \approx 0.5$.

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