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# Rapid preparation method of bulk nanostructured $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$ compounds and their improved thermoelectric performance

Han Li,<sup>1</sup> Xinfeng Tang,<sup>1,a)</sup> Qingjie Zhang,<sup>1</sup> and Ctirad Uher<sup>2</sup>

<sup>1</sup>State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, People's Republic of China

<sup>2</sup>Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, USA

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A synthetic route was introduced to speed up the preparation of high performance nanostructured  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  ( $y=0.3$  and  $0.6$ ) compounds. Compared with the samples prepared by a traditional method, the processing time is reduced from the typical 10 days to less than 40 h, the Yb filling fraction limit increases, and the resulting thermoelectric transport properties are improved significantly. As a consequence, the dimensionless figure of merit of our bulk nanostructured  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.3}$  reaches 1.3 at 800 K. The enhanced thermoelectric performance coupled with the dramatically reduced processing time will be of considerable significance to the commercial-scale production of skutterudite-based thermoelectric materials. © 2008 American Institute of Physics. [DOI: 10.1063/1.3054158]

Recently, filled skutterudite compounds have attracted notable attention as prospective novel thermoelectric materials for intermediate temperature power generation applications.<sup>1</sup> An important aspect of the skutterudite structure are two icosahedron-shaped voids in the unit cell that can be filled with foreign species such as rare-earth or alkaline-earth ions.<sup>2–4</sup> Slack<sup>5</sup> postulated that such filled skutterudites may be candidate materials for his “phonon glass-electron crystal” paradigm; i.e., they might possess very low glasslike thermal conductivity while preserving good crystalline character in their electronic transport behavior. Subsequent experimental studies, particularly those related to thermal transport, have proven the point.<sup>6–13</sup> Significantly lower thermal conductivity of filled skutterudites is often explained<sup>14,15</sup> in terms of “rattling” of the filler ions in the oversized voids and their ability to resonantly scatter the normal phonon modes responsible for heat transport.

Ytterbium is one of the fillers that drew particular attention. Its intermittent valence<sup>16</sup> ( $\text{Yb}^{2+}$  or  $\text{Yb}^{3+}$ ) provides for a higher fractional occupancy (about 0.2) than is possible with an ordinary 3+ rare earth, and its smaller ionic size is responsible for large amplitude displacements in the cage. Used either as a single filler<sup>17–21</sup> or in combination with other rare-earth or alkaline-earth ions,<sup>22</sup> Yb-filled skutterudites have achieved some of the highest figures of merit.

The skutterudite structure—the  $\epsilon$ -phase  $\text{CoSb}_3$  in the case of cobalt antimonides—is obtained in a peritectic reaction at 873 °C from the  $\delta$ -phase ( $\text{CoSb}_2$ ) and the liquid phase.<sup>23,24</sup> Because of very slow kinetics, the peritectic reaction is rarely completed, and long annealing times are required to achieve the  $\text{CoSb}_3$  phase. To ensure full densification, the ingots are crushed and hot pressed with further annealing below the peritectic temperature. The process is time and energy consuming and typically takes 1 week to 10 days to prepare a fully densified single-phase skutterudite structure.<sup>7,17,20,22</sup>

In this paper we make use of a synthetic route to obtain single-phase, fully densified filled skutterudites that dramati-

cally shortens the processing time. The technique relies on a combination of melt quenching with melt spinning and spark plasma sintering (MMS) and cuts the preparation time to less than 2 days. Moderately excess Sb doping is considered an effective way to adjust the electrical properties for  $n$ -type skutterudites.<sup>25–27</sup> Moreover, the highly nonequilibrium nature of the synthesis process allows for a higher filling fraction of Yb than is otherwise possible via the traditional synthesis routes. The outcome is an efficient synthesis process that yields high quality samples with outstanding thermoelectric properties.

Starting materials are high purity Yb (99.98% ingot), Co (99.99% shot), and Sb (99.9999% shot) that are weighed to achieve  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  (with a slight excess of Sb,  $y=0.3$  and  $0.6$ ) and loaded into a carbon-coated silica tube. The tube was sealed under a pressure of  $10^{-3}$  Pa, heated to 1373 K, kept at this temperature for 20 h, and then quenched in a supersaturated salt water solution. The obtained ingots were melt spun to get the supercooled ribbon-shaped samples.<sup>21</sup> The ribbons were collected and loaded into a graphite die and sintered by spark plasma sintering (SPS) method. The sintering temperature and time were 823 K and 5 min, respectively. The resulting single-phase bulk nanostructured  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  with a nearly 100% theoretical density took less than 40 h to prepare.

The samples were examined by powder x-ray diffraction (XRD) (PANalytical: X'Pert PRO,  $\text{Cu K}\alpha$ ), and the actual composition of all samples was determined by electron probe microanalysis (EPMA). Densities of the samples were measured using the Archimedes method. The fine microstructure of the bulk materials was studied using field emission scanning electron microscopy (FESEM) (Sirion 200 FESEM). The electric conductivity ( $\sigma$ ) and Seebeck coefficient ( $\alpha$ ) were measured simultaneously by the standard four-probe method (Sinkuriko: ZEM-1) in Ar atmosphere. The thermal conductivity ( $\kappa$ ) was calculated from the measured thermal diffusivity  $D$ , specific heat  $C_p$ , and density  $d$  according to the relationship  $\kappa=DC_p d$ . Thermal diffusivity and specific heat were determined using a laser flash method (NETZSCH: LFA 457) and a power-compensation differential scanning calorimeter (TA: DSC Q20) in a vacuum, re-

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: tangxf@whut.edu.cn.

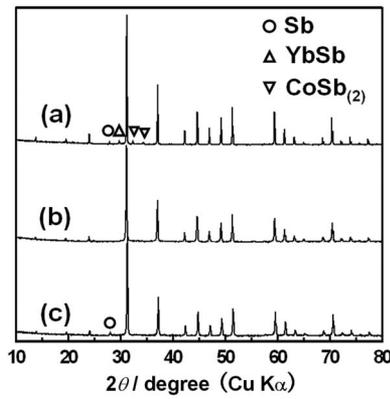


FIG. 1. XRD patterns of bulk  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$ : (a)  $y=0$ , the sample prepared by the traditional method of synthesis; (b)  $y=0.3$ ; (c)  $y=0.6$ .

spectively. All measurements were performed in the temperature range from 300 to 800 K.

Figure 1 shows the XRD patterns of all bulk  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  samples after SPS. The XRD pattern of a sample with no Sb excess that was prepared by the traditional method (sample  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}$ ) is shown in Fig. 1(a). Although this sample went through a 168 h annealing process, a small quantity of YbSb and  $\text{CoSb}_2$  impurities was detected. This is due to the Yb filling fraction of 0.3 that exceeds the theoretically and experimentally estimated<sup>28</sup> critical filling fraction of 0.2 in this near-equilibrium prepared sample. Figures 1(b) and 1(c) show the XRD patterns of bulk  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.3}$  and  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.6}$  samples synthesized by the MMS method in this research. There are no traces of YbSb and  $\text{CoSb}_2$  impurities detected by XRD in these samples. However, a small amount of pure Sb is observed in the XRD pattern of the  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.6}$  sample. The EPMA analysis shows that the actual compositions of the  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.3}$  and  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.6}$  samples are  $\text{Yb}_{0.285}\text{Co}_4\text{Sb}_{12.268}$  and  $\text{Yb}_{0.289}\text{Co}_4\text{Sb}_{12.583}$ , respectively; i.e., the Yb content indeed exceeds the theoretical and experimental filling fraction limit of 0.2. The vital difference between the MMS and the traditional preparation methods is that the material prior to SPS are supercooled ribbons made by melt spinning (a highly nonequilibrium synthesis with the cooling rate on the order of  $10^5$  K/s) rather than skutterudite powders prepared by long time annealing. The ribbons contain a large fraction of nanocrystalline and amorphous phases, and the rapid formation of the skutterudite structure is likely due to this fine and homogeneously distributed nanostructure. The reason why there is a 50% enhancement in the critical filling fraction of Yb awaits further detailed structural studies.

FESEM photographs of the bulk  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  samples after SPS are shown in Fig. 2. Samples prepared by MMS

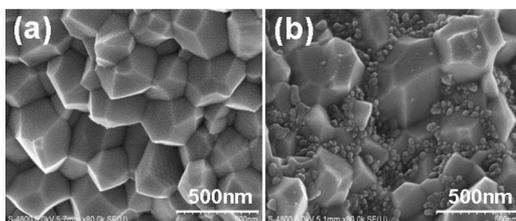


FIG. 2. FESEM photographs of bulk nanostructured  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  after SPS: (a)  $y=0.3$ ; (b)  $y=0.6$ .

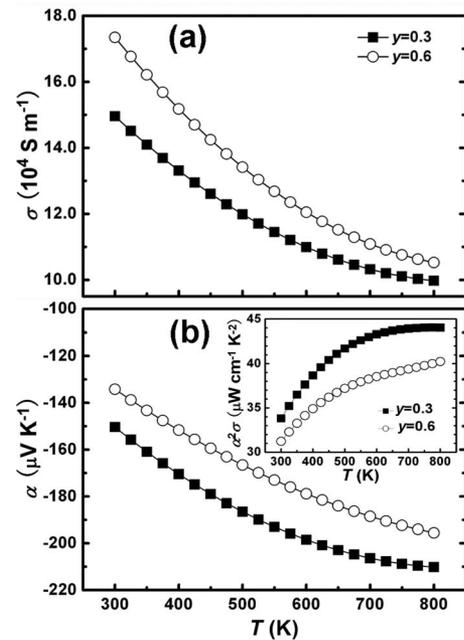


FIG. 3. Temperature dependence of (a) electrical conductivity and (b) Seebeck coefficient for  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$ .

show very high density approaching the theoretical 100%. As seen in Figs. 2(a) and 2(b), the grain size of the samples varies between 250 and 300 nm. The sample with  $y=0.3$  possesses evenly distributed grain sizes and clear and sharp grain boundaries. However, when  $y=0.6$ , the excess of Sb is too large, and antimony segregates in the form of nanoparticles ( $\sim 30$  nm) at the grain boundaries, as confirmed by energy dispersive x-ray analysis.

The temperature dependence of electrical conductivity, Seebeck coefficient, and power factor for  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  compounds are shown in Figs. 3(a) and 3(b), respectively. Both  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  compounds show a metallic conduction behavior, and  $\sigma$  increases with the increasing excess of Sb. The absolute value of the Seebeck coefficient  $\alpha$  increases with the increasing temperature and decreases with the increasing excess of Sb. Compared with other literature values of the Seebeck coefficient for high Yb filling fraction samples,<sup>17–19</sup> because of the presence of a nanostructure,  $\alpha$  values in this research are higher,<sup>29</sup> and another cause is that the carrier concentrations of our  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.3}$  and  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.6}$  are  $7.159 \times 10^{20}$  and  $7.971 \times 10^{20} \text{ cm}^{-3}$ , respectively, which are, for example, lower than the carrier concentration of  $8.4 \times 10^{20} \text{ cm}^{-3}$  for the  $\text{Yb}_{0.25}\text{Co}_4\text{Sb}_{12.69}/\text{Yb}_2\text{O}_3$  composite material.<sup>19</sup> Overall, electrical transport properties are markedly improved by the higher Yb filling fraction and nanostructural features in the bulk matrix.

Figure 4(a) displays the temperature dependence of the thermal conductivity and the lattice thermal conductivity of  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  compounds. Compared with  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12}$  prepared by the traditional method,<sup>7,25</sup>  $\kappa$  of the nanostructured  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  samples is decreased remarkably. Taking as an example  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.3}$ , the thermal conductivity is reduced by 30% at room temperature and by 22% at 800 K. These values of thermal conductivity obtained on our bulk nanostructured  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  samples are comparable with those measured on double-filled  $\text{Ba}_{0.08}\text{Yb}_{0.09}\text{Co}_4\text{Sb}_{12}$ ,<sup>22</sup> which suggests that even lower thermal conductivity might

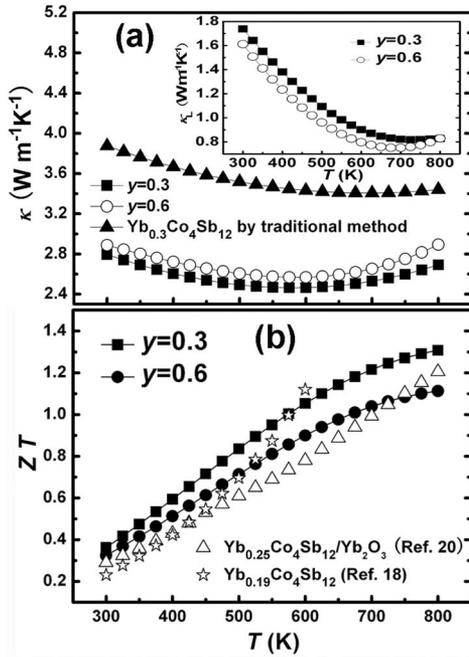


FIG. 4. Temperature dependences of (a) thermal conductivity and (b)  $ZT$  for  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  and some representative Yb single-filled skutterudites from the literature.

be achieved by preparing nanostructured double-filled skutterudite compounds. Moreover, the overstoichiometric amount of Sb does not seem to increase thermal conductivity significantly. Using the Wiedemann–Franz law and taking the Lorenz number at its Sommerfeld value of  $2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$ , we subtract the electronic thermal conductivity from the total thermal conductivity, and the resulting lattice thermal conductivity is plotted in the inset in Fig. 4(a). It should be noted that the sample with  $y=0.6$  possesses lower lattice thermal conductivity compared with the  $y=0.3$  sample. We attribute this to the enhanced scattering of phonons on the nanometer-scale precipitates of Sb at the grain boundaries of the sample with  $y=0.6$  [see Fig. 1(b)]. The value of  $\kappa_L$  is comparable to that of the  $\text{Yb}_{0.25}\text{Co}_4\text{Sb}_{12}/\text{Yb}_2\text{O}_3$  composite material.<sup>19</sup>

The dimensionless thermoelectric figure of merit  $ZT$  of our  $n$ -type  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  is calculated based on the above transport data and is presented in Fig. 4(b) together with other representative values of  $ZT$  for Yb single-filled skutterudites. As evident from Fig. 4(b), the bulk nanostructured  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12+y}$  ( $y=0.3$  and  $0.6$ ) prepared by the MMS method show higher  $ZT$  values, and  $(ZT)_{\text{max}}$  reaches values of at least 1.3 at 800 K for the  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.3}$  compound. It is worth mentioning that the  $ZT$  of  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.3}$  exceeds the value of unity already at 570 K and keeps rising with the increasing temperature. For comparison, so far the best  $n$ -type skutterudite—the double-filled  $\text{Ba}_{0.08}\text{Yb}_{0.09}\text{Co}_4\text{Sb}_{12}$  compound<sup>22</sup>—exceeds the value of unity at 600 K. Thus, the bulk nanostructured  $\text{Yb}_{0.3}\text{Co}_4\text{Sb}_{12.3}$  material seems to show high performance over a marginally wider temperature range in spite of being merely single filled.

In summary, a rapid processing method that combines melt quenching with melt spinning and SPS cuts the synthesis time of high performance filled skutterudites to less than 2 days and yet yields superior quality bulk nanostructured materials. The highly nonequilibrium nature of the synthesis process provides an additional benefit by significantly en-

hancing the critical filling fraction that is beneficial to the thermoelectric properties. Much reduced lattice thermal conductivity due to a significantly smaller grain size structure contributes to the high figure of merit of the compounds that reach values of  $ZT=1.3$  at 800 K. This processing route holds great promise for commercial-scale production of skutterudite-based thermoelectric materials. Applied to multiple-filled skutterudites and using even faster cooling rates to reduce the grain size to a few tens of nanometers, the technique should yield record-high performance filled skutterudites with considerable savings in time and energy.

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