Andrea Amaldi · Francois Tang Editors

Proceedings of the 11th European Conference on Thermoelectrics



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Preface

The growing energy demands and the urgent necessity to curb greenhouse gas emissions have promoted the advancements of a broad range of possible solutions meant to mitigate the impact of our society on our environment. Among the different approaches to limit our footprint, thermoelectric materials have been positioned as a prime candidate to recover energy from heat that would otherwise deemed wasted. The physics of thermoelectricity alone, namely the Seebeck effect, is unambiguously appealing. However, the engineering and commercial realities have been a major obstacle to the wider acceptance of thermoelectrics in practical applications. *Economically* viable generators have so far evaded the thermoelectric community.

The 11th European Conference on Thermoelectrics provided an international forum for discussion and a dissemination venue for thermoelectrics. Under the mandate of the European Thermoelectric Society, the event was organized by the European Space Agency at the European Science and Technology Centre (ESTEC) in Noordwijk, The Netherlands on November 18–20th, 2013. The Proceedings from the 11th European Conference on Thermoelectrics are a collection of 26 manuscripts that cover topics from material syntheses, the measurement of thermoelectric properties, and the design of modules and generators. The proceedings are being complemented by fully peer-reviewed manuscripts that will appear in a special issue of the *Journal of Electronic Materials*.

The large emphasis of these proceedings on the design of thermoelectric modules and generators reflects the need to grow thermoelectricity beyond investigations limited to the fundamental physical understanding and the material characterization. The future of thermoelectricity may lie in the discovery of new high-ZT material, but we believe that it resides as much, and perhaps even more, in the design of modules and generators where these materials can be best exploited.

We are thankful to all the participants and the authors who submitted manuscripts to the 2013 European Conference on Thermoelectrics. We hope that these proceedings correctly reflect the time and effort that each invested to achieve these results.

Noordwijk, The Netherlands

Andrea Amaldi Francois Tang

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Chapter 1 Effect of Structure and Microstructure on the Thermoelectric Properties of Yb_{0.19}Co₄Sb₁₂ Alloy

A. Castellero, M. Ostorero, A. Ziggiotti, M. Brignone, and M. Baricco

Abstract In this work, we report the results of the synthesis and characterisation of the n-type $Yb_{0.19}Co_4Sb_{12}$ thermoelectric alloy that is among the most promising materials for automotive applications with a value of ZT ranging around 1 at 600 K.

Sample preparation consisted of a sequence of three steps: (1) a solid/liquid reaction between the individual elements at 660 °C in a resistance furnace, (2) complete melting in an induction furnace, and (3) annealing at 730 °C in a resistance furnace for 0.75, 1.5, 3 and 6 h.

The unannealed samples consist of a mixture of Sb, YbSb₂, CoSb, CoSb₂ and CoSb₃. Only a fraction (about 50 %) of the thermodynamically stable CoSb₃-type phase could be obtained by free cooling of the melt. This is due to the complex solidification path, involving two peritectic transformations, that does not allow the system to reach the equilibrium.

Annealing at 730 °C promotes the formation of the desired $CoSb_3$ -type phase up to fractions ~98 % after 3–6 h.

Thermoelectric properties were measured between 300 and 500 K. Longer annealing time caused an increase of the absolute values of the Seebeck coefficient as a consequence of the higher fraction of the $Yb_xCo_4Sb_{12}$ thermoelectric phase. In the case of electrical conductivity, no clear trend as a function of annealing time was observed.

Keywords Skutterudite • Processing • Thermoelectric material

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Introduction

Filled skutterudites emerged as potential candidates for thermoelectric (TE) power generation in the 700–800 K temperature range [1]. In the case of n-type CoSb₃, a figure of merit (ZT) exceeding unity could be achieved with suitable Yb doping [2, 3]. Processing routes for obtaining the CoSb₃ single phase consist of several steps and are often time and energy consuming. Alloying of the elements can be typically obtained by ball milling (BM) [3], by continuous reaction between solid Co and liquid Sb [4] or by direct melting of the pure elements [5, 6]. BM processing allows complete alloying in one step and the as-milled powders are ready for subsequent compaction. However, BM processing typically favours contamination and surface oxidation of the powder. On the other hand, samples prepared from the liquid are often not homogeneous from the microstructural point of view. In fact, a complex solidification path, involving two peritectic reactions, slows down the kinetics of phase transformations. Therefore, extremely long annealing time (up to 10 days) is currently used for promoting the formation of the CoSb₃ single phase [6].

Attempts to shorten the synthesis were made by non-equilibrium techniques such as rapid solidification [7, 8], that also promotes nanostructuring and supersaturation of the phase with the dopant [7].

Despite the technological importance of controlling and optimising the synthesis of CoSb₃ single phase, only few systematic studies have been carried out. For example, Kim et al. [9] performed isochronal annealing in vacuum of undoped CoSb₃ at temperatures between 300 and 800 °C. Complete formation of the single phase was achieved after annealing at 400 °C for 24 h [9].

In this work, $Yb_{0.19}Co_4Sb_{12}$ was synthesised with a sequence of three steps: (1) a solid/liquid reaction between the pure elements, (2) complete melting in an induction furnace, and (3) annealing at 730 °C. The effect of the annealing time on the evolution of phase structure and microstructure is studied and correlated to the thermoelectric properties. It is shown that annealing for 6 h at 730 °C promotes the formation of $Yb_{0.1}Co_4Sb_{12}$ single phase. However, the samples are characterised by porosity (10–20 vol.%) that is detrimental for thermoelectric applications.

Experimental

Samples with nominal composition $Yb_{0.19}Co_4Sb_{12}$ (at.%) were prepared using elemental Co (Alfa Aesar, 99.8 % powder), Sb (Alfa Aesar, 99.999 % shot), and Yb (Aldrich, 99.9 % chip). A small excess of Sb (about 3 at.%) was added in order to compensate the loss of this element as a consequence of its evaporation during the thermal treatments. The elements were sealed in a BN-coated quartz crucible under an Ar atmosphere (6.1 kPa) and were heated at 660 °C for 2.5 h in a resistance furnace. The melting reaction was then completed in an induction furnace, under an Ar atmosphere. Finally, samples in bulk form (rods with diameter 9 mm and height 30 mm) were annealed at 730 °C for 0.75, 1.5, 3 and 6 h.

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Structural analysis on ground powders obtained from the bulk samples was performed by X-ray diffraction (XRD) in transmission geometry (PANalytical X' Pert PRO, Cu K α), using a rotating capillary. The experimental patterns were refined by Rietveld analysis using the MAUD software [10].

Microstructure and phase compositions were investigated by scanning electron microscopy (SEM) (Leica Stereoscan 420) equipped with an energy dispersive spectroscopy (EDS) microprobe (Oxford Instruments).

The density of the samples was measured with a pycnometer.

The electrical conductivity (σ) was measured with the four-probe method. The Seebeck coefficient (α) was measured with a homemade apparatus where the sample is held between two plates. The whole sample holder can be inserted inside a vertical electrical furnace under an inert atmosphere. The temperature difference between the two plates during a heating ramp is maintained by heating the lower plate by Joule effect. Thermocouple wires were used to measure both the temperature of the plates and the potential difference generated by the sample. The Seebeck coefficient was obtained by the following equation:

$$\alpha = \alpha_{\text{wires}} - \frac{\Delta V}{\Delta T} \tag{1.1}$$

where α_{wires} represents the Seebeck coefficient of the thermocouple wires, ΔV is the measured potential difference and ΔT is the measured temperature difference. All the measurements were performed in an Ar atmosphere in a temperature range between 25 and 300 °C.

Results and Discussion

Figure 1.1 shows XRD patterns related to the phase evolution in the bulk samples after annealing at 730 °C for different times. The XRD pattern of the non-annealed sample clearly shows the crystallographic reflections of additional phases to CoSb₃ (i.e. Sb, CoSb and CoSb₂). As expected, increasing the annealing time promotes the formation of the desired CoSb₃-type phase. The evolution of the volume fraction of the various phases is shown in Fig. 1.2 as a function of annealing time. It can be seen that, after only 3–6 h of annealing, the formation of the CoSb₃-type single phase is almost completed. Table 1.1 shows the values of the lattice parameter for the CoSb₃type phase after different annealing times, together with the values of R_w indicating the quality of the fit for the Rietveld refinement. The increase of the lattice parameter with annealing time indicates that the CoSb₃-type phase progressively solubilises a larger amount of Yb. From the comparison of the lattice parameter for the sample annealed for 6 h (a=9.0462 Å) with those reported in literature for undoped Co_4Sb_{12} (a=9.0347 Å [11]) and $Yb_{0.18}Co_4Sb_{12}$ (a=9.0531 Å [6]), we estimated that the maximum amount of Yb solubilised in $Yb_xCo_4Sb_{12}$ is $x \sim 0.1$ indicating that the annealing is not enough for obtaining a complete dissolution (i.e. $Yb_{0.19}Co_4Sb_{12}$).



Fig. 1.1 X-ray diffraction patterns for Yb_xCo₄Sb₁₂ for selected annealing times. *Scattered curves*: experimental patterns; *continuous curves*: fitted patterns



Fig. 1.2 Evolution of the phase volume fraction as a function of annealing time

The microstructural evolution as a function of the annealing time is shown by the backscattered electron SEM images in Fig. 1.3. In the unannealed sample, Fig. 1.3a, large dendrites of the primary CoSb phase are surrounded by CoSb₂ and CoSb₃ phases, where CoSb, CoSb₂ and CoSb₃ are immersed in an Sb matrix. The inset of Fig. 1.3a shows a eutectic microstructure consisting of YbSb₂ and Sb, showing that the Yb atoms were not fully dissolved in the skutterudite structure. After 0.75 h of annealing, Fig. 1.3b, CoSb, CoSb₂ and Sb tend to disappear in favour of CoSb₃, while a small fraction of the YbSb₂/Sb eutectic is still present (see inset).

Annealing time (h)	Lattice parameter of Yb _x Co ₄ Sb ₁₂ , a (Å)	$R_{\mathrm{w}}\left(\% ight)$
0	9.0403	2.5
0.45	9.0422	5.8
1.5	9.0428	5.4
3	9.0455	3.9
6	9.0462	6.1

Table 1.1 Values of the lattice parameter, a, of Yb_xCo₄Sb₁₂ and R_w for the Rietveld refinement of the X-ray diffraction patterns at different annealing times

After 3 h of annealing, Fig. 1.3c, only residual traces of CoSb and CoSb₂ are present, whereas the YbSb₂/Sb eutectic fully disappears. Finally, after 6 h of annealing, the microstructure shown in Fig. 1.3d becomes more homogeneous, with only a small fraction of Sb segregated at the grain boundaries of CoSb₃.

According to the Co-Sb equilibrium phase diagram [12], the sequence of reactions upon cooling is the following:

$$\sim 1065^{\circ}\text{C}:\text{L} \to \text{CoSb} + \text{L}' \tag{1.2}$$

$$936^{\circ}C:L'+CoSb \to CoSb_2 \tag{1.3}$$

$$874^{\circ}\text{C}:\text{L}''+\text{CoSb}_2 \to \text{CoSb}_3 \tag{1.4}$$

where L, L' and L" represent the liquid phase with different compositions. The presence of significant amounts of Sb, CoSb and CoSb₂ in the unannealed sample indicates that the two peritectic reactions (1.3) and (1.4) were not completed during the uncontrolled cooling after induction melting, due to the need of long-range diffusion. The effect of annealing is to homogenise the microstructure progressively, favouring the formation of the expected CoSb₃-type phase. The presence of residual Sb in the sample annealed for 6 h indicates that the excess of Sb added at the beginning did not evaporate completely. All the samples show a significant amount of porosity (ranging between 10 and 20 vol.%) irrespective of the annealing time. The measured density ranges between 6.2 and 7.0 g.cm⁻³, corresponding to 81–92 % of the theoretical density (7.60 g.cm⁻³). According to Geng et al. [5], the mechanism of the formation of porosity is the one explained below. During the peritectic reaction (1.3), CoSb₂ dendrites form inside the network of primary dendrites of CoSb formed from reaction (1.2). As a consequence of the solidification contraction, empty volumes remain between the solid phases because the pores cannot be easily filled by the remaining liquid. Since the pore fraction does not show a trend with annealing time, it can be supposed that porosity is caused by the mechanism described by Geng et al. [5] rather than from the evaporation of Sb. This is also supported by the fact that the excess of Sb was not fully evaporated, as evidenced in Fig. 1.3d. Finally, pores tend to become more rounded when the annealing time increases as a consequence of the reduction of the surface area.

The results of the thermoelectric properties are reported in Fig. 1.4. The evolution of the Seebeck coefficient, α , and of the electrical conductivity, σ , measured at different temperatures in function of the annealing time is reported in Fig. 1.4a, b, respectively.



Fig. 1.3 SEM backscattered electron images of the microstructure evolution in $Yb_4Co_4Sb_{12}$ at different annealing times: (a) 0 h, (b) 0.75 h, (c) 3 h, and (d) 6 h. The *numbers* in the micrographs indicate the corresponding phases: (*1*) CoSb₃, (*2*) CoSb₂, (*3*) CoSb, (*4*) Sb, (*5*) YbSb₂