

## Characterization of post-annealed CoSb<sub>3</sub> grown by vertical Bridgman method

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Crystal of CoSb<sub>3</sub> were grown using the vertical Bridgman method with a relatively fast growth a rate of 2.8 mm/h. Thermoelectric properties of the as-grown and post-annealed samples were measured from room temperature (RT) to 673 K. In as-grown conditions, p-type polycrystalline CoSb<sub>3</sub> grains surrounded by Sb metal were obtained. Post-annealing was used to remove excess Sb because residual Sb degrades thermoelectric properties. Subsequent heat treatment at 1073 K for 5 h removed the residual Sb successfully, resulting in a significant increase in the Seebeck coefficients at RT. The increase was from 40 to 300  $\mu\text{V/K}$  (500  $\mu\text{V/K}$  in maximum). This typical Seebeck coefficient was still higher than the nominal value of 200  $\mu\text{V/K}$  in single crystal CoSb<sub>3</sub>, though samples with much higher Seebeck coefficient exhibited lower electrical conductivity [1-5]. Temperature dependent thermoelectric properties for the post-annealed samples showed a high Seebeck coefficient of 300  $\mu\text{V/K}$  over a temperature range from RT to 673 K, and the power factor estimated for the samples was one order of magnitude higher than has been reported so far.

Key words: CoSb<sub>3</sub>, skutterudite structure, thermoelectric material

### 1. INTRODUCTION

Thermoelectric materials have attracted a great deal of attention recently due to their applications in solid state power generation from exhaust or waste heat sources, resulting in an improvement of energy efficiency. The efficiency of a thermoelectric device is characterized with the dimensionless figure of merit,  $ZT=S^2\sigma T/\kappa$ , of its constituent thermoelectric material where  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity, and  $T$  is the absolute temperature. For thermoelectric device operation, the use of a material exhibiting  $ZT$  more than unity is desirable to realize a conversion efficiency of ~10% [6,7]. For decades, many studies have been made on skutterudite compounds as materials used for thermoelectric energy conversion [1-13]. Several bulk skutterudite materials have been reported to exhibit  $ZT$  more than unity in the temperature range of 800 to 1000 K [8].

Cobalt triantimonide (CoSb<sub>3</sub>), skutterudite structure, has been known as a promising high efficiency thermoelectric conversion material in temperature range from 500 to 700 K, because of its relatively low thermal conductivity due to its complex crystal structure and high electrical conductivity due to the considerably high mobility of holes in the material [1-5,9,10].

We fabricated bulk CoSb<sub>3</sub> with a conventional vertical Bridgman (VB) method [10-12]. While a single-like crystal was obtained with a growth rate of 0.4 mm/h, CoSb<sub>3</sub> grains of crystals grown under a faster rate of 2.8 mm/h were surrounded by residual Sb metal. Residual Sb causes the electrical conductivity to increase and the Seebeck coefficient to decrease, leading to degradation of the  $ZT$  value of the grown crystal. In order to improve  $ZT$  value, a post thermal

process was performed. As a result, the residual Sb was removed, and thereby a significant increase in the Seebeck coefficient was obtained, that exceeded the nominal value expected from the evaluated carrier concentration. In this report, we describe the growth process and effects of the subsequent annealing on the temperature dependence of the thermoelectric properties of CoSb<sub>3</sub>.

### 2. EXPERIMENT

The CoSb<sub>3</sub> crystals were grown using the VB method. As source materials, 10 atomic% Co (99.995%) and 90 atomic% Sb (99.9999%) were charged into a quartz ampoule under a vacuum ( $\sim 10^{-3}$  Pa) condition. Prior to the growth, rocking at 1373 K for 20 h was performed to obtain a homogeneous melt. The CoSb<sub>3</sub> was grown at a growth rate of 2.8 mm/h and with a linear temperature gradient of 85 °C/cm near the melt-solid interface for a control-set point of 1146 K. The grown ingot was sliced and then polished to form wafers of 0.6 to 1.0 mm thickness. Subsequently, as-grown samples were annealed in a vacuum ampoule. The annealing temperature was set to 1073 K at the sample position and to 800-1075 K at the Sb deposition region (Sb-DR) for 1 to 40 h to evaporate efficiently the residual Sb from the sample. An x-ray diffraction (XRD) analysis was performed using CuK $\alpha$  radiation. The microstructure of the samples was analyzed using an optical microscope, and their composition was determined by electron-probe microanalysis (EPMA). Thermoelectric properties such as Seebeck coefficient and electrical conductivity were measured over a temperature range from room temperature (RT) to 673 K. Using these results, the power factor was determined.

### 3. RESULTS AND DISCUSSION

Figure 1 shows surface micrographs of as-grown samples. In the grown ingot, CoSb<sub>3</sub> coexisted with metal Sb, this was mainly due to the Sb-rich growth condition, and no other phase such as CoSb or CoSb<sub>2</sub> was observed. At the tip of ingot, CoSb<sub>3</sub> was highly cohesive as shown in Fig. 1(a); at the middle of the ingot the CoSb<sub>3</sub> grains appeared to be encompassed by the residual Sb (Fig. 1(b)), and the amount of Sb increased along the growth direction. Toward the rear end of the ingot, Sb-rich eutectic was observed (Fig. 1(c)). For the as-grown samples, the estimated Seebeck coefficient,  $S$ , at RT was about 40  $\mu\text{V}/\text{K}$ , which was much lower than the nominal value of  $\sim 200 \mu\text{V}/\text{K}$  expected from evaluating the carrier concentration, and was close to the  $S$  value of metal Sb [1-5]. This dominating residual Sb condition implies a high electrical conductivity,  $\sigma$ , and a large thermal conductivity,  $\kappa$ , resulting in a small figure of merit,  $ZT$ . In order to obtain large  $S$ , small  $\kappa$  and high  $\sigma$  desirable for an ideal thermoelectric material, a post annealing process was performed to remove the residual Sb in the sample. Samples cut from the ingot represented in Fig. 1(b) were used for the following experiments performed to minimize the effects resulting from the proportion of CoSb<sub>3</sub> grain to Sb.

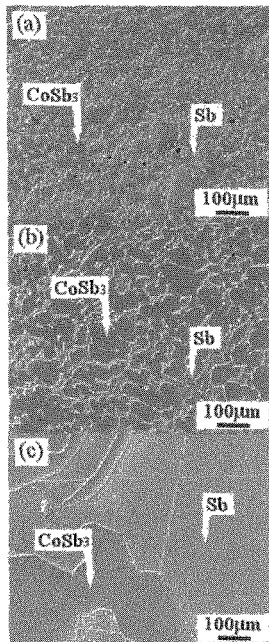


Fig. 1. Surface micrographs of as-grown samples; (a) at tip of ingot, (b) at middle of ingot, (c) at end of ingot.

The Seebeck coefficient as a function of the temperature in Sb-DR is shown in Fig. 2, for samples post-annealed for 20 h. During the annealing at 1073K, the residual Sb evaporated from the sample, and then deposited as a solid metal Sb in Sb-DR. As shown in the inset, temperature at Sb-DR was set lower than the sample temperature to draw out the Sb. For samples annealed at a temperature less than 860 K in Sb-DR, the  $S$  was a small value corresponding to the metallic value and rose with increased Sb-DR temperature. For Sb-DR temperature of 970 to 1050 K, the  $S$  exceeded the

nominal value, and reached as high as 270  $\mu\text{V}/\text{K}$  at the Sb-DR temperature of 1005 K. At higher Sb-DR temperature, the  $S$  decreased to as low as  $\sim 50 \mu\text{V}/\text{K}$ . Surface micrographs of post-annealed samples are shown in Fig. 3. As for Sb-DR temperature less than 860 K, the CoSb<sub>3</sub> grain became lean compared with the initial condition, as shown in Fig. 3(a), although residual Sb was eliminated. The XRD revealed that the sample consisted of CoSb<sub>3</sub>, CoSb, and a slight amount of Sb; this indicated that CoSb<sub>3</sub> might have decomposed to CoSb due to excess Sb evaporation from the sample. Indeed, the low  $S$  observed showed that the property of the sample was predominated by a metallic substance that might be composed of CoSb, a metallic phase, and slight residual Sb. For the sample annealed at Sb-DR temperature of 1005 K,  $S$  as high as 270  $\mu\text{V}/\text{K}$  was observed, and only CoSb<sub>3</sub> peaks appeared in the XRD spectrum, indicating no CoSb was formed and residual Sb was sufficiently eliminated. Figure 3 (b) is a micrograph of the sample annealed at 1005 K. After residual Sb was removed, voids were formed without notable change in the CoSb<sub>3</sub> grain externals and EPMA measurement also indicated that the amount of residual Sb at the void/CoSb<sub>3</sub> interface was negligibly small.

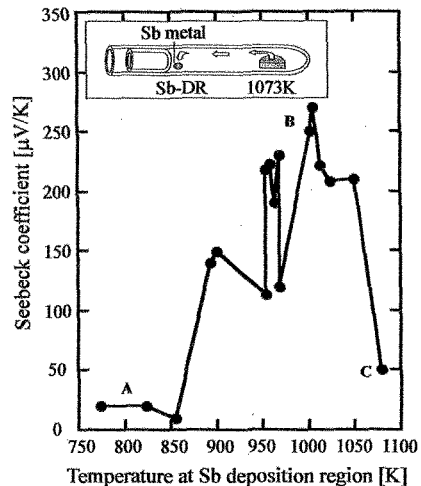


Fig. 2. The variation of  $S$  as a function of the temperature at Sb deposition region; Annealing temperature was set to 1073 K at sample position and 800-1075 K at Sb-DR for 20 h to make residual Sb evaporate from the sample efficiently.

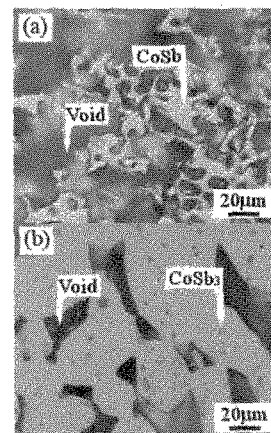


Fig. 3. Surface micrographs of the post annealed samples; (a) annealed at 770K, (b) annealed at 1005K.

An effect of post annealing duration was examined using samples for Sb-DR temperature of 1073 K and 1005 K. Figure 4 shows micrographs of samples as-grown (a), annealed for 1 h (b) and 5 h (c). Examination of the sample annealed for 1 h indicated that the  $\text{CoSb}_3$  was entirely surrounded by the residual Sb and no distinct structural variation was found as compared with the as-grown sample. After 5 h annealing, the residual Sb was evaporated to form voids, which were also observed for samples annealed for 20 h. The XRD and EPMA measurements showed that only  $\text{CoSb}_3$  remained in the post annealed sample. Concerning samples that were annealed for longer durations: 10, 20, and 40 h, the obtained properties were quite similar to those for samples annealed for 5 h.

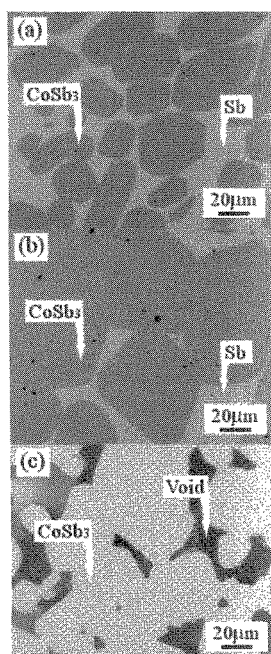


Fig. 4. Surface micrographs of as-grown and post annealed samples; (a) as-grown, (b) annealed for 1 h, (c) annealed for 5 h. Void was formed after Sb evaporation for sample (c).

For these annealed samples,  $S$  and  $\sigma$  measurements were conducted in a temperature range from RT to 673 K. Using these values, the power factor,  $S^2\sigma$ , was estimated (Fig. 5). When the annealing duration was 1 h, the  $S$  was nearly identical to that for as-grown sample over the whole temperature range, and the  $\sigma$  was slightly lower than that for as-grown sample, but was still higher than that for a nominal value of a bulk  $\text{CoSb}_3$  [1-5]. We considered that this arose from the following two effects of residual Sb: (1) the formation of phonon and (2) the career path on the metallic portion. The samples annealed for more than 5 h demonstrate that the observed  $S$  exhibited high value exceeding the nominal value of  $\sim 200 \mu\text{V/K}$  at a relatively lower temperature range of 370 to 600 K, although  $\text{CoSb}_3$  sintered typically exhibits the maximum  $S$  at 600 to 750 K [1-5,13]. In contrast to the sample annealed for 1 h, the highest  $S$  observed was  $310 \mu\text{V/K}$  at 423 K for the sample post annealed for 5 h, although  $\sigma$  was decreased due to the complete

elimination of Sb. For the sample annealed for 20 h, the temperature dependent characteristics of  $S$  were very comparable to those observed for 5 h; showing the highest  $S$  of  $310 \mu\text{V/K}$  at the same temperature. This demonstrates that post annealing for 5 h is sufficient for removing residual Sb under present conditions.

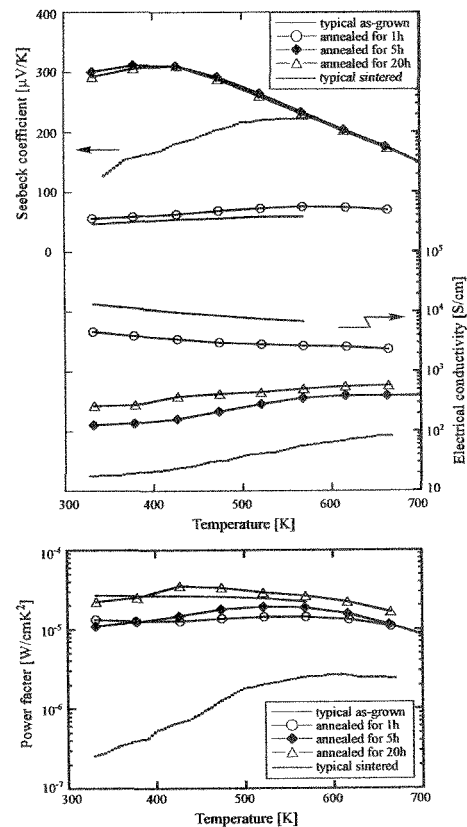


Fig. 5. Thermoelectric properties of annealed samples in temperature range from RT to 700 K; typical sintered  $\text{CoSb}_3$  data reported by Matsubara *et al.* is shown (see Ref. 13).

Variation of power factor as a function of temperature was relatively small at an order of  $10^{-5} \text{ W/cmK}^2$ , and no significant temperature dependence was observed over the whole measured temperature. In the temperature range of 323 to 600 K, the observed power factor was approximately two orders of magnitude larger than that of  $\text{CoSb}_3$  sintered typically [13]. The maximum value was  $3.5 \times 10^{-5} \text{ W/cmK}^2$  at 423 K for samples annealed for 5 h. This slightly large power factor observed for the sample annealed for 20 h was due to its having higher  $\sigma$  than that of the 5 h sample, although the  $S$  for the samples annealed for 5 and 20 h were nearly identical. We attribute this mainly to a difference in cohesion values of  $\text{CoSb}_3$  grains.

To investigate the effect of  $\text{CoSb}_3$  condensation in the sample, three samples possessing  $\text{CoSb}_3$  grains with different cohesion value were prepared and their thermoelectric properties were measured. Figure 6 shows surface micrographs of two samples in which we observed the most condensed and sparse  $\text{CoSb}_3$  grains. The  $S$ ,  $\sigma$ , and power factor in the temperature range from RT to 673 K are shown in Fig. 7. Larger  $S$  was obtained for the sparse sample and a slight difference

was observed at temperature below ~500 K. For  $\sigma$ , the condensed sample exhibited higher value than the sparse one, although the difference between their values is rather small. The largest power factor was obtained from the condensed sample, and again the difference between the condensed and sparse samples was not very large.

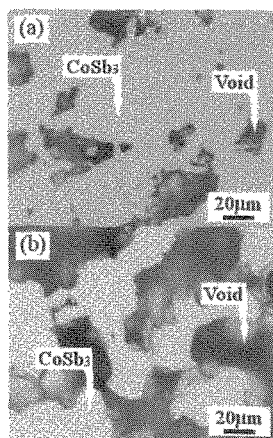


Fig. 6. Surface micrographs of post annealed samples; (a) the most condensed CoSb<sub>3</sub> grains, (b) the most sparse CoSb<sub>3</sub> grains.

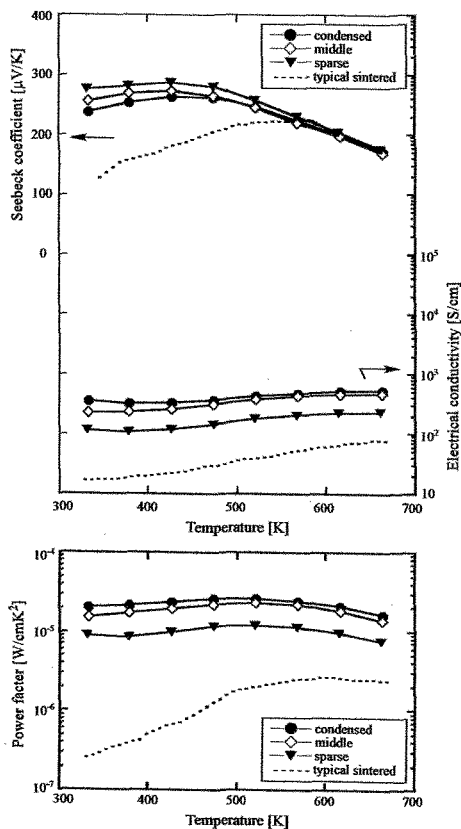


Fig. 7. Thermoelectric properties of annealed samples in a temperature range from RT to 700 K; typical sintered CoSb<sub>3</sub> data reported by Matsubara *et al.* is shown (see Ref. 13). The largest power factor was obtained from the condensed sample. But the difference between the condensed and sparse samples was not very large.

#### 4. CONCLUSION

Crystals of CoSb<sub>3</sub> were grown using the vertical Bridgman method. With a relatively fast growth rate 2.8 mm/h, p-type polycrystalline CoSb<sub>3</sub> surrounded by Sb metal was obtained. Post annealing removed the residual Sb and improved the Seebeck coefficient considerably, since the presence of residual Sb resulted in a decreased Seebeck coefficient and increase electrical conductivity. The variation in the obtained power factor as a function of temperature was rather small at an order of  $10^{-5}$  W/cmK<sup>2</sup>, and no significant temperature dependence was observed over the whole range of measured temperature. In the temperature range of 323 to 600 K, the observed power factor was approximately two orders of magnitude larger than that of a typical sintered CoSb<sub>3</sub>. For annealed sample, the maximum  $S^2\sigma$  value was  $3.5 \times 10^{-5}$  W/cmK<sup>2</sup> at 423 K.

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