

## Preparation and Thermoelectric Properties of p and n-type CoSb<sub>3</sub>

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### ABSTRACT

For the first time, large single crystals of the compound CoSb<sub>3</sub> were grown from antimony rich melts by the Bridgman gradient freeze technique. CoSb<sub>3</sub> has the skutterudite crystal structure and a peritectic decomposition temperature of 873 °C. Samples were characterized by X-ray diffractometry, microprobe analysis and density measurements. A Debye temperature of 306 K was calculated from speed of sound measurements. As-grown CoSb<sub>3</sub> crystals show p-type conductivity. N-type samples were obtained over a wide range of doping level by addition of Tc. Seebeck coefficient, electrical resistivity, thermal conductivity and Hall effect measurements were performed between room temperature and 500 °C. The results of these measurements are presented and discussed. Exceptionally high Hall mobilities were obtained on p-type samples which is consistent with the covalency of the skutterudite crystal structure. A maximum room temperature Hall mobility of about 3445 cm<sup>2</sup>.V<sup>-1</sup>.s<sup>-1</sup> was measured on a sample with a carrier concentration of 4 x 10<sup>17</sup> cm<sup>-3</sup>. N-type samples were found to have substantially lower Hall mobilities in the range of temperature investigated. A bandgap of 0.55 eV was estimated from the high temperature electrical resistivity and Hall effect measurements. The hole and electron effective masses were also estimated and are presented. Based on the experimental data obtained, the potential of CoSb<sub>3</sub> as a thermoelectric material is discussed.

### INTRODUCTION

CoSb<sub>3</sub> belongs to a large family of materials having the skutterudite structure. This structure is composed of a cubic lattice, space group *Im*3 and the unit cell contains 8 AB<sub>3</sub> groups. The lattice constant of CoSb<sub>3</sub> is 9.0385 Å and its peritectic decomposition temperature is 873 °C [1]. Some properties of this compound were previously investigated and it was found that CoSb<sub>3</sub> is a semiconductor and its bandgap was estimated to 0.5 eV from high temperature electrical resistivity measurements on n-type polycrystalline samples [2]. However, results obtained on small single crystals prepared by chemical vapor transport techniques showed that CoSb<sub>3</sub> had a metallic behavior. To clarify these contradictory results, we attempted to grow, for the first time, large crystals of CoSb<sub>3</sub> from

non-stoichiometric melts using the gradient freeze technique. The samples were characterized by microprobe analyses, density and X-ray measurements. A variety of electrical and thermal measurements were also performed on these samples over a wide range of temperature. The experimental data obtained show that  $\text{CoSb}_3$  is indeed a semiconductor. The results of the measurements are presented and the potential of this compound as a thermoelectric material is discussed.

## EXPERIMENTAL DETAILS

The Co-Sb phase diagram shows that the growth of the compound can be initiated from Sb rich melts between 91 and 97 at. % Sb [1]. Samples were grown using the gradient freeze technique from melts with 93 at. % Sb in sealed quartz ampoules coated with graphite and with a pointed bottom. A temperature gradient of about  $50\text{ }^\circ\text{C/cm}$  was maintained at the growth interface and the growth rate was  $0.7\text{ }^\circ\text{C/h}$  [3]. Doping studies were also conducted by adding different amounts of Te in the melt. Typical ingots obtained after the growth were composed of two parts: the bottom part corresponding to the compound  $\text{CoSb}_3$  and the upper part corresponding to the Sb rich eutectic. An overall number of 20 samples in the form of disks about 2 mm thick and 10 mm in diameter were cut from the ingots. Typical samples were composed of a few very large grains but single crystals (10 mm in diameter, 2 mm thick) were obtained as indicated by Laue patterns. Selected samples were polished and their microstructure was investigated under an optical microscope. Microprobe analyses were also performed on the same samples to check their composition. Finally, some samples were ground for X-ray diffractometry (XRD) analyses. XRD experiments showed that the samples were single phase and the lattice constant calculated from the pattern showed that the stoichiometry of the samples was 1:3. The density of all samples was measured by the immersion technique using toluene as liquid. The measured densities were found to be about 99.5% of the theoretical density ( $7.69\text{ g.cm}^{-3}$ ) which also indicates that the stoichiometry of the samples was 1:3.

Samples were characterized at room temperature by speed of sound, Hall effect and Seebeck coefficient measurements. High temperature Seebeck coefficient, electrical resistivity, thermal conductivity and Hall effect measurements were also performed on selected samples.

## RESULTS AND DISCUSSION

The velocity of sound was measured at room temperature in a single crystal of  $\text{CoSb}_3$  about 8 mm long and using a frequency of 5 MHz. The longitudinal sound velocity was found to be  $4.62 \times 10^3\text{ m.s}^{-1}$  and the transversal  $2.64 \times 10^3\text{ m.s}^{-1}$ . The calculated average sound

velocity is  $2,93 \times 10^3 \text{ m.s}^{-1}$  and the calculated Debye temperature using this average sound velocity is 306 K.

Room temperature van der Pauw, Hall effect and Seebeck coefficient measurements are summarized in Table I and the results clearly show that  $\text{CoSb}_3$  is a semiconductor. As grown samples show p-type conductivity while doping with Te concentration between 0.08 and 0.15 at. % changed the conductivity to n-type. All p-type samples were cut from the same ingot and are single crystals. The change in properties from one end of the ingot to the other might be attributed to changes in the stoichiometry of the samples inherent of the growth process or segregation of residual impurities towards the end of the ingot. N-type samples cut from the same ingot have different carrier concentration because of the segregation of Te during the directional crystallization.

Table I. Room temperature properties of n and p-type  $\text{CoSb}_3$  samples.

Sample #	Nominal dopant (at.%)	Conductivity type	$\rho$	$R_H$	$n/p$	$\mu_H$	$\alpha$
1NB13	-	p	0.8412	1.735	0.360	2062.5	141
2NB13	-	p	0.8117	1.605	0.389	1981.0	139
3NB13	-	p	0.7367	1.429	0.437	1944.0	138
4NB13	-	p	0.6997	1.299	0.481	1856.0	135
5NB13	-	p	0.7353	1.379	0.453	1877.0	139
6NB13	-	p	1.076	2.316	0.270	2153.3	159
71NB13	-	p	1.894	5.372	0.116	2835.7	189
72NB13	-	p	4.523	15.580	0.040	3445.5	233
1CS10	0.08 Te	n	14.2	-1.374	0.454	-101.0	-500
3CS10	0.08 Te	n	7.627	-0.644	0.969	-84.4	-380
1CS7	0.1 Te	n	11.64	-1.266	0.494	-108.8	-450
2CS9	0.12 Te	n	5.99	-0.408	1.520	-68.0	-270
2CS9A	0.12 Te	n	9.2	-0.620	0.920	-70.0	-410
1CS11	0.15 Te	n	5.572	-0.485	1.287	-87.0	-373

Electrical resistivity  $\rho$  ( $\text{m}\Omega\cdot\text{cm}$ ), Hall coefficient  $R_H$  ( $\text{C}\cdot\text{cm}^{-3}$ ), Hall carrier concentration  $n/p$  ( $\times 10^{19}\cdot\text{cm}^{-3}$ ), Hall mobility  $\mu_H$  ( $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ), Seebeck coefficient  $a$  ( $\mu\text{V}/\text{K}$ ).

P-type samples have exceptionally high carrier mobility and a maximum of  $3445 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$  was measured on a sample with a Hall carrier concentration of about  $4 \times 10^{17} \text{ cm}^{-3}$ . Figure 1 shows the room temperature Hall mobility for p-type skutterudite compounds  $\text{CoSb}_3$  and  $\text{IrSb}_3$  and also for p-type Si and Ge. Skutterudite compounds have significantly higher mobility than state-of-the-art semiconductors such as Si, Ge and III-V's. These high mobilities are consistent with the covalent bonds in the skutterudite structure and also to the fact that the valence band is essentially derived from pnictogen-pnictogen bonds in these materials [4]. N-type mobilities are substantially lower resulting in higher electrical resistivity values. Large Seebeck coefficients were measured on n-type samples. An estimation of the effective masses can be made from the room temperature values of the

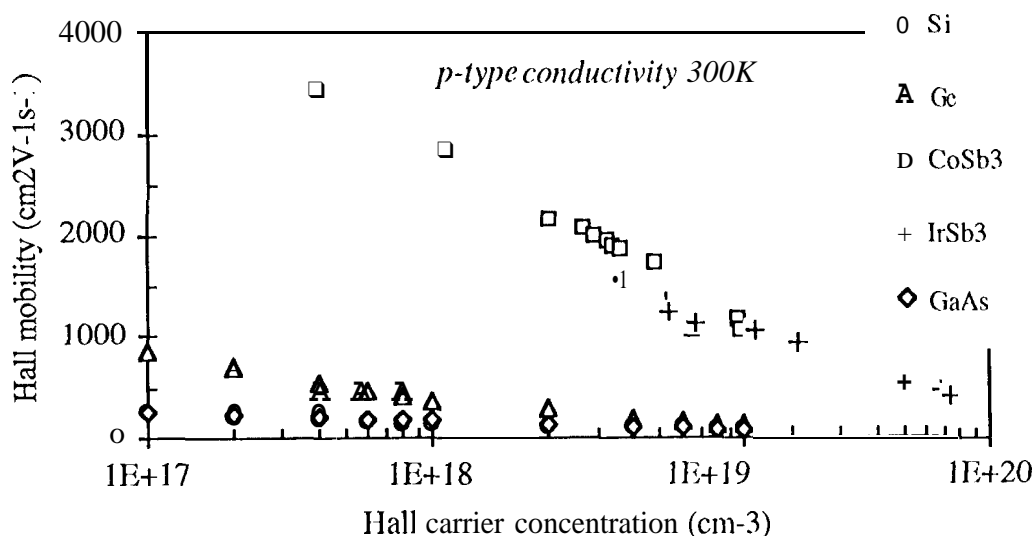
1 Hall coefficient and Seebeck coefficient as follows. The Seebeck coefficient ( $\alpha$ ) can be expressed using Fistul formalism as:

$$\alpha = \pm \frac{k}{c} \left( \frac{\Phi_4(\xi, b)}{\Phi_3(\xi, b)} - \xi \right) \quad (1)$$

where  $k$  is the Boltzmann constant,  $c$  the electron charge,  $\xi$  the Fermi level,  $\Phi_4$  and  $\Phi_3$  are Fistul integrals and  $b$  is a factor which depends on the scattering mechanisms. Assuming that the dominant scattering mechanism is acoustic phonons,  $b=0$ . Using the same formalism, the Hall coefficient ( $R_H$ ) can be expressed as:

$$R_H = \pm \frac{3h^3}{8\pi c (2m^* kT)^{3/2}} \frac{\Phi_{9,2}(\xi, b)}{[\Phi_3(\xi, b)]^2} \quad (2)$$

Using the room temperature values of the Seebeck coefficient and assuming acoustic phonon scattering, the Fermi level  $\xi$  can be calculated from equation (1) and used in equation (2) to calculate the effective mass  $m^*$ . Using the data tabulated in table 1, an average mass of 0.16 and 1.65  $m_0$  was calculated for the holes and the electrons, respectively.



**Figure 1:** Room temperature Hall mobility for p-type CoSb<sub>3</sub> and IrSb<sub>3</sub> as a function of Hall carrier concentration. Values for p-type Si and Ge are also shown for comparison.

Figure 2 shows the electrical resistivity values as a function of the temperature for several n and p-type CoSb<sub>3</sub> samples with different doping levels. N-type samples have higher resistivity values than p-type which do not show any intrinsic behavior in the investigated range of temperature. Above 260°C, the variations of the electrical resistivity of n-type

samples are practically linear with temperature and a bandgap value of 0.55 eV was estimated from the slopes of the curves.

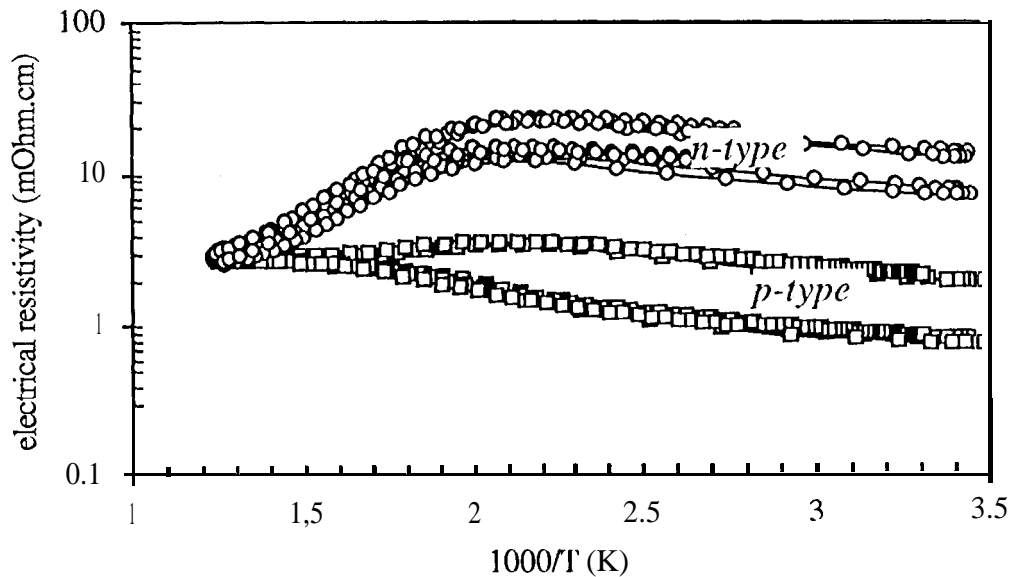


Figure 2: Electrical resistivity as a function of temperature for p and n-type  $\text{CoSb}_3$ .

Figures 3 and 4 show the variations of the Hall mobility and Seebeck coefficient as a function of temperature for n and p-type  $\text{CoSb}_3$  samples. The Hall mobility of p-type samples decreases with temperature as  $T^{-1.9}$  indicating that acoustic phonons is the dominant scattering mechanism. The Hall mobility of n-type samples is negative up to about  $200^\circ\text{C}$  and becomes positive for higher temperatures, increasing up to about  $400^\circ\text{C}$  and decreasing for higher temperatures. The Seebeck coefficient variations of n and p-type  $\text{CoSb}_3$  samples with temperature are quantitatively similar to the variations of the Hall mobility. However, the Seebeck coefficient of n-type samples changes sign at a temperature of about  $300^\circ\text{C}$ , higher than for the Hall mobility, This unusual feature needs to be understood and will be addressed in the future.

The thermal conductivity of two p-type and one n-type  $\text{CoSb}_3$  samples was calculated from thermal diffusivity and heat capacity measurements up to  $700^\circ\text{C}$  and the results are shown in Figure 5. The thermal conductivity decreases from room temperature up to about  $400^\circ\text{C}$ , reaches a minimum value of about  $4 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  and then increases due to increasing minority carrier conduction (bipolar contribution). The average value of the thermal conductivity at room temperature is  $11.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ . An estimation of the lattice thermal conductivity of  $\text{CoSb}_3$  can be made by calculating the electronic contribution to the total thermal conductivity using the Wiedemann-Franz law, the value of the Lorenz number

being calculated using the Fermi level value obtained from equation (1). The lattice thermal conductivity ( $\lambda_{ph}$ ) was estimated at  $10.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ .

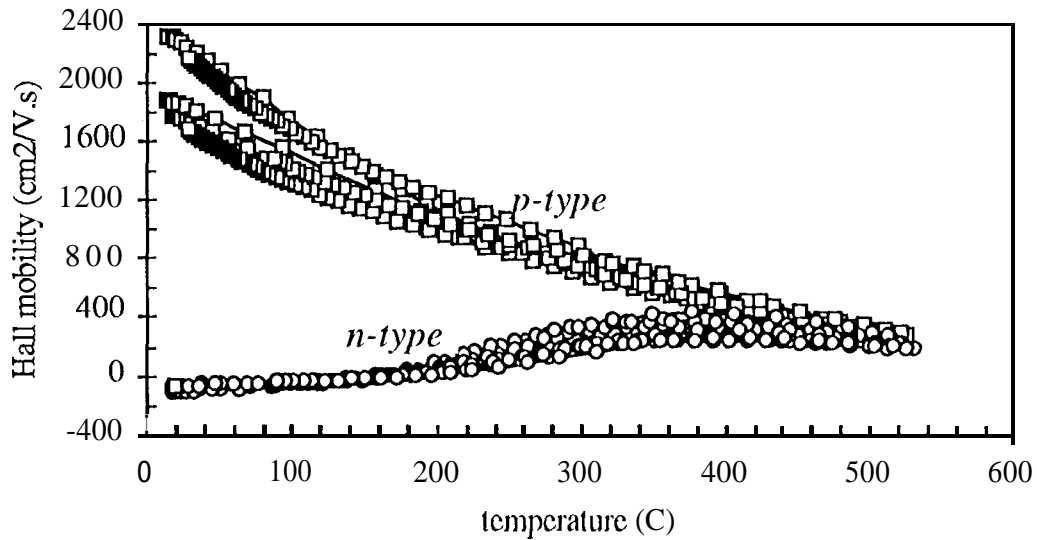


Figure 3: Hall mobility as a function of temperature for p and n-type  $\text{CoSb}_3$ .

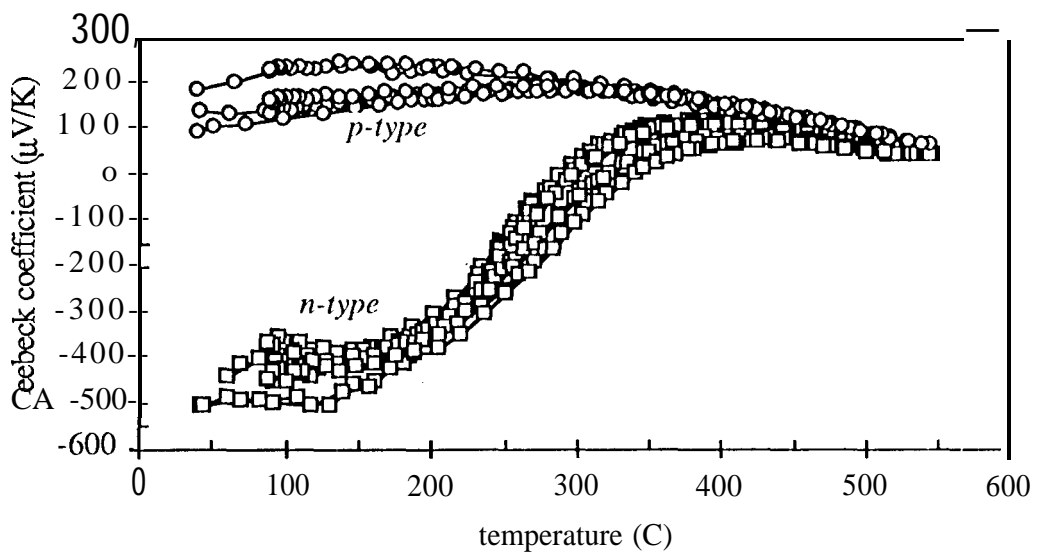


Figure 4: Seebeck coefficient as a function of temperature for p and n-type  $\text{CoSb}_3$ .

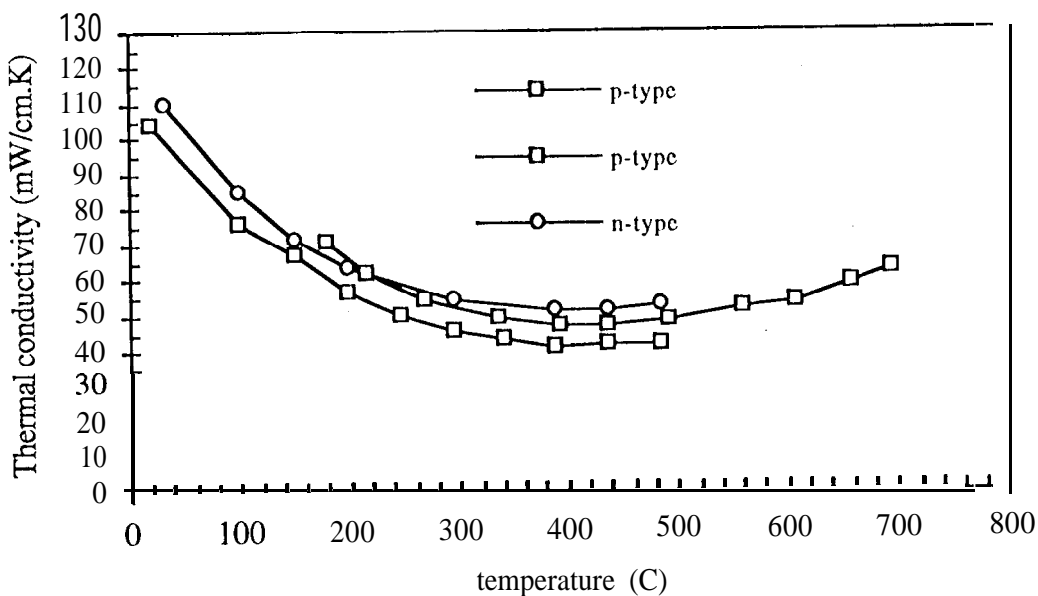


Figure 5: Thermal conductivity as a function of temperature for p and n-type  $\text{CoSb}_3$ .

Figure 6 shows the calculated  $ZT$  values for two p-type samples and one n-type samples as a function of temperature. A maximum  $ZT$  value of 0.15 was achieved at about  $300^\circ\text{C}$ . This value is relatively low but no efforts at this time were made to optimize the doping level of the samples.

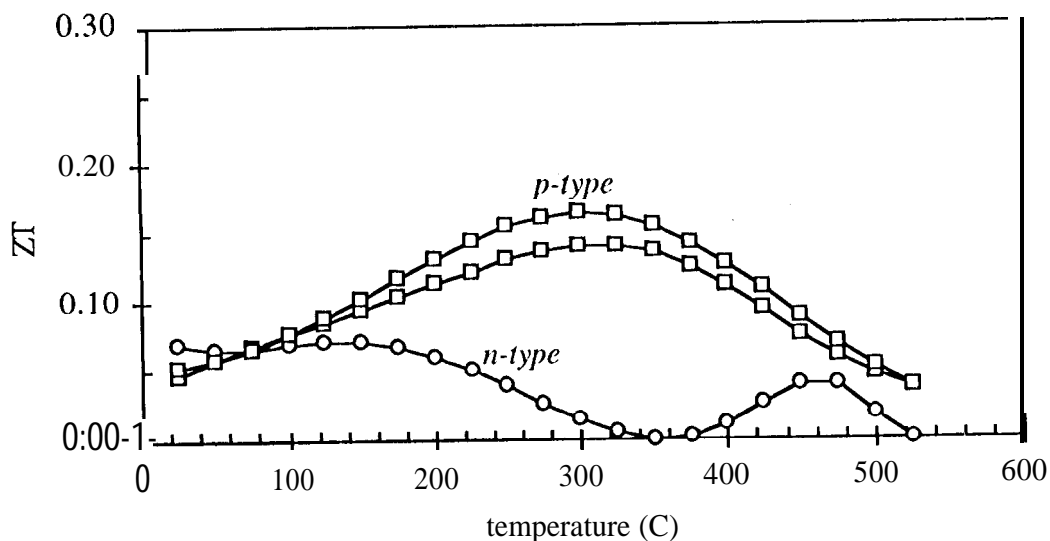


Figure 6:  $ZT$  values as a function of temperature for some p and n-type  $\text{CoSb}_3$  samples.

Conventional theory for a single band semiconductor indicates the optimum thermoelectric figure of merit depends on the scattering mechanism and a material parameter  $\beta = m^{*3/2} \mu / \lambda_{ph}$  where  $m^*$  is the carrier effective mass,  $\mu$  is the carrier mobility and  $\lambda_{ph}$  is the lattice thermal conductivity.  $\beta$  can be calculated from the estimated electron and hole masses, the estimated lattice thermal conductivity of  $10.3 \text{ W.m}^{-1}.\text{K}^{-1}$  and the measured values of the Hall mobilities for the holes and electrons. The Hall mobilities were extrapolated at a carrier concentration of  $10^{17} \text{ cm}^{-3}$  using the variations of the Hall mobility as a function of carrier concentration determined in this study. The results of the calculations are reported in Table 2.

Table 2. Some properties of n and p-type  $\text{CoSb}_3$ .

	$m^*/m_0$	$\mu$ (at $10^{17} \text{ cm}^{-3}$ ) ( $\text{cm}^2.\text{V}^{-1}.\text{s}^{-1}$ )	$\lambda_{ph}$ ( $\text{W.m}^{-1}.\text{K}^{-1}$ )	$\beta$
J)-type	0.16	5000	10.3	31.06
n-t ypc	1.65	250	10.3	51.44

The results in Table 2 show that n-type samples might have higher  $ZT$  values than p-type despite the exceptionally Hall mobilities of p-type samples.  $\text{CoSb}_3$  is definitively an interesting material with a good thermoelectric potential, However, relatively low  $ZT$  values were obtained mainly because the lattice thermal conductivity of  $\text{CoSb}_3$  is too large. High  $ZT$  values might be possible for material with the skutterudite structure if one can find a skutterudite material with a substantially lower thermal conductivity, retaining the good basic properties of  $\text{CoSb}_3$ . Considering the large number of materials having the skutterudite structure [5] and the possibilities of tailoring composition and bandgap in these materials, one should be able to find a material with a good potential for high  $ZT$  values. Reduction of the thermal conductivity can be achieved, for example, by increasing phonon scattering by alloying isostructural compounds [6] or developing ternary or even quaternary skutterudite related phases [5].

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