Preparation and Thermoelectric Properties of p and n-type CoSb₃

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ABSTRACT

For the first time, large single crystals of the compound CoSb₃ were grown from antimony rich melts by the Bridgman gradient freeze technique. CoSb₃ 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 CoSb₃ 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 cm²/V·s was measured on a sample with a carrier concentration of 4 x 10¹⁷ cm⁻³. 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 CoSb₃ as a thermoelectric material is discussed.

INTRODUCTION

CoSb₃ belongs to a large family of materials having the skutterudite structure. This structure is composed of a cubic lattice, space group Im³ and the unit cell contains 8 AB₃ groups. The lattice constant of CoSb₃ 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 CoSb₃ 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 CoSb₃ had a metallic behavior. To clarify these contradictory results, we attempted to grow, for the first time, large crystals of CoSb₃ from...
non-stoichiometric melts using the gradient freeze technique. The samples were
categorized 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 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 show 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 scaled quartz ampoules coated with graphite and
with a pointed bottom. A temperature gradient of about 50 °C/cm was maintained at the
growth interface and the growth rate was 0.7 °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 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 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 CoSb$_3$ about
8 mm long and using a frequency of 5 MHz. The longitudinal sound velocity was found to
be $4.62 \times 10^3$ m.s$^{-1}$ and the transversal $2.64 \times 10^3$ 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 Paw, Hall effect and Seebeck coefficient measurements are summarized in Table I and the results clearly show that CoSb$_3$ is a semiconductor. As grown samples show p-type conductivity while doping with Tc 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 Tc during the directional crystallization.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Nominal dopant (at. %)</th>
<th>Conductivity type</th>
<th>$\rho$ (m$\Omega$.cm)</th>
<th>$R_H$ (C.cm$^{-2}$)</th>
<th>$n/p$</th>
<th>$\mu_H$ (cm$^2$.V$^{-1}$.s$^{-1}$)</th>
<th>$\alpha$ (\muV/K)</th>
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<tr>
<td>1NB13</td>
<td>-</td>
<td>p</td>
<td>0.8412</td>
<td>1.735</td>
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<td>-</td>
<td>p</td>
<td>0.8117</td>
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<td>1981.0</td>
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<td>-</td>
<td>p</td>
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<td>0.437</td>
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<td>1.379</td>
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<td>0.040</td>
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<td>1CS10</td>
<td>0.08 Tc</td>
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<td>-500</td>
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<tr>
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<td>-380</td>
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<td>0.1 Tc</td>
<td>n</td>
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<td>-1.266</td>
<td>0.494</td>
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<td>5.99</td>
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<td>1.520</td>
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<td>1CS11</td>
<td>0.15 Tc</td>
<td>n</td>
<td>5.572</td>
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<td>1.287</td>
<td>-87.0</td>
<td>-373</td>
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Electrical resistivity $\rho$ (m$\Omega$.cm), Hall coefficient $R_H$(C.cm$^{-2}$), Hall carrier concentration $n/p$ (x 10$^{19}$.cm$^{-3}$), Hall mobility $\mu_H$(cm$^2$.V$^{-1}$.s$^{-1}$), Seebeck coefficient $\alpha$ (\muV/K).

Figure 1 shows the room temperature Hall mobility for p-type skutterudite compounds CoSb$_3$ and 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 (et) can be expressed using Fistul formalism as:

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

where \( k \) is the Boltzmann constant, \( e \) 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 \( (R_{HH}) \) can be expressed as:

$$R_{HH} = \frac{3h^3}{8\pi e(2\pi^2 kT)^3 / 2 \left[ \Phi_3(\xi, b) \right]^2}$$  \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 CoSb3 and IrSb3 as a function of 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 CoSb3 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.

![Graph](image)

**Figure 2**: Electrical resistivity as a function of temperature for p and n-type 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 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°C and becomes positive for higher temperatures, increasing up to about 400°C and decreasing for higher temperatures. The Seebeck coefficient variations of n and p-type 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°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 CoSb$_3$ samples was calculated from thermal diffusivity and heat capacity measurements up to 700°C and the results are shown in Figure 5. The thermal conductivity decreases from room temperature up to about 400°C, reaches a minimum value of about 4 W.m$^{-1}$.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 W.m$^{-1}$.K$^{-1}$. An estimation of the lattice thermal conductivity of 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 W.m$^{-1}$.K$^{-1}$.

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

**Figure 4:** Seebeck coefficient as a function of temperature for p and n-type CoSb$_3$. 
Figure 5: Thermal conductivity as a function of temperature for p and n-type CoSb₃.

Figure 6 shows the calculated ZT values for two p-type samples and one n-type sample as a function of temperature. A maximum ZT value of 0.15 was achieved at about 300°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 CoSb₃ samples.
Conventional theory for a single band semiconductor indicates the optimum thermoelectric figure of merit depends on the scattering mechanism and a material parameter \( \beta = m^* \mu / \lambda_{ph} \) 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 W m\(^{-1}\) 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\(^{17}\) 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>
<thead>
<tr>
<th></th>
<th>( m^*/m_0 )</th>
<th>( \mu ) ( (\text{at } 10^{17} \text{ cm}^{-3}) )</th>
<th>( \lambda_{ph} ) ( (\text{W m}^{-1}\text{K}^{-1}) )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>J-type</td>
<td>0.16</td>
<td>5000</td>
<td>10.3</td>
<td>31.06</td>
</tr>
<tr>
<td>n-type</td>
<td>1.65</td>
<td>250</td>
<td>10.3</td>
<td>51.44</td>
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</table>

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. 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 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 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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REFERENCES


