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Antimony desinsertion reaction from $\text{Sb}_x\text{CoSb}_{3-x}$

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The compound $\text{Sb}_x\text{CoSb}_{3-x}$ was produced at 7.7 GPa and 550°C in a self-insertion reaction from the binary skutterudite $\text{CoSb}_3$. This self-insertion reaction is characterized by the collapse of some framework Sb atoms into the cages formed by the Co and Sb atoms in the skutterudite structure, as was further confirmed by Bader’s analysis of maximum-entropy charge density maps obtained from synchrotron radiation x-ray powder diffraction data. The opposite reaction (i.e., Sb desinsertion, $\text{Sb}_x\text{CoSb}_{3-x} \rightarrow \text{CoSb}_3$) occurs when $\text{Sb}_x\text{CoSb}_{3-x}$ is heated above 180°C at ambient pressure. This desinsertion reaction was followed by means of differential scanning calorimetry, x-ray diffraction, and electrical resistivity measurements. Differential scanning calorimetry measurements revealed the presence of two thermal events in samples rich in the $\text{Sb}_x\text{CoSb}_{3-x}$ phase. An endothermic peak around 150°C was assigned to a small change in the position of the guest Sb atoms inside the cages of $\text{Sb}_x\text{CoSb}_{3-x}$. This assignment was based on the analysis of charge density maps obtained from synchrotron x-ray diffraction measurements carried out both at room temperature and at 155°C. Accordingly, the guest Sb atoms in $\text{Sb}_x\text{CoSb}_{3-x}$ shift from the 12d ($x,0,0$) site of $\text{Im}^3$ space group (in a position distant about 0.35 Å from the center of the cages), at room temperature, to the 2a ($0,0,0$) site (i.e., to the center of the cages) above 150°C. An exothermic event starting at 180°C is the thermal signature of the desinsertion of guest Sb atoms from the $\text{Sb}_x\text{CoSb}_{3-x}$ skutterudite cages, as confirmed by x-ray diffraction analysis and further verified by electrical measurements. After heating to 350°C, $\text{Sb}_x\text{CoSb}_{3-x}$ samples fully convert back to $\text{CoSb}_3$. The Sb desinsertion reaction from $\text{Sb}_x\text{CoSb}_{3-x}$ follows a first order kinetics, with a transition enthalpy of approximately 21 kJ/mol and an activation energy of 83 kJ/mol.


I. INTRODUCTION

For some time now, skutterudite compounds have been considered as potential candidates for thermoelectric materials with high figure of merit.¹–¹¹ These compounds exhibit cubic crystal structures, with space group $\text{Im}^3$ and general formula $\text{M}_x\text{x}_3$, where M is a transition metal (Co, Fe, Ir, Rh) occupying site 8c and X = P, As or Sb (site 24 g). The symbol $\square$ represents a vacancy (situated into a cage formed by the atoms in the 8c and 24 g sites), which can be empty or partially occupied by alkaline earth or lanthanide ions.¹–⁵ To be a useful thermoelectric material, it must have a large thermoelectric figure of merit, defined as $ZT = \frac{x^2}{\kappa}T/\rho k$, where $x$ is the Seebeck coefficient, $\rho$ is the electrical resistivity, $k$ is the thermal conductivity, and $T$ is the absolute temperature. Relatively large $ZT$ values, around 2.5 at room temperature, have been obtained for nanostructured thermoelectric materials.⁵ By filling the cages in the skutterudite structure with elements that are loosely bound to the framework and are able to rattle around the equilibrium position, one have an efficient phonon-scattering mechanism that reduces significantly the lattice thermal conductivity, thus increasing the figure of merit.⁵–⁹,¹² Recently, a kind of self-insertion reaction induced by high pressure was observed for the compound $\text{CoSb}_3$.¹⁰,¹¹ In fact, at room temperature and above about 20 GPa, cobalt antimonide undergoes an irreversible isosymmetric transition to a phase with molar volume at ambient pressure greater than that of pristine $\text{CoSb}_3$. This anomalous behavior was interpreted as a pressure-induced self-insertion reaction, in which antimony atoms from the $\text{CoSb}_3$ framework collapses and partially fills the cages formed by Sb and Co atoms. From now on, the phase obtained by self-insertion of Sb into the cages of $\text{CoSb}_3$ will be referred to as $\text{Sb}_x\text{CoSb}_{3-x}$. This self-insertion reaction was also observed at lower pressures and moderate temperatures in experiments carried out in a toroidal high pressure cell. Also, further evidence of this transition has been provided by Matsui et al. in a recent study of the pressure behavior of $\text{TSb}_3$ ($T = \text{Co, Rh, and Ir}$).¹³

In this work, samples of $\text{Sb}_x\text{CoSb}_{3-x}$ were produced at high pressure and high temperature aiming to obtain further insight on the nature of the guest atom. Also, the change with temperature of the crystallographic site occupied by the atoms that collapses into the skutterudite cages was explored by means of model-independent charge density maps derived from synchrotron radiation x-ray powder diffraction data. In fact, in spite we already referred to the high pressure phase as $\text{Sb}_x\text{CoSb}_{3-x}$, conclusive evidence that Sb atoms actually

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collapse to the interior of the CoSb$_3$ cages under high pressure will be provided by Bader’s analysis of the charge density distribution of the high pressure phase, as will be described in this work. Furthermore, to study the inverse reaction, i.e., the desinsertion of guest atoms from the cages of the Sb$_x$CoSb$_{3-x}$ skutterudite, samples prepared at high pressure and high temperature were studied at ambient pressure by x-ray powder diffraction, differential scanning calorimetry analysis, and electrical resistivity measurements, both in situ and after heating up to 350 °C.

II. EXPERIMENTAL PROCEDURE

The samples of CoSb$_3$ used in this work were prepared from the elements as described in previous works.$^{11,14}$ Five different samples of Sb$_x$CoSb$_{3-x}$ were prepared from CoSb$_3$ in a toroidal-type chamber assembled in a 400 ton hydraulic press. Sample #1 was prepared by submitting CoSb$_3$ to 7.7 GPa and 550 °C for 20 min. Samples #2, #3, #4, and #5 were produced from CoSb$_3$ pre-treated at 2.5 GPa, and 500 °C for 60 min and then were submitted to 7.7 GPa and 550 °C for 60 min in an attempt to increase the relative amount of the Sb$_x$CoSb$_{3-x}$ phase. Despite all efforts in obtaining single phase Sb$_x$CoSb$_{3-x}$ samples, this has proven to be unfeasible within the limits of pressure imposed by the toroidal high pressure cell used in this work. In fact, at least two parallel reactions occur when CoSb$_3$ samples are submitted to 7.7 GPa and 550 °C. The first one is the self-insertion reaction already mentioned before. The second one is the decomposition reaction CoSb$_3$ → CoSb$_2$ + Sb, which leaves some contaminant phases (CoSb$_2$ and Sb) present in the samples. The results obtained so far suggest that to produce a sample of Sb$_x$CoSb$_{3-x}$ free of contaminant phases, it would be necessary to submit CoSb$_3$ samples to pressures higher than 7.7 GPa, while keeping the temperature below 550 °C. As we shall see, the free Sb from the decomposition of CoSb$_3$ also contributes to form Sb$_x$CoSb$_{3-x}$ at high pressure and high temperature. The phase composition and Sb$_x$CoSb$_{3-x}$ lattice parameter for the samples used in this work were determined by Rietveld analysis of their x-ray powder diffraction patterns at ambient conditions and are given in Table I.

X-ray powder diffraction patterns were collected using a Shimadzu 6000 diffractometer, with Cu Kα radiation (λ = 0.15404 nm), in the angular range from 12° to 56° (2θ), with a step size of 0.05° and 4 s integration time. The diffractometer was equipped with Soller slits in the incident and diffracted beams, an 1° divergence slit, a 0.30 mm receiving slit, and a graphite monochromator in the diffracted beam.

Further angle-dispersive x-ray diffraction measurements of Sb$_x$CoSb$_{3-x}$ were carried out in the x-ray powder diffraction (XPD) beamline at D10B in the Laboratório Nacional de Luz Síncrona (LNLS) (Campinas, Brazil).$^{15}$ In this experiment, synchrotron radiation was monochromatized by a double-bounce Si(111) monochromator. The wavelength (λ = 0.123 857 nm) was determined from the analysis of the Bragg peaks from a sample of silicon standard (NIST SRM640c). The measurements were performed in θ − 2θ geometry, employing a Ge(111) crystal analyzer installed in front of a scintillation detector. Step-scan data were collected over the angular range between 10° and 120° (2θ). The samples, mounted on an aluminum sample holder for measurements at room temperature and on a copper sample holder for measurements at 155 °C, were attached to a goniometer head with four adjustable axes on a Huber 4-circle diffractometer. Measurements at 155 °C and 10$^{-5}$ Pa were carried out with a commercial closed-cycle He cryostat with vibration damping and temperature control. Structural parameters were obtained by Rietveld analysis of the x-ray powder diffraction patterns using the computer program Fullprof.$^{16,17}$ Charge density distribution of Sb$_x$CoSb$_{3-x}$ was determined by the maximum-entropy method (MEM) using the MEM-based pattern fitting (MPF) method, with the programs Rietan-FP and PRIMA.$^{18,19}$ Split pseudo-Voigt functions were used to fit Bragg peaks and the peak profile was calculated within 15 ± FWHM (full width at half maximum) of peak position. A Legendre polynomial was fitted to background intensities with 10 adjustable parameters.$^{21}$ The unit cell was divided into 100 × 100 × 100 pixels for MPF calculations. In this iterative procedure, the charge density distribution is first calculated from a set of structure factors obtained from Rietveld refinement of the x-ray diffraction pattern. The structural parameters of CoSb$_3$ were used as a starting point for the iterative MPF calculations to avoid any bias toward a pre-defined structural model for Sb$_x$CoSb$_{3-x}$. The refinement proceeds by calculating the charge density distribution compatible with the set of structure factors that maximize information entropy. A new set of structure factors is thus calculated from this charge density distribution, and this iterative procedure goes on until convergence is achieved. The three-dimensional charge density distribution was visualized as isosurfaces with the computer program VESTA.$^{23}$ An estimate of the electronic charge of the guest atom inside the high pressure and high temperature skutterudite cages was obtained from the maximum-entropy charge density distribution according to Bader’s theory of atoms in molecules.$^{24}$

A total of 215 structure factors were extracted from the x-ray powder diffraction data, and these were used in the MPF analysis. This relatively small set of structure factors (which was limited by the experimental conditions available at the D10B beamline in the LNLS) imposes a severe limitation on the precise determination of the charge of the guest atom inside the cages of the high pressure phase and also on the detailed mapping of the charge distribution in

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**TABLE I. Phase composition and Sb$_x$CoSb$_{3-x}$ lattice parameter and 2a site fractional occupancy for samples #1 to #5. The figures in parentheses are the uncertainties in the last significant digit.**

<table>
<thead>
<tr>
<th>Sample #</th>
<th>CoSb$_3$ (wt%)</th>
<th>CoSb$_2$ (wt%)</th>
<th>Sb$<em>x$CoSb$</em>{3-x}$ (wt%)</th>
<th>a (Å)</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13(1)</td>
<td>2(1)</td>
<td>85(4) 9.127(4) 0.72(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5(1)</td>
<td>5(2)</td>
<td>90(6) 9.125(1) 0.59(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7(1)</td>
<td>12(1)</td>
<td>81(3) 9.126(1) 0.63(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>9(1)</td>
<td>15(2)</td>
<td>76(4) 9.1265(5) 0.68(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>9(1)</td>
<td>18(2)</td>
<td>73(2) 9.127(1) 0.67(6)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Sb, CoSb3−x. Despite these limitations, the synchrotron x-ray powder diffraction data has enough quality as for a conclusive identification of the atom collapsed to the interior of the CoSb3 cages under high pressure. The XPD data also allowed the study of the effect of temperature on the position of the guest atom inside the skutterudite cages.

The desinsertion reaction Sb, CoSb3−x → CoSb3 was followed in situ by differential scanning calorimetry analysis (DSC), which was performed with a TA Instruments Q2000 heat flux calorimeter. The Sb, CoSb3−x sample was placed into a sealed aluminum pan on the sample furnace of the calorimeter and scanned from 10°C up to 380°C, at a heating rate of 10°C/min, using argon as purge gas. The reaction order and activation energy of the desinsertion reaction was estimated by the method of Borchardt and Daniels. Reaction enthalpies and activation energies were corrected for the actual amount of Sb, CoSb3−x present in the samples, as determined by Rietveld analysis of their x-ray diffraction patterns. Electrical resistivity was measured using a four-point technique suitable for cylindrical samples with high thickness-to-diameter ratio.

III. RESULTS AND DISCUSSION

Figure 1 shows synchrotron radiation x-ray powder diffraction patterns of pristine CoSb3 and Sb, CoSb3−x (sample #1) at room temperature. The Sb, CoSb3−x phase is characterized by the displacement of cobalt antimonide Bragg peaks toward lower angles and by the reduction of the intensity of 110, 200, and 211 Bragg peaks. The separation of Bragg peaks from CoSb3 and Sb, CoSb3−x, can be better appreciated in the inset of Fig. 1(a), while the reduction of the intensity of 110, 200, and 211 Bragg peaks can be seen in the inset of Fig. 1(b).

Besides the product from the self-insertion reaction, CoSb3 → Sb, CoSb3−x, one should note in the powder pattern shown in Fig. 1(b) the presence of CoSb2 resultant from a parallel decomposition reaction, CoSb3 → CoSb2 + Sb. However, there is no evidence of free Sb from the decomposition reaction in the x-ray powder diffraction pattern shown in Fig. 1(b). This observation suggests that the Sb resulting from decomposition of CoSb3 at high pressure and high temperature may also be inserted into the cages of cobalt antimonide, thus forming some fraction of the Sb, CoSb3−x phase present in the sample. A similar behavior was previously observed with tin. Nevertheless, it must be stressed that the insertion reaction of CoSb3 with free Sb cannot account for all Sb, CoSb3−x formed at high pressure and high temperature, as the amount of the latter in our samples is much greater than it would be expected solely on the basis of the insertion reaction with free Sb formed from CoSb3 decomposition. Also, the amount of free Sb present in the as-synthesized CoSb3 is actually very small (less than 2%wt), as inferred from Rietveld analysis of data shown in Fig. 1(a).

Furthermore, in experiments conducted with CoSb3 (and related compounds) at high pressure and room temperature, Sb, CoSb3−x is observed with no apparent contamination from CoSb2. As we shall see, Bragg peaks from free Sb formed by decomposition of CoSb3 will be identified in the x-ray powder diffraction pattern of samples previously rich in Sb, CoSb3−x, after heating to temperatures high enough to promote the desinsertion reaction.

The room temperature CoSb3 lattice parameter [a0 = 9.036(2) Å] is in good agreement with literature. On the other hand, the Sb, CoSb3−x lattice parameter is about 0.011 Å smaller than previously reported. The Sb, CoSb3−x lattice parameter varies with the actual value of x for each sample. However, the origin of the above-mentioned discrepancy is mainly due to the fact that in our previous work, based on conventional x-ray powder diffraction data, we supposed that the sample consisted of a mix of two Sb, CoSb3−x phases with distinct 2a site occupancies (two different values of x) and, thus, two slightly distinct lattice parameters. The improved resolution and overall quality of the synchrotron radiation XPD data, shown in Fig. 1, now
allows us to conclude that the samples obtained by processing cobalt antimonide at high pressure and high temperature actually consists of \(\text{Sb}_x\text{CoSb}_3\), some unmodified \(\text{CoSb}_3\) and \(\text{CoSb}_2\). The refinement of XPD data under this assumption leads to a slightly smaller \(\text{Sb}_x\text{CoSb}_{3-x}\) lattice parameter.

Charge density distribution analysis was performed with synchrotron radiation x-ray diffraction data taken at room
temperature for sample #1, according to the MEM-based pattern fitting approach. The evolution of the MPF analysis is shown in Fig. 2. Starting from above, Fig. 2(a) shows the result of a Rietveld analysis in which the high pressure phase \( \text{Sb}_x \text{CoSb}_3 \), was refined using a structural model identical to that of \( \text{CoSb}_3 \), i.e., with empty cages around the Im\(^3\) 2a (0,0,0) site in the skutterudite structure and no vacancies in the framework. One should note the significant difference between experimental and calculated patterns, shown as a red solid line at the bottom. The inset in Fig. 2(a) shows the regression between experimental and calculated patterns, shown as a red line, as the MPF analysis converges with a clear improvement in the agreement between experimental and calculated diffraction patterns, as shown in Fig. 2(b). The 3D charge density distribution, shown in the inset of Fig. 2(b), now exhibits a non-spherical charge buildup around the 2a (0,0,0) site. It worth to emphasize that this charge buildup around the 2a site resulted from a model-independent iterative MPF analysis which started from a charge density distribution calculated for \( \text{Sb}_x \text{CoSb}_3 \) with empty cages (i.e., from \( \text{CoSb}_3 \), with no bias toward charge accumulation at the center of the cages).

The MPF analysis of synchrotron radiation x-ray diffraction data for the skutterudite phase produced at high pressure and high temperature thus provides further evidence that this phase is formed by the collapse of some atoms from the framework into the cages of the \( \text{CoSb}_3 \) structure. Moreover, the non-spherical shape of the charge density distribution near the center of the cage suggests that, at ambient conditions, the collapsed atom may actually occupy a site near the center of the cage, other than the 2a site.

Accordingly, in order to accelerate the convergence of the iterative MPF process and also to improve the overall agreement between the experimental and calculated synchrotron x-ray diffraction powder patterns, a new MPF analysis was started with a set of structure factors derived from Rietveld analysis of the powder data in which the structure of the high pressure and high temperature phase has guest Sb atoms partially occupying the general site 48 h (x,y,z) near the center of the cage (the Co and Sb atoms in the framework were kept at the 8c and 24 g sites of Im\(^3\) space group, respectively, the latter partially occupied). The structure factors from this Rietveld analysis were taken again as the starting point for a model-free MPF iterative procedure. Figure 2(c) shows the result after convergence of the MPF calculation. Besides the appreciable improvement in reproducing the experimental results, the charge density distribution shown in the inset of Fig. 2(c) now exhibits a set of six maxima off the center of the cage. The total charge inside the cage depicted in the inset of Fig. 2(c), obtained from the sum over the atomic basins in the charge density distribution determined by Bader’s analysis, amounts to approximately 50.6e. This strongly suggests that Sb atoms from the framework indeed collapses to the interior of the \( \text{CoSb}_3 \) cages, forming a high pressure and high temperature phase that can be retained at ambient conditions, thus giving support to our previous identification of this phase as \( \text{Sb}_x \text{CoSb}_3 \).
heated to 170°C, but the $Sb_2CoSb_{3-x}$ lattice parameter remains identical within the uncertainty of measurement. In situ measurements of electrical resistivity at high temperature revealed no abrupt change within the temperature range of the first event observed on DSC analysis (i.e., up to 180°C). All these observations are in accordance with the results from DSC. Indeed, the first heating to 170°C may provide enough thermal energy to promote a small fraction of the guest Sb atoms out of the cages. The desinsertion of a small fraction of the guest Sb atoms from $Sb_2CoSb_{3-x}$ may be responsible for the slight reduction of the integrated intensity of the endothermic peak in the second DSC run and, also, for the small increase of room temperature electrical resistivity in samples previously heated to 170°C. On the other hand, for the sample previously heated above 180°C, the room temperature electrical resistivity increases toward that of CoSb3, as a consequence of the progress of the desinsertion reaction. It is worth noting the almost twenty-fold increase in room temperature electrical conductivity in going from CoSb3 to $Sb_2CoSb_{3-x}$, which prompts for measurements of thermal conductivity and Seebeck coefficient in order to assess the thermoelectric figure-of-merit for this promising high pressure phase.

To further investigate the nature of the first endothermic event observed in the DSC signal of samples rich in the $Sb_2CoSb_{3-x}$ phase, charge density distribution analysis was performed with synchrotron radiation x-ray diffraction data taken at 155°C (sample #5). The result of the MPF analysis can be seen in Fig. 2(d). The charge density distribution associated to the guest Sb atom is now evenly spread over about 0.5 Å from the center of the cage, along six equivalent directions. One possible explanation for the shape of the charge density distribution shown in the inset of Fig. 2(d) is that at high temperature, before the onset of the desinsertion reaction, the guest Sb atoms jump from the $12d$ ($x,0,0$) to the $2a$ $(0,0,0)$ site. At the center of the cages, the guest Sb atoms oscillate with high amplitude along the directions dictated by the anisotropic potential to which they are submitted, as the result of the remnant defects on the cage walls. In other words, above 150°C the guest Sb anisotropic atomic displacement around the equilibrium position at the center of the cage should be very asymmetric and should be oriented along the line that goes from the center of the cage to the defect in the wall left by the atom that collapsed in the self-insertion reaction. The random distribution of these defects among six equivalent directions pointing from the center of the cage thus gives rise to the guest Sb charge distribution

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**TABLE II.** Room temperature lattice parameter and electrical resistivity for polycrystalline samples of CoSb3 and $Sb_2CoSb_{3-x}$, this latter previously heated to $T_{max}$. The figures in parentheses are the uncertainties in the last significant digit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{max}$ (°C)</th>
<th>CoSb3 a(Å)</th>
<th>Sb2CoSb3 a(Å)</th>
<th>$\rho$ ($\mu$Ω·m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#4</td>
<td>RT</td>
<td>–</td>
<td>9.125(1)</td>
<td>45(4)</td>
</tr>
<tr>
<td>#4</td>
<td>170</td>
<td>–</td>
<td>9.124(2)</td>
<td>76(5)</td>
</tr>
<tr>
<td>#4</td>
<td>400</td>
<td>9.038(5)</td>
<td>–</td>
<td>523(6)</td>
</tr>
<tr>
<td>CoSb3</td>
<td>RT</td>
<td>9.033(9)</td>
<td>–</td>
<td>818(4)</td>
</tr>
</tbody>
</table>

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Fig. 4. (Color online) Conventional XRD patterns of sample #3 previously heated at different temperatures and comparison with pristine CoSb3. The inset (in which the XRD patterns are ordered in the same way as in the main graph) shows the disappearance of the 310 Bragg peak from the $Sb_2CoSb_{3-x}$ phase in the XRD data for the sample previously heated to 350°C. The presence of a minor contamination from $Sb_2O_3$ is due to residual oxygen in the purge gas used in the thermal treatment of the sample.
depicted in the inset of Fig. 2(d). The reversible transition of the guest Sb atom from the 12d to the 2a site thus should account for the endothermic peak in the DSC signal at about 150 °C.

IV. CONCLUSIONS

The skutterudite phase obtained by processing CoSb$_3$ at 7.7 GPa and 550 °C was studied by means of conventional and synchrotron radiation x-ray diffraction, DSC and electrical resistivity measurements. The analysis of the charge density distribution for the high pressure and high temperature phase allowed its unambiguous identification as Sb$_{x}$CoSb$_{3-x}$. Attempts to refine this defect structure according to space group Im$\overline{3}$ have lead to the conclusion that, at room temperature, the guest Sb atoms partially occupy the 12d site, 0.35 Å off the center of the cage in the skutterudite framework. The desinsertion reaction Sb$_{x}$CoSb$_{3-x} \rightarrow$ CoSb$_3$ at room pressure follows a first-order kinetics, with an onset temperature near 180 °C. The desinsertion reaction is preceded by an endothermic event that was related to the displacement of the guest Sb atoms from the 12d site toward the center of the cage. The room temperature electrical resistivity for samples rich in the self-insertion phase is about 20 times smaller than that of polycrystalline CoSb$_3$. This suggests that measurements of thermal conductivity and Seebeck coefficient should be performed to evaluate the potential of Sb$_{x}$CoSb$_{3-x}$ as a high performance thermoelectric material.

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