



HAL
open science

Reaction mechanism and thermoelectric properties of $\text{In}_{0.22}\text{Co}_4\text{Sb}_{12}$ prepared by magnesiothermy

Sylvain Le Tonquesse, Eric Alleno, Valérie Demange, Carmelo Prestipino,
Olivier Rouleau, Mathieu Pasturel

► **To cite this version:**

Sylvain Le Tonquesse, Eric Alleno, Valérie Demange, Carmelo Prestipino, Olivier Rouleau, et al..
Reaction mechanism and thermoelectric properties of $\text{In}_{0.22}\text{Co}_4\text{Sb}_{12}$ prepared by magnesiothermy.
Materials Today Chemistry, 2020, 16, pp.100223. 10.1016/j.mtchem.2019.100223 . hal-03048178

HAL Id: hal-03048178

<https://univ-rennes.hal.science/hal-03048178v1>

Submitted on 9 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Reaction mechanism and thermoelectric properties of $\text{In}_{0.22}\text{Co}_4\text{Sb}_{12}$ prepared by magnesiothermy

Sylvain Le Tonquesse^a, Éric Alleno^b, Valérie Demange^a, Carmelo Prestipino^a,
Olivier Rouleau^b, Mathieu Pasturel^a,

^aUniv Rennes, CNRS, Institut des Sciences Chimiques de Rennes - UMR6226, F-35000, Rennes, France

^bUniversité Paris-Est, Institut de Chimie et des Matériaux Paris-Est, UMR 7182 CNRS - UPEC, 2 rue H. Dunant, 94320 THIAIS, France

Abstract

The magnesiothermy synthesis of $\text{In}_{0.22}\text{Co}_4\text{Sb}_{12}$ with high In-rattler concentration from Sb_2O_4 and In-doped Co_3O_4 precursors is reported. This process directly yields a submicronic powder in a single step of 96 h at 810 K. The reaction mechanism has been investigated by stopping the reaction every 12 h and quantifying the existing phases by X-ray diffraction and Rietveld refinements. The precursors are first reduced in CoO and Sb_2O_3 lower oxides, then form CoSb_2O_6 and CoSb_2O_4 intermediates which are finally reduced in $\text{In}_x\text{Co}_4\text{Sb}_{12}$. A powder with 350 nm average size and mostly composed of In-filled skutterudite phase with composition close to $\text{In}_{0.17}\text{Co}_4\text{Sb}_{12}$ is obtained. Upon spark plasma sintering, small residual amount of InSb reacts with the skutterudite matrix to form a single-phase densified pellet with composition close to $\text{In}_{0.22}\text{Co}_4\text{Sb}_{12}$. The resulting densified material with 1.8 μm average grain size shows a figure-of-merit ZT_{max} of 0.95 at 750 K.

Keywords: Skutterudites; Magnesiothermy synthesis; Reaction mechanism; Thermoelectric properties.

*mathieu.pasturel@univ-rennes1.fr; Institut des Sciences Chimiques de Rennes, Campus de Beaulieu, bat. 10A, 263 avenue Général Leclerc, 35042 Rennes Cedex, France

1. Introduction

Thermoelectric (TE) materials enable the direct conversion of heat into electricity through the Seebeck effect. The conversion efficiency is directly related to the figure-of-merit ZT defined as:

$$ZT = \frac{\alpha^2}{\rho (\kappa_L + \kappa_e)} T \quad (1)$$

with α the Seebeck coefficient, ρ the electrical resistivity, κ_L and κ_e the lattice and electronic contributions to the total thermal conductivity κ and T the temperature. CoSb₃-based skutterudites are well-known TE materials with a band gap of about 0.2 eV [1]. They are considered as promising candidates for mid-temperature (600 - 800 K) TE applications because of their excellent electronic properties, good mechanical properties and relatively abundant constituting elements. Large power factors, $PF = \alpha^2/\rho$, reaching 4 - 5 mW m⁻¹ K⁻² can be obtained for compositions with optimized charge carrier concentration. In order to achieve high ZT , the intrinsic high thermal conductivity (≈ 9 W m⁻¹ K⁻¹ at 298 K for CoSb₃ [2]) must be reduced as much as possible without simultaneously degrading the electronic properties. This can be effectively done by partially filling the empty isocahedral voids of the structure with rare-earth, alkaline metal or III - IV group elements [1]. The additional mass contrast induced by the partial occupancy as well as the ‘rattling’ behavior of the filling atoms in the oversized voids effectively scatter acoustic heat-carrying phonons. For example, lattice thermal conductivities as low as 1 - 2 and ≈ 0.5 W m⁻¹ K⁻¹ were reported for single Ba-, Ca- and Yb-filled [3, 4, 5] and nanostructured multi-filled skutterudites [6], respectively.

Indium is among the most studied filler atom for n -type skutterudites because (i) it acts as an electron donor enabling large increase of PF and (ii) it

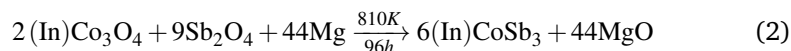
25 efficiently reduces κ_L due to its heavy atomic mass. While some controversy ex-
26 ists about its true solubility limit ($0.16 < x < 0.27$) [7, 8, 9], all authors agree
27 that the best performances are obtained by maximizing the In concentration
28 [2, 10]. ZT_{max} of about 1.1 are usually reported for materials with composi-
29 tion close to $\text{In}_{0.25}\text{Co}_4\text{Sb}_{12}$ and synthesized by conventional fusion/solidification
30 processes [11, 2]. However, due to the peritectic formation of CoSb_3 , long an-
31 nealing (> 100 h) at high temperature (1100 K) are required to form a single
32 phase product. In addition, the ingots are composed of microns sized grains
33 which need to be reduced by milling in order to reduce κ_L . κ reduction were
34 attempted using such conventional approach by *in situ* formation of InSb nano-
35 precipitates [12, 13, 14] or by designing mesostructured materials with oxide
36 nanoinclusions [11, 15]. These additional annealing and milling steps, to be
37 performed under unreactive atmosphere, cost time and energy cost and could
38 become an obstacle to the large scale production of this material.

39

40 Alternative processes have been developed to overcome the problematic syn-
41 thesis of this material. For example, hydrothermal [16, 17] or melt-spinning/reactive
42 spark plasma sintering approaches [18] have been adapted to the synthesis of
43 nanostructured $\text{In}_x\text{Co}_4\text{Sb}_{12}$ with high concentration of interfaces between the
44 grains and lattice thermal conductivity as low as $1.5 \text{ W m}^{-1} \text{ K}^{-1}$. Most im-
45 portantly, these alternative routes do not require any post-reaction annealing
46 which considerably speed up the synthesis. However, nanostructured materi-
47 als often suffer from largely higher electrical resistivity usually attributed to the
48 lower density of the sintered materials [19, 16] or to the enhanced charge car-
49 riers scattering at the numerous interfaces/defects, considerably reducing the
50 beneficial effect of the microstructure on ZT .

51 In a previous article [20], we reported a new magnesio-reduction synthesis

52 for $\text{In}_x\text{Co}_4\text{Sb}_{12}$ with $x = 0.13$ according to the reaction:



53 This process, also applied to the production of TE-silicides [21], possesses
54 many advantages such as the direct synthesis of high purity skutterudite pow-
55 ders with submicronic average grain sizes without additional long annealing or
56 milling step, high yield, relatively low reaction temperature and the use of cheap
57 and air-stable oxide precursors. Moreover, magnesiothermy is already used to
58 industrially produce metals via the Kroll [22] or Ames [23] processes and of-
59 fer thus interesting scalability perspectives. In the present article, this magne-
60 sioreduction process is adapted to the synthesis of saturated $\text{In}_{0.22}\text{Co}_4\text{Sb}_{12}$. The
61 discussion will mainly focus on the comprehension of the reaction mechanism
62 which was investigated by X-ray diffraction (XRD). Finally, the thermoelectric
63 properties were measured and compared to those of reference samples from the
64 literature.

65 2. Experimental procedures

66 The detailed procedure for the magnesio-reduction synthesis of In-filled skut-
67 terudites according to reaction (2) is described in a previous work [20]. For
68 preparation of the ' $\text{In}_{0.18}\text{Co}_{2.81}\text{O}_4$ ' precursor, stoichiometric amounts of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
69 (Prolabo, 99.9 %) and $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (home-made by dissolving In in concen-
70 trated HNO_3) are dissolved in distilled water and then precipitated using NaOH.
71 The precipitate is washed with water and ethanol several times, dried at 363 K
72 and calcined at 723 K for 4 h in air. XRD pattern (fig. SI 1) shows broad diffrac-
73 tion peaks corresponding to Co_3O_4 and In_2O_3 . Rietveld refinement converges to
74 a lattice parameter $a = 8.137(9)$ Å significantly larger than for pristine Co_3O_4
75 ($a = 8.076$ Å [24]) suggesting the insertion of In in the structure [25]. The pres-

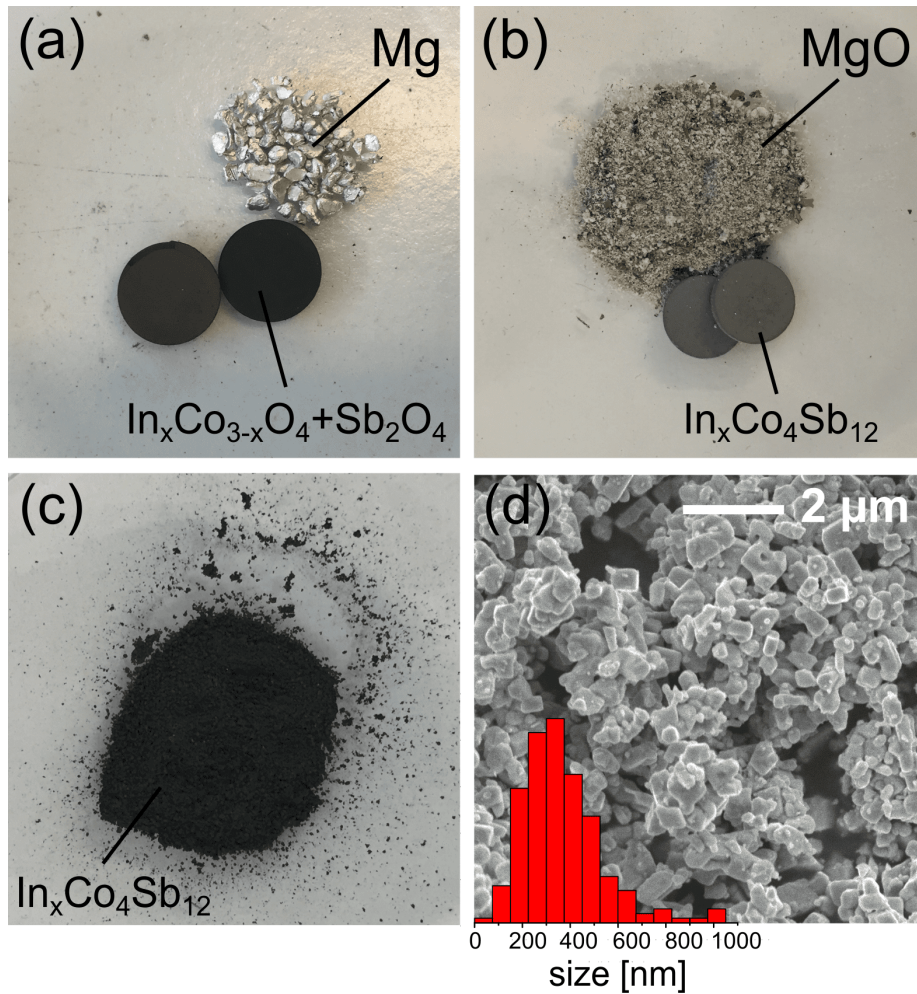


Figure 1: Pictures of (a) the reaction precursors, (b) reaction products after 96 h at 810 K and (c) crushed as-synthesized $\text{In}_x\text{Co}_4\text{Sb}_{12}$ pellets. (d) Secondary electron SEM image of the as-synthesized powder with histogram showing the grain size distribution.

76 ence of remaining In_2O_3 indicates that the solubility limit has been reached. A
 77 mixture of this precursor and Sb_2O_4 (Sigma-Aldrich, 99.995 %) with 1:5.4 mo-
 78 lar composition, required to counterbalance the loss of antimony by evaporation
 79 during the MR process and obtain phase pure samples [20], is thoroughly milled
 80 in an agate mortar. The oxide mixture is cold-pressed at 250 MPa into Ø 10 mm
 81 pellets with about 2 mm height (fig. 1a). The pellets (usually 2 stacked on top

82 of each other) are placed with Mg chunks (2 - 3 % excess) in a clamped Mo
83 crucible. The crucible is heated to 810 K for 96 h under protective Ar atmo-
84 sphere before being cooled down to room temperature. After the reaction, the
85 skutterudite remains in the shape of compact pellets and can easily be separated
86 from the loose MgO (fig. 1b). The powder (fig. 1c,d) is then spark plasma sin-
87 tered (FCT HP-D-10 system) in \varnothing 10 mm graphite dies at 1000 K and 66 MPa
88 for 10 min.

89 Powder X-ray diffraction was performed on a Bruker D8 Advance diffrac-
90 tometer in the θ - 2θ Bragg-Brentano geometry working with a monochroma-
91 tized Cu $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$), equipped with a LynxEye detector
92 which enables photon energy discrimination around 20 %, thus reducing the
93 cobalt fluorescence signal. Lattice parameters and phase fractions were deter-
94 mined by the Rietveld method using the FullProf software [26]. Scanning elec-
95 tron microscopy (SEM) images and energy dispersive spectroscopy (EDS) were
96 performed on a JEOL JSM 7100 F microscope equipped with an Oxford EDS
97 SDD X-Max spectrometer. Transport properties measurements were carried out
98 using a home-made apparatus described elsewhere [27]. Thermal diffusivity
99 measurements were performed using a Netzsch LFA 457 equipment under Ar
100 atmosphere. The thermal conductivity was determined from $\kappa = D C_p d$ with
101 D the thermal diffusivity, C_p the specific heat of the sample calculated using
102 the Dulong-Petit law and d the sample density determined by the Archimede
103 method in absolute ethanol.

104 **3. Results and discussion**

105 **3.1. Reaction mechanism and skutterudite characterizations**

106 $\text{In}_x\text{Co}_4\text{Sb}_{12}$ (targeted $x = 0.25$) has been synthesized, along with some InSb
107 and Sb impurities, from Sb_2O_4 and In-doped Co_3O_4 after 96 h heat treatment

108 at 810 K in presence of Mg. To elucidate the reaction mechanism, the synthe-
 109 sis was repeated several times and stopped every twelve hours. Each time, the
 110 phases in the samples were quantified by the Rietveld method and their relative
 111 concentrations are represented in fig. 2. Figure 3 shows some selected XRD
 112 patterns while all refined patterns and parameters can be found in supplement-
 113 ary information (fig. SI 2, tables SI. 1 - 9). Up to 6 different phases have been
 114 identified in some patterns indicating a complex reaction mechanism. The full
 115 reduction of the precursors is realized in three steps: (i) the partial reduction
 116 of the precursors in lower oxides (0 h - 24 h), (ii) the formation of CoSb_2O_6
 117 and CoSb_2O_4 intermediates (0 h - 48 h) and (iii) the complete reduction of the
 118 intermediates and the formation of $\text{In}_x\text{Co}_4\text{Sb}_{12}$ (38 h - 96 h).

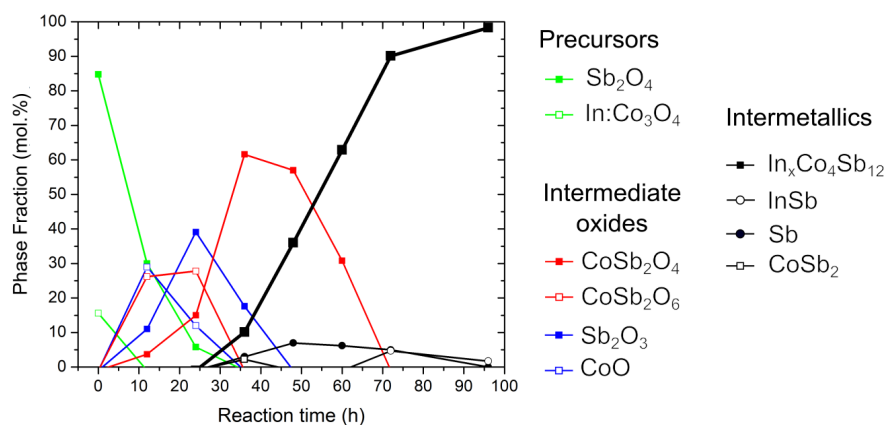


Figure 2: Evolution of the sample composition during the magnesio-reduction synthesis of $\text{In}_x\text{Co}_4\text{Sb}_{12}$, determined by the Rietveld method, as a function of the reaction time. In the present case and according to [28], the relative standard deviation on the concentrations are considered to be well below 5 %.

119 The precursors mixture is initially composed of Sb_2O_4 [Sb^{3+} , Sb^{5+}] and
 120 $\text{In:Co}_3\text{O}_4$ [Co^{2+} , Co^{3+}]. After 24 h at 813 K, $\text{In:Co}_3\text{O}_4$ and Sb_2O_4 almost com-
 121 pletely disappeared. Instead, freshly formed CoO [Co^{2+}] and Sb_2O_3 [Sb^{3+}] rep-
 122 resent almost 50 % of the reaction media. This suggests the partial reduction of

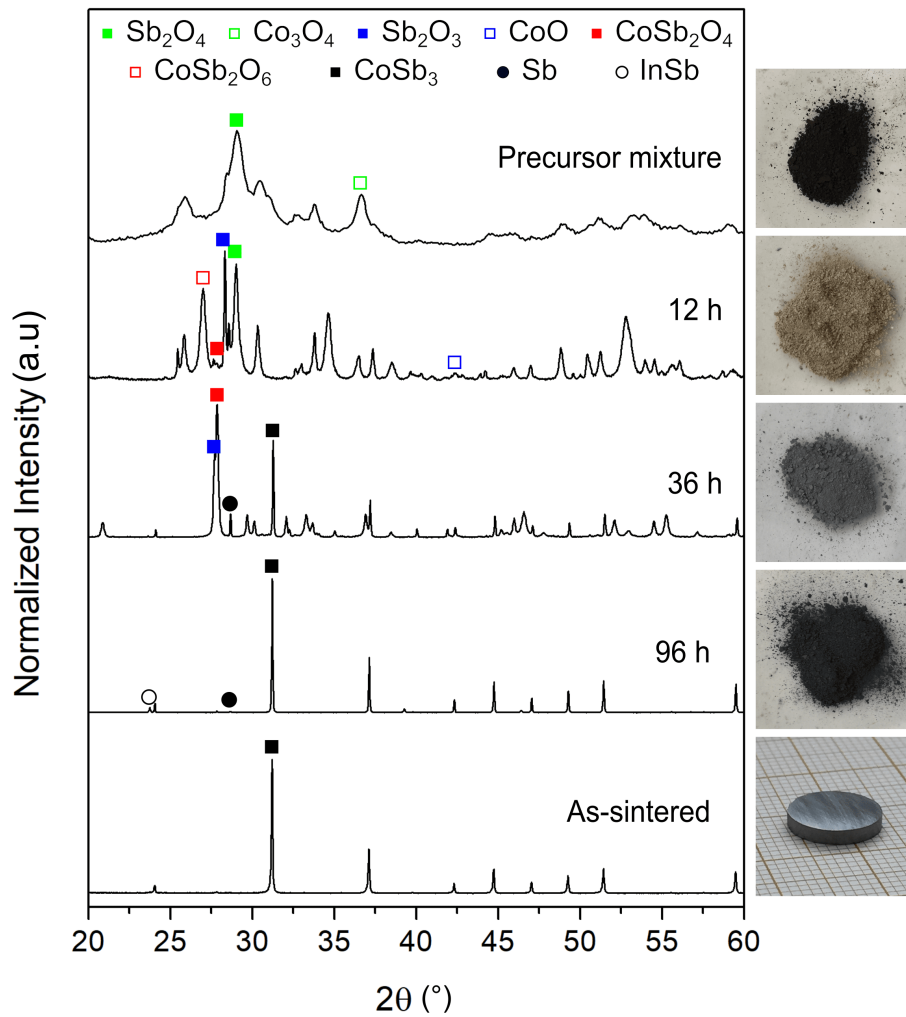


Figure 3: XRD patterns of the $\text{In}_x\text{Co}_4\text{Sb}_{12}$ magnesio-reduction synthesis after 0 h, 12 h, 36 h, 96 h reaction time and after spark plasma sintering. The symbols indicate the most intense reflections of each constituting phases. The images shows the evolution of the product color with the reaction time.

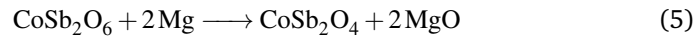
123 the precursors in lower oxides by Mg according to the reactions:





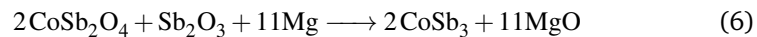
124 These reductions are thermodynamically possible at 810 K as indicated by
 125 the large negative Gibbs free energy of reaction. In addition, CoSb_2O_6 [Co^{2+} ,
 126 Sb^{5+}] ($P4_2/mnm$) and CoSb_2O_4 [Co^{2+} , Sb^{3+}] ($P4_2/mbc$) ternary intermediates
 127 are formed most likely by solid state reactions between the various binary ox-
 128 ides in presence. This is supported by several works reporting the synthesis of
 129 these mixed oxides by conventional solid-state reaction starting from CoO and
 130 $\text{Sb}_2\text{O}_3/\text{Sb}_2\text{O}_5$ powders between 973 and 1073 K [30, 31, 32].

131 After 36 h, no trace of CoSb_2O_6 remains in the XRD pattern (fig. 3) and
 132 CoSb_2O_4 is the major phase representing 60 mol.% of the sample. According to
 133 the simultaneous decrease of CoSb_2O_6 and increase of CoSb_2O_4 contents, one
 134 might expect CoSb_2O_4 to be formed from the reduction of CoSb_2O_6 according
 135 to:

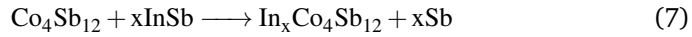


136 More interestingly, skutterudite starts forming ($\approx 10\%$) and the lattice pa-
 137 rameter $a = 9.0384(8) \text{ \AA}$ corresponds well to $\text{In}_x\text{Co}_4\text{Sb}_{12}$ with low In-content
 138 ($x < 0.05$) [7, 8]. At this point of the reaction, Sb^{5+} and Co^{3+} are no more
 139 present in the reaction media and Sb^{3+} and Co^{2+} are consecutively reduced in
 140 metallic Co and Sb.

141 The complete reduction of CoSb_2O_4 and Sb_2O_3 into CoSb_3 takes another 36
 142 hours according to:



143 Traces of InSb appear on the diffraction patterns after 72 h. We hypothesize
 144 that In was solubilized in CoSb_2O_4 because (i) the formation of InSb corre-
 145 sponds to the total reduction of CoSb_2O_4 , (ii) the refined lattice parameters of
 146 the latter, $a = 8.5078(5) \text{ \AA}$ and $c = 5.9316(5) \text{ \AA}$, are significantly larger than
 147 literature data, $a = 8.49285(7) \text{ \AA}$ and $c = 5.92449(5) \text{ \AA}$ [30] and (iii) other ele-
 148 ments such as Pb^{2+} can substitute Sb to a great extent in CoSb_2O_4 [30]. In pres-
 149 ence of InSb, the lattice parameter of In_xCoSb_3 increases from $9.0384(2) \text{ \AA}$ after
 150 48 h to $9.04872(4) \text{ \AA}$ after 96 h. This can be explained by the insertion of In in
 151 the CoSb_3 structure according to:



152 The slow diffusion of In in CoSb_3 was already stressed out by Grytsiv *et*
 153 *al.* [8]. After 96 h, the reaction media is mostly composed of $\text{In}_x\text{Co}_4\text{Sb}_{12}$ with
 154 $a = 9.04872(4) \text{ \AA}$ which corresponds to $x = 0.17 - 0.18$ [7, 8] and of a small
 155 amount of InSb ($\approx 4 \text{ mol.}\%$) and Sb ($\approx 2 \text{ mol.}\%$). No traces of MgO or Mg
 156 containing compound are visible at any time on the diffraction patterns. For this
 157 reason, we hypothesize that the reduction reactions occur *via* the slow oxidation
 158 of the Mg chunks by the equilibrium O_2 vapor pressure of the oxides. This is
 159 consistent with the general aspect of the Mg chunks between 24 h to 48 h which
 160 are clearly oxidized at the surface (powdery and white) but remain metallic and
 161 relatively shiny in the core.

162 The as-synthesized powder was spark plasma sintered to obtain pellets with
 163 97 % relative density. The XRD pattern of the as-sintered pellet (fig. 3) is
 164 fully indexed with the skutterudite structure type. Rietveld refinement results
 165 in a lattice parameter $a = 9.0527(2) \text{ \AA}$ which is significantly larger than that of
 166 the as-synthesized powder. Along with the disappearance of the InSb secondary
 167 phase, whose melting point (789 K) is lower than the sintering temperature, this

168 suggests that InSb reacts with the skutterudite matrix during the sintering step
 169 thus increasing the inserted In content. According to literature data, this lattice
 170 parameter corresponds to a true $\text{In}_x\text{Co}_4\text{Sb}_{12}$ composition close to $x = 0.20 - 0.22$
 171 [7, 8]. The scenario is very similar to the synthesis of $\text{In}_{0.13}\text{Co}_4\text{Sb}_{12}$ where about
 172 20 % of In was inserted in the structure during the sintering step [20].

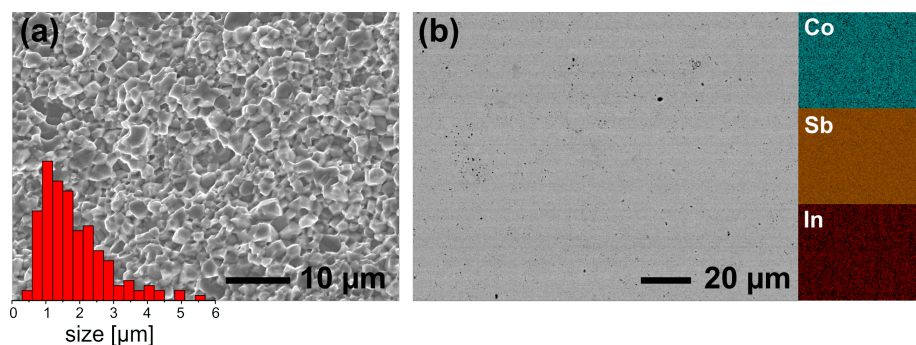


Figure 4: (a) Secondary electron SEM image of a broken cross-section of a densified $\text{In}_{0.22}\text{Co}_4\text{Sb}_{12}$ pellet and histogram showing the distribution of the apparent grain size. (b) Backscattered electron SEM image and corresponding EDS elementary mappings of the pellet polished surface.

173 Backscattered electron image and EDS mapping of the pellet (fig. 4b) reveal
 174 homogeneous chemical composition. Indium filling fraction could however not
 175 be accurately quantified by EDS because of its low concentration and the partial
 176 overlapping of the In L_α and the intense Sb L_α peaks. The magnesioreduc-
 177 tion synthesis of $\text{In}_{0.30}\text{Co}_4\text{Sb}_{12}$ was also attempted but InSb in excess leaked out
 178 of the die during sintering and the resulting skutterudite lattice parameter re-
 179 maind close to $a = 9.053 \text{ \AA}$. As a result, $\text{In}_{0.22}\text{Co}_4\text{Sb}_{12}$ would be the In-richest
 180 composition accessible by magnesioreduction synthesis in these reaction condi-
 181 tions. It is in agreement with the solubility limit usually reported for In-filled
 182 CoSb_3 prepared by conventional melting/annealing [8] or solid state diffusion
 183 [33] syntheses. The SEM secondary electron image of the broken cross-section
 184 of a pellet is shown in fig. 4a. The microstructure is typical for magnesiore-
 185 duced skutterudite with well-faceted grains and size distribution characterized

186 by an average value of $1.8 \mu\text{m}$. The present grain size is significantly larger than
 187 our previous work [20]. This is mostly attributed to the 90 K higher sintering
 188 temperature found necessary to complete the reaction. Also the higher content
 189 of liquid InSb might have favored grain growth by accelerating matter transport
 190 during the sintering [34].

191 3.2. Thermoelectric properties

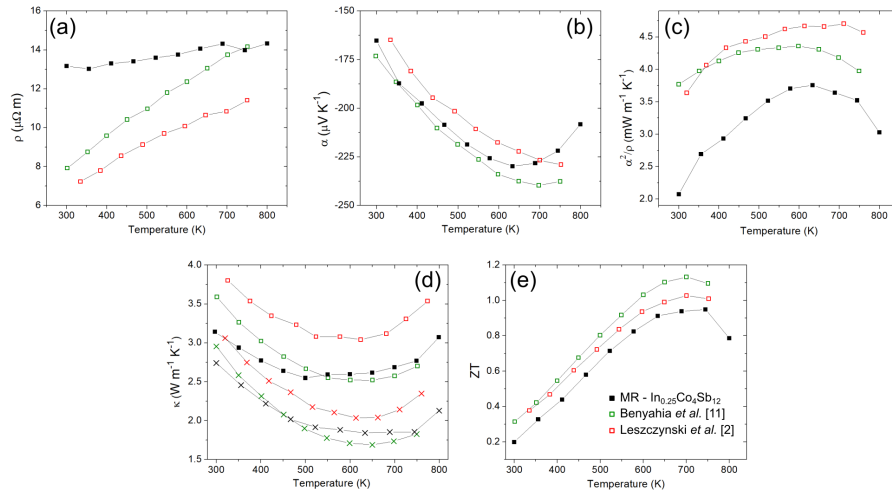


Figure 5: High-temperature dependence of (a) the electrical resistivity, (b) Seebeck coefficient, (c) power factor, (d) total (squares) and lattice (crosses) thermal conductivities and (e) figure-of-merit of $\text{In}_{0.22}\text{Co}_4\text{Sb}_{12}$ synthesized by magnesioreduction (filled black squares) along with literature data for $\text{In}_{0.25}\text{Co}_4\text{Sb}_{12}$ taken from [11] (green empty squares) and $\text{In}_{0.28}\text{Co}_4\text{Sb}_{12}$ taken from [2] (red empty squares).

192 The thermoelectric properties of $\text{In}_{0.22}\text{Co}_4\text{Sb}_{12}$ are shown in fig. 5 and com-
 193 pared to data from the literature on compounds with similar compositions. Data
 194 reported by Benyahia *et al.* [11] and Leszczynski *et al.* [2] were obtained for
 195 materials synthesized by melting/annealing/sintering method. Although the
 196 Seebeck coefficient of our sample compares well to literature data, the resistiv-
 197 ity is more elevated, especially near room temperature. As a direct consequence,
 198 the PF_{max} is 7 to 20 % lower at 750 K. Despite its apparent purity and density,
 199 small cracks appeared on our sample upon thermal cycles that could explain

200 the higher measured resistivity. Such deterioration is attributed to the melting
201 around 800 K [8] during the measurement cycle of small residual amount of
202 InSb usually observed at the grain boundaries of saturated In-filled skutterudite
203 [12, 35]. However, the In content in the structure remains constant as indi-
204 cated by the similar lattice parameter, $a = 9.0520(3) \text{ \AA}$, determined after the
205 thermoelectric characterization.

206 The room temperature thermal conductivity of MR sample is about $3.2 \text{ W m}^{-1} \text{ K}^{-1}$
207 and reaches its minimum value of $2.6 \text{ W m}^{-1} \text{ K}^{-1}$ in the 450 - 650 K range. The
208 simultaneous decrease of α and upturn of κ at about 650 K is attributed to
209 the bipolar effect *i.e.* to the contribution of two types of charge carriers to the
210 material transport properties. The lattice thermal conductivity was determined
211 by subtracting κ_e to κ and κ_e was calculated using the the Wiedemann-Franz
212 law $\kappa_e = L T/\rho$ with L taken from [2] as $1.7 \cdot 10^{-8} \text{ W } \Omega \text{ K}^{-2}$. The κ_L of the
213 magnesiosynthesized sample agrees with the lower κ_L values of the literature
214 over the entire temperature range. No significant decrease of κ_L is measured
215 at room temperature contrary to our previous work on $\text{In}_{0.13}\text{Co}_4\text{Sb}_{12}$ certainly
216 because of the larger average grain size, $1.8 \text{ }\mu\text{m}$ vs. 600 nm , respectively, and
217 the stronger influence of the rattlers over the mesostructure at such elevated
218 concentration. As a consequence of the lower PF , a ZT_{max} of 0.95 at 750 K is
219 obtained which remains 5 and 15 % lower than the reference samples made by
220 conventional melting/annealing process.

221 Further comparison of the MR-materials performance with literature data
222 is not a straightforward task as long as the TE properties of In-filled skutteru-
223 dites strongly depends on the precise In-content inserted in the cages up to its
224 solubility limit [9, 33, 13, 36]. In the present case, we confirm that increasing
225 the In-content from 0.13 [20] to 0.22 in the MR-samples decreases the thermal
226 conductivity and increases the ZT_{max} from 0.75 to 0.95. Oversaturating In in

227 CoSb₃ induces the formation of InSb and/or CoSb₂ (nano)precipitates that are
228 playing a significant role in decreasing the thermal conductivity and improving
229 the ZT_{max} of these composite materials [37, 38, 39, 40]. MR-In_{0.22}Co₄Sb₁₂ do
230 not show the presence of such precipitates after spark plasma sintering. The
231 measured TE properties can thus be considered as intrinsic to the material and
232 slightly deteriorated by the microcracks appearing in the pellets during physi-
233 cal properties measurements. The submicron particle size distribution obtained
234 after magnesio-reduction corresponds well to that reported by Benyahia *et al.*
235 on mesostructured $ZT = 1.4$ In_{0.25}Co₄Sb₁₂. Unfortunately, the grain growth in-
236 duced during sintering cancels this microstructural feature and both thermal
237 conductivity and figure-of-merit are much closer from those obtained by fusion-
238 solidification-long term annealing [2, 18] or most recently by scanning laser
239 melting for higher In-content [41]. Nevertheless, our ZT value is most of the
240 time higher than those reported after solid state diffusion [39, 42, 43] or HPHT
241 technique [44]. Improving the SPS step to limit the grain growth, stabilizing
242 In_{0.22}Co₄Sb₁₂/InSb nanocomposites or trying to form multifilled skutterudites
243 by magnesiothermy are the perspectives of this work.

244 4. Conclusions

245 The investigation of the reaction mechanism for the magnesio-reduction syn-
246 thesis of In-filled skutterudite from Sb₂O₄ and In-doped Co₃O₄ evidenced a
247 complex scenario involving intermediate species: CoO, Sb₂O₃, CoSb₂O₆ and
248 CoSb₂O₄. The formation of CoSb₃ precedes the insertion of In-rattler in the
249 cage. After spark plasma sintering, the resulting material is single phase skut-
250 terudite with composition close to In_{0.22}Co₄Sb₁₂ which corresponds to the In-
251 richest composition which could be synthesized by this technique in these con-
252 ditions. A ZT_{max} of 0.95 is measured at 750 K due to limited PF resulting from
253 elevated ρ caused by microcracks appearing in the pellets. In addition to im-

254 portant energy and time saving, the relatively mild reaction conditions used in
255 this process prevent high Mg vapors pressure inside the reactor thus avoiding
256 the formation of deleterious Mg-containing side-products which often limits the
257 up-scaling perspectives of magnesioreduction processes. Finally, the knowledge
258 gained on the reaction mechanism will be a precious help for the development of
259 optimized reaction conditions (multi-step heat treatment, mixed oxide precur-
260 sors) enabling the insertion of other filler atoms (*e.g.* Ba, rare earths elements)
261 whose respective oxides are often too stable to be reduced by Mg in the present
262 reaction conditions.

263 **Acknowledgements**

264 Loic Joanny and Francis Gouttefangeas are acknowledged for SEM images and
265 EDS analyses performed on the CMEBA platform belonging to the ScanMAT unit
266 (UMS 2001, University of Rennes 1) which received a financial support from the
267 European Union (CPER-FEDER 2007-2014).

268 **Declaration of interest**

269 The authors declare no conflict of interest.

270 **References**

- 271 [1] G. Rogl, P. Rogl, Skutterudites, a most promising group of thermoelectric
272 materials, *Curr. Opin. Green Sustainable Chem.* 4 (2017) 50–57.
- 273 [2] J. Leszczynski, V. D. Ros, B. Lenoir, A. Dauscher, C. Candolfi, P. Mass-
274 chelein, J. Hejtmanek, K. Kutorasinski, J. Tobola, R. I. Smith, C. Stiewe,
275 E. Müller, Electronic band structure, magnetic, transport and thermody-
276 namic properties of In-filled skutterudites $\text{In}_x\text{Co}_4\text{Sb}_{12}$, *J. Phys. D: Appl.*
277 *Phys.* 46 (2013) 495106.

- 278 [3] X. Li, Q. Zhang, Y. Kang, C. Chen, L. Zhang, D. Yu, Y. Tian, B. Xu, High
279 pressure synthesized Ca-filled CoSb_3 skutterudites with enhanced thermo-
280 electric properties, *J. Alloys Compd.* 677 (2016) 61–65.
- 281 [4] Y. Kang, F. Yu, C. Chen, Q. Zhang, H. Sun, L. Zhang, D. Yu, Y. Tian, B. Xu,
282 High pressure synthesis and thermoelectric properties of Ba-filled CoSb_3
283 skutterudites, *J. Mater. Sci.: Mater. Electron.* 28 (2017) 8771–8776.
- 284 [5] G. S. Nolas, M. Kaeser, R. T. Littleton, T. M. Tritt, High figure of merit
285 in partially filled ytterbium skutterudite materials, *Appl. Phys. Lett.* 77
286 (2000) 1855.
- 287 [6] G. Rogl, A. Grytsiv, K. Yubuta, S. Puchegger, E. Bauer, C. Raju, R. Mallik,
288 P. Rogl, In-doped multified n-type skutterudites with $ZT = 1.8$, *Acta*
289 *Mater.* 95 (2015) 201–211.
- 290 [7] Y. Tang, Y. Qiu, L. Xi, X. Shi, W. Zhang, L. Chen, S.-M. Tseng, S. wen
291 Chend, G. J. Snyder, Phase diagram of In-Co-Sb system and thermoelectric
292 properties of In-containing skutterudites, *Energy Environ. Sci.* 7 (2014)
293 812.
- 294 [8] A. Grytsiv, P. Rogl, H. Michor, E. Bauer, G. Giester, $\text{In}_y\text{Co}_4\text{Sb}_{12}$ skutterudite:
295 phase equilibria and crystal structure, *J. Electron. Mater.* 42 (2013) 2940–
296 2952.
- 297 [9] E. Visnow, C. P. Heinrich, A. Schmitz, J. de Boor, P. Leidich, B. Klobes, R. P.
298 Hermann, W. E. Müller, W. Tremel, On the true indium content of In-filled
299 skutterudites, *Inorg. Chem.* 54 (2015) 7818–7827.
- 300 [10] R. C. Mallik, J. Y. Jung, S. C. Ur, I. H. Kim, Thermoelectric properties of
301 $\text{In}_2\text{Co}_4\text{Sb}_{12}$ skutterudites, *Met. Mater. Int.* 14 (2008) 223.

- 302 [11] M. Benyahia, V. Ohorodniichuk, E. Leroy, A. Dauscher, B. Lenoir, E. Alleno,
303 High thermoelectric figure of merit in mesostructured $\text{In}_{0.25}\text{Co}_4\text{Sb}_{12}$ n-type
304 skutterudite, *J. Alloys Compd.* 735 (2018) 1096–1104.
- 305 [12] J. Eilertsen, S. Rouvimov, M. Subramanian, Rattler-seeded InSb nanoin-
306 clusions from metastable indium-filled $\text{In}_{0.1}\text{Co}_4\text{Sb}_{12}$ skutterudites for high-
307 performance thermoelectrics, *Acta Mater.* 60 (2012) 2178–2185.
- 308 [13] G. Li, K. Kurosaki, Y. Ohishi, H. Muta, S. Yamanaka, Thermoelectric prop-
309 erties of Indium-added skutterudites $\text{In}_x\text{Co}_4\text{Sb}_{12}$, *J. Electron. Mater.* 42
310 (2013) 1463.
- 311 [14] H. Li, X. Su, X. Tang, Q. Zhang, C. Uher, G. J. Snyder, U. Aydemir,
312 Grain boundary engineering with nano-scale InSb producing high per-
313 formance $\text{In}_x\text{Ce}_y\text{Co}_4\text{Sb}_{12+z}$ skutterudite thermoelectrics, *J Materiomics* 3
314 (2017) 273–279.
- 315 [15] C. Chubilleau, B. Lenoir, C. Candolfi, P. Masschelein, A. Dauscher,
316 E. Guilmeau, C. Godart, Thermoelectric properties of $\text{In}_{0.2}\text{Co}_4\text{Sb}_{12}$ skut-
317 terudites with embedded PbTe or ZnO nanoparticles, *J. Alloys Compd.*
318 589 (2014) 513–523.
- 319 [16] Y. Du, K. Cai, S. Chen, Z. Qin, S. Shen, Investigation on Indium-Filled
320 Skutterudite Materials Prepared by Combining Hydrothermal Synthesis
321 and Hot Pressing, *J. Electron. Mater.*, year =.
- 322 [17] A. Gharleghi, P.-C. Hung, F.-H. Lin, C.-J. Liu, Enhanced ZT of $\text{In}_x\text{Co}_4\text{Sb}_{12}$ -
323 InSb nanocomposites fabricated by hydrothermal synthesis combined with
324 solid-vapor reaction: a signature of phonon-glass and electron-crystal ma-
325 terials, *ACS Appl. Mater. Interfaces* 8 (2016) 35123–35131.
- 326 [18] S. Lee, K. H. Lee, Y.-M. Kim, H. S. Kim, G. J. Snyder, S. Baik, S. W. Kim,

- 327 Simple and efficient synthesis of nanograin structured single phase filled
328 skutterudite for high thermoelectric performance, *Acta Mater.* 142 (2018)
329 8–17.
- 330 [19] M. S. Toprak, C. Stiewe, D. Platzek, S. Williams, L. Bertini, E. Müller,
331 C. Gatti, Y. Zang, M. Rowe, M. Muhammed, The impact of nanostruc-
332 turing on the thermal conductivity of thermoelectric CoSb₃, *Adv. Funct.*
333 *Mater.* 14 (2004) 1189–1196.
- 334 [20] S. Le Tonquesse, E. Alleno, V. Demange, V. Dorcet, L. Joanny, C. Prestipino,
335 O. Rouleau, M. Pasturel, Innovative one-step synthesis of mesostructured
336 CoSb₃-based skutterudites by magnesio-reduction, *J. Alloys Compd.* 796
337 (2019) 176–184.
- 338 [21] S. Le Tonquesse, V. Dorcet, L. Joanny, V. Demange, C. Prestipino, Q. Guo,
339 D. Berthebaud, T. Mori, M. Pasturel, Mesostructure - thermoelectric prop-
340 erties relationships in V_xMn_{1-x}Si_{1.74} (x = 0, 0.04) higher manganese
341 silicides prepared by magnesiothermy, *J. Alloys Compd.* in press (2020)
342 doi:10.1016/j.jallcom.2019.152577.
- 343 [22] W. Kroll, Verformbares Titan und Zirkon, *Z. Anorg. Allg. Chem.* 234
344 (1937) 42–50.
- 345 [23] F. H. Spedding, H. A. Wilhelm, W. H. Keller, Production of Uranium, U.S.
346 Patent no. 2830894.
- 347 [24] E. Antolini, M. Ferretti, Synthesis and Thermal Stability of LiCoO₂, *J. Solid*
348 *State Chem.* 117 (1995) 1–7.
- 349 [25] L. Ma, C. Y. Seo, X. Chen, K. Sun, J. W. Schwank, Indium-doped Co₃O₄
350 nanorods for catalytic oxidation of CO and C₃H₆ towards diesel exhaust,
351 *Appl. Catal. B-Environ.* 222 (2018) 44–58.

- 352 [26] J. Rodriguez-Carvajal, Recent advances in magnetic-structure determina-
353 tion by neutron powder diffraction, *Physica B* 192 (1993) 55–69.
- 354 [27] O. Rouleau, E. Alleno, Measurement system of the Seebeck coefficient or of
355 the electrical resistivity at high temperature, *Rev. Sci. Instrum.* 84 (2013)
356 105103.
- 357 [28] H. Toraya, Estimation of statistical uncertainties in quantitative phase
358 analysis using the Rietveld method and the whole-powder-pattern decom-
359 position method, *J. Appl. Cryst.* 33 (2000) 1324–1328.
- 360 [29] O. Knacke, O. Kubaschewski, K. Hesselmann, *Thermo-chemical Properties*
361 *of Inorganic Substances* (1991) Springer Ed.
- 362 [30] B. P. de Laune, C. Greaves, Structural and magnetic characterisation of
363 CoSb_2O_4 and the substitution of Pb^{2+} for Sb^{3+} , *J. Solid State Chem.* 187
364 (2012) 225–230.
- 365 [31] D. Larcher, A. S. Prakash, L. Laffont, M. Womes, J. C. Jumas, J. Olivier-
366 Fourcade, M. S. Hedge, J.-M. Tarascon, Reactivity of antimony oxides and
367 MSb_2O_6 ($M = \text{Cu, Ni, Co}$) trirutile-type phases with metallic lithium, *J.*
368 *Electrochem. Soc.* 153 (2006) A1778–A1787.
- 369 [32] J. N. Reimers, J. E. Greedan, C. V. Stager, R. Kremer, Crystal structure
370 and magnetism in CoSb_2O_4 and CoTa_2O_6 , *J. Solid State Chem.* 83 (1989)
371 20–30.
- 372 [33] T. He, J. Chen, H. D. Rosenfeld, M. A. Subramanian, Thermoelectric prop-
373 erties of indium-filled skutterudites, *Chem. Mater.* 18 (2006) 759–762.
- 374 [34] S.-J. L. Kang, *Sintering: densification, grain growth and microstructure*
375 (2004) Elsevier Ed.

- 376 [35] J. Eilertsen, Y. Surace, S. Balog, L. Sagarna, G. Rogl, J. Horky,
377 M. Trottmann, P. Rogl, M. A. Subramanian, A. Weidenkaff, From occu-
378 pied voids to nanoprecipitates: synthesis of skutterudite nanocomposites
379 in situ, *Z. Anorg. Allg. Chem.* 641 (2015) 1495–1502.
- 380 [36] J.-Y. Jung, K.-H. Park, S.-C. Ur, I.-H. Kim, Thermoelectric and transport
381 properties of In-filled CoSb_3 skutterudites, *Mater. Sci. Forum* 658.
- 382 [37] R. C. Mallik, C. Stiewe, G. Karpinski, R. Hassdorf, E. Müller, Thermoelec-
383 tric properties of $\text{Co}_4\text{Sb}_{12}$ skutterudite materials with partial In filling and
384 excess In additions, *J. Electron. Mater.* 38 (2009) 1337–1343.
- 385 [38] A. Sesselmann, T. Dasgupta, K. Kelm, E. Müller, S. Perlt, S. Zastrow, Trans-
386 port properties and microstructure of indium-added cobalt-antimony-
387 based skutterudites, *J. Mater. Res.* 26 (2011) 1820–1826.
- 388 [39] J. Peng, X. Liu, L. Fu, W. Xu, Q. Liu, J. Yang, Synthesis and thermoelectric
389 properties of $\text{In}_{0.2+x}\text{Co}_4\text{Sb}_{12+x}$ composite, *J. Alloys Compd.* 521 (2012)
390 141–145.
- 391 [40] V. V. Khovaylo, T. A. Korolkov, A. I. Voronin, M. V. Gorshenko, A. T.
392 Burkov, Rapid preparation of $\text{In}_x\text{Co}_4\text{Sb}_{12}$ with a record-breaking $ZT=1.5$:
393 the role of the In overfilling fraction limit and Sb overstoichiometry, *J.*
394 *Mater. Chem. A* 5 (2017) 3541–3546.
- 395 [41] F. Chen, R. Liu, Z. Yao, Y. Xing, S. Bai, L. Chen, Scanning laser melting for
396 rapid and massive fabrication of filled skutterudites with high thermoelec-
397 tric performance, *J. Mater. Chem. A* 6 (2018) 6772–6779.
- 398 [42] K. Biswas, M. A. Subramanian, M. S. Good, K. C. Roberts, T. J. Hendricks,
399 Thermal cycling effects on the thermoelectric properties of *n*-type In,Ce-
400 based skutterudite compounds, *J. Electron Mater.* 41 (2012) 1615–1621.

- 401 [43] A. Sesselmann, B. Klobes, T. Dasgupta, O. Gourdon, R. Hermann,
402 E. Müller, Neutron diffraction and thermoelectric properties of in-
403 dium filled $\text{In}_x\text{Co}_4\text{Sb}_{12}$ ($x = 0.05, 0.2$) and indium cerium filled
404 $\text{Ce}_{0.05}\text{In}_{0.1}\text{Co}_4\text{Sb}_{12}$, *Phys. Status Sol. A* 213 (2016) 766–773.
- 405 [44] L. Deng, L. B. Wang, J. M. Qin, T. Zheng, Effects of indium-filling and
406 synthesis pressure on the thermoelectric properties of CoSb_3 , *Mod. Phys.*
407 *Lett. B* 28 (2014) 1450118.