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## Thermoelectric Properties of $\text{In}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$ Skutterudite Compounds

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### ABSTRACT

The preparation of partially filled n-type  $\text{In}_x\text{Co}_4\text{Sb}_{12}$  skutterudite compounds has been recently reported. The results were particularly promising, the materials exhibiting a ZT value far higher than one at moderated temperature. In this paper, we propose to investigate another way to tune the electrical and thermal properties by substituting Co atoms by Ni atoms in  $\text{In}_x\text{Co}_4\text{Sb}_{12}$ .  $\text{In}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$  polycrystalline samples have been prepared by a conventional metallurgical route. Structural analyses have been carried out by X-ray diffraction. The chemical composition and micro-homogeneity have been checked by electron probe microanalysis. Measurements of the electrical resistivity, thermoelectric power and thermal conductivity have been performed between 300 and 800 K. The influence of the presence of Ni on the thermoelectric properties of  $\text{In}_x\text{Co}_4\text{Sb}_{12}$  compounds is presented and discussed.

### INTRODUCTION

The  $\text{CoSb}_3$ -based filled skutterudites continue to attract a lot of attention as potential thermoelectric materials for elevated temperature applications. Particular interest is focused on n-type skutterudites as their thermoelectric properties are still not as good as in p-type skutterudites. A variety of approaches were applied to improve skutterudite thermoelectric properties involving partial filling of the structural voids, formation of  $\text{CoSb}_3$  isoelectronic solid solutions and doping by proper substitution at the metal or pnictogen sites. Among all these diverse methods void filling was found to be the most efficient. The presence of a filler element leads to a strong reduction of the thermal conductivity as compared to the parent composition and also affects its electrical properties by introducing additional electrons and modifying band structure yielding high power factors. The best improvement of the thermoelectric properties was achieved by partial filling with rare earth elements (Yb, Eu [1,2]) and alkaline metals (Ca, Ba[3-6]) and ZT values exceeding 1 at  $T \geq 600\text{K}$  were reported. In case of alkaline filling elements it was shown that further improvement of thermoelectric figure of merit can be obtained by careful tuning of carrier concentration accomplished by Ni doping. Quite recently H. Lee et al. [7] published very promising results of thermoelectric performance of indium partially filled  $\text{CoSb}_3$ . For composition  $\text{In}_{0.25}\text{Co}_4\text{Sb}_{12}$  they have measured maximum ZT value of 1.2 at 600 K. The aim

of this work was to synthesize indium partially filled  $\text{CoSb}_3$  pure and Ni doped samples to study Ni influence on thermoelectric properties of In filled compounds.

## EXPERIMENT

Polycrystalline  $\text{In}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$  samples were prepared by a combination of melting and sintering techniques. Stoichiometric amounts of high purity In shots 99.99%, Sb shots 99.999%, Co 99.998%, and Ni 99.995% powders were loaded into a quartz ampoule. Because it is known that even small Ni impurity has strong effect on Seebeck coefficient and electrical resistivity of skutterudites high purity cobalt (Ni free) powder was used. The ampoule was sealed under reducing He-10%  $\text{H}_2$  atmosphere and placed in a vertical oscillating furnace. Following that it was heated to 950°C at 10°C/min, left at 950°C for 4 hours and quenched in a water bath. The obtained ingot was ground into fine powder using an agate mortar, cold-pressed into pellets and once again loaded into quartz ampoule and annealed at 670°C for several days. The completely reacted pellets were crushed, pulverized and sieved to obtain grain fraction <50  $\mu\text{m}$ . Final densification was carried out in a graphite die by hot pressing in an argon atmosphere at 650°C for 2 h under 50 MPa.

Structural and chemical characterization of all the polycrystalline samples was accomplished by x-ray diffraction XRD as well as electron probe micro analysis EPMA. XRD measurements were conducted with a Siemens d500 diffractometer using monochromatic  $\text{CoK}\alpha$  radiation in the  $2\Theta$  range 20-120° with  $2\Theta$  step 0.032° and silicon powder as an internal standard for lattice constant calculation. The real compositions presented herein were obtained from EPMA analysis as an average of measurements taken at 30 random points, and normalized to full occupancy at the cobalt site. Electrical resistivity measurements were made on square-shape samples 4x4x1 mm<sup>3</sup> between 300 and 800 K using a standard Van der Paw method. Seebeck coefficient was measured in the temperature range 320 K – 800 K. The carrier concentration was calculated from the Hall coefficient  $R_H$ , assuming a single-carrier model and unity as a Hall factor. Thermal conductivity was determined for temperatures between 300 and 810 K by measuring the thermal diffusivity on a 10 mm diameter disc by a laser flash technique, the specific heat values for thermal conductivity evaluation were calculated from Dulong-Petit law.

## DISCUSSION

Based on XRD measurements and EPMA analysis, it was confirmed that the samples consists of one main phase with skutterudite structure and some secondary phases. Sb and InSb

**Table I.** Nominal and real compositions and physical properties of the  $\text{In}_x\text{Ni}_y\text{Co}_{4-y}\text{Sb}_{12}$  samples at room temperature.

Nominal composition	Real composition from EPMA measurements	Lattice parameter $a$ (Å)	Relative density (%)	Carrier concentration $n$ (cm <sup>-3</sup> )	Carrier mobility $\mu$ (cm <sup>2</sup> /Vs)
$\text{In}_{0.1}\text{Co}_4\text{Sb}_{12}$	$\text{In}_{0.041}\text{Co}_4\text{Sb}_{12}$	9.0407	98.8	$2.3 \cdot 10^{19}$	107
$\text{In}_{0.2}\text{Co}_4\text{Sb}_{12}$	$\text{In}_{0.1}\text{Co}_4\text{Sb}_{12}$	9.0442	92.4	$7.5 \cdot 10^{19}$	70.2
$\text{In}_{0.3}\text{Co}_4\text{Sb}_{12}$	$\text{In}_{0.18}\text{Co}_4\text{Sb}_{12}$	9.0504	98.7	$9.6 \cdot 10^{19}$	83.7
$\text{In}_{0.22}\text{Ni}_{0.03}\text{Co}_{3.97}\text{Sb}_{12}$	$\text{In}_{0.12}\text{Ni}_{0.02}\text{Co}_{3.98}\text{Sb}_{12}$	9.0474	96.5	$1.25 \cdot 10^{20}$	41.5
$\text{In}_{0.22}\text{Ni}_{0.05}\text{Co}_{3.95}\text{Sb}_{12}$	$\text{In}_{0.13}\text{Ni}_{0.05}\text{Co}_{3.95}\text{Sb}_{12}$	9.0454	97.2	$1.47 \cdot 10^{20}$	30.1
$\text{In}_{0.22}\text{Ni}_{0.08}\text{Co}_{3.92}\text{Sb}_{12}$	$\text{In}_{0.11}\text{Ni}_{0.06}\text{Co}_{3.94}\text{Sb}_{12}$	9.0457	93.1	$1.23 \cdot 10^{20}$	29.6
$\text{In}_{0.3}\text{Ni}_{0.03}\text{Co}_{3.97}\text{Sb}_{12}$	$\text{In}_{0.14}\text{Ni}_{0.02}\text{Co}_{3.98}\text{Sb}_{12}$	9.046	98.9	$1.25 \cdot 10^{20}$	44.6
$\text{In}_{0.3}\text{Ni}_{0.08}\text{Co}_{3.92}\text{Sb}_{12}$	$\text{In}_{0.11}\text{Ni}_{0.07}\text{Co}_{3.93}\text{Sb}_{12}$	9.0437	87	-	-

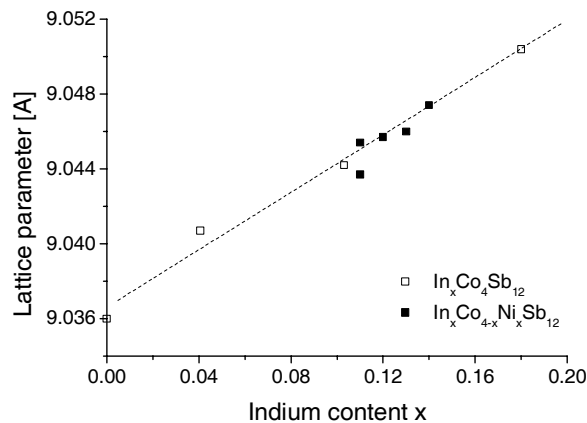


Figure 1. Lattice constant vs. indium content in  $\text{In}_x\text{Co}_4\text{Sb}_{12}$  samples.

impurities were observed in XRD measurements and the amount of these phases was estimated to be below 2% vol.. Electron microprobe results revealed that for all samples In and Ni distribution was homogeneous with compositions for all elements close to the nominal except In,

where the real content was only about 50% of the nominal composition (see Table I). Single grains of Sb and InSb were observed likewise in the X-ray diffraction measurements and the observed amount of the impurity phases was less than 1% vol.. Presence of indium-rich phases explains the deviation between real and nominal composition.

Fig. 1 shows the lattice constant  $a$  as a function of the real indium content  $x$ . The lattice parameter  $a$  is increasing with increasing  $x$  linearly and follows a Vegard's law. This was observed for all filling atoms. In the indium case, the  $a$  parameter is smaller than for Tl, Ba [8,3] and for most rare-earth filler elements but is comparable with Ca[5] and Yb[1] at the same filling fraction. Similar relation of lattice constant and composition was reported by He et al.[7]. However, they were able to introduce more In into the skutterudite structure and that was reflected in higher lattice parameters they obtained for the same nominal compositions. The addition of nickel seems to have a small influence on the lattice parameter.

### **Transport properties of $\text{In}_x\text{Co}_4\text{Sb}_{12}$ series**

The Seebeck and resistivity data for indium partially filled  $\text{CoSb}_3$  are shown in figures 2 and 3 respectively. The pure  $\text{CoSb}_3$  exhibits positive sign of Seebeck coefficient. Introduction of small amount of indium into the structural cages switch the dominant type of carriers from holes to electrons resulting in a negative Seebeck coefficients. At room temperature absolute Seebeck coefficient decreases with In filling fraction. For the samples with the real composition  $x=0.1-0.18$  the magnitude of the thermopower monotonically increases with increasing temperature. This behavior is typical for heavily doped semiconductors. For the sample with the lowest indium content  $x=0.04$  at temperature close to 500 K the Seebeck coefficient reaches its maximum and begins to decrease with temperature reflecting the influence of holes. Intrinsic conductivity tends to play a role also for other indium filled samples at highest temperatures leading to flattening of the temperature dependence of the thermopower. The temperature dependence of the  $\text{CoSb}_3$  electrical resistivity is typical semiconducting behavior. Indium insertion into the voids decreases

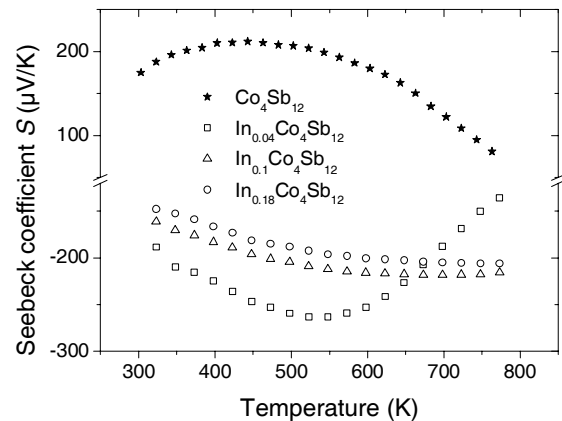


Figure 2. Seebeck coefficient vs. temperature in  $\text{In}_x\text{Co}_4\text{Sb}_{12}$  samples.

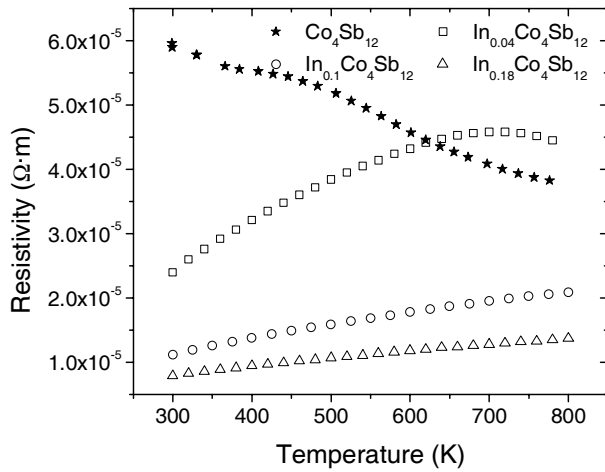


Figure 3. Resistivity vs. temperature in  $\text{In}_x\text{Co}_4\text{Sb}_{12}$  samples.

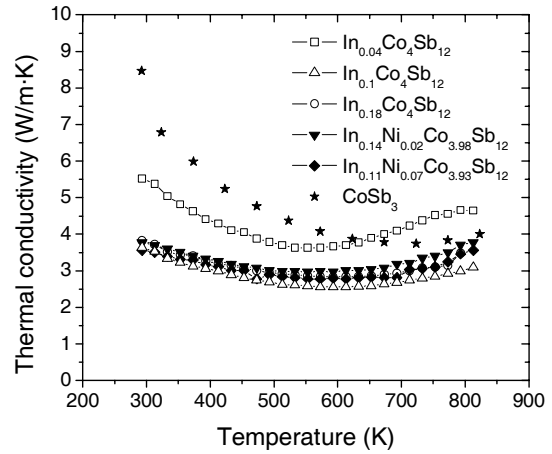


Figure 4. Thermal conductivity vs. temperature in In-filled  $\text{CoSb}_3$  samples.

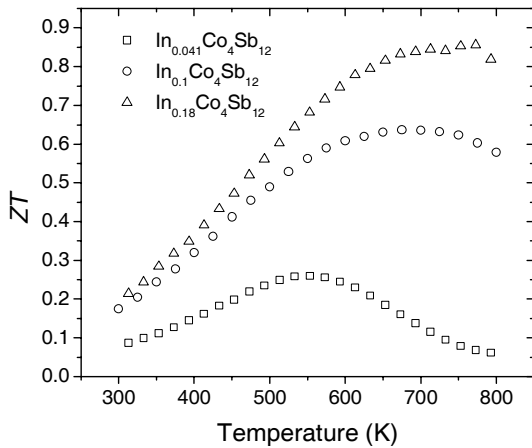


Figure 5. ZT vs. temperature in  $\text{In}_x\text{Co}_4\text{Sb}_{12}$  samples.

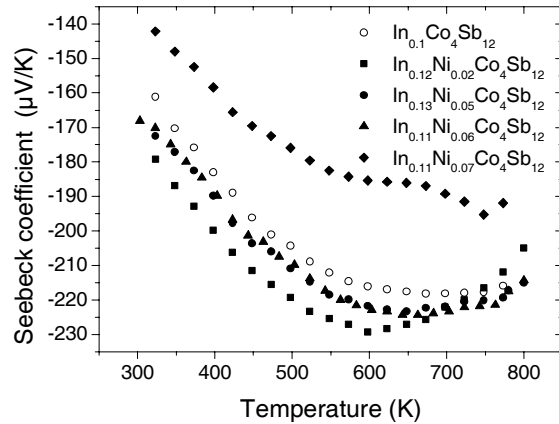


Figure 6. Seebeck coefficient vs. Temperature in  $\text{In}_x\text{Ni}_y\text{Co}_{4-y}\text{Sb}_{12}$  samples.

resistivity and change the temperature dependence to a more semi-metallic like with almost linear resistivity increase with temperature. The Hall measurements results are consistent with the Seebeck coefficient results. The Hall mobility follows roughly a  $T^{-3/2}$  dependence from 100 K to 300 K indicating acoustic phonon scattering. The electron mobility in the  $\text{In}_x\text{Co}_4\text{Sb}_{12}$  samples is one of the highest in the n-type skutterudites and at room temperature the values are 107, 70 and 83  $\text{cm}^2/\text{V}\cdot\text{s}$  for indium content  $x=0.04, 0.1, 0.18$  respectively. This is a little bit higher than for polycrystalline Th-filled  $\text{CoSb}_3$  [7]. The indium insertion cause an increase of the electronic carrier concentration but the number of electrons given to the structure is much lower then in case of other filler atoms. The highest carrier concentration  $n = 9.6 \cdot 10^{19} \text{ cm}^{-3}$  is obtained for the sample with highest indium content  $x=0.18$ .

The thermal conductivity temperature dependence is shown in Fig. 4. Thermal conductivity is significantly decreased by In filling. For In content higher than 0.1 it remains almost unchanged with further In introduction. Small deviations are probably the result of microstructural and density differences between samples. Such a strong effect on thermal conductivity reduction is probably due to combination of multiple phonon scattering mechanisms

like point defect scattering by mass fluctuation, strain field scattering and certainly phonon resonance scattering what was suggested in case of Ca[9].

Figure 5 shows that thermoelectric performance expressed by  $ZT$  is increasing with temperature and presents the maximum close to the Seebeck coefficient maximum.  $ZT$  coefficient is improved by increasing the filling fraction of In and the highest value is obtained in  $\text{In}_{0.18}\text{Co}_4\text{Sb}_{12}$  with  $ZT$  close to 0.85 at 700-780 K.

### Transport properties of $\text{In}_x\text{Ni}_y\text{Co}_{4-y}\text{Sb}_{12}$ series

Studying the Ni influence on thermoelectric properties of  $\text{In}_x\text{Co}_4\text{Sb}_{12}$  was not an easy task because of large deviations between nominal and real indium concentration. Finally a group of samples with indium content close to 0.1 was chosen for comparison but in some cases it was not possible to distinguish effect of In content variations and Ni concentration. As a reference sample  $\text{In}_{0.1}\text{Co}_4\text{Sb}_{12}$  sample is used. The temperature dependence of the Seebeck coefficient of  $\text{In}_x\text{Ni}_y\text{Co}_{4-y}\text{Sb}_{12}$  samples is shown in Fig. 6. The overall thermopower behavior is not changed by Ni doping. Introduction of Ni  $y = 0.02$  shifts the Seebeck coefficient about  $-20 \mu\text{V/K}$  increasing the absolute value. For higher Ni content thermopower magnitude decreases to the values close to the reference sample ( $y = 0.05, 0.06$ ) and then falls  $20 \mu\text{V/K}$  down. Nickel provides additional electrons to the structure increasing charge carrier concentration from  $7.5 \cdot 10^{19} \text{ cm}^{-3}$  to  $1.47 \cdot 10^{20}$  in  $\text{In}_{0.13}\text{Ni}_{0.05}\text{Co}_{3.95}\text{Sb}_{12}$ . However, it is not quite clear how many electrons is given by Ni atom as In content is also varying. More evident effects are observed for carrier mobility which is strongly depressed by Ni impurity and is about a half of the value for reference sample at  $T = 300 \text{ K}$  (see table I). The mobility decrease is proportional to Ni content. The temperature dependence of the mobility is also altered and is less steeper than for the reference sample revealing that ionized impurity scattering has a great importance even at temperatures above 100K. As a result of the carrier concentration and mobility changes, the resistivity at room temperature is initially reduced by introducing Ni and then increases above the resistivity value of the reference sample. At  $T > 300 \text{ K}$  the temperature dependence of the resistance (Fig. 7) is more or less metallic like. Increasing the Ni content reduce the TCR and makes resistivity less temperature sensitive that could be qualitatively explained by the change in carrier scattering

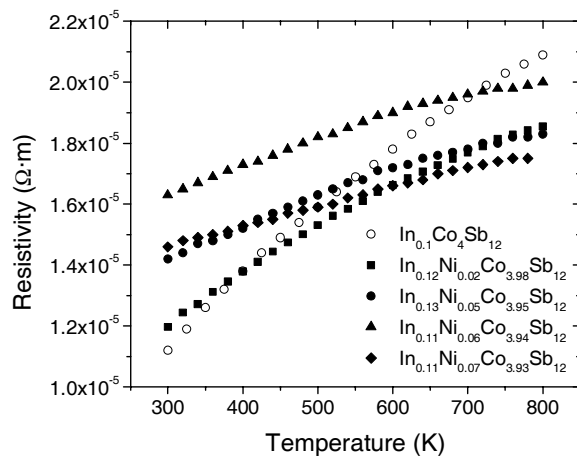


Figure 7. Resistivity vs. temperature in  $\text{In}_x\text{Ni}_y\text{Co}_{4-y}\text{Sb}_{12}$  samples.

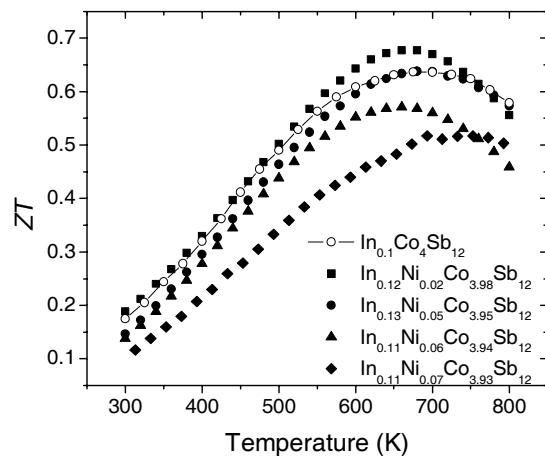


Figure 8.  $ZT$  vs. temperature in  $\text{In}_x\text{Ni}_y\text{Co}_{4-y}\text{Sb}_{12}$  samples.

mechanism from acoustic phonons to both acoustic phonons and ionized impurities. The thermal conductivity of  $\text{In}_x\text{Ni}_y\text{Co}_{4-y}\text{Sb}_{12}$  samples is not modified significantly with the introduction of Ni as exemplified in Fig. 4.

The ZT versus temperature plot for  $\text{In}_x\text{Ni}_y\text{Co}_{4-y}\text{Sb}_{12}$  samples is presented in Fig. 8. Depending of the Ni doping one can see that it is possible to control the thermoelectric properties. It can be observed that small amount of nickel enhances thermoelectric figure of merit and gives the maximum value of ZT 0.68 at 650 K compared to ZT 0.64 for the reference sample  $\text{In}_{0.1}\text{Co}_4\text{Sb}_{12}$ .

## CONCLUSIONS

The influence of indium filling on thermoelectric properties of  $\text{CoSb}_3$  and following that influence of Ni substitution for Co on the properties of In partially filled cobalt triantimonide were investigated. It was found that In plays the role of a *n*-type dopant yielding high electron mobility values at room temperature close to  $100 \text{ cm}^2/\text{V}\cdot\text{s}$  and reducing significantly the thermal conductivity. This results in strong improvement of the thermoelectric properties and the maximum ZT value of 0.85 is reached at 700K for the sample  $\text{In}_{0.18}\text{Co}_4\text{Sb}_{12}$ . In the  $\text{In}_x\text{Ni}_y\text{Co}_{4-y}\text{Sb}_{12}$  system Ni acts as the *n*-type dopant and affects mainly on the electronic properties. These changes can be explained in terms of enhanced carriers scattering on ionised impurities. Doping  $\text{In}_x\text{Co}_4\text{Sb}_{12}$  by small nickel amounts ( $y \approx 0.02$ ) seems to have the beneficial effect on the thermoelectric properties. The maximum ZT value for  $\text{In}_{0.12}\text{Ni}_{0.02}\text{Co}_{3.98}\text{Sb}_{12}$  sample was increased of 6% compared to the reference sample. It will be interesting to investigate the influence of Ni on samples with higher indium content as they give a prospect of achieving figures of merit higher than one.

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