Effect of the Ni substitution on $CoSb_3$ partially filled with In and Yb

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Abstract

In the field of skutterudites, and more precisely in the group of cobalt triantimonides, it has been proved that the substitution of Co by a small amount of Ni has a positive influence on the thermoelectric properties of the skutterudites [1]. This fact was clearly illustrated in the case of partial filling with several alkaline earth like for example Ca [2].

It has been estimated that the Yb partially filled $CoSb_3$ can present very good high-temperature properties [3], and more recently, very encouraging results were obtained with the insertion of In into the voids of the structure [4]. With the objective to further improve these performances, and to determine if Ni has also a positive influence in these cases, we synthesized and measured the high temperature (300 – 800 K) thermoelectric properties of two series of samples : $Yb_xCo_{4-y}Ni_ySb_{12}$ and $In_xCo_{4-y}Ni_ySb_{12}$.

Introduction

These last ten years, materials with a skutterudite structure have aroused great interest from a fundamental point of view because of their unusual physical properties (superconductivity, long-distance magnetic ordering, "exotic spin state"), but also for engineers because of their potential as active branche in thermoelectric generators at moderated temperature [5].

One of the striking feature distinguishing skutterudites from conventional thermoelectric materials is the possibility they offer to reduce their lattice thermal conductivity through the partial filling of the "voids" of the open structure [5]. The filling atoms can rattle around their equilibrium position and thus actively contribute to phonon scattering.

Many sorts of atoms have been identified as possible filler elements : alkaline earths (Ba, Ca) [6,7] and rare-earths (Ce, La, Eu, Nd) [8-12]. More recently, alkaline elements like K or Na were studied because of their high theoretical filling fraction limit [13,14]. Once partially filled, one can still try to improve the thermoelectric performance of the obtained materials through doping. For example, the substitution of Co by Ni was found to be particularly efficient [1].

In this study, we focus on the influence of Ni-substitution on the Co site in Yb- and In-doped $CoSb_3$. These two ternary materials were already studied in the literature [3,4], but the optimization by doping and the full study at high temperature were not completed. We report here on the physico-chemical characterizations, and on the high temperature properties of several $Yb_xCo_{4-y}Ni_ySb_{12}$ and $In_xCo_{4-y}Ni_ySb_{12}$ samples. The results are compared to value obtained for binary $CoSb_3$ and ternary $Yb_xCo_4Sb_{12}$ we synthesized, and to $In_xCo_4Sb_{12}$ values from the literature [4].

Preparation and analysis

Polycrystalline samples of $CoSb_3$, $Yb_xCo_4Sb_{12}$, $Yb_xCo_{4-y}Ni_ySb_{12}$ and $In_xCo_{4-y}Ni_ySb_{12}$ were elaborated using a combination of solid-liquid reaction, grinding process, annealing and uniaxial hot pressing. A detailed description of the synthesis is given with all the details elsewhere [12].

Structural and chemical characterizations of the samples were realized through X-ray diffraction (XRD) and electron microprobe analyses (EPMA). All the compositions reported below result from EPMA analyses and were normalized to full occupancy of the cobalt site.

Transport properties have been performed in the 300-800 K temperature range. Thermal conductivity was determined by measuring the thermal diffusivity by a laser flash technique; the density was measured via a geometrical method, and the specific heat was deduced from the Dulong-et-Petit law. The electrical resistivity was measured by a four probes technique based on the Van der Pauw method, and the Seebeck coefficient was determined using a standard method [15].

Results and discussion

Structural and chemical characterization

All the peaks of the X-ray diffraction patterns were indexed on the space group Im3 characteristic of the skutterudite $CoSb_3$. Presence of minor secondary phases (< 3% vol.) can be detected thanks to the presence of some extra peaks of weak intensity. As indicated on Figure 1, they are representative of Sb and oxides such as In_2O_3 and Yb_2O_3.

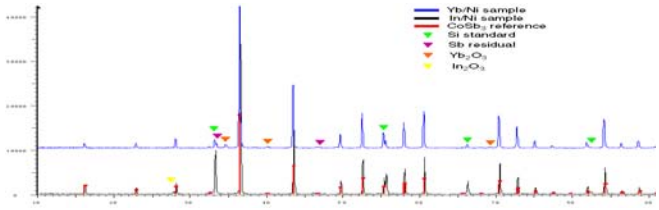


Figure 1: Typical X-ray diffraction patterns of $Yb_xCo_{4-y}Ni_ySb_{12}$ and $In_xCo_{4-y}Ni_ySb_{12}$ samples

The lattice parameter of the ternary compounds is determined thanks to the different XRD acquisitions. This parameter is increased in the case of partial filling with regard to $CoSb_3$. This is a first indice of the insertion of In and Yb into the cages of the structure, but this information has to be confirmed by neutron diffraction.

Maps obtained by EDS analysis (see Figure 2) show Co and Sb homogeneity and the presence of In-rich or Yb-rich phases. One can also observe the excellent distribution of Ni into the matrix. The presence of In or Yb oxides explains the deviation of the real composition from the nominal value.

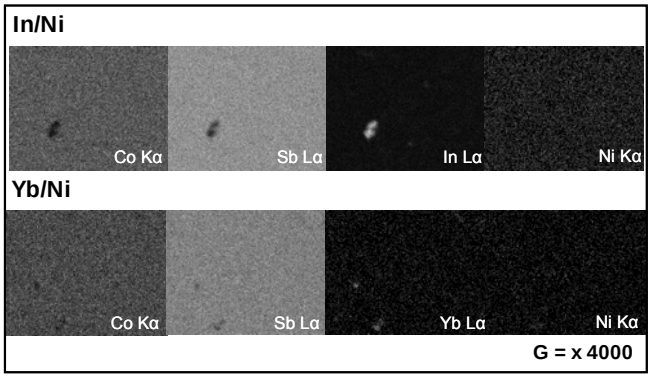


Figure 2: EDS maps EPMA showing Co, Sb and Ni homogeneity and the presence of In- and Yb-rich phases

Transport properties

Figure 3 shows the temperature dependences of the Seebeck coefficient for all the samples. Contrary to the binary compound $CoSb_3$ which is p-type, both In/Ni and Yb/Ni-containing compounds exhibit n-type conductivity. This inversion of the type of dominant carriers is already caused by the presence of Yb or In into the voids of the structure. One can deduce that the filling atoms give electrons to the structure. High thermopower values are reached, suggesting high effective masses of the carriers. The inversion of the slope for In/Ni-containing compounds indicates the participation of minority carriers from ≈ 600 K. The addition of Ni to $Yb_xCo_4Sb_{12}$ and $In_xCo_4Sb_{12}$ results in a decrease (in absolute value) of the thermopower. The reduction is moderate in the case of Yb samples but is marked for the In containing compounds.

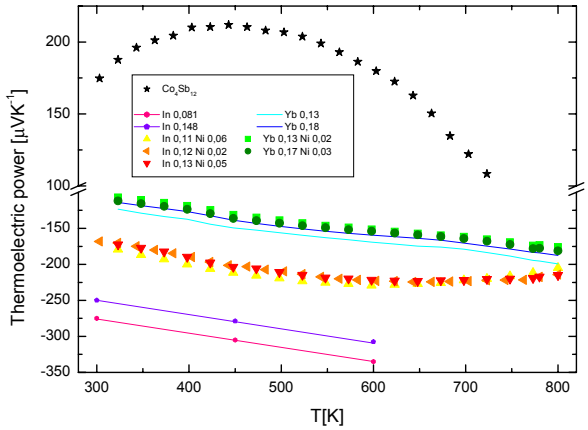
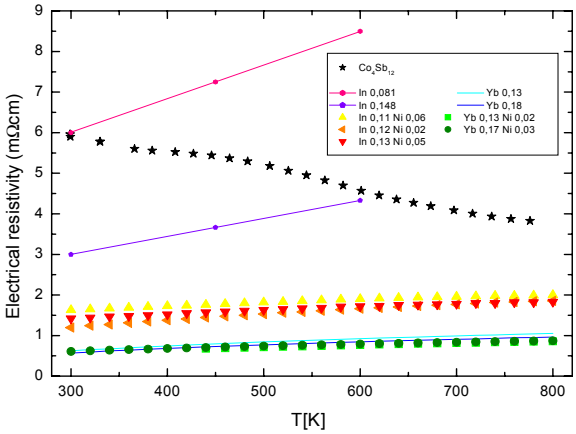


Figure 3: Thermoelectric power versus temperature for the binary, ternary and quaternary compounds.

The temperature dependence of the electrical resistivity is reported on Figure 4. The binary $CoSb_3$ compound exhibits an electrical resistivity that diminishes as a function of temperature, characteristic of a semiconducting behaviour. All the other samples present a metal-like temperature evolution. In the case of Yb, the impact of Ni is not significant. Hall data measurement have shown that carrier concentration increases but that at the same time, carrier mobility is depressed. The situation is notably different in the case of In, where the impact of Ni is marked : the resistivity is decreased at least by a factor of two at



room temperature.

Figure 4: Temperature dependence of the electrical resistivity for all the samples

On Figure 5 is presented the evolution of the thermal conductivity with temperature. Compared to the total thermal conductivity of $CoSb_3$, the values for In/Ni and Yb/Ni-containing compounds are divided approximately by a factor of two at room temperature. This reduction can be firstly attributed to resonant scattering caused by the rattling of In and Yb atoms included into the cages. The presence of these elements also cause mass fluctuations and strain field fluctuations which can be responsible for point defect scattering of the phonons.

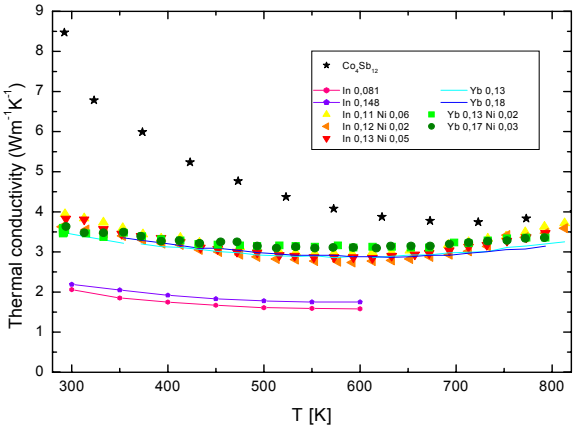


Figure 5: Temperature dependence of the thermal conductivity

From the S(T), ρ(T) and λ(T) temperature dependences, we have calculated the temperature dependence of the dimensionless figure of merit in the 300 – 800 K range. The results are reported on Figure 7.

Due to the participation of the minority carriers to the conduction phenomenon over 600 K, the ZT value of the In/Ni series reaches a maximum ($0.57 < \max < 0.67$) at about 650 K and then decreases. This is not the case for the Yb/Ni series whose ZT is still increasing, reaching values of 0.8 -0.9 at 800 K. In this series, the substitution by Ni do not result in a global increase of the performance of $Yb_xCo_4Sb_{12}$. The same conclusion seems to hold for the In/Ni doped samples.

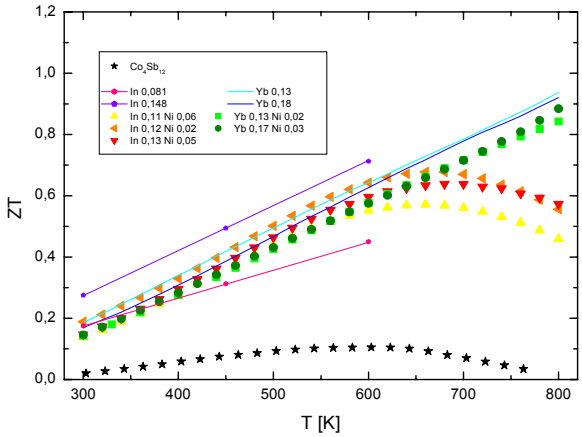


Figure 7: Temperature evolution of the dimensionless figure of merit ZT

Conclusion

We have successfully prepared $Yb_xCo_{4-y}Ni_ySb_{12}$ and $In_xCo_{4-y}Ni_ySb_{12}$ skutterudites via a metallurgical route and measured their thermoelectric properties between 300 and 800 K. Fairly good homogeneity of the samples was observed. As expected, In and Yb play the role of dopants (n-type), and Ni is thought to substitute to Co and further add electron to the structure.

The positive influence of Ni demonstrated in Ba and Ca partially filled Co_4Sb_{12} skutterudites is not observed for the $Yb_xCo_{4-y}Ni_ySb_{12}$ and $In_xCo_{4-y}Ni_ySb_{12}$ compounds.

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