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

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Abstract

In an effort to further understand the influence of Nd on the thermoelectric properties of the binary compound CoSb_3 and try to optimize them through doping, we prepared and investigated $\text{Nd}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$ compounds. The samples have been prepared by a conventional metallurgical route. Structural analysis has 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, thermal conductivity and Hall coefficient have been performed. The influence of both Nd and Ni on the thermoelectric properties of the binary parent CoSb_3 is presented and discussed. Nd plays the role of a dopant (n-type) and the presence of Ni contributes to decrease significantly the electrical resistivity.

Introduction

Among narrow band gap semiconductors, skutterudites have received particular attention over the last ten years. This interest was motivated first by their outstanding properties as engineering materials for power generation applications, but also because they exhibit intriguing physical features from a fundamental point of view (e.g. Kondo behaviour or superconductivity). [1]

The potential of a material for thermoelectric applications is determined by the material's dimensionless figure of merit $ZT = S^2T/\rho\lambda$, where S is the thermoelectric power, T the absolute temperature, ρ the electrical resistivity and λ the total thermal conductivity ($\lambda = \lambda_L + \lambda_E$ the lattice and electronic contributions, respectively).

Skutterudites based on CoSb_3 have been identified as being particularly interesting for thermoelectric applications at moderated temperatures. [2] The skutterudite structure offers many possibilities to tune the electrical and thermal properties by appropriate filling of the constitutional voids and/or substitutions on the Co or Sb sites. [1, 3] N-type or p-type materials with ZT values exceeding unity have been obtained in this way making skutterudites outstanding materials. The development of segmented thermoelectric unicouples using advanced thermoelectric materials, e.g., is currently under investigation. [4]

Several rare-earth elements can be inserted into the cages of the CoSb_3 structure. [1, 2] If many studies were performed with La and Ce, [5, 6] the case of Nd remains little explored if

we except the work of Kuznetsov et al. [7] Thus, no attempt was made to optimize this interesting material system through doping or compensation.

In this paper, we are reporting on the preparation and the characterization of polycrystalline $\text{Nd}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$. The influence of the filler element Nd and of the doping atom Ni on the electrical and thermal properties is discussed.

Experimental

The synthesis of $\text{Nd}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$ skutterudites was achieved by a metallurgical technique we developed. [8] High purity Nd powder (99.9 %), Co nickel-free powder (99.998 %), Sb shots (99.999 %) and Ni powder (99.995 %) were used as the starting materials. Stoichiometric amounts of these elements were loaded into a quartz ampoule in an argon-atmosphere glovebox. The tube was sealed under a He/H₂ atmosphere and transferred into an oscillating furnace. The ampoule was heated-up to a temperature T ($750^\circ\text{C} < T < 1050^\circ\text{C}$) at a rate of $1^\circ\text{C}/\text{min}$ and maintained at T for 84 h. The obtained solid was then ground in an agate mortar into fine powders ($< 100 \mu\text{m}$) that were further compacted into pellets without any lubricant in a steel die. To achieve completely the reaction and to obtain the expected crystallographic phase, the pellets were annealed in a quartz ampoule under a He/H₂ atmosphere at 620°C for 3 to 10 days. These materials were powdered again and densified. The densification was accomplished by uniaxial hot-pressing using graphite dies in an argon atmosphere at 600°C under 51 MPa.

The crystallographic structure and the chemical composition of all samples were carefully checked using respectively a Siemens D-500 diffractometer (X-Ray diffraction) and a CAMECA SX 100 electron microprobe (EPMA analyses).

To perform the transport property measurements, samples of various shapes (parallelepiped and cylindrical) were cut with a diamond wire saw from the hot-pressed ingots.

The thermoelectric power was measured between 300 – 800 K by a standard method using a home-made apparatus. The thermal conductivity was evaluated by the combination of the thermal diffusivity measured by a laser flash apparatus (Netzsch LFA 427) and the heat capacity measured by differential scanning calorimetry (Netzsch DSC 404) in the 300 – 800 temperature range. The density of our samples was

determined by a measure of their mass and volume at ambient temperature. We made no corrections for thermal expansion at high temperature. Low temperature electrical measurements (4 – 300 K) were performed using a PPMS (Quantum Design) in the AC mode.

Results and discussion

The X-ray diffraction patterns of all the samples can be indexed with a unit cubic cell corresponding to the skutterudite structure, space group $Im\bar{3}$, as illustrated in figure 1. The results show that all the samples are predominantly single phase. A small amount of a Sb-rich secondary phase, that never exceeds 2 vol. %, detected at $2\theta = 33.4$, may also be present.

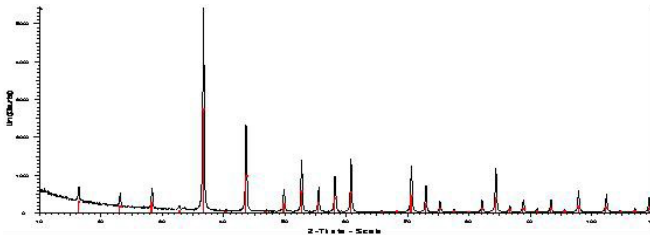


Figure 1: Typical X-ray diffraction pattern of $Nd_xCo_4Sb_{12}$ skutterudite

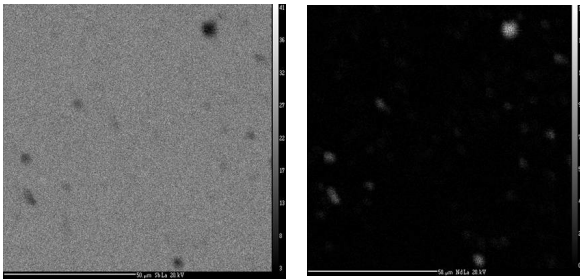


Figure 2: Sb-L β and Nd-La maps as obtained by EPMA showing Sb homogeneity and the presence of Nd-rich phases

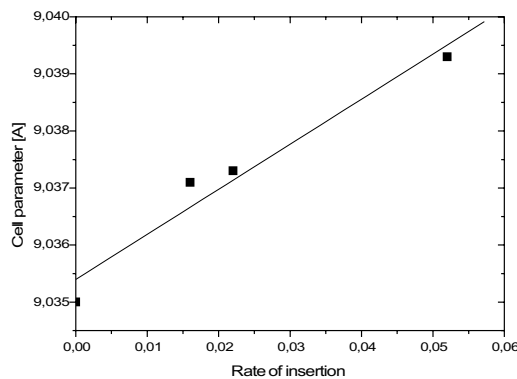


Figure 3: Lattice parameter versus x in $Nd_xCo_4Sb_{12}$: the line is just a guide for the eye.

X-ray maps reveal that the major elements, Co and Sb, are homogeneously distributed in the samples while small Nd-rich precipitates are systematically detected (figure 2) making

the Nd content of the matrix in deficit relative to the nominal composition. In the next of the text, x and y in $Nd_xCo_{4-y}Ni_ySb_{12}$ will always refer to the actual composition as determined by EPMA.

For the Ni-free samples, the variation of the lattice parameter versus the content of Nd, x , was found to be linear (see figure 3), suggesting a Vegard's law. This behaviour is consistent with the findings of Kuznetsov et al. [7] However, while these authors find a solubility limit of $x \sim 0.1$, our investigations concluded on $x \sim 0.05$.

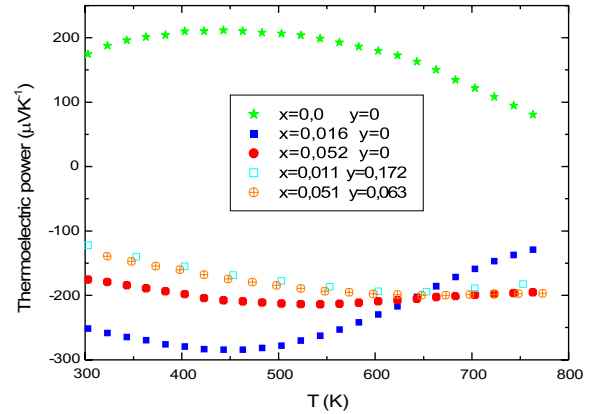


Figure 4: Temperature dependence of the thermoelectric power for the $Nd_xCo_{4-y}Ni_ySb_{12}$ compounds.

The temperature dependence of the thermoelectric power, of the different $Nd_xCo_{4-y}Ni_ySb_{12}$ samples is reported in figure 4. The $CoSb_3$ binary compound exhibits a positive thermoelectric power that decreases with the enhancement of the temperature. As it can be seen, the introduction of neodymium in the cavities of the skutterudite structure has a strong effect on the temperature-dependent thermoelectric power behaviour. The presence of Nd at a content as low as $x = 0.016$ leads to a negative thermoelectric power, meaning that the electrical conduction goes from a conduction dominated by the holes in $CoSb_3$ to a conduction dominated by the electrons in the $Nd_xCo_4Sb_{12}$ compounds. A higher content of Nd ($x = 0.052$), decreases the thermopower in absolute values as a result of an increase of the carrier concentration. It can be seen that all curves exhibit a more or less pronounced inversion of the slope between 450-550 K according to the compound, revealing the participation of the minority carriers to the conduction, i.e. electrons for the binary compounds and holes for samples containing Nd. The influence of the substitution of Co by Ni on the thermopower of $Nd_xCo_4Sb_{12}$ samples is also shown in figure 4. The presence of Ni results in an increase of the carrier concentration (as seen in table 1) since Ni has one electron more than Co. For this reason, it is expected that the thermopower (in absolute value) of the samples containing Ni will be lower in comparison that of samples without Ni. This is effectively what we observe but we can note that for $x \sim 0.05$, the doping does not drastically decrease S. This point

has already been underlined by other authors when fillers other than Nd, for instance alkaline earths, have been used. [3, 9]

In figure 5 are plotted the temperature dependences of the electrical resistivity between 4 – 800 K. The binary CoSb_3 compound exhibits an electrical resistivity that diminishes as a function of temperature, characteristic of a semiconducting behaviour. These observations coincide with the results of Puyet et al. [10] obtained with polycrystalline p type CoSb_3 . Neodymium insertion in the cavities of the crystalline structure modifies somewhat this behaviour since the electrical resistivity decreases, exhibits a minimum and then increases slowly when the temperature increases to further decrease at high temperature. We can note that the values are quite comparable to the values obtained with other filler elements (alkaline earths or rare earths) for similar filling fractions. [1, 10] More spectacular is the effect of Ni, which decreases substantially the values of the electrical resistivity. The room temperature values of the electrical resistivity, Hall carrier concentration and Hall mobility are listed in table 1 for the $\text{Nd}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$ compounds studied.

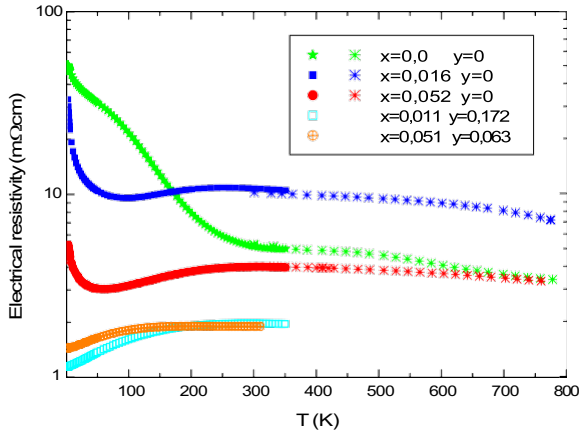


Figure 5: Temperature dependence of the electrical resistivity for the $\text{Nd}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$ compounds

Sample	Hall carrier concentration (cm^{-3})	Hall mobility ($\text{cm}^2/\text{V.s}$)	Resistivity ($\text{m}\Omega.\text{cm}$)
$x = 0 \quad y = 0$	$p = 1.90 \cdot 10^{18}$	641	5.14
$x = 0.016 \quad y = 0$	$n = 6.51 \cdot 10^{18}$	91	10.55
$x = 0.052 \quad y = 0$	$n = 3.18 \cdot 10^{19}$	59	3.33
$x = 0.051 \quad y = 0.063$	$n = 1.78 \cdot 10^{20}$	18	1.89

Table 1: Hall carrier concentration, Hall mobility and Hall resistivity measured at room temperature for the different $\text{Nd}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$ skutterudites studied

Looking now to the thermal conductivity (figure 6), we can see that the insertion of Nd has particularly a beneficial effect at room temperature, lowering the thermal conductivity by roughly a factor 2. The effect is less marked at high temperature. The phononic contribution plays a major role

near 300 K while this contribution is less pronounced at high temperature. Samples with or without Ni display quite similar thermal conductivity. This trend seems reasonable since Ni and Co have similar atomic masses that should not conduct to strong point defect scattering.

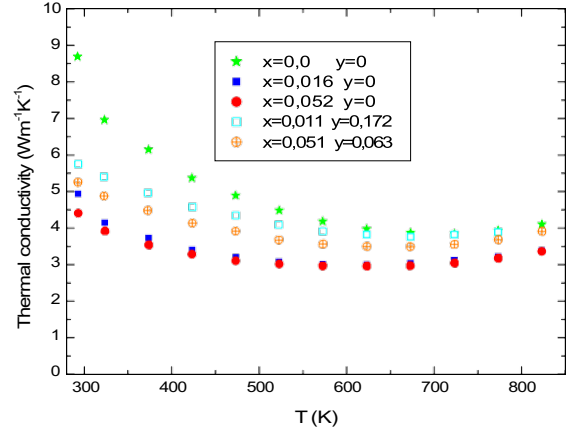


Figure 6: Temperature dependence of the thermal conductivity for the $\text{Nd}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$ compounds.

From the $S(T)$, $\rho(T)$ and $\lambda(T)$ temperature dependences, we have calculated the temperature dependence of the dimensionless figure of merit in the 300 – 800 K range. An extrapolation of the electrical resistivity for the Ni samples at high temperatures has been performed based on previous results. [3] The results are reported in figure 7. For the $\text{Nd}_x\text{Co}_4\text{Sb}_{12}$ samples, ZT is maximum for the higher filling fraction. The value is about 0.28 near 800 K. The presence of Ni is expected to improve significantly this value as it is illustrated in figure 7 from the estimation of ZT .

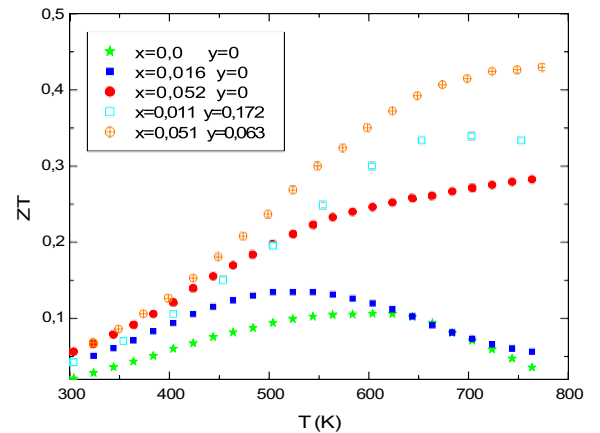


Figure 7: Temperature dependence of the dimensionless figure of merit ZT for the $\text{Nd}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$ compounds.

Conclusion

We investigated the transport properties of $\text{Nd}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$ polycrystalline samples obtained via a metallurgical route. It was found that the solubility limit of Nd in CoSb_3 is relatively low (~ 0.05) relative to other filler elements. Moreover, neodymium plays the role of a dopant (n type). Due to the low filling fraction, the ZT values of the $\text{Nd}_x\text{Co}_4\text{Sb}_{12}$ remain moderate. Doping this system by Ni seems to be favourable. This investigation should be pursued in more detail to have a better insight about the role of Ni on the transport properties of the $\text{Nd}_x\text{Co}_4\text{Sb}_{12}$ samples.

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