

# Improved Thermoelectric Properties in the Double Filled Skutterudites (Ce-Yb)<sub>y</sub>(Fe-Co-Ni)<sub>4</sub>Sb<sub>12</sub>

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## Abstract:

We have investigated the thermal and electrical properties of filled skutterudites belonging to the series Ce<sub>1-z</sub>Yb<sub>z</sub>Fe<sub>4</sub>Sb<sub>12</sub> and Ce<sub>y/2</sub>Yb<sub>y/2</sub>Fe<sub>4-x</sub>(Co/Ni)<sub>x</sub>Sb<sub>12</sub>, as well as their potential for thermoelectric power generation. The power factor and the dimensionless thermoelectric figure of merit are significantly improved in double filled skutterudites as compared to single filled ones, and the double filling happens to be a promising path to provide good thermoelectric performance.

## Introduction:

The skutterudite family has been extensively studied in the past few years because of its very promising properties for high temperature thermoelectric applications<sup>1, 2</sup>. The efficiency of a thermoelectric material used for power generation or cooling applications is usually characterized by the dimensionless thermoelectric figure of merit ZT defined as

$$ZT = \frac{\sigma S^2 T}{\lambda} = \frac{\sigma S^2 T}{\lambda_e + \lambda_L}, \text{ where } \sigma, S \text{ and } \lambda \text{ are the}$$

electrical conductivity, Seebeck coefficient or thermopower, and total thermal conductivity respectively.  $\lambda_e$  and  $\lambda_L$  are the electronic and lattice part of the thermal conductivity.  $\lambda_e$  and  $\sigma$  are related by the Wiedemann-Franz law  $\lambda_e = L_0 T \sigma$  valid for metals, with the Lorentz number  $L_0 = 2.44 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ . The energy conversion efficiency increases when increasing ZT. Therefore, the requirements for an optimum thermoelectric material will be to conduct heat like a glass (low  $\lambda_L$ ) and the electrons like a crystal (high  $\sigma$ ) rendering the PGEC (Phonon Glass and Electron Crystal) concept<sup>3</sup>.

Binary skutterudites crystallize in a body-centred cubic (bcc) structure with space group Im3<sup>4</sup> and have a general formula MX<sub>3</sub> (M=Co, Rh or Ir and X=P, As or Sb)<sup>5</sup> with M occupying the 8c and X the 24g positions of the crystallographic structure. They are small band gaps semiconductors with high thermopower and high charge carrier mobilities<sup>2</sup>. However, their dimensionless figures of merit ZT remain too low for thermoelectric applications because of their high lattice thermal conductivities (the room

temperature lattice thermal conductivity is about ten times higher in CoSb<sub>3</sub> than in state of the art Bi<sub>2</sub>Te<sub>3</sub> based alloys<sup>6, 7</sup>).

An effective way to reduce the lattice thermal conductivity of the skutterudites and to make them viable for thermoelectric applications is to fill the large icosahedral void in the 2a site of the crystallographic structure with an electropositive element to form filled skutterudites with general formula RM<sub>4</sub>X<sub>12</sub> (R=electropositive element, M=Fe, Ru or Os). Many electropositive elements have been explored to optimise ZT, including most of the rare-earths<sup>2</sup>, Ba<sup>8</sup>, Tl<sup>9</sup>, Sn<sup>10</sup>... The lattice thermal conductivity of filled skutterudites is strongly reduced as compared to that of binary skutterudites<sup>1</sup>. This decrease originates from the possibility for the filler atom to "rattle" around its equilibrium position in the oversized cage and thus to effectively scatter the heat conducting phonons<sup>11</sup>. However, a tetravalent element would be necessary to keep the semi-conducting behaviour which is required for a high thermopower but the major part of the possible filler atoms are divalent or trivalent. Therefore, the semi-conducting behaviour is lost and the thermopower is strongly reduced (for instance, the room temperature thermopower is ~75  $\mu\text{V} \cdot \text{K}^{-1}$  in CeFe<sub>4</sub>Sb<sub>12</sub><sup>12</sup> as compared to ~230  $\mu\text{V} \cdot \text{K}^{-1}$  in non-intentionally doped CoSb<sub>3</sub><sup>6</sup>). A way to restore a high thermopower is to reduce the carrier concentration n by substituting Co or Ni for Fe on the M site of the structure. With a simple electrons count, the substitution of one Fe atom by one Co (Ni) atom would increase the valence electrons number by one (two). However the R atom filling rate decreases as the iron fraction decreases<sup>13, 14</sup>, which leads to partially filled skutterudites with general formula R<sub>y</sub>M<sub>4-x</sub>M'<sub>x</sub>Sb<sub>12</sub><sup>15</sup>. Lattice thermal conductivity is strongly reduced in partially filled skutterudites as compared to fully filled ones, with a minimum close to y~0.6<sup>15</sup>. This is related to a scattering of the heat conducting phonons by mass fluctuations on the R site (due to mass differences between the filler atom and a vacancy)<sup>16</sup>. In state of the art skutterudites, a dimensionless figure of merit ZT=1.25 has been obtained at 900K for n-type Ba<sub>0.3</sub>Ni<sub>0.05</sub>Co<sub>3.95</sub>Sb<sub>12</sub><sup>17</sup>, and ZT=1.1 has been obtained at 750K for p-type Ce<sub>0.28</sub>Co<sub>2.48</sub>Fe<sub>1.52</sub>Sb<sub>12</sub><sup>18</sup>. However, even in this compounds the lattice thermal conductivity remains quite high and could lead to further improvements. It

has been shown recently in  $R_yCo_4Sb_{12}$  that multi-filling is an effective approach to generate additional phonons scattering and thus to decrease the lattice thermal conductivity<sup>19</sup>. Furthermore, this reduction is more pronounced when the valence states of the two filler atoms are different<sup>19</sup>.

Recently, we have shown the possibility of mixing cerium and ytterbium on the 2a site of the structure to form a complete solid solution  $Ce_{1-y}Yb_yFe_4Sb_{12}$ <sup>20</sup>, and of tuning the carrier concentration by substituting Co or Ni for Fe to form partially filled skutterudites with general formula  $Ce_{y/2}Yb_{y/2}Fe_{4-x}(Co/Ni)_xSb_{12}$ <sup>21</sup>. We have shown that Ce is always in a trivalent state whereas Yb is in a mixed valence state that depends on the Yb fraction<sup>22</sup>. This paper presents the thermal and electrical transport properties of these series from 4K to 800K. The effect of double-filling on the thermoelectric properties is analysed. Finally, the potential of double-filled skutterudites with respect to the thermoelectric performance as well as possible improvements are discussed.

### Experimental:

All samples described in this study were prepared by standard arc melting on a water-cooled copper hearth under Ar atmosphere and subsequent annealing as described in ref.<sup>22</sup>. For physical properties measurements, densification of the samples was achieved by two techniques as described in ref.<sup>22</sup>. Structural and chemical characterisations of the samples were performed by X-ray diffraction (XRD) and electron probe microanalysis (EPMA) and are also described in ref.<sup>22</sup>. All the compositions reported in this article are final compositions measured by EPMA and normalized to full occupancy of the transition metal site. The antimony fraction has been fixed to full occupancy, as the observed deviation is not significant. XRD and EPMA show that every sample is constituted by one single skutterudite phase and faint amounts of  $Sb$ ,  $Fe_{1-x}(Co/Ni)_xSb_2$  and/or  $Ce_{1-z}Yb_zSb_2$ . All samples contain more than 95% of the skutterudite phase. No broadening or shift of the Bragg peaks can be observed, thus revealing that the skutterudite phases are well crystallized and homogeneous.

For electrical conductivity and thermopower, all samples were measured in a direction perpendicular to the pressing direction. Details are given in ref.<sup>22</sup>. Hall effect measurements were performed on the same samples as electrical resistivity between 4K and 300K and up to 7 teslas using a Quantum Design PPMS. The Hall coefficient was deduced from the slope of the Hall resistivity versus field curves,  $\rho_H(H)$ . The carrier concentration (n or p) was calculated from the Hall coefficient  $R_H$ , assuming a single-carrier model and a Hall factor of unity. Hall mobility  $\mu_H$  was obtained using

$$\mu_H = \left| \frac{1}{\rho n e} \right|$$

with  $\rho$  the electrical resistivity. Above room

temperature, thermal conductivity was determined by measuring the thermal diffusivity on a 12mm diameter disc by a laser flash technique and the specific heat by differential scanning calorimetry. Thermal conductivity measurements below room temperature were performed in a flow cryostat on cuboid-shaped samples.

### Results and discussion :

Figure 1 shows the temperature dependences of the thermopower (bottom) and of the electrical resistivity (top) for three samples belonging to the series  $Ce_{1-z}Yb_zFe_4Sb_{12}$ . As expected from a simple electrons count, all samples appear p type, as can be deduced from the positive values of the thermopower. For all samples, the thermopower grows continuously up to 520K (limit of our measurement setup). For samples with  $z=0$  and  $z=1$ , its magnitude is consistent with the results reported by Sales et al. for  $CeFe_4Sb_{12}$ <sup>1</sup> and by Anno et al. for  $YbFe_4Sb_{12}$ <sup>23</sup>. Except in the low temperature part (under about 100K) where magnetism may contribute, the thermopower of the mixed compound  $Ce_{0.40}Yb_{0.53}Fe_4Sb_{12}$  lies between that of the two former compounds. This result is consistent with Hall effect measurements reported in table 1, which shows that the holes' concentration increases when the ytterbium fraction increases. This behaviour is related to the variation of the valence of the rare-earth : whereas Ce is always trivalent, the Yb valence state decreases from 2.7 in  $Ce_{0.85}Yb_{0.05}Fe_4Sb_{12}$  to 2.2 in  $Yb_{0.92}Fe_4Sb_{12}$ <sup>20</sup>. The electrical resistivity increases with increasing temperature for all samples belonging to the  $Ce_{1-z}Yb_zFe_4Sb_{12}$  series as can be expected for semimetals. The high temperature values measured for  $Yb_{0.92}Fe_4Sb_{12}$  and  $Ce_{0.85}Fe_4Sb_{12}$  are slightly lower than those reported in the literature<sup>24,25</sup>, thus revealing a very good densification of our samples. The resistivity of  $Ce_{0.40}Yb_{0.53}Fe_4Sb_{12}$  lies between that of  $Yb_{0.92}Fe_4Sb_{12}$  and  $Ce_{0.85}Fe_4Sb_{12}$ , in agreement with the dependence of the thermopower with substitution. The hole mobility decreases with increasing carrier concentration (see Table 1), as it has been observed in the series  $Yb_yFe_{4-x}Ni_xSb_{12}$ <sup>23</sup> where this behaviour has been attributed to an increase of the effective mass with increasing carrier concentration<sup>23</sup>. However, this decrease of  $\mu$  does not dominate the increase of  $[p]$  and  $\rho$  decreases.

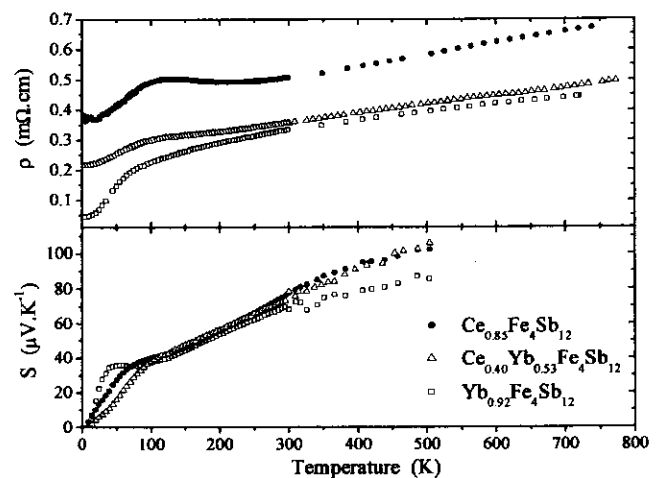


Fig. 1 : Temperature dependence of the electrical resistivity (top) and of the thermopower (bottom) in  $Ce_{1-z}Yb_zFe_4Sb_{12}$ .

Figure 2 shows the low temperature dependence of the thermal conductivity in the series  $Ce_{1-z}Yb_zFe_4Sb_{12}$ . The thermal conductivity of  $Yb_{0.92}Fe_4Sb_{12}$  is higher than that of  $Ce_{0.85}Fe_4Sb_{12}$ . This is related to an increase of the electronic

part of the thermal conductivity  $\lambda_e$  with increasing Yb fraction. However, although the electrical resistivity of  $Ce_{0.40}Yb_{0.53}Fe_4Sb_{12}$  is lower than that of  $Ce_{0.85}Fe_4Sb_{12}$ , its thermal conductivity is lower too.

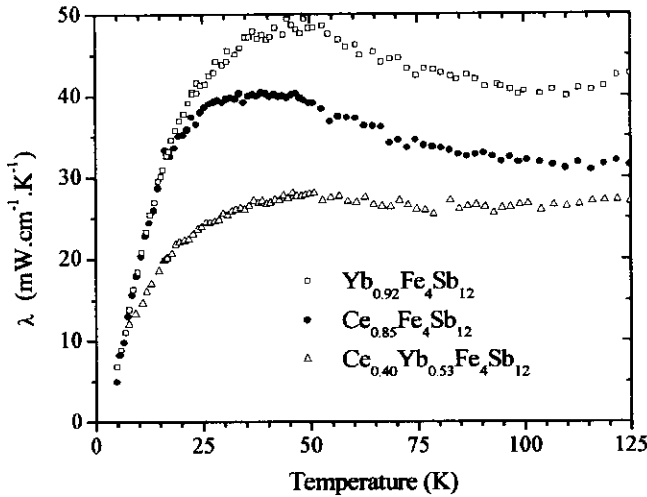


Fig. 2 : Temperature dependence of the thermal conductivity in  $Ce_{1-x}Yb_xFe_4Sb_{12}$ .

Therefore, the double filling of the cage with two filler atoms of different valence states appears to be an effective path to reduce the thermal conductivity, as was first shown by Chen et al. in  $(R-R')_yCo_4Sb_{12}$ <sup>19</sup>. The thermal conductivity is almost constant from room temperature up to 825K in  $Ce_{0.40}Yb_{0.53}Fe_4Sb_{12}$  (not shown).

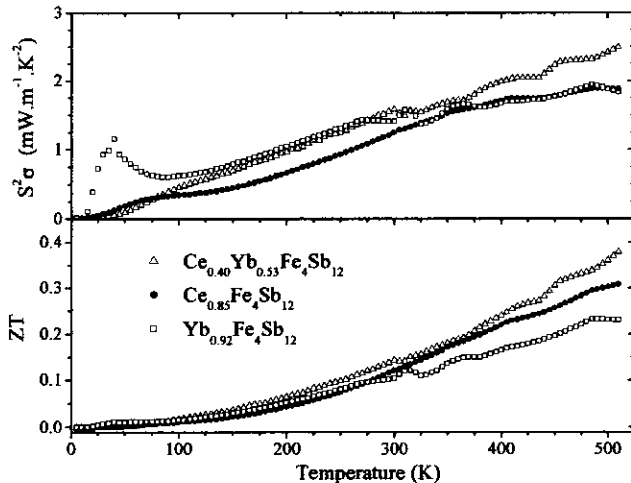


Fig. 3 : Temperature dependence of the power factor (top) and of the dimensionless thermoelectric figure of merit (bottom) in  $Ce_{1-x}Yb_xFe_4Sb_{12}$ . ZT data for  $Ce_{0.85}Fe_4Sb_{12}$  and  $Yb_{0.92}Fe_4Sb_{12}$  have been extrapolated from low temperature thermal conductivity measurements.

Figure 3 shows the temperature dependence of the power factor  $S^2\sigma$  (top) and of the dimensionless thermoelectric figure of merit (bottom). ZT data for  $Ce_{0.85}Fe_4Sb_{12}$  and  $Yb_{0.92}Fe_4Sb_{12}$  have been extrapolated from low temperature thermal conductivity measurements. At 520K, the power factor is close in  $Yb_{0.92}Fe_4Sb_{12}$  and  $Ce_{0.85}Fe_4Sb_{12}$  : the

electrical resistivity is lower in the former one and the thermopower is higher in the last one, thus resulting in similar power factor. However, it is clearly enhanced in the double filled compound  $Ce_{0.40}Yb_{0.53}Fe_4Sb_{12}$ .

Moreover, as can be seen in figure 3, the figure of merit ZT is enhanced in  $Ce_{0.40}Yb_{0.53}Fe_4Sb_{12}$  by more than 20% as compared to  $Ce_{0.85}Fe_4Sb_{12}$  and by more than 60% as compared to  $Yb_{0.92}Fe_4Sb_{12}$ . Therefore, double filled skutterudites seems to be of significant interest to improve the power generation efficiency.

To reach higher ZT values, it is mandatory to tune the charge carrier concentration. This can be achieved by substituting Co or Ni for Fe on the metal site. Figure 4 shows the room temperature thermopower in the series  $(Ce-Yb)_yFe_{4-x}(Co/Ni)_xSb_{12}$  as a function of the equivalent cobalt fraction defined in ref.<sup>14</sup>. It is considered from a simple electrons count that the substitution of one iron atom by one nickel atom is equivalent to the substitution of two iron atoms by two cobalt atoms. This enables us to directly compare the results obtained for the Fe-Ni and the Fe-Co series.

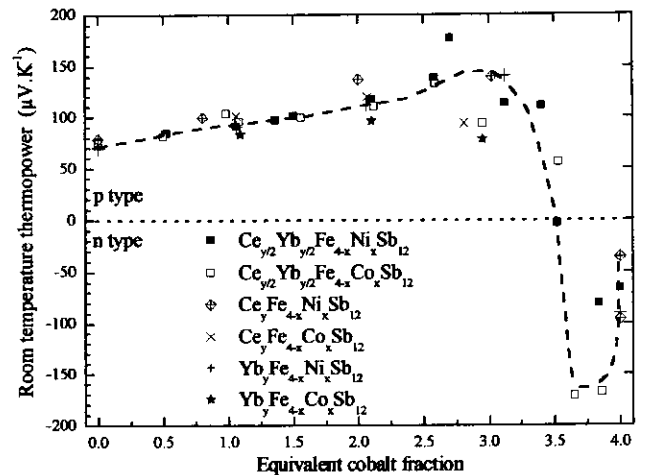


Fig. 4 : Room temperature thermopower in the series  $(Ce-Yb)_yFe_{4-x}(Co/Ni)_xSb_{12}$  versus equivalent cobalt fraction as described in text. The dashed line is a guide for the eyes.

Figure 4 shows a crossover from p to n type conductivity for an equivalent cobalt fraction of about 3.5, which can be easily explained by a simple carriers count: the Fe-Co or Fe-Ni substitution reduces the holes' concentration which is eventually overcompensated by the electrons provided by the filler atom(s) for rich Co or Ni skutterudites. This simple count also explains the increase of S before the p-n transition. The thermopower reaches its highest absolute values close to the p-n transition, and its magnitude very weakly depends on the nature of the filler atom.

The thermal dependence of the thermopower and of the electrical resistivity are shown in Fig. 5 for some samples belonging to the series  $Ce_{y/2}Yb_{y/2}Fe_{4-x}(Co/Ni)_xSb_{12}$ . As can be deduced from Fig. 4, iron rich samples appear p type whereas cobalt rich or nickel rich samples appear n type. Similarly to the series  $Ce_{1-x}Yb_xFe_4Sb_{12}$ , the absolute value of the thermopower grows continuously up to 520K and no evidence of a maximum can be observed, except for  $Ce_{0.05}Yb_{0.12}Fe_{2.08}Ni_{1.92}Sb_{12}$  whose thermopower decreases at

high temperature. The latter is probably related to the semi-conducting nature of this compound (see Fig. 5 top). All other samples are semimetals with low resistivity values, which increase with increasing temperature. These values are similar to those reported in the literature for skutterudites with similar cobalt or iron fraction (see for example <sup>23, 26</sup>).

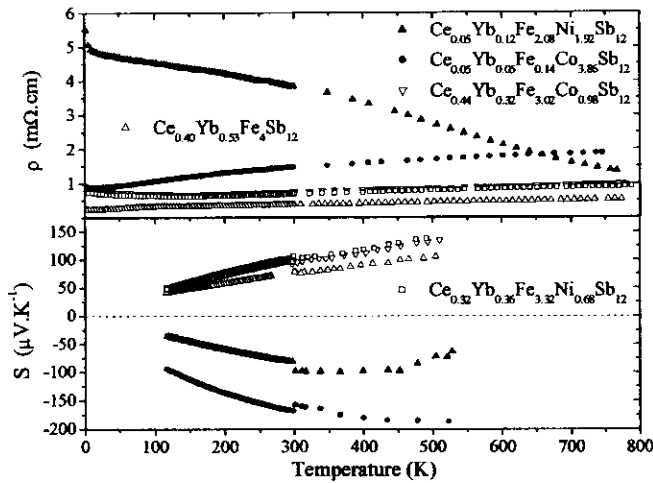


Fig. 5 : Temperature dependence of the electrical resistivity (top) and of the thermopower (bottom) in  $Ce_{y/2}Yb_{y/2}Fe_{4-x}(Co/Ni)_xSb_{12}$ .

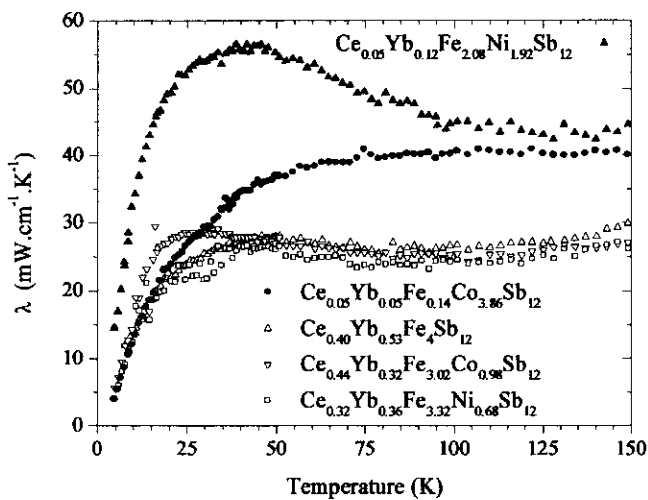


Fig. 6 : Temperature dependence of the thermal conductivity in  $Ce_{y/2}Yb_{y/2}Fe_{4-x}(Co/Ni)_xSb_{12}$ .

Figure 6 shows the low temperature dependence of the thermal conductivity. The thermal conductivity first decreases when substituting cobalt or nickel for iron to form partially filled skutterudites, and then increases when the rare-earth concentration further decreases. This behaviour is consistent with the “mass fluctuation scattering” model proposed by Meisner et al. <sup>15</sup>, which showed that the minimum thermal conductivity in  $Ce_yFe_{4-x}Co_xSb_{12}$  occurs for  $y \sim 2/3$ . The thermal conductivity is almost constant from room temperature up to 825K in  $Ce_{0.44}Yb_{0.32}Fe_{3.02}Co_{0.98}Sb_{12}$  (not shown).

The temperature dependence of the power factor  $S^2\sigma$  and of the thermoelectric figure of merit are shown in figure 7. Whereas the power factor and ZT are similar in p type  $Ce_{0.44}Yb_{0.32}Fe_{3.02}Co_{0.98}Sb_{12}$  and  $Ce_{0.32}Yb_{0.36}Fe_{3.32}Ni_{0.68}Sb_{12}$ , with similar equivalent cobalt fraction, this is not the case in n type  $Ce_{0.05}Yb_{0.12}Fe_{2.08}Ni_{1.92}Sb_{12}$ ;  $Ce_{0.05}Yb_{0.05}Fe_{0.14}Co_{3.86}Sb_{12}$ . They are strongly degraded in the Ni-based n type skutterudite. While the holes concentration and mobility are similar in iron rich Ni-based and Co-based skutterudites, the electrons concentration and mobility are very different in iron poor skutterudites (see Table 2). Especially, the mobility is strongly decreased in the Ni-rich skutterudite as compared to the Co-rich ones. Several mechanisms could explain this behaviour. This decrease could be related to the theoretical calculations performed by Lassalle et al. <sup>27</sup> on  $Fe_2Ni_2Sb_{12}$ , which shows that the disorder induced by the random distribution of iron and nickel atoms has a strong effect on antimony atoms position and charge, and therefore on the band structure and on the effective mass. This could also be related to the huge structural disorder induced by the substitution of iron by nickel : whereas less than 4% of the cobalt atoms are substituted by iron in  $Ce_{0.05}Yb_{0.05}Fe_{0.14}Co_{3.86}Sb_{12}$ , almost 50% of the iron atoms are substituted by nickel in  $Ce_{0.05}Yb_{0.12}Fe_{2.08}Ni_{1.92}Sb_{12}$ . Nevertheless, it appears that cobalt substitutions are more relevant than nickel substitutions to achieve good thermoelectric properties in n type skutterudites. The best figure of merit is observed in  $Ce_{0.44}Yb_{0.32}Fe_{3.02}Co_{0.98}Sb_{12}$  with  $ZT=0.55$  at 525K. However, one must keep in mind that this composition has not been optimized and that important enhancements are certainly possible with higher cobalt fractions.

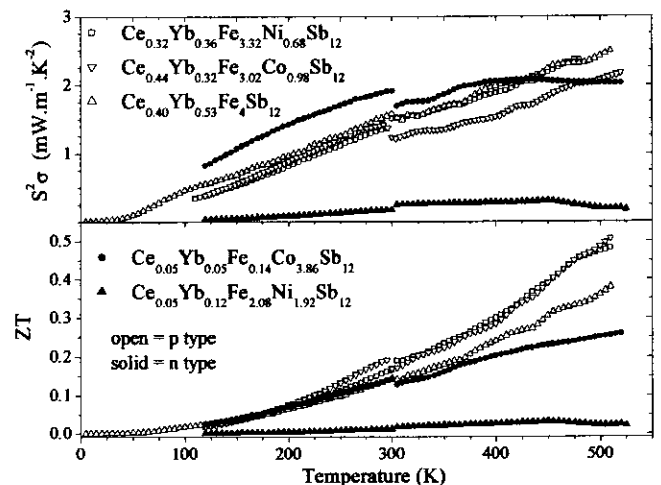


Fig. 7 : Temperature dependence of the power factor (top) and of the thermoelectric figure of merit (bottom) in  $Ce_{y/2}Yb_{y/2}Fe_{4-x}(Co/Ni)_xSb_{12}$ . ZT data for  $Ce_{0.32}Yb_{0.36}Fe_{3.32}Ni_{0.68}Sb_{12}$ ,  $Ce_{0.05}Yb_{0.05}Fe_{0.14}Co_{3.86}Sb_{12}$  and  $Ce_{0.05}Yb_{0.12}Fe_{2.08}Ni_{1.92}Sb_{12}$  have been extrapolated from low temperature thermal conductivity measurements.

Figure 8 shows the figure of merit of  $Ce_{0.44}Yb_{0.32}Fe_{3.02}Co_{0.98}Sb_{12}$  (thermopower has been extrapolated above 550K). We have also plotted the figure of

merit of  $Ce_{0.74}Fe_{2.98}Co_{1.02}Sb_{12}$  (same cobalt fraction) and  $Ce_{0.28}Fe_{1.52}Co_{2.48}Sb_{12}$  (state of the art) published by Tang et al.<sup>18</sup> for comparison. For a similar cobalt fraction, the figure of merit is strongly enhanced in the double filled skutterudite : it increases from  $ZT=0.4$  at 700K in  $Ce_{0.74}Fe_{2.98}Co_{1.02}Sb_{12}$  to  $ZT=0.85$  at 700K in  $Ce_{0.44}Yb_{0.32}Fe_{3.02}Co_{0.98}Sb_{12}$ . The latter exhibits a figure of merit very close to that of state of the art  $Ce_{0.28}Fe_{1.52}Co_{2.48}Sb_{12}$ , although the composition has not been optimized. From this result, high  $ZT$  values are expected in double filled skutterudites, probably significantly higher than  $ZT=1$ .

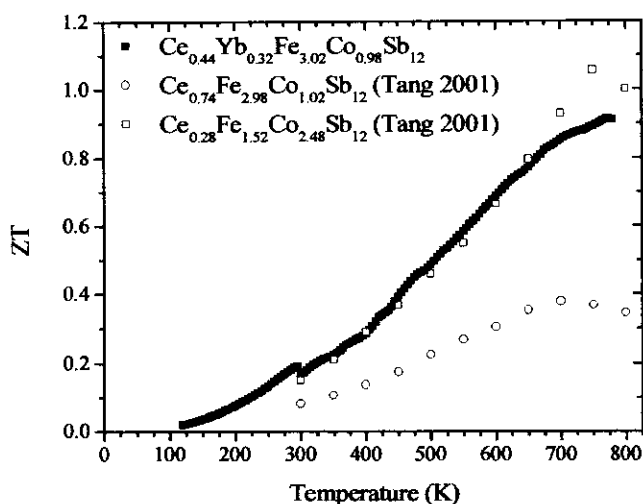


Fig. 8 : Temperature dependence of  $ZT$  in  $Ce_{0.44}Yb_{0.32}Fe_{3.02}Co_{0.98}Sb_{12}$ . Thermopower has been extrapolated above 550K.

### Conclusion :

We have studied the thermoelectric properties of skutterudites belonging to the series  $Ce_{y/2}Yb_{y/2}Fe_{4-x}(Co/Ni)_xSb_{12}$ , where Ce is trivalent whereas the Yb valence decreases when the Yb fraction increases. The power factor and the thermoelectric figure of merit are clearly enhanced in  $Ce_{0.40}Yb_{0.53}Fe_4Sb_{12}$  as compared to  $Ce_{0.85}Fe_4Sb_{12}$  and  $Yb_{0.92}Fe_4Sb_{12}$ . The carrier concentration can be tuned by substituting Co or Ni on the Fe site, which also diminishes the thermal conductivity. It has been shown that the cobalt substitution is more effective than the nickel substitution to achieve high power factor or figure of merit in n-type samples.  $ZT=0.5$  has been observed at 500K in  $Ce_{0.44}Yb_{0.32}Fe_{3.02}Co_{0.98}Sb_{12}$  and an extrapolation leads to  $ZT=0.95$  at 800K, which is close to state of the art  $Ce_{0.28}Fe_{1.52}Co_{2.48}Sb_{12}$  although the composition is far from being optimized. Therefore, double filled Ce+Yb skutterudites appear to be very promising with respect to thermoelectricity, and  $ZT$  values significantly above unity could possibly be reached.

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