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Partially filled $CoSb_3$ skutterudite compounds are emerging materials for thermoelectric energy conversion at high temperature. $Ca_xCo_4Sb_{12}$ with different Ca contents has been prepared by the conventional metallurgical route. The temperature dependences of the electrical resistivity, Seebeck coefficient, and thermal conductivity have been measured on these compounds in the 300–800 K temperature range. These measurements have identified Ca as being a true *n*-type filler atom and offer, for this family of skutterudite, several valuable insights into the potential of Ca to provide good thermoelectric performance. © *2004 American Institute of Physics.*
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I. INTRODUCTION

Extensive efforts have been devoted over the last several years to study the physical properties of a class of materials called skutterudites. It was demonstrated that some semiconducting skutterudite compounds have a great potential for thermoelectric applications.[1,2] The principal characteristics for ''good thermoelectric materials'' are given by the definition of the dimensionless figure of merit ZT, where T is the absolute temperature and $Z=\alpha^2/\rho\lambda$. In this equation, α is the Seebeck coefficient, ρ the electrical resistivity, and λ the total thermal conductivity ($\lambda=\lambda_E+\lambda_L$ where λ_E is the electronic contribution and λ_L the lattice contribution). Finding more efficient thermoelectric materials for either refrigeration or power generation applications corresponds to finding materials with higher values of ZT than state-of-the-art materials.

Skutterudites are binary compounds of general formula MX_3 where M is a transition metal such as Co, Rh, or Ir and X stands for a picnogen atom such as P, As, or Sb. Binary skutterudites crystallize in the body-centred cubic structure in the space group Im 3. It is an open crystalline structure typified by the presence of two voids. This feature is the key point for making skutterudite material with interesting thermoelectric properties. Actually, by filling the voids with foreign species, one may modify both the electronic and lattice properties and enhance the thermoelectric performances.[1–24] In this connection, the greatest efforts were conducted with cobalt triantimonide. Several kinds of atoms were used to fill the voids of the structure, including rare earths,[3–13] alkaline earths,[24] Sn,[15–17] or Tl elements.[14] High ZT values, compared to the state-of-the-art Si–Ge alloys, were obtained with the $Ce_yFe_{4-x}Co_xSb_{12}$[25] and $Ba_{0.3}Co_{4-x}Ni_xSb_{12}$[26] compounds for achieving *p* and *n* type semiconductors, respectively.

In this article, we present an investigation of $CoSb_3$ partially filled with an alkaline earth, namely calcium. All the transport measurements necessary to calculate the value of ZT were performed within the temperature range 300–800 K. This work offers several valuable insights into the potential of this family of compounds for thermoelectric applications.

II. EXPERIMENT

Preparation of the samples used in this study was performed by a metallurgical route and is described in detail elsewhere.[27] High purity Co (free of Ni), Sb, and Ca were used as starting materials. The densification (>80% of the theoretical density) of the samples was accomplished by hot pressing in graphite dies under an argon atmosphere at 600 °C for 2 h and under a pressure of 660 kg/cm^2.[27]

Structural and chemical characterisations of the samples were realized through x-ray diffraction (XRD), neutron diffraction and electron microprobe analyses (EPMA). All the compositions reported in this article result from EPMA analyses and were normalized to full occupancy of the cobalt site.

It was shown that the maximum filling fraction of $Ca_xCo_4Sb_{12}$ is at least $x=0.2$ with the preparation method we developed. This value is only half of the maximum filling fraction of the other alkaline earth filler atom barium, but is consistent with that obtained for Tl, La, Yb filler atom.[30] XRD and EPMA revealed the single phase and chemically homogeneous samples. Rietveld refinement performed on

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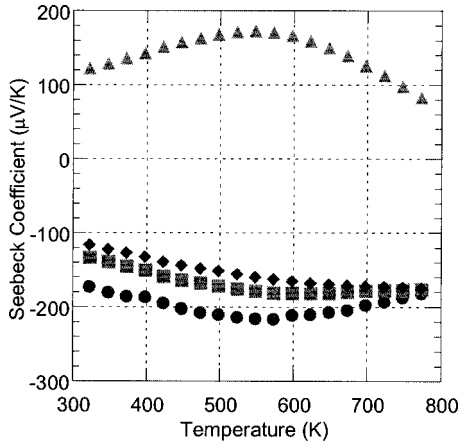

FIG. 1. Temperature dependence of the Seebeck coefficient: (▲) $Co_4Sb_{12.24}$ *p* type, (●) $Ca_{0.05}Co_4Sb_{12.43}$, (■) $Ca_{0.08}Co_4Sb_{12.45}$, and (♦) $Ca_{0.2}Co_4Sb_{12.46}$.

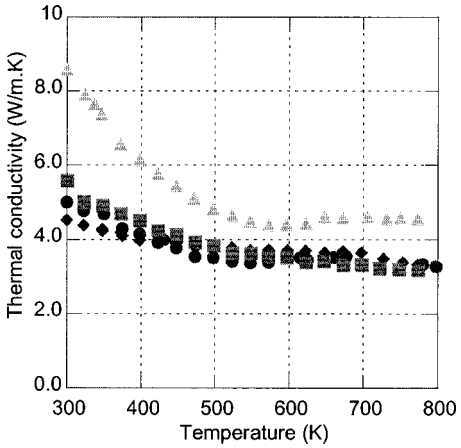

FIG. 3. Temperature dependence of the thermal conductivity of: (▲) $Co_4Sb_{12.24}$ *p* type, (●) $Ca_{0.05}Co_4Sb_{12.43}$, (■) $Ca_{0.08}Co_4Sb_{12.45}$, and (♦) $Ca_{0.2}Co_4Sb_{12.46}$.

neutron data proved that the calcium is located in the voids of the structure.[27]

Transport properties have been performed in the 300–800 K temperature range. All the samples were measured in a direction perpendicular to the pressing direction except for thermal conductivity. Thermal conductivity was determined by measuring the thermal diffusivity by a laser flash technique, the specific heat by differential scanning calorimetry, and the density by an immersion technique. The electrical resistivity was measured by a four probes technique based on the Van der Pauw method, whereas the Seebeck coefficient was determined using a standard method.[28]

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of the Seebeck coefficient for several $Ca_xCo_4Sb_{12}$ samples ($x=0,0.05,0.08,0.2$). The binary compound $CoSb_3$ appears *p* type by this way of synthesis. The value of the Seebeck coefficient becomes negative for all samples containing Ca between 300 and 800 K. Filling the voids of the structure with Ca atoms provides the possibility of changing the sign of the Seebeck coefficient. The Ca atoms give electrons to the structure and thus change the carrier concentration and its nature. Under these circumstances, typical of doped semiconductors, we observe a weak decrease of magnitude of the Seebeck coefficient with the increase of calcium content. Nevertheless, the values of S remain important in the whole temperature range. These values of Seebeck coefficients are similar to those observed for $CoSb_3$ partially filled with Ce,[4] La,[6] Ba,[24] and are presumably due to the large electron effective masses. We estimated the electron effective mass in $Ca_xCo_4Sb_{12}$ using a single parabolic band model with acoustic phonon scattering. In this model, the Seebeck coefficient α can be expressed as

$$\alpha = -\frac{k}{e}\left(2\frac{F_1(\xi)}{F_0(\xi)} - \xi\right), \tag{1}$$

where ξ is the reduced Fermi level and F_x is the Fermi integral of order *x*. Using the same formalism, the electron carrier concentration *n* can be expressed as

$$n = \frac{4}{\sqrt{\pi}}\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2} F_{1/2}(\xi), \tag{2}$$

where m^* is the electron effective mass.

The reduced Fermi levels were determined from the experimental data using Eq. (1) and were applied to Eq. (2), together with the experimental Hall carrier concentration values (measured at room temperature), to calculate the effective masses. Employing this simple model, the effective masses obtained are comprised between 2 and 3 m_0 (m_0 is the free electron mass) for $Ca_xCo_4Sb_{12}$ compounds. These values are in good agreement with those obtained for partially filled Ce,[4] La,[12] Ba,[24] $CoSb_3$ compounds. The relatively large values of m^* are also consistent with band structure calculations performed on $Ca_xCo_4Sb_{12}$.[29]

Figure 2 shows the temperature dependences of the electrical resistivity for the same samples. The *p*-type $CoSb_3$ resistivity behavior is consistent with previously published results for similar carrier concentration ($p \sim 3\times10^{18}\,\mathrm{cm}^{-3}$ at room temperature).[21] The electrical resistivity of the three samples containing Ca is relatively high, with room tempera-

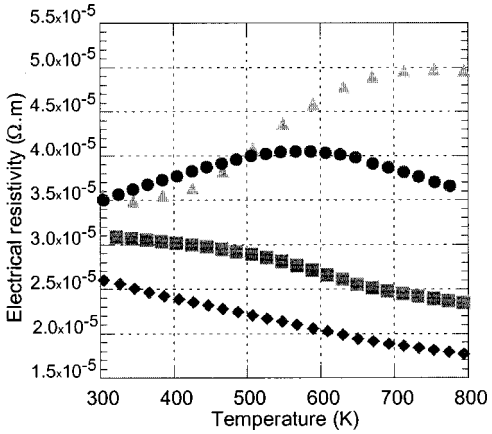

FIG. 2. Temperature dependence of the electrical resistivity of: (▲) $Co_4Sb_{12.24}$ *p* type, (●) $Ca_{0.05}Co_4Sb_{12.43}$, (■) $Ca_{0.08}Co_4Sb_{12.45}$, and (♦) $Ca_{0.2}Co_4Sb_{12.46}$.

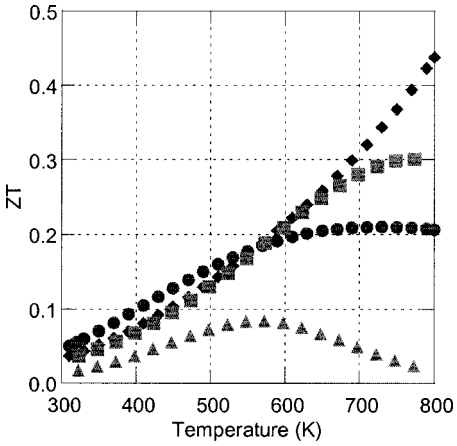

FIG. 4. Temperature dependence of the dimensionless figure of merit (ZT) of: (▲) $Co_4Sb_{12.24}$ p type, (●) $Ca_{0.05}Co_4Sb_{12.43}$, (■) $Ca_{0.08}Co_4Sb_{12.45}$, and (◆) $Ca_{0.2}Co_4Sb_{12.46}$.

ture values around 30 $\mu\Omega$ m, compared to Ba,[24] Eu,[9] or Yb-filled[12] skutterudites. Filling the voids of $CoSb_3$ with Ca may therefore lead to less optimized electrical resistivity as compared to the other divalent atoms.

The most interesting properties of these partially filled skutterudites are their thermal conductivity. The binary p-type $CoSb_3$ compound has a thermal conductivity of about 8.4 W/m K at room temperature. As shown in Fig. 3, the total thermal conductivity of the $Ca_xCo_4Sb_{12}$ compounds is lower than that of $CoSb_3$ over all the temperature range investigated. The electronic thermal conductivity λ_E has been estimated from the Wiedeman–Franz law ($\lambda_E = L_0 T/\rho$, where $L_0 = 2.44\times10^{-8}$ V^2/K^2). Taking into account the relatively high value of the electrical resistivity, the total thermal conductivity of the $Ca_xCo_4Sb_{12}$ compounds reflects essentially the lattice thermal conductivity. The lowering of the lattice thermal conductivity can be attributed to the rattling motion of the Ca ions inside the voids as it was already suggested by the large atomic displacement parameter (ADP) obtained for Ca in $Ca_xCo_4Sb_{12}$ compounds (ADP=0.68 Å^2 at 300 K).[27] However, the lattice thermal conductivity remains relatively large in comparison to skutterudites partially filled with rare-earth atoms (Ce,[4] La,[6] Yb)[12] and other species (Tl).[14] To decrease the lattice thermal conductivity of $Ca_xCo_4Sb_{12}$-based compounds even more, further substitution of Co by Ni and multifilling approaches might be interesting ways of investigation.[30]

From the results of the three transport properties, we have calculated the dimensionless figure of merit ZT for each sample. For all samples, the ZT values increase with increasing temperature within the temperature range investigated (Fig. 4). A maximum ZT value of 0.45 was achieved at 800 K for the compounds presenting the maximum filling fraction.

IV. CONCLUSION

Ca partially filled skutterudite compounds have been synthesized until $x=0.2$ by a metallurgical route. Transport properties measurement put forward that Ca can be identified as a true n-type filler atom. Despite the thermoelectric performance of these compounds being quite decent, they remain less attractive than the Ba partially filled compounds in the same range of temperature.[24] Further improvement may be forthcoming in these materials, particularly if the lattice thermal conductivity and the electrical resistivity can be further reduced.

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