Transport Properties of $Ca_xCo_4Sb_{12-y}Te_y$ Skutterudite Compounds

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Abstract

We have prepared a series of Te doped $Ca_xCo_4Sb_{12-y}Te_y$ skutterudite materials partially filled with Ca by a powder metallurgy route. The chemical composition and crystallographic structure have been checked by electron probe microanalyses and x-ray diffraction, respectively. It was found that the presence of Te strongly affects the Ca insertion compared to Te free samples. Preliminary transport properties (electrical and thermal) of these new skutterudite compounds are reported in the 4 – 300 K temperature range and discussed. Some electrical resistivity measurements have also been performed up to 800 K.

Introduction

During this last decade, many efforts have been provided in the search of new high efficient thermoelectric materials. Several promising families have attracted much attention including semi-Heusler phases [1], skutterudites [2], lamellar oxides [3], clathrates [4], and more recently the $AgPb_mSbTe_{2+m}$ system [5]. The performance of thermoelectric materials is usually evaluated in terms of their dimensionless figure of merit, $ZT = \alpha^2 T/\varrho\lambda$, where α is the thermopower, T the absolute temperature, ϱ the electrical resistivity, and $\lambda = \lambda_L + \lambda_E$ the total thermal conductivity with its lattice and electronic contributions, respectively.

Skutterudite compounds based on cobalt triantimonide display an exceedingly rich spectrum of physical properties. The electrical and thermal properties of skutterudites can be significantly modified either through partial or total filling of the open "cages" of their crystalline structure by different atoms and/or via substitutions of constituent atoms of the framework structure. In the past few years, a lot of combinations have been investigated [2, 6-19]. Both n and p-type skutterudite materials exhibiting ZT values exceeding those of the current standard thermoelectrics, namely PbTe based compounds and SiGe alloys, have been evidenced [6,17]. Quite recently, Ca ions were identified as new filler elements [20]. At moderated temperatures, these partially-filled $Ca_xCo_4Sb_{12}$ compounds keep high thermopower values and a favourable thermal conductivity but, unfortunately to the detriment of an excessive electrical resistivity. Consequently, the thermoelectric performance remains moderated up to high temperatures ($ZT \sim 0.45$ at 800 K) [21]. In an effort to further reduce the electrical resistivity of the $Ca_xCo_4Sb_{12}$ compounds, we have investigated the influence of tellurium doping on the antimony sites. Previous results showed that the addition of tellurium in unfilled $CoSb_3$ increases the thermoelectric properties [22,23].

In this paper, we report on the preparation and the physico-chemical characterizations of a series of $Ca_xCo_4Sb_{12-y}Te_y$ samples. Low temperature transport properties are also presented and discussed.

Experimental

The $Ca_xCo_4Sb_{12-y}Te_y$ samples have been prepared by a solid-state reaction method. Two nominal Ca contents were considered ($x = 0.2$ and $x = 0.3$) while y was varied between 0 and 0.15. Appropriate quantities of high purity Ca pellets (99.5 %), Sb and Te shots (99.999 %) and Co (99.998 %) powders were loaded into a quartz ampoule. The ampoule was sealed under reducing $He-H_2$ atmosphere and heated in a vertical furnace up to 630 or 750°C for 84 h with the heating rate fixed at 1°C/min. The grown ingot was then ground in an agate mortar into powders (~100 μm) that were again annealed and powdered under the same conditions for samples with $x = 0.3$. Resulting powders were pressed into pellets that were annealed at 430 or 620°C for 84 hours. These pellets were crushed and powdered into 25 μm grains. Final compaction was performed in graphite dies by uniaxial hot pressing in an argon atmosphere at 600°C for 2 hours under 51 MPa.

The crystallographic structure of the samples was investigated by x-ray diffraction (XRD) conducted on a Siemens D-500 diffractometer with the Co $K_{\alpha 1}$ radiation. Silicon powder was used as a standard and was mixed with the powdered samples. The density of the samples was measured by the immersion technique or with a picnometer. The samples were also characterized by electron-microprobe analysis (EPMA) that was performed using a CAMECA SX 50 electron superprobe.

Parallelepipedic shaped samples (typically 9x2x2 mm^3) were cut with a diamond wire saw from the sintered ingot for transport property measurements. The electrical resistivity, thermopower and thermal conductivity were measured simultaneously on selected samples between 10 – 300 K. A dc four probe method was used to extract the resistivity while a four probe steady state heater and sink method was used to measure the thermal conductivity and the thermopower. Galvanomagnetic measurements (Hall effect) were also performed on an AC transport measurement system option of a PPMS (Quantum Design) over the temperature range of 2-350 K and with magnetic field ranging up to 7 T. The Hall mobility, μ_H, was calculated from the Hall coefficient and the resistivity values. Preliminary high temperature electrical resistivity measurements were performed on some samples using a Van der Pauw technique on square shaped sample (4x4x1 mm^3).

Sample	Nominal composition $Ca_xCo_4Sb_{12-y}Te_y$	Actual composition	Relative density (%)	Lattice parameter (Å)
1	x = 0.2; y = 0.02	x = 0.04; y = -	91	9.0392
2	x = 0.2; y = 0.05	x = 0.03; y = -	95	9.0385
3	x = 0.2; y = 0.08	x = 0.02; y = -	98	9.0377
4	x = 0.3; y = 0.10	x = 0.03; y = 0.06	99	9.0419
5	x = 0.3; y = 0.15	x = 0.01; y = 0.09	99	9.0410
6	x = 0.3; y = 0.24	x = 0.01; y = 0.05	97	9.0390

Table 1 *Nomimal and actual chemical compositions determined by EPMA, lattice parameters deduced from X-ray diffraction data, relative densities of the $Ca_xCo_{4-y}Ni_ySb_{12}$ samples. (-) means that the composition was not quantitatively determined.*

Results and discussion

The X-ray diffraction patterns of all the samples were indexed with a unit cubic cell corresponding to the skutterudite structure, space group Im3. The results showed that the samples were predominantly single phase with a small amount of a secondary Sb rich phase that never exceeds 2 vol. %. X-ray EPMA maps revealed that the Co and Sb elements are homogeneously distributed in the samples while small precipitates of Ca were systematically detected as illustrated in Fig. 1. Te-rich phases were also identified in some samples. Even in the absence of Te, the presence of Ca precipitates has been observed in Ca-partially filled skutterudite compounds prepared by this method [20].

Due to the presence of the Ca-rich phase, the actual composition of the skutterudite compounds shows a deficiency in calcium relatively to the nomimal composition (see table 1). However, the deviation is much more pronounced than that expected. The Ca-filling fraction x is always less than 0.05 whatever the series of samples while the maximum solubility determined by Puyet et al. in $Ca_xCo_4Sb_{12}$ compounds was x ~ 0.2 [20]. These observations seem to indicate that the substitution of Sb by Te limits the insertion of Ca in the voids of the crystalline structure. The link between the Te content y and the Ca content x is however not clearly established here and further investigations seem necessary before we can conclude. But it is not unlikely that the Ca fraction is fixed by the Te content in the same way that it was demonstrated in other skutterudite systems [8].

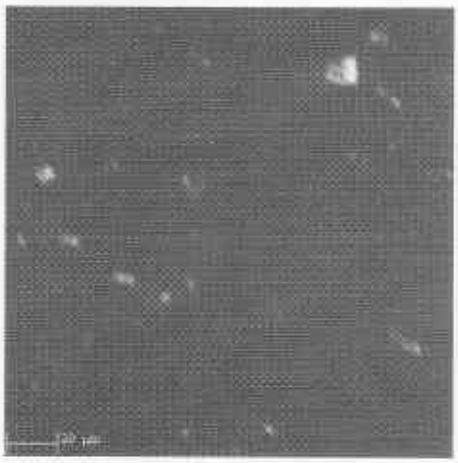

Figure 1 *Ca-Kα map as obtained by EPMA showing Ca-rich phases.*

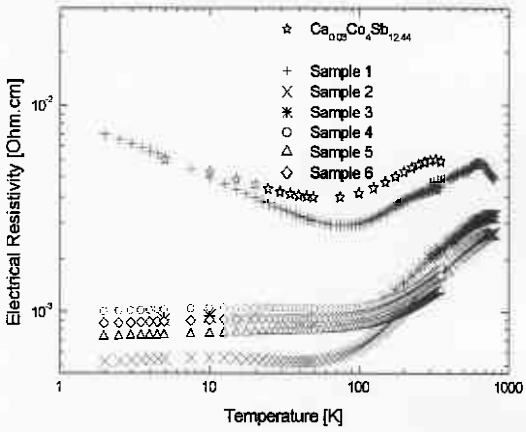

Figure 2 *Dependence of the electrical resistivity with temperature for $Ca_xCo_4Sb_{12-y}Te_y$ compounds.*

The temperature dependence of the electrical resistivity of the $Ca_xCo_4Sb_{12-y}Te_y$ samples is shown in Fig. 2. The measurements were performed between 2 – 350 K but some of them were extended up to 800 K. We also add in this figure the resistivity of the $Ca_{0.03}Co_4Sb_{12}$ compound for comparison. For the Te-doped samples, the resistivity is quite constant at low temperature and increases above 100 K. This increase is typical of heavily doped semiconducors. Above 600 K, the resistivity begins to decrease likely due to the onset of the intrinsic conduction.

As expected, the Hall coefficient of the Te-doped samples is negative. Both the Ca and the Te atoms give electrons to the structure. The Hall carrier concentration (see Fig. 3) is in the range $3x10^{19} - 2x10^{20}$ cm^{-3} at T = 300 K.

The Hall mobility as a function of temperature for these samples is reported in Fig. 4. Room temperature values lie between 30 – 50 $cm^2/V.s$ which are higher than those for Ca partially filled-Te undoped samples with comparable carrier concentration [24]. For all the Te-containing samples, the mobility follows a $T^{-3/2}$ dependence law near room temperature suggestive of scattering by the acoustic phonons.

As shown in Fig. 5, the thermopower values indicate that electrons are the majority charge carriers in the $Ca_xCo_4Sb_{12-y}Te_y$ compounds in agreement with our Hall data. All samples display a nearly linear increase in magnitude with temperature, aspects which are consistent with degenerate electron transport. Although the carrier concentration increases by a factor of about 10 among

the samples studied, the room temperature values do not change by more than 15%. Moreover, the values remain important presumably due to high electron effective masses.

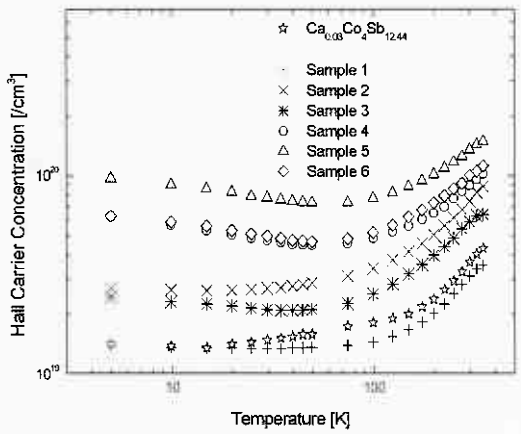

Figure 3 *The Hall carrier concentration values as a function of temperature for* $Ca_xCo_4Sb_{12-y}Te_y$.

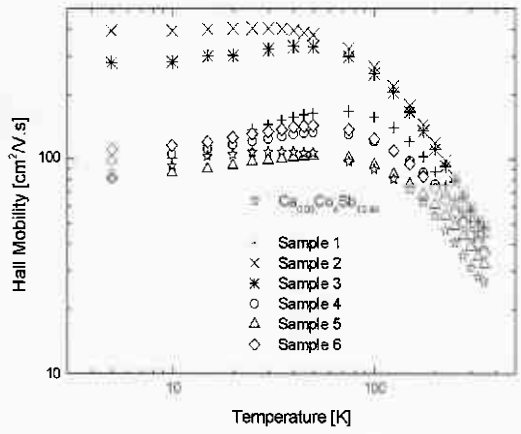

Figure 4 *The Hall mobility values as a function of temperature for* $Ca_xCo_4Sb_{12-y}Te_y$.

The dependence with temperature of the thermal conductivity is reported in Fig. 6 for some Te-doped samples. Also shown are the data for the binary skutterudite Co_4Sb_{12} and for $Ca_{0.03}Co_4Sb_{12}$. Note that the total thermal conductivity of all the samples reflects essentially the lattice thermal conductivity. The data in Fig. 6 illustrate the strong effect the Ca occupancy has on the peak near 25 K. The subsequent effect of Te is difficult to establish because we were not able to ensure the exact reproducibility of the filling fraction of Ca. However, we may anticipate that the substitution of Sb by Te should produce little additional phonon scattering because of the low mass difference (less than 5%) between this two atoms.

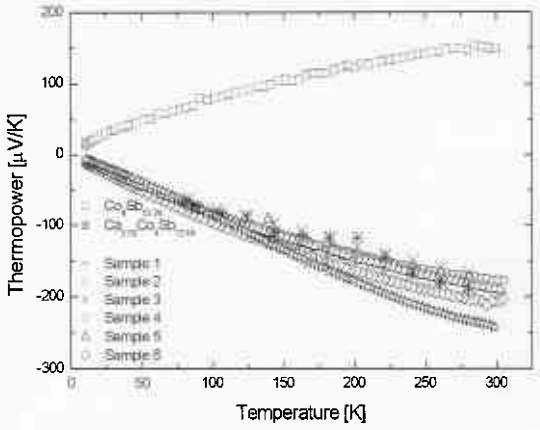

Figure5 *The thermopower values as a function of temperature for* $Ca_xCo_4Sb_{12-y}Te_y$.

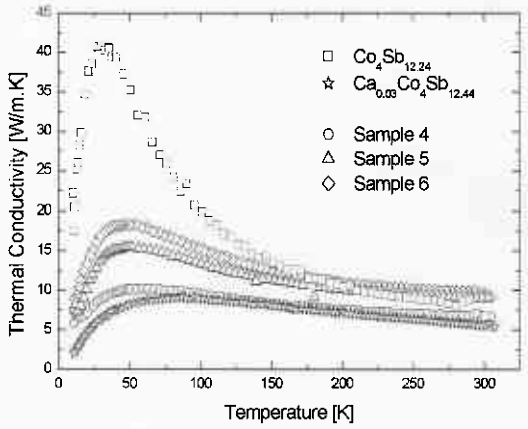

Figure 6 *The thermal conductvity values as a function of temperature for* $Ca_xCo_4Sb_{12-y}Te_y$.

Conclusion

We have prepared $Ca_xCo_4Sb_{12-y}Te_y$ samples via a metallurgical route. It was shown that the presence of Te atoms prevents the achievement of a high Ca filling fraction. The relation between x and y is not clearly established yet. The low temperature transport properties of these compounds were found to be typical of those of heavily doped semiconductors.

Acknowledgments

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