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Thermoelectric Promise of $(\mathrm{In}_x\mathrm{Sn}_x)\mathrm{Co}_4\mathrm{Sb}_{12}$ Materials

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We report on a new series of filled skutterudites derived from $\mathrm{CoSb_3}$ with double filling of the cage (by In, Sn) in order to lower the thermal conductivity. As expected for Co-rich side samples, the Seebeck coefficient indicates n-type, with surprisingly high values at 300 K.

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1. Introduction

The development of alternative technologies is of prime necessity to reduce the dependence in fossil fuels and to preserve the climate. In a thermoelectric generator (TG), electricity can be generated by the direct action of heat on the constituting materials, which are n- and p-type semiconductors connected electrically in series and thermally in parallel. These systems are simple, compact, silent and highly reliable (no moving parts).

Qualitatively, the efficiency of a TG is related to the dimensionless figure of merit $ZT = S^2\sigma T/\lambda$ (T — average temperature of use; S — Seebeck coefficient; σ and λ — electrical and thermal conductivities, respectively). Z is a parameter intrinsic to each material which depends on its thermal and electrical properties.

Over past few years, much effort has been devoted to achieve higher ZT in new series of materials. Among them $\mathrm{A}_y(\mathrm{Co,Fe,Ni})_4\mathrm{Sb}_{12}$ (A = electropositive element) skutterudites probe to be specially promising as (i) both n- and p-type exist and (ii) $ZT > 1$ in various series. For n-types the best performances have been obtained in $\mathrm{A}_x(\mathrm{Co, Fe, Ni})_4\mathrm{Sb}_{12}$, on the Co-rich side with A = Ba, Ca, Yb, Eu, In, and (Ce, In) [1]. For p-type, materials on the Fe-richer side have high ZT [2]. In order to further decrease λ, and consequently increase ZT, double filling has been proposed in $(\mathrm{Ce,Yb})_y\mathrm{Fe}_4\mathrm{Sb}_{12}$ and it turns out to be efficient in the series (Ce,Yb)$_y$(Fe, Co, Ni)$_4$Sb$_{12}$ [3]. In Ln-based skutterudites, the ZT maximum occurs between 600 and 900 K, often bound with a maximum of S. However, the TG efficiency is not only related to the maximum value of ZT at a certain T but the value of ZT has to be as high as possible in the full temperature range of use. Materials with higher ZT at lower T can also be very useful for segmented TG. This has been recently obtained with a ZT of 1.2 in In$_x$Co$_4$Sb$_{12}$ [4] and of 1.7 in In$_{0.2}$Ce$_{0.2}$Co$_4$Sb$_{12}$ at 575 K [5]. In the frame of our effort to continue the exploration of new thermoelectric materials — and of the effect of double filling — we here report the preliminary results on the preparation, X-ray diffraction (XRD) characterization and electrical transport properties obtained on the (In$_x$Sn$_x$)Co$_4$Sb$_{12}$ series.

2. Experimental

(In$_x$Sn$_x$)Co$_4$Sb$_{12}$ ($0.05 \leq x \leq 0.2$) samples with 2 g were prepared by reaction of the elements at 800°C under vacuum, in a sealed quartz ampoule. Examination of the Ce–Sb phase diagram leads to the annealing of the samples at 600°C for 8 days. No significant weight losses ($< 0.5\%$) were observed. Powder XRD patterns of the annealed samples were collected at room temperature using Cu K_α radiation using a Philips PW1150 diffractometer, with a 2θ-step size of 0.02°, from 10° to 100°, and a constant counting time of 10 s per step. The XRD patterns were studied using the Rietveld method with the help of the FULLPROF software [6]. Electrical resistivity measurements were attempted at room temperature using a PPMS (9 Tesla) system equipped with transport setup. The Seebeck coefficient was determined in the 100–300 K temperature range by using a home-made apparatus [7] on samples made by pressing powder at 300°C under 400 MPa during two hours (P.O. Weber hot-press tool HS10) which lead to solid bars ($10 \times 2 \times 2$ mm) with a density equal to 80% of the theoretical density.

3. Results and discussion

The samples were homogeneous, but porous, fragile, and brittle. Figure 1 shows the X-ray diffraction patterns of the (In$_x$Sn$_x$)Co$_4$Sb$_{12}$ ($x = 0.05$, 0.1, and 0.2) samples. The skutterudite CoSb$_3$-type structure (cubic, $Im3$ space group) was confirmed for all the samples, with lattice parameter values ranging from $a = 9.046$ Å to 9.054 Å ($x = 0.05$ and 0.2, respectively). No significant amounts of impurity phases (typically $< 1\%$) were detected.

No reliable electrical resistivity measurements could be obtained: the measurements were not reproducible, probably due to the porous and fragile quality of the samples. However, a semiconductor behavior is expected for these samples, similarly to other skutterudites.

The temperature dependence of the thermoelectric coefficient is shown in Fig. 2. All samples have high absolute values at room temperature, with a negative sign, which decrease with the decreasing temperature. The increase in the In

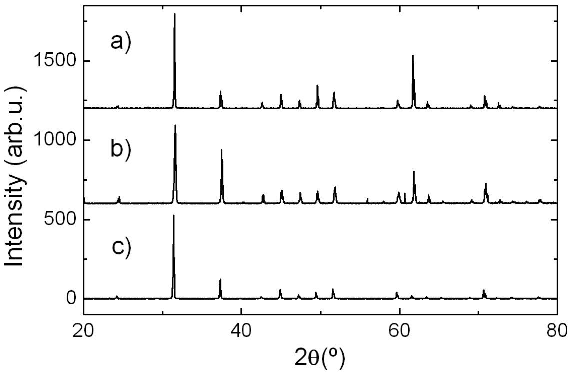

Fig. 1. (In_xSn_x)Co_4Sb_{12} powder XRD patterns: (a) $x = 0.05$; (b) $x = 0.1$; (c) $x = 0.2$.

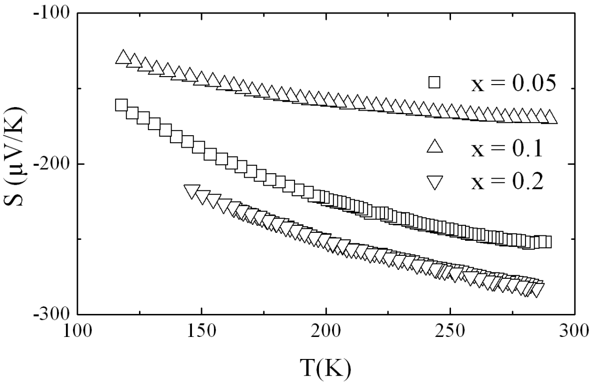

Fig. 2. Seebeck coefficient versus temperature in (In_xSn_x)Co_4Sb_{12}.

and Sn amounts first lead to decrease in the thermoelectric coefficient, down to a minimum of ≈ 170 μV/K at 280 K, for $x = 0.1$, and then increases again, reaching a maximum of ≈ 280 μV/K at room temperature for $x = 0.2$. These values compare well with those obtained for $(Ce,Yb)_x(Fe, Co, Ni)_4Sb_{12}$ at the same temperature (around ±150 μV/K) [8].

4. Conclusions

We have studied the preparation, X-ray diffraction and reported on preliminary electrical transport properties of (In_xSn_x)Co_4Sb_{12} ($0.05 \leq x \leq 0.2$). The samples were homogeneous and crystallize in the cubic $CoSb_3$-type structure. However, they are very brittle, and no reliable resistivity measurements could be obtained, pointing for the need of more dense and stronger materials. The Seebeck coefficients as high as ≈ 280 μV/K at 300 K could be obtained at room temperature for $x = 0.2$, which indicate these materials as good candidates for thermoelectrical applications. The synthesis of stronger and denser materials, needed for a better characterization of the samples, is now under way.

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