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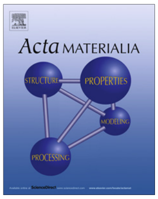

In-doped multifilled n-type skutterudites with $ZT = 1.8$

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ABSTRACT

In this paper we maximize the thermoelectric (TE) figure of merit, ZT, of n-type skutterudites, $(\mathrm{In,Sr,Ba,Yb})_y\mathrm{Co_4Sb_{12}}$, via three different routes: (i) find the optimum fraction of In as fourth filler (ii) check the influence of powder particle, grain, and crystallite size on the TE properties and (iii) check thermal stability. Filled n-type $(\mathrm{Sr,Ba,Yb})_y\mathrm{Co_4Sb_{12}}$ was mixed in three different proportions with $\mathrm{In_{0.4}Co_4Sb_{12}}$, ball milled (regular or high-energy (HB) ball milling) and hot-pressed. Particle size analyses and SEM pictures of the broken surfaces of the hot pressed samples document that only HB produces uniform particles/grains with average crystallite sizes ~100 nm, proven by transmission electron microscopy. X-ray Rietveld refinements combined with EDX indicate that in all cases indium entered the icosahedral voids of the skutterudite. Temperature dependent physical properties of all three regularly ball-milled samples show that increasing In-content infers an increasing electrical resistivity, increasing Seebeck coefficient but a decreasing total thermal conductivity. Although ZT (823 K) is in the same range as for the sample without In, the ZT values in the whole temperature range are higher and consequently the TE-conversion efficiency, η is at least 10% higher. Annealing the samples at 600 °C for three days shows minor changes in structure and thermoelectric properties, indicating TE stability. The HB sample, due to uniformly small particles, equally sized grains and crystallites, exhibits a high power factor (4.4 $\mathrm{mW/m\,K^{-2}}$ at 730 K) and a very low thermal conductivity leading to an outstanding high $ZT = 1.8$ at 823 K ($\eta_{max} = 17.5\%$).

1. Introduction

The last years have seen intense research devoted to skutterudites, most of them with the goal to enhance the efficiency of this thermoelectric material for power generation. The quality of a TE material is characterized by the dimensionless figure of merit $ZT = S^2T/[\rho(\lambda_e + \lambda_{ph})]$, where S, ρ and λ are the Seebeck coefficient, the electrical resistivity and the thermal conductivity, respectively, the latter consisting of an electronic, λ_e, and a phonon part, λ_{ph}. The higher the ZT over a wide temperature range, the higher the thermal-electric conversion efficiency η, calculated from the expression

$$\eta = \frac{T_h - T_c}{T_h}\,\frac{\sqrt{1+(ZT)_a}-1}{\sqrt{1+(ZT)_a}+\frac{T_c}{T_h}} \tag{1}$$

including the Carnot efficiency, where T_h and T_c are the temperatures on the hot and the cold side (in this paper 823 K and 300 K), respectively, as well as $(ZT)_a$, which is the average ZT value between T_c and T_h. This means, the goal is to increase the power factor S^2/ρ and in parallel reduce λ i.e. particularly its phonon part, as the electronic part of the thermal conductivity is connected to the electrical resistivity via the Wiedemann–Franz law

$$\lambda_e(T) \approx \frac{L(T)T}{\rho(T)} \tag{2}$$

where the temperature dependent Lorenz number is given by

$$L(T) = \left(\frac{k_B}{e}\right)^2\left[\frac{(s+7/2)F_{s+5/2}(\xi)}{(s+3/2)F_{s+1/2}(\xi)} - \left(\frac{(s+5/2)F_{s+3/2}(\xi)}{(s+3/2)F_{s-1/2}(\xi)}\right)^2\right] \tag{3}$$

as proposed by D.M. Rowe et al. [1].

To find the correct $L(T)$ value, the reduced Fermi energy, ξ, has to be extracted from the measured Seebeck coefficient values following the relation

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$$S = \pm \frac{k_B}{e}\left[\frac{(s+5/2)F_{s+3/2}(\xi)}{(s+3/2)F_{s+1/2}(\xi)} - \xi\right] \tag{4}$$

where $F_n(\xi)$ is the n^{th} order Fermi integral,

$$F_n(\xi) = \int_0^\infty \frac{\chi^n}{1+e^{\chi-\xi}}d\chi, \quad \xi = \frac{E_F}{k_B T}, \tag{5}$$

and $k_B = 1.3807 \times 10^{-23}$ JK^{-1} is the Boltzmann constant, $e = 1.6022 \times 10^{-19}$ As is the electron charge, E_F is the Fermi energy and s is the scattering parameter. By assuming acoustic phonon scattering, as the main carrier scattering mechanism, $s = -1/2$, and the temperature dependent Lorenz number can be calculated by substituting the values of ξ and s in Eq. (3).

In the last decade indium filled skutterudites have attracted serious attention as promising n-type TE materials. He and co-workers [2] were the first with a thorough investigation of single filled (indium) skutterudites, stating a decrease of the thermal conductivity with an increase of the filling level resulting in $ZT > 1$. A series of In-filled skutterudites of various groups prepared with various methods followed [3–28] and confirmed that indium was useful as a filler. These investigations were extended to double-filled skutterudites of In with Sn [29], with Ba [3,16,30–37], with Tl [38], with Pb [35], with Ce [6,39–42], with Pr [27], with Nd [21,43], with Yb [7,8,16,19,44–49], with Lu [50], and to triple filled skutterudites of In with Ba and Ce [51], with Ba and Yb [16,52], with La and Yb [47], with Ce and Yb [41,42,53] and Ga and Tl [26]. There are also attempts to improve the TE properties by doping and/or alloying e.g. substituting Co by Fe [33,54–58], by Ni [31,59,60] and by Rh [61–63] or doping of the Sb site by Ge [20,64], by Se [65] and by Te [66–69]. Also double filled (Ba, In), substituted (Fe, Co) and doped (Sb by Ge) were investigated [36]. The highest ZT values gained so far in all these afore mentioned endevours were $ZT = 1.34$ for $Ba_{0.14}In_{0.23}Co_4Sb_{12}$ at 850 K [30] and $ZT = 1.43$ for $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ at 800 K [6].

Many authors attribute the good TE performance of indium filled skutterudites to the low thermal conductivity originating from enhanced phonon scattering on low energy vibrations of weakly bonded indium atoms rattling in the large icosahedral voids of the lattice [46] and/or the enhanced boundary scattering of phonons on InSb nano-precipitates or secondary phases with grain sizes of 10–80 nm [6].

In this paper we investigated multifilled n-type skutterudites by adding $In_{0.4}Co_4Sb_{12}$ (nominal) in three different weight portions to triple-filled $(Sr,Ba,Yb)_yCo_4Sb_{12}$ and by using two different ball milling conditions for thorough powder blending prior to a final hot-pressing step for homogenization and densification. The structural and physical properties of these In-filled skutterudites were compared with each other and with a reference sample without In, prepared under the same conditions in a previous investigation [70]. Particular attention is paid to the dependence of the total filling level as well as the In-content on the added wt.% of $In_{0.4}Co_4Sb_{12}$ and the grain and crystallite size.

In order to check the thermal and thermoelectric stability of the new $(Sr,Ba,Yb,In)_yCo_4Sb_{12}$ skutterudites the samples were annealed at 600 °C for 3 days and afterward structural and physical properties were elucidated. This procedure was performed twice.

2. Experimental

All In-filled skutterudites were prepared in parallel starting from two different master alloys, i.e. samples with the nominal compositions: a) $(Sr_{0.33}Ba_{0.33}Yb_{0.33})_{0.35}Co_4Sb_{12.3}$ and b) $In_{0.4}Co_4Sb_{12}$.

Ad a) The $(Sr_{0.33}Ba_{0.33}Yb_{0.33})_{0.35}Co_4Sb_{12.3}$ samples were prepared from Sr, Ba (99 + mass%, Sigma–Aldrich, Germany), Yb (99.9 mass%, Rhône-Poulenc, Shelton, CT, USA) and Sb ingots (99.8 mass% metals basis, Alfa Aesar, Germany), Co-powder (99.9 mass%, particle size < 150 μm, Sigma–Aldrich, Germany) and Co pieces (99.9 mass%, Alfa Aesar, Germany) as described in detail earlier [70,71]. The bulk was (i) ball milled in tungsten carbide vessels (volume = 80 ml, Ar filled) in a Fritsch planetary mill (Pulverisette 4) with 25 balls of a diameter of 10 mm for 2 h at 200 rpm (main disk) and −500 rpm (vessels) followed by (ii) hot pressing (HP) under argon in a FCT uniaxial hot-press system HP W 200/250 2200–200-KS with the following press conditions: 700 °C and 56 MPa (2 h).

Ad b) The $In_{0.4}Co_4Sb_{12}$ samples were synthesized from CoSb, InSb and (Sb) using In pieces (99.9 mass%; Ögussa Austria), Sb ingot (99.8 mass% metals basis; Alfa Aesar, Germany) and Co powder (99.9 mass%, particle size < 150 μm, Sigma–Aldrich, Germany) as described in detail in an earlier reference [24].

Afterward the crushed pieces of $(Sr_{0.33}Ba_{0.33}Yb_{0.33})_{0.35}Co_4Sb_{12.3}$ and $In_{0.4}Co_4Sb_{12}$ were mixed as described in Table 1 and ball milled and hot pressed under the same conditions as already used for the production of $(Sr_{0.33}Ba_{0.33}Yb_{0.33})_{0.35}Co_4Sb_{12.3}$. Samples, later referred to as HB, were high-energy ball milled under modified conditions: 4 h at 400 rpm (main disk) and −1000 rpm (vessels). The HB samples were hot pressed (HP) under the same conditions as the other samples.

All work with powders was performed in a glove box under argon with less than 3 ppm O_2 and 5 ppm H_2O. For the three days of annealing at 600 °C the sample was sealed into a quartz tube under vacuum and air quenched after annealing.

X-ray powder diffraction data were obtained from a Huber Guinier powder camera and monochromatic CuK$_{\alpha 1}$ radiation ($\lambda = 0.154056$ nm) with an image plate recording system. Precise lattice parameters were calculated by least squares fits to the indexed 2θ values (calibrated with respect to Ge as internal standard; $a_{Ge} = 0.565791$ nm at room temperature) using the program STRUKTUR [72]. Quantitative Rietveld refinement was performed in order to determine the total filling level, y_{RV}, (occupancy of the sum of the various filler atoms in the 2a site) employing the program FULLPROF [73] by introducing the atomic ratios of the fillers from the electron probe microanalyses, (EPMA), energy dispersive X-ray spectroscopy (EDX) with an Oxford Instruments X-Max 80 equipment.

The particle sizes were determined with a HELOS Laser diffraction system, from Sympatec, Germany, analyzing all samples at least three times. The crystallite sizes were evaluated from the XRD patterns (spectra from FeK$_{\alpha 1}$-radiation) relying on the MDI JADE 6.0 software (Materials Data Inc., Liverpool, CA) and Silicon as standard. This method allows to calculate the crystallite size from the full width at half-maximum (FWHM) of a single diffraction peak referring to the formula developed by Scherrer [74]. The calculations of the crystallite sizes were performed for three well separated reflections, (240), (332) and (422) within a 2θ range from 51° to 58°. For details see reference 75. Grain sizes were determined from SEM images of the broken surfaces of the samples (see Fig. 2 in the section "Results and discussion", 3.1).

The density d_m of each sample was obtained by the Archimedes' method, using distilled water. The relative densities d_{rel} (in %) were calculated from the X-ray density $d_X = (MZ)/(VN)$ where M is the molar mass, Z is the number of formula units per cell, N is Loschmidt's number and V is the volume of the unit cell.

Electrical resistivity in the range of 4.2 K to room temperature as well as room temperature measurements for all samples were carried out with an "in house" equipment using a Lebeflore a. c. bridge. Resistivity and Seebeck coefficient above room temperature to 823 K were measured simultaneously in an ULVAC-ZEM3 (Riko, Japan) equipment. The high-energy ball milled sample, In9.1HB, in addition was measured with a LSR-3 measurement system (LINSEIS, Germany) at the Indian Institute of Science, Dept. of Physics in Bangalore, India. Electrical resistivity data, measured