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Influence of filler element and Ni-substitution on thermoelectric properties of multi-filled skutterudites

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ABSTRACT

The influence of multi-filling on the thermoelectric properties was investigated for skutterudites $(Ca,Sr,Ba,Mm)_yCo_4Sb_{12}$, where Mm is Mischmetal, a naturally mixed rare earth (Ce,La,Nd,Pr), which throughout this work was treated for convenience as one filler element. Regardless of the filling elements, triple filling shows lower electrical resistivity as well as lattice thermal conductivity and consequently a higher figure of merit ZT than single and double filling, indicating the positive influence of multi-filling on thermoelectric performance. Investigations of triple-filled alloys $(Sr,Ba)_AYb_RCo_4Sb_{12}$ point out that Yb-filling in multi-filled skutterudites entails better thermoelectric properties than Mm-filling. Also the ratio A:R is a critical parameter to achieve high ZT. Moreover, for $(Sr,Ba,Yb)_yCo_4Sb_{12}$, a larger filling level y leads to lower electrical resistivity. Although Ni substitutions for Co in double-filled $Ca_yMm_y(Co_{1-x}Ni_x)_4Sb_{12}$ result in complicated compositional dependences for the electrical resistivity and the Seebeck coefficient, they exert almost no influence on the thermal conductivity, and the Ni-free sample shows the highest ZT in $Ca_yMm_y(Co_{1-x}Ni_x)_4Sb_{12}$, indicating a different impact of Ni with respect to unfilled $(Co_{1-x}Ni_x)_4Sb_{12}$.

1. Introduction

Although filled skutterudite, $R_yT_4Pn_{12}$ (R is a rare-earth or alkaline earth, T is a transition metal, Pn is one of Sb, P or As), was discovered a long time ago [1], it has not been developed as a thermoelectric material until Slack [2] proposed the concept of "phonon-glass electron-crystal" (PGEC), which Morelli et al. verified experimentally for $CeFe_4Sb_{12}$ [3]. Subsequently skutterudites were developed rapidly as a promising thermoelectric (TE) material [4–7]. One advantage of skutterudites regarding TE efficiency is that the two voids in the unit cell can be filled by loosely bound ("rattling") atoms, for example, rare-earth or alkaline-earth ions, which (i) suppress the lattice thermal conductivity via enhanced interaction with low frequency phonons [8], and simultaneously (ii) reduce the electrical resistivity by increasing the carrier density n [5,9]. TE efficiency is determined by the dimensionless figure of merit $ZT=(S^2/(\rho\kappa))T$ (S means the Seebeck coefficient, ρ the electrical resistivity and κ the thermal conductivity).

Recently, multi-filled skutterudites attracted broad attention, since multi-filling reduces thermal conductivity and decreases electrical resistivity when compared to single filling due to the impacts of intrinsic properties such as, ionic radii, atomic mass, and resonant phonon scattering frequencies for double fillers [10–16] and for triple fillers [17,18]. These investigations have set the strategies to (i) reduce the lattice thermal conductivity (κ_l) via enhanced phonon scattering by complex atom filling and to (ii) reduce electrical resistivity through additional doping. The large difference in resonance frequencies of filler atoms, such as of Ba and Yb, has found to be a better route to suppress thermal conductivity than via filler atoms with similar resonance frequencies [12].

In addition, it is well known that Ni-doping in $CoSb_3$-based skutterudites not only controls the conduction type but also enhances ZT through reduction of both electrical resistivity and thermal conductivity [19–26]. Therefore, it is of interest to investigate the impact of Ni on multi-filled skutterudites.

In our previous work [18], we have synthesized high ZT triple-filled skutterudites from low-grade Sb (99.8 mass%), cheaper than standard high-grade 4N-material. The results have confirmed the multi-filling strategies: triple-filled $(Ba,Sr,Yb)_yCo_4Sb_{12}$ achieves distinctly lower electrical resistivity and lower lattice thermal conductivity than single-filled $Ba_yCo_4Sb_{12}$ and double-filled $(Ba,Yb)_yCo_4Sb_{12}$. Furthermore, our results [27] show that Mm, available at a price lower than that of single rare earths, can be used to replace Ce as fillers for skutterudites with the same or even better TE performances. Therefore the aims of the current work are: (i) to use Mm instead of Yb and 99.8 mass% Sb in order to reduce material costs, (ii) to study the influence of various additional alkaline earth fillers (Ca, Sr, or Ba) on the TE properties of

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Mm-filled Co_4Sb_{12} in comparison with those Yb-filled, in which the filling limit of Ce is half of that of Yb [28,29], (iii) to investigate the effect of the ratio alkaline earth to rare earth on TE properties, and (iv) to investigate the influence of Ni-doping on TE performance for $Ca_{0.2}Mm_{0.2}Co_4Sb_{12}$ exploiting the large difference of atomic mass between Mm and Ca. Although Mm contains four different rare earth elements, for simplicity we consider it as a single-filler. The filling level (FL, the amount of alkaline earth and rare earth) was optimised in our previous paper [18], where the highest ZT appears for the sample with FL = 0.2. Additionally, ball milling and hot pressing were employed for preparation considering a substantial increase of ZT for nanostructured materials [27,30].

2. Experimental procedures

Fig. 1 displays the schematic diagram of nominal compositions for the double- and triple-filled skutterudites. The extended "x" axis refers to the x values (Ni content) in $Ca_{0.2}Mm_{0.2}(Co_{1-x}Ni_x)_4Sb_{12}$.

Alloys with a weight of 8 g each were prepared by melting pieces of Ca, Sr, Ba (99+ mass%, Sigma–Aldrich, Germany) and Mm (Ce-50.8%, La-28.1%, Nd-16.1%, Pr-5.0%, Treibacher Industrie AG, Austria), Co powder (99.9 mass%, particle size <150 μm, Sigma–Aldrich, Germany), Ni-wire (99.9 mass%, from Alfa Aesar, Germany), and Sb-ingot (99.8 mass% metals basis, Alfa Aesar, Germany) in evacuated silica ampoules at 980 °C (for details see [18]). After melting the specimens were transferred to tungsten carbide ball-mill containers (volume = 80 ml, Ar atmosphere with less than 3 ppm O_2 and H_2O), ball milled with a Fritsch planetary mill (Pulverisette 4, and balls of ⌀ = 10 mm) for 1 h at 200 rpm (main disc) and 500 rpm (vessels). The milled powders were loaded in a 10 mm diameter graphite die inside a glove box and hot pressed under Ar via a FCT hotpress system HP W 200/250 2200-200-KS at 600 °C and 56 MPa during 2 h.

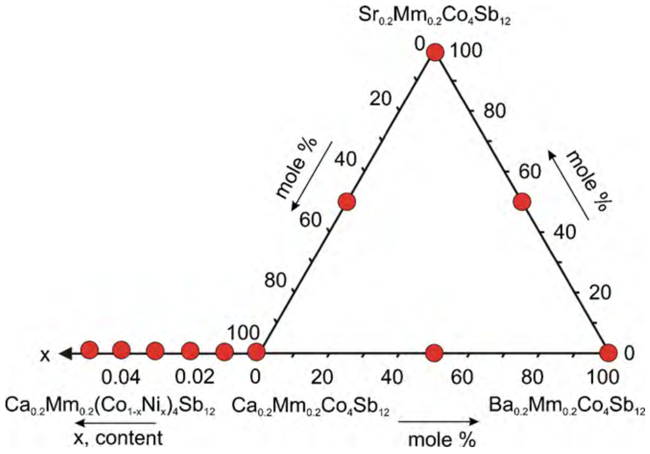

Fig. 1. Schematic diagram of nominal alloy compositions. The red circles represent the compositions of the compounds investigated. The "x" axis extended from the triangle phase diagram denotes the x value in $Ca_{0.2}Mm_{0.2}(Co_{1-x}Ni_x)_4Sb_{12}$ and increases from right to left.

X-ray powder diffraction data were obtained from a Huber Guinier camera and monochromatic Cu $K_{\alpha1}$ radiation (λ = 0.154051 nm) with an image plate recording system. Precise lattice parameters were calculated by least squares fits to the indexed 2θ values using Ge as internal standard (a_{Ge} = 0.565791 nm). The filling level was derived from Rietveld refinements employing the FULLPROF program [31] with the assumption that the ratio among filler elements is the same as for the nominal

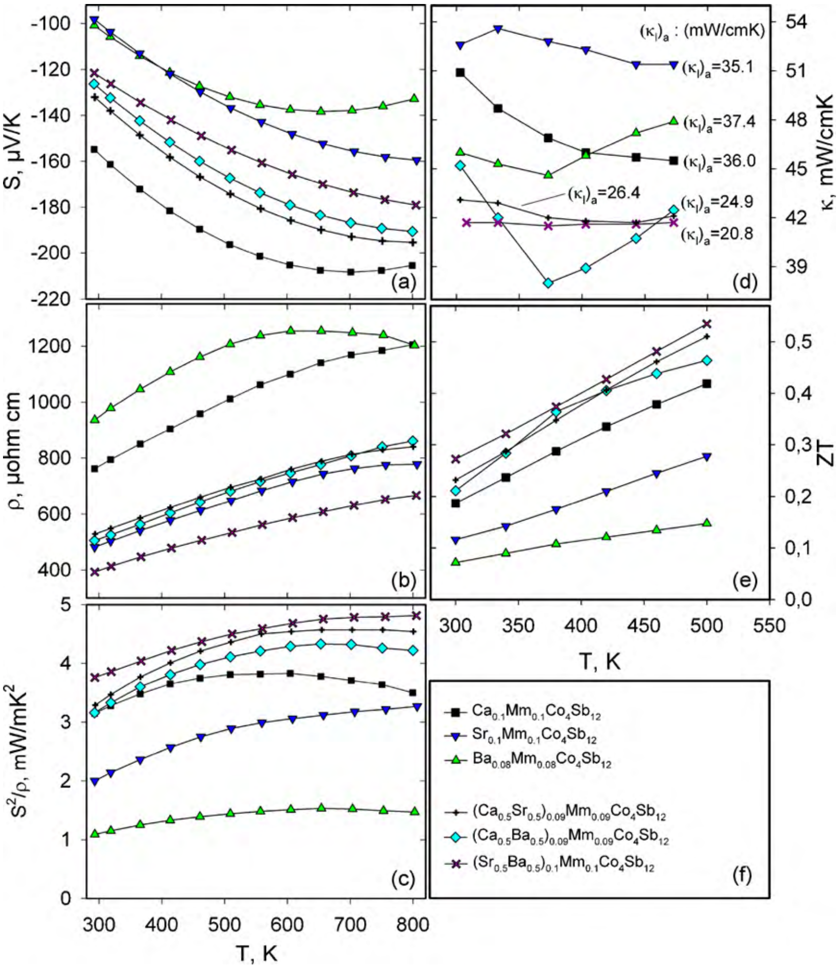

Fig. 2. Temperature dependency of the Seebeck coefficient S (a), the electrical resistivity ρ (b), the power factor S^2/ρ (c), the thermal conductivity κ (d), and ZT (e) for multi-filled $(Ca,Sr,Ba)_yMm_yCo_4Sb_{12}$. For legend see figure (f).

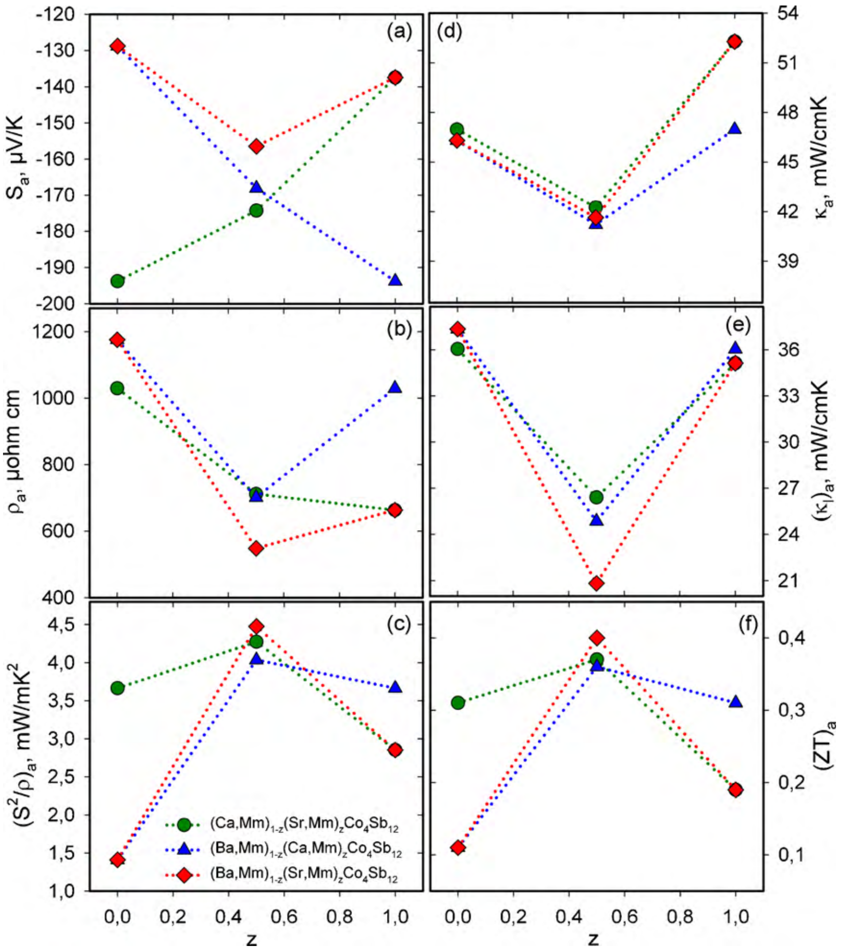

Fig. 3. Average value of the Seebeck coefficient S_a (a), the electrical resistivity ρ_a (b), the power factor $(S^2/\rho)_a$ (c), the thermal conductivity κ_a (d), the lattice thermal conductivity $(\kappa_l)_a$ (e), and figure of merit $(ZT)_a$ (f) for multi-filled skutterudites as a function of composition. $z = 0, 1$ represent double-filled skutterudites and $z = 0.5$ represents the triple-filled skutterudites. The dotted lines are guides for the eyes.

Table 1

Filling level FL, lattice parameter a, and transport parameters for $Ca_yMm_y(Co_{1-x}Ni_x)_4Sb_{12}$ and multi-filled $(Ca,Sr,Ba,Mm,Yb)_yCo_4Sb_{12}$ n-type skutterudites. S_a, ρ_a, $(S^2/\rho)_a$, and $(ZT)_{a2}$ are averaged S, ρ, S^2/ρ, ZT in the temperature range from 300 K to 800 K in steps of 10 K. κ_a, $(\kappa_l)_a$, and $(ZT)_{a1}$ are averaged κ, κ_l, and ZT in the temperature range from 300 K to 500 K in steps of 10 K.

Composition	FL	S_a µV/K	ρ_a µΩ cm	$(S^2/\rho)_a$ mW/m K^2	κ_a mW/cm K	$(\kappa_l)_a$ mW/cm K	$(ZT)_{a1}$ 300–500 K	$(ZT)_{a2}$ 300–800 K	a nm
$Ca_{0.1}Mm_{0.1}Co_4Sb_{12}$	0.20	−194	1029	3.66	47.0	36.0	0.31	–	0.90418(3)
$Ca_{0.08}Mm_{0.08}Co_{3.96}Ni_{0.04}Sb_{12}$	0.16	−196	1644	2.34	41.0	35.1	0.22	–	0.90411(2)
$Ca_{0.09}Mm_{0.09}Co_{3.92}Ni_{0.08}Sb_{12}$	0.18	−172	1173	2.53	48.2	39.4	0.19	–	0.90439(2)
$Ca_{0.08}Mm_{0.08}Co_{3.88}Ni_{0.12}Sb_{12}$	0.16	−158	1047	2.41	47.8	38.0	0.18	–	0.90436(3)
$Ca_{0.075}Mm_{0.075}Co_{3.84}Ni_{0.16}Sb_{12}$	0.15	−149	975	2.28	43.1	32.6	0.17	–	0.90439(2)
$Ca_{0.07}Mm_{0.07}Co_{3.8}Ni_{0.2}Sb_{12}$	0.14	−145	1150	1.84	43.8	35.3	0.14	–	0.90444(4)
$Sr_{0.1}Mm_{0.1}Co_4Sb_{12}$	0.20	−137	663	2.85	52.3	35.1	0.19	–	0.90480(3)
$Ba_{0.08}Mm_{0.08}Co_4Sb_{12}$	0.16	−129	1175	1.41	46.3	37.4	0.11	–	0.90474(4)
$(Ca_{0.5}Sr_{0.5})_{0.09}Mm_{0.09}Co_4Sb_{12}$	0.18	−174	711	4.27	42.2	26.4	0.37	–	0.90503(2)
$(Ca_{0.5}Ba_{0.5})_{0.09}Mm_{0.09}Co_4Sb_{12}$	0.18	−168	701	4.04	41.2	24.9	0.36	–	0.90538(2)
$(Sr_{0.5}Ba_{0.5})_{0.1}Mm_{0.1}Co_4Sb_{12}$	0.20	−157	548	4.47	41.6	20.8	0.40	–	0.90557(2)
$(Sr_{0.66}Ba_{0.33})_{0.05}Yb_{0.05}Co_4Sb_{12}$	0.10	−153	1462	1.60	–	–	–	–	0.90402(3)
$(Sr_{0.5}Ba_{0.5})_{0.05}Yb_{0.05}Co_4Sb_{12}$	0.10	−157	1215	2.04	40.5	31.4	0.19	–	0.90411(1)
$(Sr_{0.5}Ba_{0.5})_{0.11}Yb_{0.11}Co_4Sb_{12}$	0.22	−140	361	5.45	35.4	3.0	0.52	0.87	0.90615(2)
$(Sr_{0.5}Ba_{0.5})_{0.17}Yb_{0.17}Co_4Sb_{12}$	0.34	−129	328	5.07	38.2	3.1	0.45	0.75	0.90686(2)
$(Sr_{0.5}Ba_{0.5})_{0.1}Yb_{0.05}Co_4Sb_{12}$	0.15	−138	858	2.21	51.4	38.3	0.16	–	0.90483(5)
$(Sr_{0.5}Ba_{0.5})_{0.12}Yb_{0.06}Co_4Sb_{12}$	0.18	−146	669	3.18	46.4	29.3	0.24	–	0.90511(4)
$(Sr_{0.5}Ba_{0.5})_{0.1}Yb_{0.1}Co_4Sb_{12}$[a]	0.2	−158	445	5.60	33.5	3.8	0.64	0.92	0.90609(3)

[a] Data from Ref. [18].

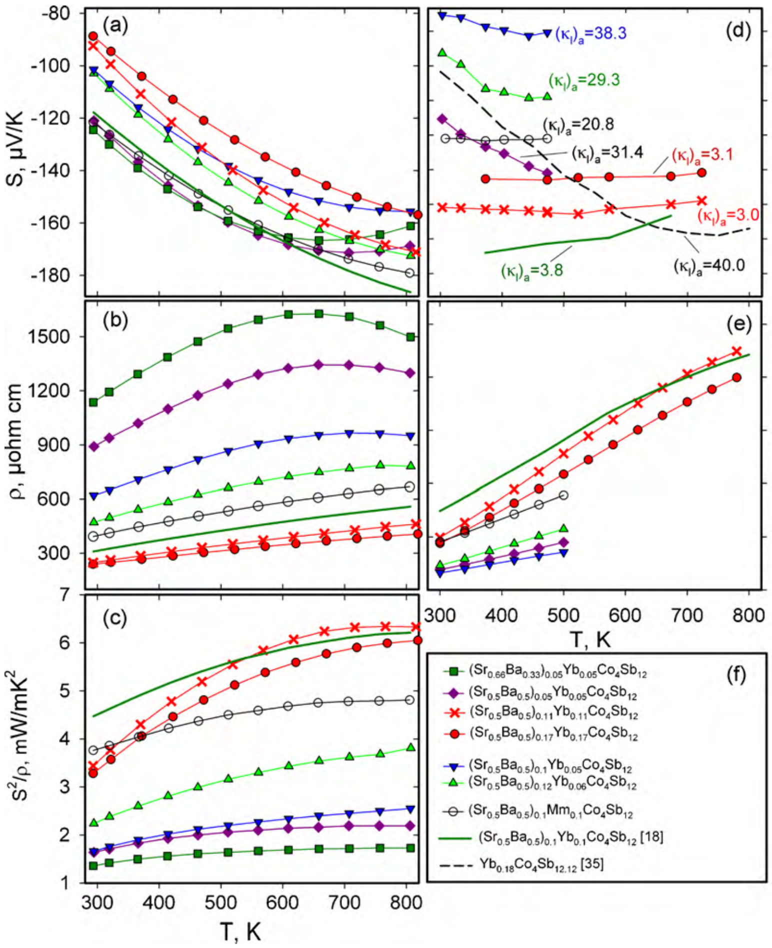

Fig. 4. Temperature dependences of the Seebeck coefficient S (a), the electrical resistivity ρ (b), the power factor S^2/ρ (c), the thermal conductivity κ (d), and ZT (e) for $(Sr,Ba,Yb)_yCo_4Sb_{12}$ compared with $(Sr_{0.5}Ba_{0.5})_{0.1}Mm_{0.1}Co_4Sb_{12}$ and the literature data for $(Sr_{0.5}Ba_{0.5})_{0.1}Yb_{0.1}Co_4Sb_{12}$ [18] and for single Yb-filled $Yb_{0.18}Co_4Sb_{12.12}$ [35]. The unit of averaged lattice thermal conductivities $(\kappa_l)_a$ in figure (d) is given in mW/cm K. For figure legend see figure (f).

composition. Since the grain size is smaller than 0.3 μm, EPMA is unsuccessful to define the composition.

Measurements of the high-temperature Seebeck coefficient and electrical resistivity were performed using a Seebeck coefficient/electric resistance measuring system (ZEM-3, Ulvac-Riko, Japan). The thermal conductivity was calculated from the thermal diffusivity D_t measured by a laser flash method (Flashline-3000, ANTER, USA), specific heat C_p and density ρ_d using the relationship $\kappa = D_t C_p \rho_d$. The density was measured in distilled water by the Archimedes method.

The lattice thermal conductivity κ_l was calculated by subtracting from the measured values κ the electronic thermal conductivity κ_e (assuming the applicability of the Wiedemann–Franz law with a temperature independent Lorenz number $L_0 = 2.44 \times 10^{-8}$ V^2/K^2). Arithmetically averaged values for S, ρ, S^2/ρ, were calculated for the temperate range from 300 K to 800 K in steps of 10°, resulting in S_a, ρ_a, $(S^2/\rho)_a$; κ, κ_l, and ZT were calculated from 300 K to 500 K in steps of 10 degrees, resulting in averaged values κ_a, $(\kappa_l)_a$, and $(ZT)_a$.

3. Results and discussion

X-ray powder diffraction data (XPD) prove a single-phase skutterudite for all samples. The relative density for all the samples is better than 98.8%.

3.1. Influence of multi-filling on TE properties

The filling levels obtained from Rietveld refinement are listed in Table 1 for alloys from the series $(Ca,Sr,Ba)_yMm_yCo_4Sb_{12}$ and $F_yMm_yCo_4Sb_{12}$ where F is either $(Ca_{0.5}Sr_{0.5})$, $(Ca_{0.5}Ba_{0.5})$ or $(Sr_{0.5}Ba_{0.5})$. Transport properties for these compounds are summarised in Fig. 2. For the convenience of observing the double and triple filling, their averaged values are displayed in Fig. 3.

The Seebeck coefficient (Figs. 2a and 3a) for triple filling is slightly larger than for double filling (except for $Ca_{0.1}Mm_{0.1}Co_4Sb_{12}$). It should be noted that the electrical resistivity (Figs. 2b and 3b) for triple filling is significantly lower than in case of double filling (except for $Sr_{0.1}Mm_{0.1}Co_4Sb_{12}$). Since the differences in FL for all these samples are smaller than 0.04, the low electrical resistivity benefits from triple filling. It was also derived from our previous investigation that triple-filled $(Sr,Ba,Yb)_yCo_4Sb_{12}$ exhibits a distinctly lower electrical resistivity than single- and double-filled skutterudites [18]. Thus, the largest power factors (Figs. 2c and 3c) are associated with the triple-filled samples.

The temperature dependent thermal conductivity κ, shown in Fig. 2d, demonstrates the impact of multi-filling on κ: κ(triple) < κ(double). The differences are clearly seen in the averaged thermal conductivity κ_a (Fig. 3d). The values are comparable to data reported for $(Ba,Ce)_yCo_4Sb_{12}$ [15] and $(Ca,Ce)_yCo_4Sb_{12}$ [16]. Nevertheless, κ is higher than the value for $(Ba,Yb)_yCo_4Sb_{12}$ [13,18]. This result might be due to the specific rare earth filler elements (Yb and Ce), which will be discussed below. Filling fractions for Mm in the present work were ~0.1, comparable to Ce in $Ba_{0.18}Ce_{0.05}Co_4Sb_{12.02}$ [15] and $Ba_{0.08}Yb_{0.09}Co_4Sb_{12.12}$ [13]. The lattice thermal conductivity (Figs. 2d, 3e and Table 1) separates in two groups: one group for triple filling at lower values compared to a second group of double-filled materials. As a consequence

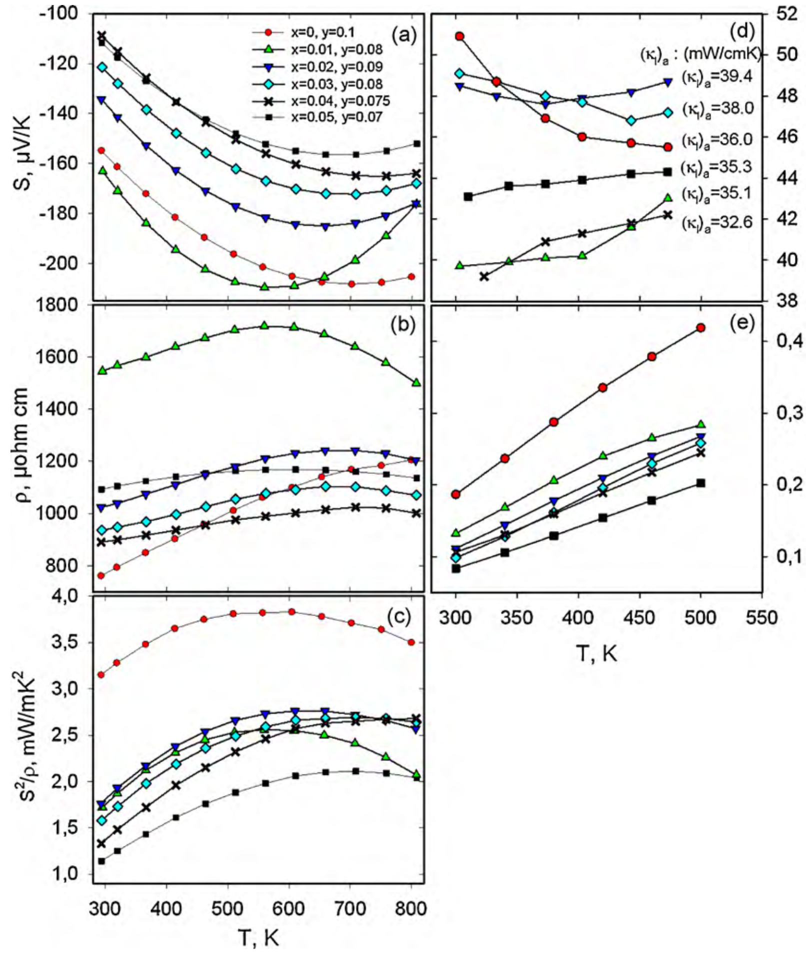

Fig. 5. Temperature dependences of the Seebeck coefficient S (a), the electrical resistivity ρ (b), the power factor S^2/ρ (c), the thermal conductivity κ (d), and ZT (e) for $Ca_yMm_y(Co_{1-x}Ni_x)_4Sb_{12}$ ($x = 0$, 0.01, 0.02, 0.03, 0.04, 0.05). Legend in figure (a) refers to all panels.

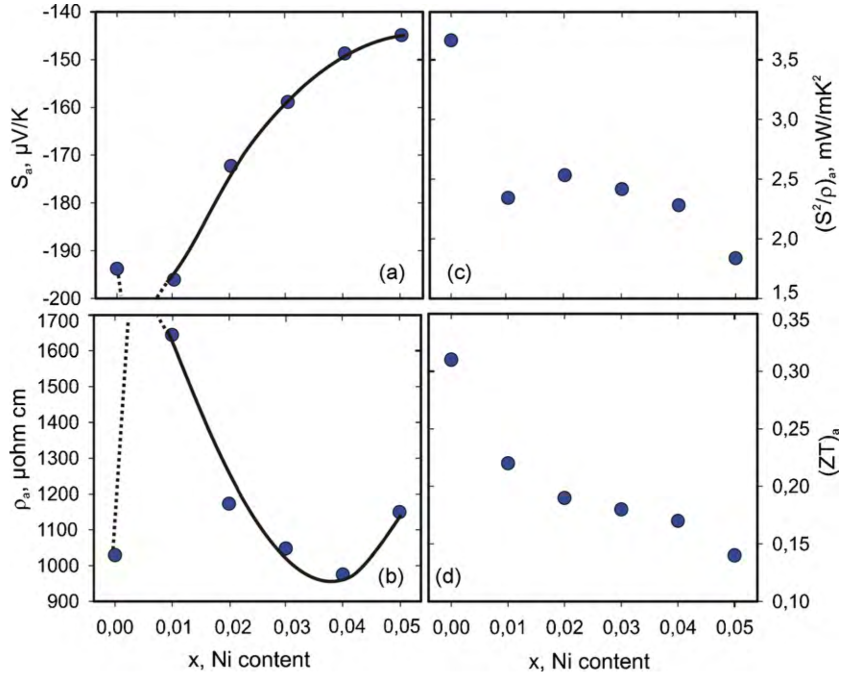

Fig. 6. Average value of the Seebeck coefficient S_a (a), the electrical resistivity ρ_a (b), the power factor $(S^2/\rho)_a$ (c), and figure of merit $(ZT)_a$ (d), for $Ca_yMm_y(Co_{1-x}Ni_x)_4Sb_{12}$ ($x = 0$, 0.01, 0.02, 0.03, 0.04, 0.05) as a function of Ni content x.

the three triple-filled skutterudites $(Sr_{0.5}Ba_{0.5})_{0.1}Mm_{0.1}Co_4Sb_{12}$, $(Ca_{0.5}Sr_{0.5})_{0.09}Mm_{0.09}Co_4Sb_{12}$, and $(Ca_{0.5}Ba_{0.5})_{0.09}Mm_{0.09}Co_4Sb_{12}$ show the highest ZT over the entire temperature range (Figs. 2e and 3f).

3.2. Influence of filling elements and the ratio of alkaline earth to rare earth for triple filling

The highest *ZT* value for $(Ca,Sr,Ba,Mm)_yCo_4Sb_{12}$ at elevated temperature (300 K < *T* < 500 K) is $ZT_{500K} = 0.53$ for triple-filled $(Sr_{0.5}Ba_{0.5})_{0.1}Mm_{0.1}Co_4Sb_{12}$, which is still lower than for $(Sr_{0.5}Ba_{0.5})_{0.1}Yb_{0.1}Co_4Sb_{12}$ ($ZT_{500K} = 0.85$ [18]). Since all these compounds exhibit the close filling level (FL ≈ 0.2), the principal contribution comes from Yb, and may be attributed to (1) intermediate valence of Yb [32–34], and/or (2) the larger difference of resonant phonon scattering frequencies between Yb and alkaline earths as compared to Ce and alkaline earths [12].

Fig. 4 compares the TE properties for triple-filled $(Sr,Ba,Yb)_yCo_4Sb_{12}$ with those of $(Sr,Ba,Mm)_yCo_4Sb_{12}$ and the thermal conductivity from the literature data for single Yb-filled $Yb_{0.18}Co_4Sb_{12.12}$ [35]. Although the absolute Seebeck coefficient (Fig. 4a) of $(Sr,Ba,Yb)_yCo_4Sb_{12}$ changes only slightly with FL, the electrical resistivity (Fig. 4b) significantly reduces until FL ≈ 0.22 and then, ρ saturates at minimum values. $(Sr_{0.5}Ba_{0.5})_{0.1}Mm_{0.1}Co_4Sb_{12}$ with FL = 0.2 locates well on this trend.

Although the thermal conductivity (Fig. 4d) for $(Sr_{0.5}Ba_{0.5})_{0.11}Yb_{0.11}Co_4Sb_{12}$ is slightly lower than for $(Sr_{0.5}Ba_{0.5})_{0.1}Mm_{0.1}Co_4Sb_{12}$, the lattice thermal conductivity κ_l (Fig. 4d and Table 1) for the former is significantly lower than for the latter. It should be noted that the ratio of alkaline earths to rare earths (A:R) significantly affects TE performances. Although the two samples with A:R = 2 ($(Sr_{0.5}Ba_{0.5})_{0.1}Yb_{0.05}Co_4Sb_{12}$ and $(Sr_{0.5}Ba_{0.5})_{0.12}Yb_{0.06}Co_4Sb_{12}$) have quite high FL, they still show much larger κ and κ_l than those with A:R = 1. Although single Yb-filled $Yb_{0.18}Co_4Sb_{12.12}$ [35] shows a quite low κ, it exhibits higher κ_l than the triple-filled skutterudites. In comparison to the thermal conductivity data reported for single-filled skutterudites and despite Sr- [36] and Ba-filled [37] skutterudites have higher κ than the Yb-filled alloys [35], they show similar κ_l. Therefore, the combination of a proper A:R ratio with a proper FL in multi-filled $(Sr,Ba,Yb)_yCo_4Sb_{12}$ may achieve a very low electrical resistivity and lattice thermal conductivity, resulting in a high *ZT* (Fig. 4e).

3.3. Transport properties of $Ca_y Mm_y(Co_{1-x}Ni_x)_4Sb_{12}$ at high temperature

Transport properties for $Ca_yMm_y(Co_{1-x}Ni_x)_4Sb_{12}$ (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05) are shown in Fig. 5 and their average values are displayed in Fig. 6. The filling fraction y is slightly different for various values x.

With increasing Ni-content in $Ca_yMm_y(Co_{1-x}Ni_x)_4Sb_{12}$, both $|S|$ and ρ show a maximum at $x \approx 0.01$ (Figs. 5 and 6). A similar situation was also observed for $Co_{1-x}Ni_xSb_3$ [19,21]. At higher Ni contents, $|S|$ decreases due to an increase of the charge carrier concentration [20,25]. Temperature dependent $|S(T)|$ and $\rho(T)$ show both a maximum in the intrinsic region near the temperature where the Hall coefficient changes from negative to positive [25]. The maxima shift to higher temperature with increasing x, which is also seen for $Co_{1-x}Ni_xSb_3$ in Ref. [25]. Such behaviour of $\rho(T)$ hints the start of intrinsic conduction as was discussed for $Co_{1-x}Ni_xSb_3$ [25] and $Ba_{0.3}(Co_{1-x}Ni_x)_4Sb_{12}$ [22]. The second extremum of ρ_a at $x \approx 0.04$ (see Fig. 6b) is similar to that reported for Ni-doped $Ba_{0.3}(Co_{1-x}Ni_x)_4Sb_{12}$ [22] and $Ca_y(Co_{1-x}Ni_x)_4Sb_{12}$ [26].

Fig. 5d displays the temperature dependent κ for $Ca_yMm_y(Co_{1-x}Ni_x)_4Sb_{12}$. Unlike the apparent suppression in the thermal conductivity for Ni-substitution in unfilled $CoSb_3$ [20,21,25] and $Ba_{0.3}(Co_{1-x}Ni_x)_4Sb_{12}$ [22], the impact of Ni-doping on κ especially on κ_l for $Ca_yMm_y(Co_{1-x}Ni_x)_4Sb_{12}$ is very weak. Similar results were reported by Puyet et al. for $Ca_{0.18}(Co_{1-x}Ni_x)_4Sb_{12}$ [24,26].

Combining all measured properties, only the Ni-free sample shows a promising power factor $(S^2/\rho)_a = 3.5$ mW/m K at 604 K (Figs. 5c and 6c). However, the resulting $(ZT)_a$ (Fig. 6d) is below 0.5 due to the high lattice thermal conductivity.

4. Conclusions

The influence of multi-filling on TE properties was investigated concerning filler element, filling level and the ratio of alkaline earth to rare earth. Triple filling shows higher ZT values than double filling owing to lower electrical resistivity and lattice thermal conductivity. The electrical resistivity decreases with increase of y for $(Sr,Ba,Yb)_yCo_4Sb_{12}$. Yb provokes an important contribution to reduce thermal conductivity in contrast to Mm in multi-filled skutterudites and hence enhancing ZT.

The influence of Ni-substitution on TE properties for $Ca_{0.2}Mm_{0.2}(Co_{1-x}Ni_x)_4Sb_{12}$ was investigated, too. The thermal conductivity is independent of the Ni-concentration; $|S|$ and ρ increase and subsequently decrease with increasing Ni-content, and consequently, the highest *ZT* is shown in Ni-free samples.

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