

# Filled Sb-Based Skutterudites from 1996–2022

Gerda Rogl  and Peter Franz Rogl 

Institute of Materials Chemistry, University of Vienna, Waehringerstraße 42, A-1090 Wien, Austria

\* Correspondence: gerda.roggl@univie.ac.at

**Abstract:** In the present review the focus is set on filled antimony-based skutterudites as they are among the most promising TE materials. Thermoelectric properties (at 300 K and 800 K) of more than 1200 compositions from more than 250 publications from 1996 to 2022 were collected and evaluated. In various figures the dependence of the peak ZT for single-filled, double-filled and multi-filled compounds of p- and n-type skutterudites on the publishing year, the peak temperature, electrical resistivity, thermal and lattice thermal conductivity, the power factor and the fillers are displayed. Together with plots of electrical resistivity versus Seebeck coefficient and especially thermal conductivity versus power factor these evaluations etc. may help to find the ideal skutterudite material for practical applications.

**Keywords:** skutterudites; physical properties; figure of merit (ZT)

## 1. Introduction

In times of energy shortage, it is necessary to exploit new energy sources. Thermoelectric (TE) materials can convert a heat flow from any external source (e.g., waste heat) into a flow of charge carriers within the material, creating electric power. There are many classes of TE materials such as tellurides, selenides, silicides, Zintl phases, clathrates, Heusler and half-Heusler alloys, oxides, antimonides, even organic semiconductors . . . and skutterudites, which qualify in various temperature ranges as TE materials.

Two properties serve to judge the quality of a TE material: the figure of merit (ZT), and the conversion efficiency ( $\eta$ ).  $ZT = S^2T/\rho(\lambda_e + \lambda_{ph})$ , where  $S$ ,  $\rho$  and  $\lambda$  are the Seebeck coefficient, the electrical resistivity and the thermal conductivity, respectively, the latter consisting of an electronic ( $\lambda_e$ ) and a phonon (lattice) part ( $\lambda_{ph}$ ). The power factor (pf) of a TE material is defined as  $pf = S^2/\rho$ . For a high ZT, a large absolute value  $S$  together with a low  $\rho$  and a low  $\lambda$  are essential.

The conversion efficiency,  $\eta$ , for thermoelectric power generation is defined as

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

where  $T_h$  and  $T_c$  are the temperatures on the hot and the cold side and  $(ZT)_a$  is the average ZT value in the temperature gradient between  $T_c$  and  $T_h$ . For  $(ZT)_a$  to be evaluated, all measured data must be integrated, as the curvature of the ZT vs. the  $T$  curve determines the result.

Skutterudites, especially filled skutterudites, not only have high ZTs and efficiencies, but they can also be used in a wide temperature range (300–900 K), have shown long-term stability as well as reasonable mechanical properties and the starting materials are abundant and cheap in comparison to most other TE materials.

The name “skutterudite” refers to a naturally occurring mineral,  $CoAs_3$ , which was first found and mined in a small town, Skutterud, in Norway. In 1928, I. Oftedal [1] identified the crystal structure as body-centered cubic, belonging to the space group  $Im\bar{3}$  No. 204. The general formula of binary skutterudites is  $TX_3$ , where the transition metal



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T = Co, Rh, Ir and the pnictogen X = P, As, Sb. The unit cell contains 32 atoms arranged in eight  $\text{TX}_3$  blocks. X-atoms in the 24g sites (0, y, z) form irregular and tilted octahedra, which are centered by the T-atoms in the 8c sites (1/4, 1/4, 1/4). The framework of corner-connected octahedra provides room for two icosahedral voids at the 2a sites, which can be filled with filler atoms (first explored in 1977 by W. Jeitschko and D. Braun [2] on  $\text{LaFe}_4\text{P}_{12}$ ). In general, the filler atoms are loosely bonded and “rattle” inside their cage, which enhances phonon scattering. Filled skutterudites have the general formula  $\text{M}_y\text{T}_4\text{X}_{12}$ , with M being an electropositive element, occupying partially or fully the icosahedral voids in the 2a sites. In certain cases, electronegative fillers may also enter the cages.

From the perspective of thermoelectricity, the optimal void fillers would be neutral atoms with large atomic displacement parameters. This would ensure a large reduction in the lattice thermal conductivity but only a minimum perturbation of electronic transport properties; however, in praxis, so far, it was not possible to keep rare gas species locked in the skutterudite cage. Generally, the weak coupling of any filler(s) with the rest of the structure and because of the fact that the pnictogen orbitals are hardly affected by the rattling ions, the carrier mobility remains large and therefore the structure can keep its crystalline character and good electronic properties. The advantage of filled skutterudites, with lanthanoids, actinoids, alkaline metals or alkaline earths as fillers, is that the rattling motions of the fillers interfere with the normal modes of the structure, thus leading to a reduction of the lattice thermal conductivity.

As proposed by Slack et al. [3], a high ZT material should be a “phonon-glass electron-crystal” (PGEC) system, with a large Seebeck coefficient and small  $\rho$ ,  $\lambda$ . It is, however, not easy to satisfy these criteria, as the three physical properties, S,  $\rho$  and  $\lambda$ , are interdependent in such a way that a modification to any of these properties often adversely affects the other properties; therefore the ZT values remained for a long time below or around ZT~1.

There are, of course, many attempts to enhance ZT and  $\eta$  as published in many articles and review articles [4–19], which focus on the following routes, as described in detail in, for example [20,21]:

- (a) Partially or fully filling of skutterudites was a big step towards high ZTs. It was found that the maximum filling fraction increases with the type of filler, which roughly follows the sequence: rare earths, alkaline earths, alkaline metals. Of course, it is also affected by the radius, the valence and the electronegativity of the filler ions. Double and multiple filling (Tables 1 and 2), due to different frequencies and masses of the fillers, enhances the phonon scattering and therefore reduces the thermal conductivity. As the filling fractions of the rare earths influence the carrier properties, lattice thermal conductivity will decrease but the power factor will remain (details are given in [5]).
- (b) Charge compensation (Tables 1 and 2) is achieved by substituting Fe by Co, Fe by Ni or in rare cases Fe by Zn (p-type), or Co by Cr, Fe, Ni, Pd, or by using Fe/Ni substitution (n-type) to control the carrier concentration and positively influence the TE properties. These substitutions alter the nature of the conduction process from that of being substantially metallic to one with a more semiconducting character, leading to a reduction in the thermal conductivity. One has additionally to take into account the interplay between the electron doping via the filler atoms and the hole doping on the Co sites.
- (c) Doping at the Sb sites (Table 3), because these dopant atoms create a perturbation on the vibration of the  $\text{Sb}_4$ -ring, introduces defects and therefore enhances the scattering of high-frequency phonons on electrons and impurities. This way the thermal conductivity can be reduced without affecting either the electrical resistivity or the Seebeck coefficient.
- (d) The possibility to enhance the Seebeck coefficient and concomitantly reduce the electrical resistivity and thermal conductivity is provided by dispersing micro- or, even better, nanoparticles within the bulk material to form nanocomposites. These “obstacles” disperse evenly at the grain boundaries of the skutterudite matrix and enhance interfacial scattering of the heat-carrying phonons in conjunction with point

defect scattering and mixed valence scattering. This should reduce the thermal conductivity more than the electrical conductivity, and should increase the Seebeck coefficient by the energy filtering of the charge carriers or by quantum confinement, more than decreasing the electrical conductivity. One may also aim at precipitating nanoparticles within the matrix from supersaturated solutions. It is important to select particles which enhance the scattering of the heat-carrying phonons of different wavelengths and reduce thermal conductivity but do not disturb the charge carriers. A good overview of additives for unfilled and filled p- and n-type skutterudites is given in [22]. The variety of additives for filled Sb-based skutterudites in this work is shown in Table 3.

- (e) Ball-milling produces very fine, even nano-sized powders. Even though during the densification (e.g., hot-pressing or spark plasma sintering) some particle growth occurs, the reduced particle size decreases the mean free path of the phonons and thereby reduces the thermal conductivity. Although the electrical resistivity increases, the net effect is in most cases positive i.e., ZT is higher.
- (f) Severe plastic deformation (SPD) via high-pressure torsion (HPT) reduces the crystallite size and in parallel increases the quantity of lattice defects—mainly dislocations. This way the scattering of the heat-carrying phonons is enhanced, which reduces the thermal conductivity more than it enhances the electrical resistivity (the Seebeck coefficient remains untouched), resulting in higher ZTs. This method was applied on hot pressed samples as well as on cold pressed skutterudite powder, the latter technique saving a lot of energy and time on samples with 10 or 30 mm in diameter and a height of ~1 mm or ~8 mm.

Freer and al. [23] recently published tables of the TE properties of various TE materials together with an evaluation of these data. The chapter “skutterudites” was handled by P. Qiu, S. Wan and L. Chen, who collected the TE parameters of about 30 publications of p- and n-type, unfilled and filled skutterudites, and plotted the thermal conductivity, carrier mobility, power factor and ZT in dependence of the electrical conductivity, as well as the carrier concentration versus the Seebeck coefficient.

In the current review the focus was set on filled antimony-based skutterudites as they are the most promising TE materials. Measured data of the electrical resistivity, total thermal and phonon thermal conductivity, Seebeck coefficient, power factor and ZT (at 300 K and at 800 K) of almost 1200 compositions from more than 250 publications from 1996 to 2022 were collected and evaluated. As the temperature ranges in various publications differ, average ZTs have not been evaluated.

In the beginning of skutterudite research, the main interest was set on structure and/or the magnetic/superconducting behavior and consequently measurements of TE properties were performed in the temperature range of 4.2 K to room temperature only. It should also be mentioned that even at the time the interest in the TE behavior and ZT was already present; the highest ZT in some cases was published for 600 K or even lower temperatures due to the fact that for various reasons measurements at higher temperatures were not possible.

## 2. Experimental Methods

There exist various production routes for filled skutterudites, such as the melt growth method, the solvothermal method, the solid phase reaction method, mechanical alloying, melt spinning, the high-temperature-high-pressure method, pulsed laser deposition, magnetron sputtering, molecular beam epitaxy, self-propagation high-temperature synthesis, microwave sintering, and high-pressure torsion. All these methods are described in detail in a recent review publication by C. Zhao et al. [24]. Single-phase skutterudites can be obtained by these preparation methods; many of them are rapid, and low-cost and provide large-scale preparation routes for high-quality TE materials.

In some publications the phonon part of the thermal conductivity is missing. The authors calculated it as suggested by Kim et al. [25]; the power factor (pf) was, in cases where it was not published, calculated from  $pf = S^2/(\rho\lambda)$ .

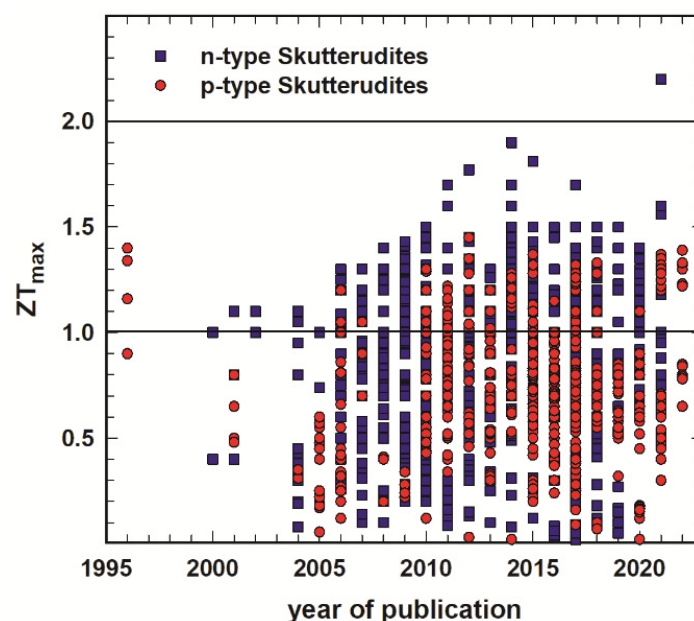
Furthermore, it should be noted that all values of p- and n-type skutterudites in Sections 3.2 and 3.3 are not substituted at the antimony site and are free of any additions.

### 3. Results and Discussion

#### 3.1. General Overview

For all figures in this chapter, data from [25–280] were used.

In Figure 1, all peak ZTs of measurements above room temperature versus the publication year are plotted. There are several features which catch the eye. One is the fact that generally n-type skutterudites have higher values than the p-type skutterudites, a fact also observed by Qiu et al. [23]. Another one is an almost linear increase in the peak ZT per year from 2003 to 2014 for the n-type and from 2006 to 2012 for the p-type, followed by an almost linear decrease with only a few exceptions. It is noticeable that as early as 1996 J.-P. Fleurial et al. [26] published ZTs > 1 for p-type  $\text{CeFe}_4\text{Sb}_{12}$ ,  $\text{CeFe}_{3.5}\text{Co}_{0.5}$  and  $\text{CeFe}_3\text{CoSb}_{12}$ . B.C. Sales et al. [27] reported a ZT of almost 1 for p-type  $\text{LaFe}_3\text{CoSb}_{12}$ . In 2006 and later a real “boom” appears; interestingly there are years (2007–2009) with no or almost no publications of p-type skutterudites, whereas in other years (2011, 2015–2017) they predominate.



**Figure 1.** ZT<sub>max</sub> vs. year of publication for p- and n-type filled skutterudites.

In Figure 2 the highest ZTs are displayed as a function of temperature. Of course, in some cases ZT<sub>max</sub> is not really the peak ZT of the respective sample but is identical to ZT of the highest measured temperature. Especially before 2005, measurements were often performed only below 600 K, but it also explains a culmination of many ZT<sub>max</sub> values at 800 K.

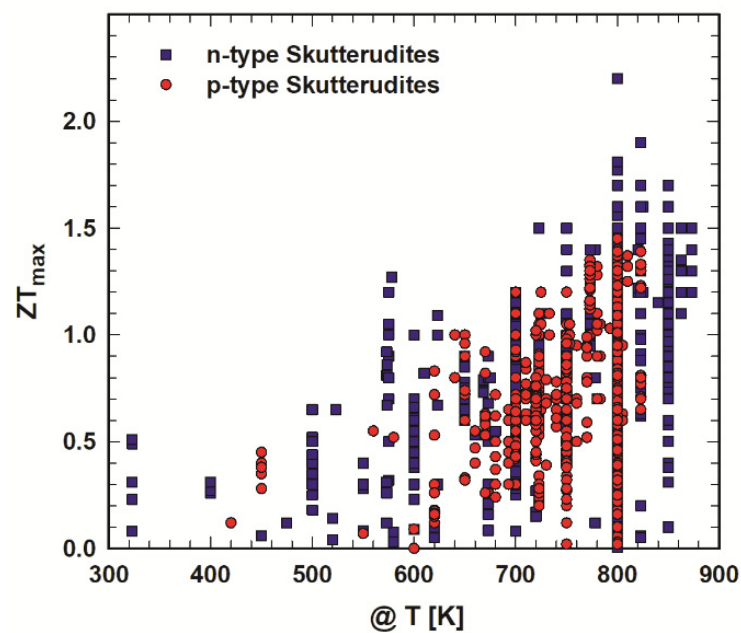


Figure 2.  $ZT_{\max}$  vs. temperature (T) of p- and n-type filled skutterudites.

In Figure 3 the dependence of the Seebeck coefficient on the electrical resistivity is depicted for the temperatures of 800 K and 300 K (insert in Figure 3). At 800 K the values of the Seebeck coefficient for the majority of p-type skutterudites are in the range of 100 to 210  $\mu\text{V/K}$  with corresponding electrical resistivities of 50 to 2000  $\mu\Omega\text{cm}$ , whereas for the n-type, the Seebeck coefficient for the majority is within a wider range,  $-110$  to  $-280$   $\mu\text{V/K}$ ; however, the electrical resistivity is in the same range as for the p-type.

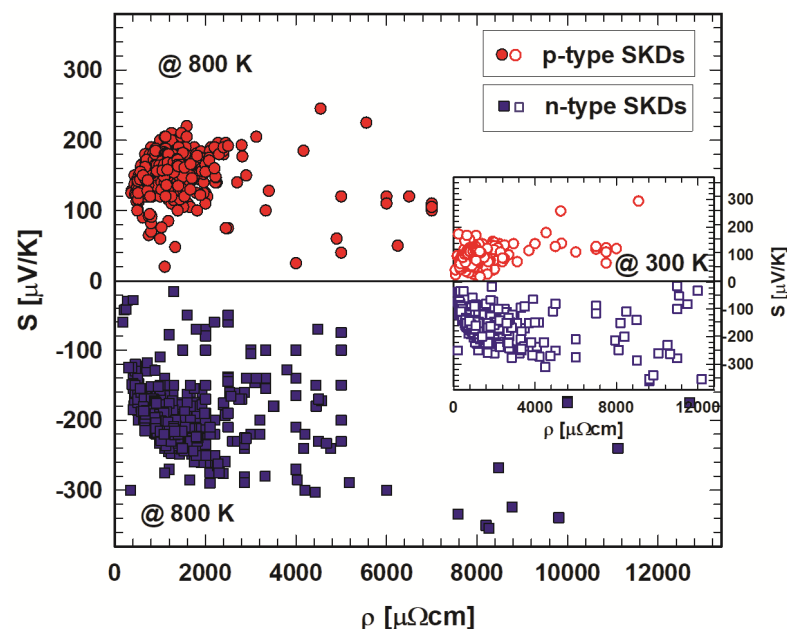
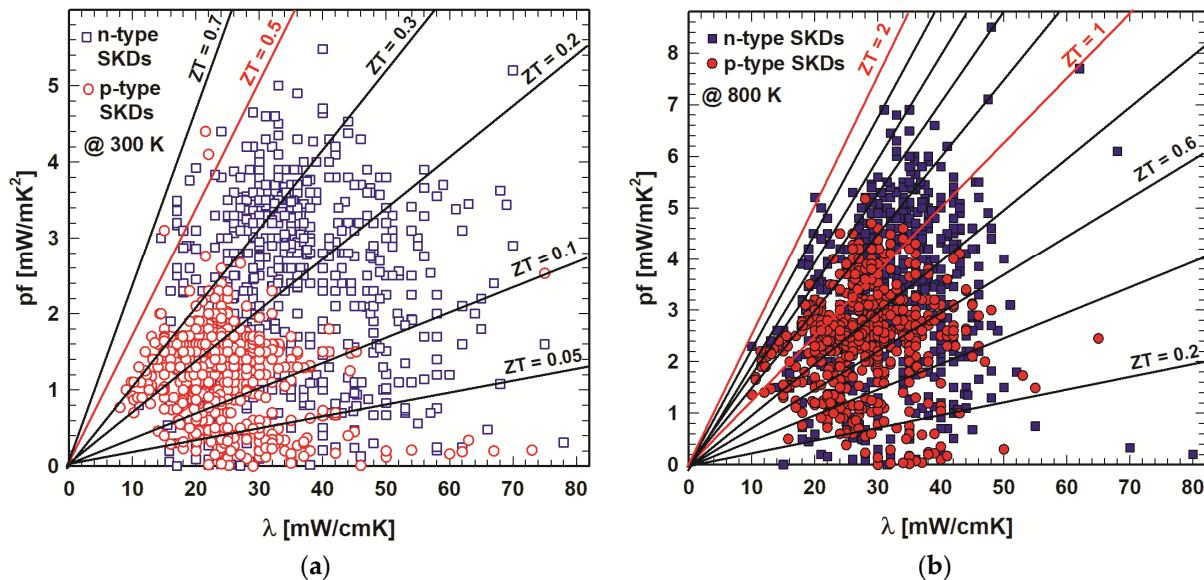


Figure 3. Seebeck coefficient (S) vs. electrical resistivity ( $\rho$ ) of p- and n-type filled skutterudites at 800 K. Insert: S vs.  $\rho$  at 300 K.

Figure 4a,b depicts the dependence of the power factor on the thermal conductivity at room temperature and at 800 K, respectively. Comparing these two figures, one finds that at 300 K the values are much more spread out than at 800 K. In addition, the level of the n-type power factors is much higher than that of the p-type, and although the level of



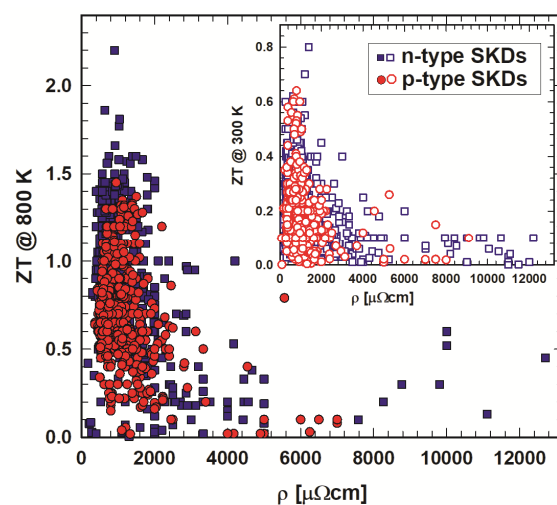
thermal conductivities for the p-type is lower than for the n-type; this is the main reason for the higher ZTs for the n-type. The lower thermal conductivities for the p-type can be explained by the usually higher filling fractions, leading to a stronger phonon scattering.



**Figure 4.** (a). Power factor (pf) vs. thermal conductivity ( $\lambda$ ) of p- and n-type filled skutterudites at 300 K. (b). Power factor (pf) vs. thermal conductivity ( $\lambda$ ) of p- and n-type filled skutterudites at 800 K.

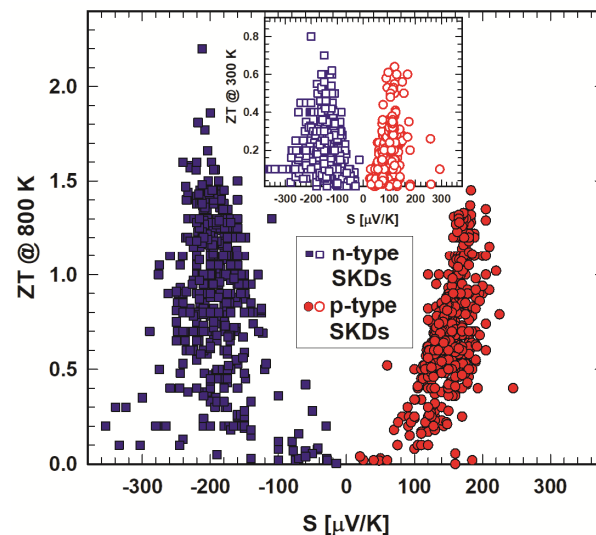
In both figures, the lines for the resulting ZT values are also drawn. These lines show that at 300 K (Figure 4a) no compound exceeds  $ZT = 0.7$  and there are only a few values above the line for  $ZT = 0.5$ . In addition, one can observe that for the n-type skutterudites the range of the power factors, as well as of the thermal conductivities, is much wider than for the p-type. This is not so much the fact for 800 K (Figure 4b) where all data are more squeezed together. Most skutterudites have a ZT between 0.6 and 1.4, and for the n-type ZT even exceeds 2 for  $(\text{Sm}, \text{Mm})_{0.13}\text{Co}_4\text{Sb}_{12}$  [275].

In Figure 5 ZT at 800 K is plotted versus the electrical resistivity ( $\rho$ ). For p- as well as for n-type skutterudites, for all high ZTs,  $\rho$  is lower than  $2000 \mu\Omega\text{cm}$ . For ZT at 300 K, (insert in Figure 5) even for  $\rho < 3000 \mu\Omega\text{cm}$ , the majority has a  $ZT > 0.3$ .



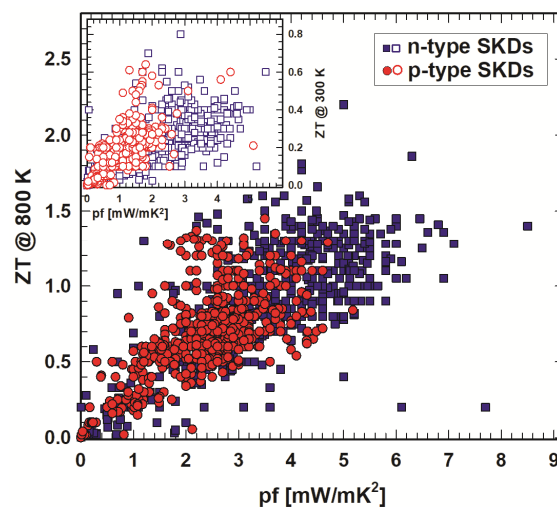
**Figure 5.** ZT vs. electrical resistivity ( $\rho$ ) of p- and n-type filled skutterudites at 800 K. Insert: ZT vs.  $\rho$  at 300 K.

Figure 6 presents the dependence of ZT on the Seebeck coefficient,  $S$ , at 800 K and in the insert at 300 K. For the n-type generally, the ideal value of  $S$  for high ZTs is around  $-200 \mu\text{Vcm}$ , with also the highest ZTs in this range (highest ZT~2.2 for HPT processed  $(\text{MmSm})_{0.15}\text{Co}_4\text{Sb}_{12}$  [275]). For the p-type this ideal range is between  $S = 140 \mu\text{Vcm}$  and  $S = 180 \mu\text{Vcm}$ , with the highest ZT = 1.45 at 800 K for  $\text{DD}_{0.6}\text{Fe}_3\text{CoSb}_{12}$  [120].

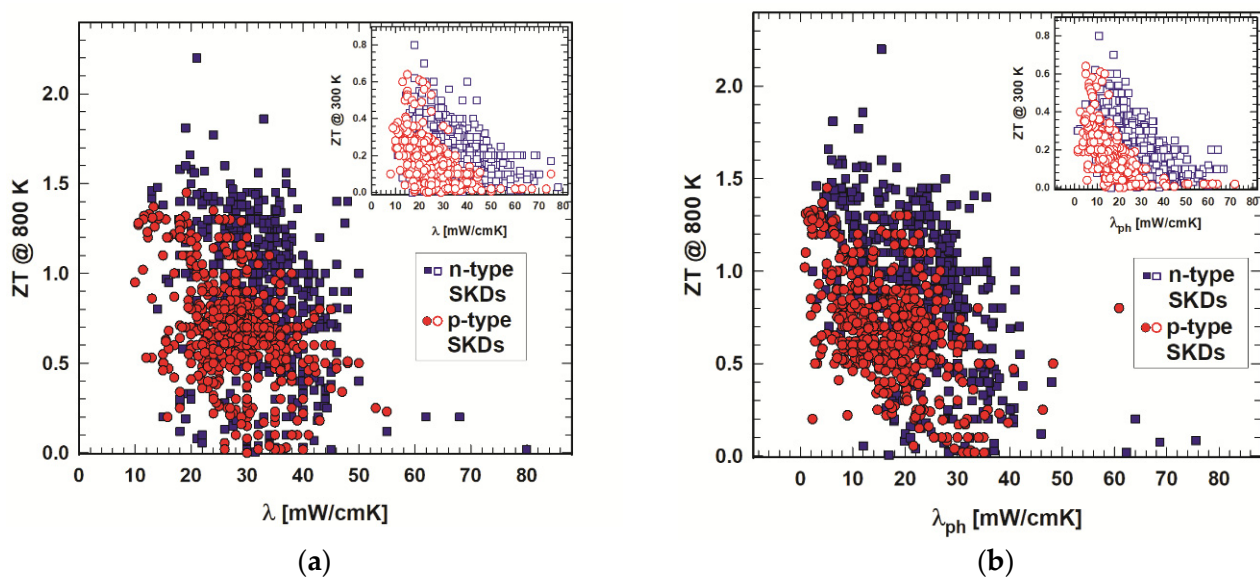


**Figure 6.** ZT vs. Seebeck coefficient ( $S$ ) of p- and n-type filled skutterudites at 800 K. Insert: ZT vs.  $S$  at 300 K.

Comparing Figure 7 with Figure 8a one can see that for ZT at 800 K the “cloud” of points looks different. For ZT at 800 K versus pf, except some outliers, there is an almost linear trend: ZT is increasing with increasing power factor, which is also the trend at 300 K (insert in Figure 7), although at room temperature the data are spread out wider. For both temperature regimes the n-type has higher power factors and ZTs. ZT at 800 K versus thermal conductivity looks different, with almost all data points for the thermal conductivity within  $15 \text{ mW/cmK}$  and  $40 \text{ mW/cmK}$ . This range is wider for the data at 300 K (insert in Figure 8a), but reveals much better that ZTs are higher the lower the thermal conductivity is.



**Figure 7.** ZT vs. power factor (pf) of p- and n-type filled skutterudites at 800 K. Insert: ZT vs. pf at 300 K.



**Figure 8.** (a). ZT vs. thermal conductivity ( $\lambda$ ) of p- and n-type filled skutterudites at 800 K. Insert: ZT vs.  $\lambda$  at 300 K. (b). ZT vs. lattice thermal conductivity ( $\lambda_{ph}$ ) of p- and n-type filled skutterudites at 800 K. Insert: ZT vs.  $\lambda_{ph}$  at 300 K.

Comparing now the total thermal conductivity versus ZT (Figure 8a) with the lattice thermal conductivity versus ZT (Figure 8b), the differences are marginal for the high as well as for the low temperature regime.

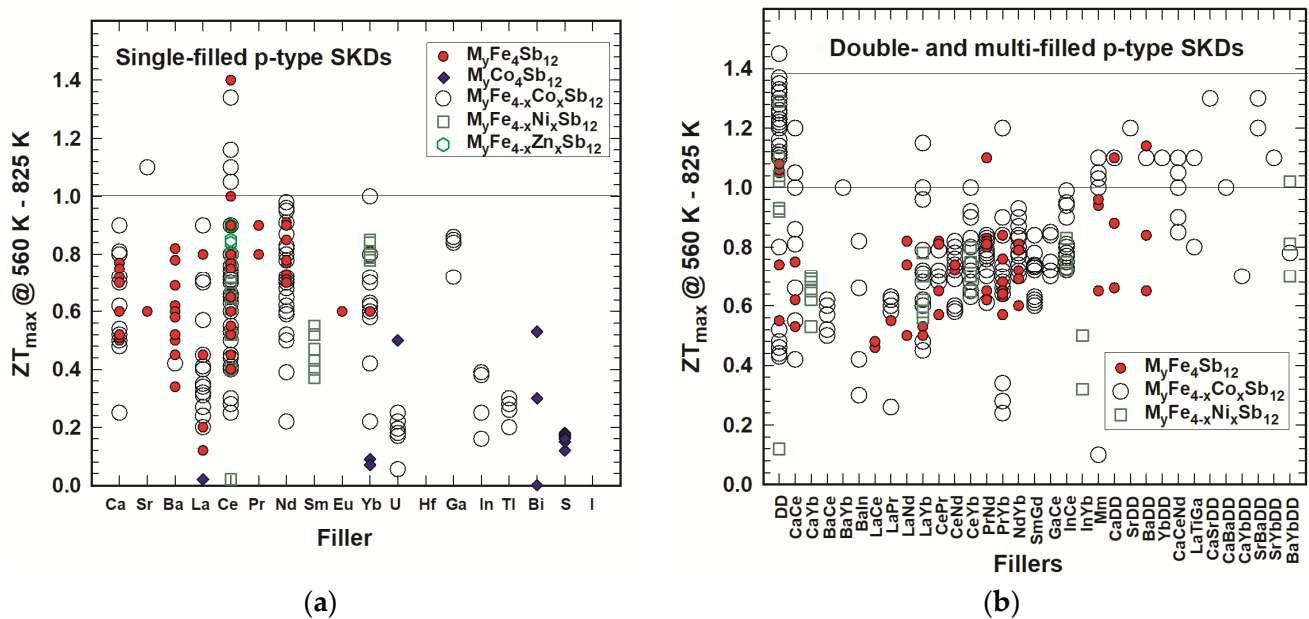
ZT generally increases with increasing temperature, therefore some values of  $ZT_{max}$  could only be taken at  $T_{max}$  of a rather reduced temperature interval and do not represent the true  $ZT_{max}$ . As ZTs of the n-type generally reach higher values than ZTs of the p-type, it is necessary to try to enhance p-type ZTs in order to construct efficient modules with p- and n-legs of comparable ZTs. The source of this imbalance is the Seebeck coefficient, which on average is higher for the n- than for the p-type.

### 3.2. P-Type Skutterudites

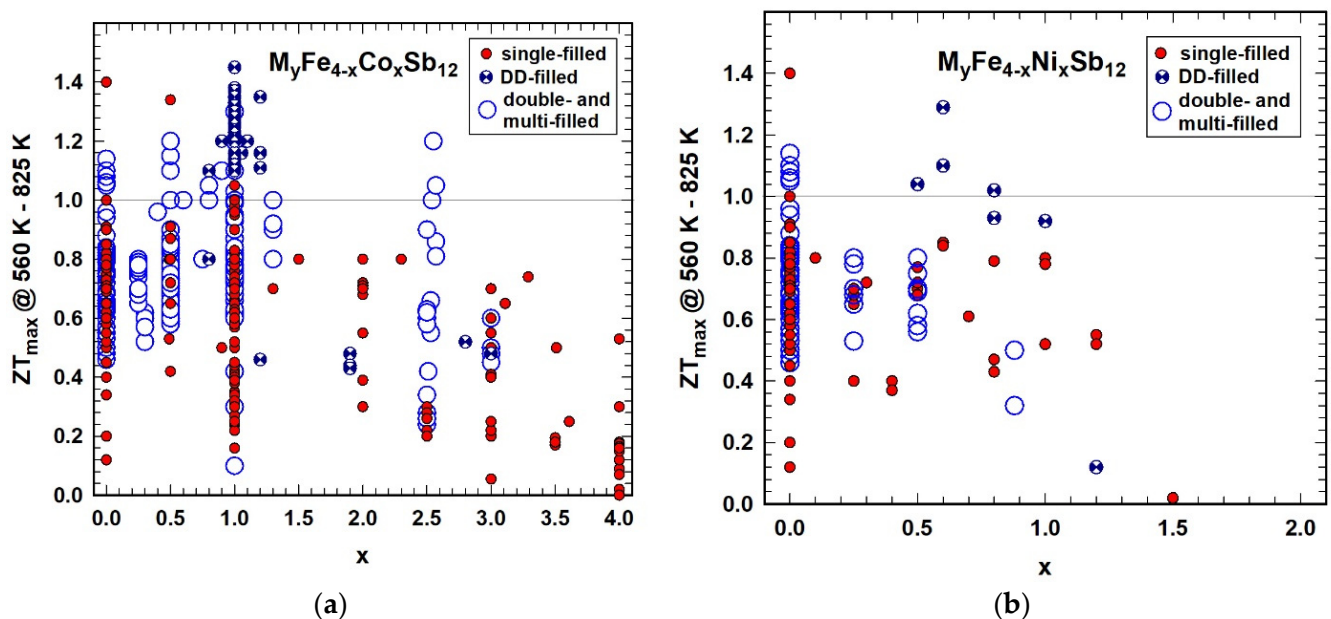
#### 3.2.1. Skutterudites $M_yCo_4Sb_{12}$

There exist only a few publications about p-type  $M_yCo_4Sb_{12}$  (Table 1); all of them are single-filled and all of them have a rather low ZT (see Figures 9a and 10a). For  $Bi_yCo_4Sb_{12}$  (Mallik and al. [131]) and for  $S_yCo_4Sb_{12}$  (Ghosh et al., [262]) the influence of the amount of filler was investigated: the highest ZTs are  $ZT = 0.53$  and  $0.175$ , respectively. Sales et al. [33] investigated  $Tl_yCo_4Sb_{12}$  as well as with Sb substituted by Sn: all ZTs  $\leq 0.1$ . P-type single-filled  $La_{0.5}Co_4Sb_{12}$  [259] as well as  $Yb_{0.25}Co_4Sb_{12}$  [211] turned into an n-type when Al as second filler was added. The same switch from p- to n-type occurred for  $Yb_{0.25}Co_4Sb_{12}$  due to the substitution of Co by Ni [228].  $U_{0.05}Co_4Sb_{12}$  was used as reference sample for Fe/Co substitution [48].





**Figure 9.** (a). ZT in dependence of the filler for  $M_yFe_4Sb_{12}$ ,  $M_yCo_4Sb_{12}$ ,  $M_yFe_{4-x}Co_xSb_{12}$ ,  $M_yFe_{4-x}Ni_xSb_{12}$  and  $M_yFe_{4-x}Zn_xSb_{12}$  (ZT of  $I_yCo_4Sb_{12}$  is only available for  $T < 300$  K). (b). ZT in dependence of the fillers for  $M_yFe_4Sb_{12}$ ,  $M_yFe_{4-x}Co_xSb_{12}$ , and  $M_yFe_{4-x}Ni_xSb_{12}$ .



**Figure 10.** (a). Maximum ZT in dependence of single-, DD-, double- and multi-filled p-type skutterudites  $M_yFe_{4-x}Co_xSb_{12}$ . (b). Maximum ZT in dependence of single-, DD-, double- and multi-filled p-type skutterudites  $M_yFe_{4-x}Ni_xSb_{12}$ .

**Table 1.** P-type skutterudites: Filler(s), References for Fe<sub>4</sub>Sb<sub>12</sub>-based, Fe/Ni substituted, Fe/Co substituted, Fe/Zn substituted and Co<sub>4</sub>Sb<sub>12</sub>-based skutterudites.

|                       | Fe <sub>4</sub> Sb <sub>12</sub><br>Refs. | Fe/Ni Refs.      | Fe/Co Refs.                                                                     | Fe/Zn<br>Refs. | Co <sub>4</sub> Sb <sub>12</sub><br>Refs. |
|-----------------------|-------------------------------------------|------------------|---------------------------------------------------------------------------------|----------------|-------------------------------------------|
| Ca                    | [25,105,107,109]                          | -                | [58,97,107,182,278]                                                             | -              | -                                         |
| Sr                    | [105]                                     | -                | [97]                                                                            | -              | -                                         |
| Ba                    | [105,107,109,267]                         | -                | [97,103,107]                                                                    | -              | -                                         |
| La                    | [52,53,105]                               | -                | [26,46,47,49,52,76,141]                                                         | -              | [261]                                     |
| Ce                    | [25,104,105,123,136,153,183,189,199,254]  | [43,152,190,195] | [25,28,29,36,49,64,101,103,104,152,183,199,202,209,217,219,232,233,247,254,274] | 123            | -                                         |
| Pr                    | [101,105,264]                             | -                | -                                                                               | -              | -                                         |
| Nd                    | [105,206,264]                             | -                | [140,164,192,194,203,205,206,222,241,242]                                       | -              | -                                         |
| Sm                    | -                                         | [185]            | -                                                                               | -              | -                                         |
| Eu                    | [34,38,105]                               | -                | [38]                                                                            | -              | -                                         |
| Yb                    | [40,105,228,280]                          | -                | [40,89,97,103,104,141,226,263]                                                  | -              | [211,228]                                 |
| U                     | -                                         | -                | [48]                                                                            | -              | [48]                                      |
| Hf                    | [50]                                      | -                | -                                                                               | -              | -                                         |
| Ga                    | -                                         | -                | [253]                                                                           | -              | -                                         |
| In                    | -                                         | -                | [215]                                                                           | -              | [119]                                     |
| Tl                    | -                                         | -                | [160]                                                                           | -              | [33]                                      |
| Bi                    | -                                         | -                | -                                                                               | -              | [131]                                     |
| S                     | -                                         | -                | -                                                                               | -              | [262]                                     |
| I                     | -                                         | -                | -                                                                               | -              | [147]                                     |
| <b>Double-fillers</b> |                                           |                  |                                                                                 |                |                                           |
| DD                    | [95,107,109]                              | [95,122]         | [95,97,106,107,120,134,151,173,174,220,239,276]                                 | [95,122]       | -                                         |
| Ca, Ce                | [156]                                     | -                | [58,156]                                                                        | -              | -                                         |
| Ca, Yb                | -                                         | [62]             | -                                                                               | [62]           | -                                         |
| Ba, Ce                | -                                         | -                | [103]                                                                           | -              | -                                         |
| Ba, Yb                | -                                         | -                | [163]                                                                           | -              | -                                         |
| Ba, In                | -                                         | -                | [124,139]                                                                       | -              | -                                         |
| La, Ce                | [272]                                     | [167]            | [49,169,187,219,272]                                                            | [167]          | -                                         |
| La, Pr                | [230]                                     | -                | [207,230]                                                                       | -              | -                                         |
| La, Nd                | [178,249]                                 | -                | [178,249]                                                                       | -              | -                                         |
| La, Yb                | [250]                                     | [168]            | [141,250]                                                                       | [168]          | -                                         |
| Ce, Pr                | [225,231]                                 | -                | [225]                                                                           | -              | -                                         |

Table 1. Cont.

|                      | Fe <sub>4</sub> Sb <sub>12</sub><br>Refs. | Fe/Ni Refs. | Fe/Co Refs.       | Fe/Zn<br>Refs. | Co <sub>4</sub> Sb <sub>12</sub><br>Refs. |
|----------------------|-------------------------------------------|-------------|-------------------|----------------|-------------------------------------------|
| Ce, Nd               | [130,224]                                 | -           | [103,130,224]     | -              | -                                         |
| Ce, Yb               | -                                         | [196]       | [89,103,219,266]  | -              | -                                         |
| Pr, Nd               | [177,204,264]                             | -           | [177,204,264]     | -              | -                                         |
| Pr, Yb               | [176,223]                                 | -           | [176,223]         | -              | -                                         |
| Nd, Yb               | [205,242]                                 | -           | [193,205,242]     | -              | -                                         |
| Sm, Gd               | -                                         | -           | [246]             | -              | -                                         |
| Ga, Ce               | -                                         | -           | [253]             | -              | -                                         |
| In, Ce               | -                                         | -           | [209]             | -              | -                                         |
| In, Yb               | -                                         | -           | [179,212]         | -              | -                                         |
| <b>Multi-fillers</b> |                                           |             |                   |                |                                           |
| Mm                   | [101,107,109]                             | -           | [101,107,162,233] | -              | -                                         |
| Ca, DD               | [107]                                     | -           | [97,107]          | -              | -                                         |
| Sr, DD               | -                                         | -           | [97]              | -              | -                                         |
| Ba, DD               | [107]                                     | -           | [97,107]          | -              | -                                         |
| Yb, DD               | -                                         | -           | [97]              | -              | -                                         |
| Ca, Ce, Nd           | -                                         | -           | [161]             | -              | -                                         |
| La, Ti, Ga           | -                                         | -           | [218,237]         | -              | -                                         |
| Ca, Sr, DD           | -                                         | -           | [97]              | -              | -                                         |
| Ca, Ba, DD           | -                                         | -           | [97]              | -              | -                                         |
| Ca, Yb, DD           | -                                         | -           | [97]              | -              | -                                         |
| Sr, Ba, DD           | -                                         | -           | [97]              | -              | -                                         |
| Sr, Yb, DD           | -                                         | -           | [97]              | -              | -                                         |
| Ba, Yb, DD           | -                                         | [122]       | [97]              | [122]          | -                                         |

### 3.2.2. Skutterudites M<sub>y</sub>Fe<sub>4</sub>Sb<sub>12</sub>

Single-filled skutterudites M<sub>y</sub>Fe<sub>4</sub>Sb<sub>12</sub> (for the filler M, see Table 1) were prepared and investigated for various reasons. Especially in the time before 2000, many measurements were performed only below room temperature and the focus was set on the investigation of magnetism and/or structural features, or the heat capacity e.g., Refs. [28,34,40,50]. In some of these publications not all measurements necessary to calculate ZT were performed for various reasons, in other cases thermoelectric properties were measured only to about 600 K or even to lower temperatures, revealing the highest ZTs at these temperatures.

Some research groups compared the influence of various fillers on the TE properties with the goal to find the best one [105,107,264]; other groups tried to enhance the filling level, which led to the conclusion that generally, keeping the same conditions for density, or grain size, ZT is higher the more of the filler is in the skutterudite cage. For example, Rogl et al. showed an increase in ZT with growing filling level for Ca<sub>y</sub>Fe<sub>4</sub>Sb<sub>12</sub> as well as for Ba<sub>y</sub>Fe<sub>4</sub>Sb<sub>12</sub> [107,109]; the latter was confirmed by Yu et al. [267]. Bao et al. arrived at the same results for La<sub>y</sub>Fe<sub>4</sub>Sb<sub>12</sub> [52] and Shin et al. for Nd<sub>y</sub>Fe<sub>4</sub>Sb<sub>12</sub> [206].

Several research groups [107,109,135,254] prepared the samples using different techniques. Tan et al. [136], for example, compared the TE properties of CeFe<sub>4</sub>Sb<sub>12</sub> prepared with the traditional melting–annealing method followed by spark plasma sintering, with melt spinning and spark plasma sintering resulting in ZTs of 0.9 and 1, respectively. Liu et al. [254] used different annealing temperatures (773–848 K) for Ce<sub>1.25</sub>Fe<sub>4</sub>Sb<sub>12</sub> and ob-

tained the best result for the lowest temperature ( $ZT = 0.8$ ). Rogl et al. [107,109] could prove that smaller grain sizes due to ball-milling of  $\text{Ca}_y\text{Fe}_4\text{Sb}_{12}$  and  $\text{Ba}_y\text{Fe}_4\text{Sb}_{12}$  result in higher ZTs, because of lower thermal conductivities, although the electrical resistivity was enhanced.

In many publications, single-filled  $\text{M}_y\text{Fe}_4\text{Sb}_{12}$  was used as reference sample to compare with multi-filled skutterudites, as shown in Refs. [156,264]. In most cases  $\text{M}_y\text{Fe}_4\text{Sb}_{12}$  was compared with single- or double- or multi-filled  $\text{M}_y\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$  [26,28,29,156,176–178,199, 204–207,223–225,230,231,242,249,250,272] or with  $\text{M}_y\text{Fe}_{4-x}\text{Ni}_x\text{Sb}_{12}$  [153,165] or  $\text{M}_y\text{Fe}_{4-x}\text{Zn}_x\text{Sb}_{12}$  [123] with M being the same filler(s).

Figure 9a shows that for single-filled  $\text{M}_y\text{Fe}_4\text{Sb}_{12}$  the most popular fillers are Ca, Ba, Ce and Nd. Most peak ZTs of the single-filled skutterudites are in the temperature range of about 600 to 800 K (Figure 2) with ZTs between 0.5 and 0.9 (Figure 9a). Besides the very high  $ZT = 1.4$  of  $\text{CeFe}_4\text{Sb}_{12}$  in Fleurial et al. [26], only one more single-filled skutterudite, which reaches  $ZT = 1$ , is published by Tan et al. [136] for  $\text{CeFe}_4\text{Sb}_{12}$ .

For  $\text{Fe}_4\text{Sb}_{12}$  based p-type skutterudites, various double fillers were used, as listed in Table 1. Didymium, DD, is a natural double filler consisting of 95.4% neodymium and 4.6% praseodymium. As the benefit of double- or multi-filling is that due to different rattling modes of different fillers the thermal conductivity is decreased, on average, peak ZTs of double-filled skutterudites are higher than those of the single-filled ones (Figure 9b). In 2011, Rogl et al. achieved  $ZT = 1.08$  at 800 K for ball-milled  $\text{DD}_{0.85}\text{Fe}_4\text{Sb}_{12}$  [107], which was confirmed about 10 years later by Limbu et al. [264] for  $\text{PrFe}_4\text{Sb}_{12}$  doped with Nd, with a  $ZT = 1.1$  at 800 K. For mischmetal, Mm, (50.8% Ce, 28.1% La, 16.1% Nd, 5.0% Pr) [101,107,109] the highest ZT is about 1 at 800 K; for multi-filled skutterudite  $\text{Ca}_{0.41}\text{DD}_{0.4}\text{Fe}_4\text{Sb}_{12}$  the highest ZT is 1.1, and for  $\text{Ba}_{0.44}\text{DD}_{0.42}\text{Fe}_4\text{Sb}_{12}$  ZT is 1.14 [107].

### 3.2.3. P-Type Skutterudites with Fe/Co, Fe/Ni and Fe/Zn Substitution

Co, Ni, are the most-used transition metals substituted for Fe, but Fe/Co substitutions are more frequent than Fe/Ni substitutions (Table 1), as can be seen by comparing Figure 10a,b. Tan et al. was the only one with an Fe/Zn substitution [123] and reached  $ZT = 0.9$  at 800 K for  $\text{CeFe}_{3.9}\text{Zn}_{0.1}\text{Sb}_{12}$ . As already explained in the introduction, the benefit of such substitutions is that due to a structural disorder, the overall thermal conductivity decreases leading to an enhancement of ZT.

Figure 10a shows that for all single-filled  $\text{M}_y\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$  skutterudites,  $ZT \geq 1$  in the case of  $x \leq 2.5$ , such as  $ZT = 1.34$  for  $\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$  and  $ZT = 1.16$  for  $\text{CeFe}_3\text{CoSb}_{12}$  (Fleurial et al. [26]),  $ZT = 1.1$  for  $\text{Sr}_{0.6}\text{Fe}_3\text{CoSb}_{12}$  and  $\text{Yb}_{0.65}\text{Fe}_3\text{CoSb}_{12}$  (Rogl et al. [97]) and  $ZT = 1.1$  or  $1.05$  for  $\text{CeFe}_3\text{CoSb}_{12}$  (Zhang et al. [101]). As already shown for  $\text{Fe}_4\text{Sb}_{12}$ -based skutterudites, for those with Fe/Co substitution,  $ZT \geq 1$  also occurs more often for double- and multi-filled skutterudites than for single-filled ones. From Figure 10a it is obvious that didymium is an excellent filler, providing very high ZTs. Hot pressed samples of  $\text{DD}_y\text{Fe}_3\text{CoSb}_{12}$  have ZTs in the range of 1.2, and after additional HPT the thermally stable  $\text{DD}_{0.6}\text{Fe}_3\text{CoSb}_{12}$  has a  $ZT \sim 1.4$  [120]. Also, commercial skutterudite powder  $\text{DD}_{0.6}\text{Fe}_3\text{CoSb}_{12}$ , cold pressed and densified by HPT, reaches  $ZT \sim 1.3$  [239], and, in the case of samples with a diameter of 30 mm and a height of about 1 mm, even  $ZT \sim 1.4$  [276]. Multi-filled compounds with DD reach high ZTs, such as  $\text{Ca}_{0.2}\text{Sr}_{0.12}\text{DD}_{0.39}\text{Fe}_3\text{CoSb}_{12}$  or  $\text{Sr}_{0.16}\text{Yb}_{0.1}\text{DD}_{0.36}\text{Fe}_3\text{CoSb}_{12}$ , which have  $ZT = 1.3$  and  $ZT = 1.1$ , respectively (Rogl et al. [97]); but also, without DD, Tang et al. [58] and Jie et al. [130] published  $ZT = 1.2$  for  $\text{Ca}_{0.18}\text{Ce}_{0.12}\text{Fe}_{1.45}\text{Co}_{2.55}\text{Sb}_{12}$  and  $\text{Ce}_{0.45}\text{Nd}_{0.45}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$ , respectively. Dahal et al. obtained  $ZT = 1.15$  for  $\text{La}_{0.68}\text{Ce}_{0.25}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$  [187] and  $ZT = 1.1$  for  $\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$  [161], a ZT value also gained by Peng et al. [218] for  $\text{La}_{0.8}\text{Tl}_{0.1}\text{Ga}_{0.1}\text{Fe}_3\text{CoSb}_{12}$ .

Generally, ZT of filled  $\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$  skutterudites becomes lower with increasing  $x$ , but, of course, ZT also depends on the filling level, the density and whether or not the sample is single phase or not. One also learns from Figure 10a that  $\text{M}_y\text{Fe}_3\text{CoSb}_{12}$  is the most frequently used composition, followed by  $\text{M}_y\text{Fe}_4\text{Sb}_{12}$ .

In case of  $M_yFe_{4-x}Ni_xSb_{12}$  (Figure 10b) all published samples have  $x \leq 1.25$ , which corresponds to  $x \leq 2.5$  in the Co series. Only Tan et al. [153] published results for a Fe/Ni substituted series i.e., for  $Ce_{0.3}Fe_{2.5}Ni_{1.5}Sb_{12}$  a very low  $ZT = 0.02$ .

$ZTs > 1$  can be found for several DD-filled skutterudites by Rogl et al. [95,122]; otherwise, for single-filled as well as for double- or multi-filled alloys,  $ZT = 0.8$  such as for  $Ce_{0.9}Fe_{3.9}Ni_{0.1}Sb_{12}$  in Tan et al. [152] or  $La_{0.75}Yb_{0.25}Fe_{3.75}Ni_{0.25}Sb_{12}$  in Jeon et al. [168].

Only a few single-filled p-type skutterudites reach a  $ZT_{max} > 1$ . In the case of double- and multi-filled p-type skutterudite, it shows that didymium is an excellent filler with almost all  $ZTs > 1$ , but also other double- and multi-filled p-types reach high  $ZTs$ . It should be mentioned that DD-filled skutterudites after additional processing via high-pressure torsion (optimization of microstructure) have excellent  $ZTs$ . Substituting Fe by Co, especially in the combination  $Fe_3Co$ , enhances the TE properties, but one can also see that for  $Fe_{4-x}Co_x$  compounds substitutions with  $x > 2.5$  do not provide any improvements. The Fe/Ni substitutions did hitherto not yield results as good as for the Fe/Co series.

### 3.3. N-Type Skutterudites

#### 3.3.1. Skutterudites $M_yCo_4Sb_{12}$

In contrast to the p-type,  $Co_4Sb_{12}$ -based skutterudites represent the majority of the n-type. In all three figures (Figure 11a–c), displaying the relation between the respective filler or fillers and the peak  $ZT$  for n-type skutterudites, one can see that  $M_yCo_4Sb_{12}$  is dominant. Figure 2 shows that n-type skutterudites were measured in some cases almost to 900 K, p-type usually only to about 800 K. Concerning the single-filled n-type skutterudites of this group, the most-used fillers are Ba, Yb and In (Table 2). Also “exotic” fillers such as Li, Na, K, Mg, Sm, Gd, Tb, Dy, Ti, Ga, Ge and Br were used, and mostly only one publication for each filler exists; fillers such as Ti, Ge, Sn or Br were used only in combination with antimony substitution.

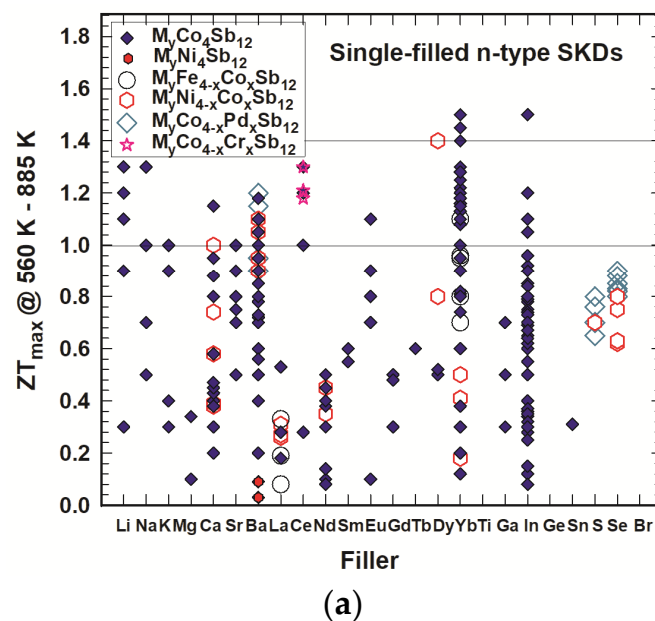
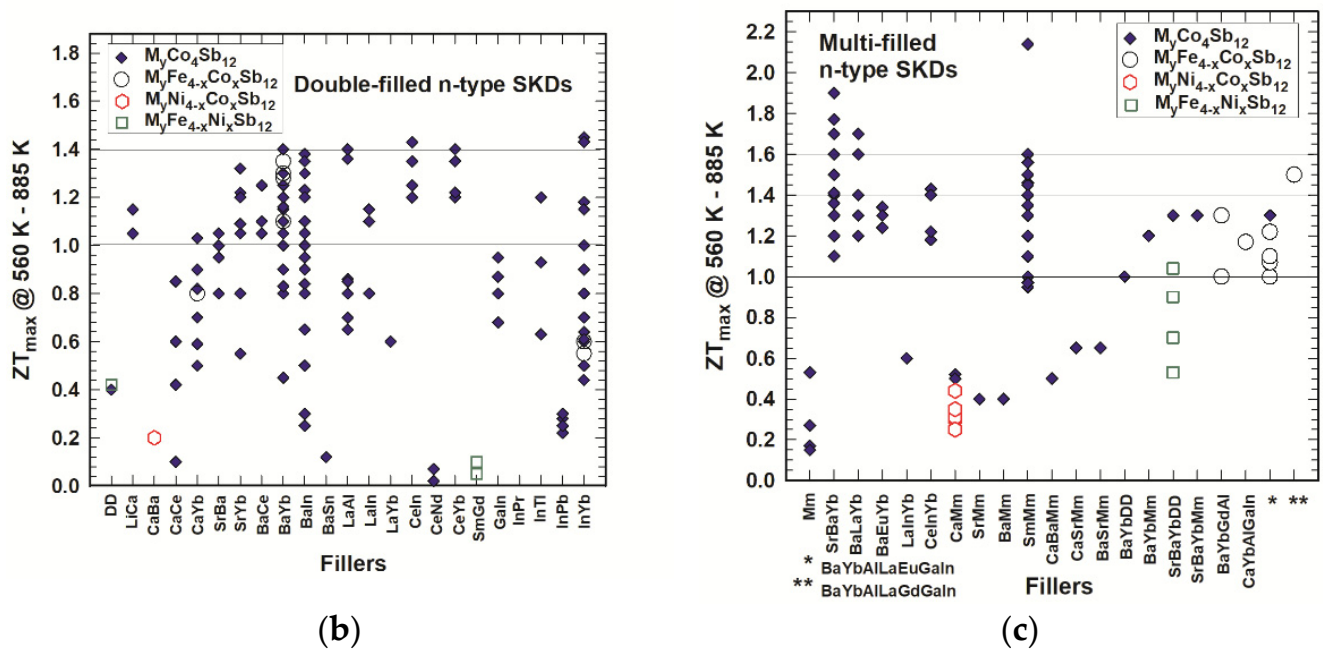


Figure 11. Cont.





**Figure 11.** (a).  $ZT$  in dependence of the filler for  $M_yCo_4Sb_{12}$ ,  $M_yNi_4Sb_{12}$ ,  $M_yFe_{4-x}Co_xSb_{12}$ ,  $M_yNi_{4-x}Co_xSb_{12}$ ,  $M_yCo_{4-x}Pd_xSb_{12}$  and  $M_yCo_{4-x}Cr_xSb_{12}$ . (b).  $ZT$  in dependence of the filler for  $M_yCo_4Sb_{12}$ ,  $M_yFe_{4-x}Co_xSb_{12}$ ,  $M_yNi_{4-x}Co_xSb_{12}$  and  $M_yFe_{4-x}Ni_xSb_{12}$ . (c).  $ZT$  in dependence of the filler for  $M_yCo_4Sb_{12}$ ,  $M_yFe_{4-x}Co_xSb_{12}$ ,  $M_yNi_{4-x}Co_xSb_{12}$  and  $M_yFe_{4-x}Ni_xSb_{12}$ .

**Table 2.** N-type skutterudites: Filler(s), references for  $Co_4Sb_{12}$ -based, Co/Cr substituted, Fe/Co substituted, Co/Ni substituted, Co/Pd substituted and Fe/Ni substituted skutterudites.

| Filler(s) of N-Type SKDs | $Co_4Sb_{12}$ Refs.                                           | Co/Cr Refs. | Fe/Co Refs. | Co/Ni Refs.   | Co/Pd Refs. | Fe/Ni Refs. |
|--------------------------|---------------------------------------------------------------|-------------|-------------|---------------|-------------|-------------|
| <b>Single-fillers</b>    |                                                               |             |             |               |             |             |
| Li                       | [113,125,216]                                                 | -           | -           | -             | -           | -           |
| Na                       | [83]                                                          | -           | -           | -             | -           | -           |
| K                        | [57]                                                          | -           | -           | -             | -           | -           |
| Mg                       | [138]                                                         | -           | -           | -             | -           | -           |
| Ca                       | [44,45,79,98,197,216]                                         | -           | -           | [45]          | -           | -           |
| Sr                       | [60,93]                                                       | -           | -           | -             | -           | -           |
| Ba                       | [35,37,65–67,74,75,77, 88,91,92,126,158,159, 174,213,260,270] | -           | -           | [37,201, 234] | [65]        | [201]       |
| La                       | [210,240]                                                     | -           | [46]        | [59,112]      | -           | -           |
| Ce                       | [28–30,181,183,184,236]                                       | [184]       | [28]        | -             | -           | -           |
| Nd                       | [42,54,198,236]                                               | -           | -           | [54]          | -           | -           |
| Sm                       | [94,198]                                                      | -           | -           | -             | -           | -           |
| Eu                       | [38,39,72]                                                    | -           | [38]        | -             | -           | -           |
| Gd                       | [137,198]                                                     | -           | -           | -             | -           | -           |
| Tb                       | [198]                                                         | -           | -           | -             | -           | -           |
| Dy                       | [198,243]                                                     | -           | -           | [243]         | -           | -           |

Table 2. Cont.

| Filler(s) of N-Type SKDs | Co <sub>4</sub> Sb <sub>12</sub> Refs.                                                                                      | Co/Cr Refs. | Fe/Co Refs. | Co/Ni Refs. | Co/Pd Refs. | Fe/Ni Refs. |
|--------------------------|-----------------------------------------------------------------------------------------------------------------------------|-------------|-------------|-------------|-------------|-------------|
| Yb                       | [31,32,61,62,68,69,71,74,75,80,84,85,90,98,100,108,121,128,129,144,145,149,166,171,175,180,181,186,208,211,255,257,258,271] | -           | [62,186]    | [228]       | -           | [40]        |
| Ti                       | [235]                                                                                                                       | -           | -           | -           | -           | -           |
| Ga                       | [132]                                                                                                                       | -           | -           | -           | -           | -           |
| In                       | [55,63,67,70,81,82,84,87,99,110,115,118,119,127,143,154,155,179,191,214,261]                                                | -           | -           | -           | -           | -           |
| Ge                       | [148]                                                                                                                       | -           | -           | -           | -           | -           |
| Sn                       | [56,78]                                                                                                                     | -           | -           | -           | -           | -           |
| S                        | [188,245,273]                                                                                                               | -           | -           | [188]       | [244]       | -           |
| Se                       | [188,227]                                                                                                                   | -           | -           | [277]       | [248]       | -           |
| Br                       | 190                                                                                                                         | -           | -           | -           | -           | -           |
| <b>Double-fillers</b>    |                                                                                                                             |             |             |             |             |             |
| DD                       | [95]                                                                                                                        | -           | -           | -           | -           | [95]        |
| Li, Ca                   | [216]                                                                                                                       | -           | -           | -           | -           | -           |
| Ca, Ba                   | -                                                                                                                           | -           | [96]        | [96]        | -           | -           |
| Ca, Ce                   | [79]                                                                                                                        | -           | -           | -           | -           | -           |
| Ca, Yb                   | [98]                                                                                                                        | -           | -           | -           | -           | -           |
| Sr, Ba                   | [93,108]                                                                                                                    | -           | -           | -           | -           | -           |
| Sr, Yb                   | [51,91,93]                                                                                                                  | -           | -           | -           | -           | -           |
| Ba, Ce                   | [77]                                                                                                                        | -           | -           | -           | -           | -           |
| Ba, Yb                   | [74,75,91,135]                                                                                                              | -           | [142]       | -           | -           | -           |
| Ba, In                   | [67,92,127,157,252]                                                                                                         | -           | -           | -           | -           | -           |
| Ba, Sn                   | [159]                                                                                                                       | -           | -           | -           | -           | -           |
| La, Al                   | [259]                                                                                                                       | -           | -           | -           | -           | -           |
| La, In                   | [229]                                                                                                                       | -           | -           | -           | -           | -           |
| La, Yb                   | [117]                                                                                                                       | -           | -           | -           | -           | -           |
| Ce, In                   | [81,146]                                                                                                                    | -           | -           | -           | -           | -           |
| Ce, Nd                   | [217]                                                                                                                       | -           | -           | -           | -           | -           |
| Ce, Yb                   | [114]                                                                                                                       | -           | -           | -           | -           | -           |
| Sm, Gd                   | -                                                                                                                           | -           | -           | -           | -           | [246]       |
| Ga, In                   | [170]                                                                                                                       | -           | -           | -           | -           | -           |
| In, Pr                   | [154]                                                                                                                       | -           | -           | -           | -           | -           |
| In, Tl                   | [116]                                                                                                                       | -           | -           | -           | -           | -           |
| In, Pb                   | [127]                                                                                                                       | -           | -           | -           | -           | -           |
| In, Yb                   | [73,84,114,117,212]                                                                                                         | -           | -           | -           | -           | -           |

Table 2. Cont.

| Filler(s) of N-Type SKDs   | Co <sub>4</sub> Sb <sub>12</sub> Refs. | Co/Cr Refs. | Fe/Co Refs.   | Co/Ni Refs. | Co/Pd Refs. | Fe/Ni Refs. |
|----------------------------|----------------------------------------|-------------|---------------|-------------|-------------|-------------|
| <b>Multi-fillers</b>       |                                        |             |               |             |             |             |
| Mm                         | [101,253]                              | -           | -             | -           | -           | -           |
| Sr, Ba, Yb                 | [91,108,120,150,175]                   | -           | -             | -           | -           | -           |
| Ba, La, Yb                 | [111,150]                              | -           | -             | -           | -           | -           |
| Ba, Eu, Yb                 | [86]                                   | -           | -             | -           | -           | -           |
| La, In, Yb                 | [117]                                  | -           | -             | -           | -           | -           |
| Ce, In, Yb                 | [114,146]                              | -           | -             | -           | -           | -           |
| Ca, Mm                     | [102]                                  | -           | -             | [102]       | -           | -           |
| Sr, Mm                     | [102]                                  | -           | -             | [102]       | -           | -           |
| Ba, Mm                     | [102]                                  | -           | -             | -           | -           | -           |
| Sm, Mm                     | [151,220,256,265,275]                  | -           | -             | -           | -           | -           |
| Ca, Ba, Mm                 | [102]                                  | -           | -             | -           | -           | -           |
| Ca, Sr, Mm                 | [102]                                  | -           | -             | -           | -           | -           |
| Ba, Sr, Mm                 | [102]                                  | -           | -             | -           | -           | -           |
| Ba, Yb, DD                 | [150]                                  | -           | -             | -           | -           | -           |
| Ba, Yb, Mm                 | [150]                                  | -           | -             | -           | -           | -           |
| Sr, Ba, Yb, DD             | [150]                                  | -           | -             | -           | -           | [133]       |
| Sr, Ba, Yb, Mm             | [150]                                  | -           | -             | -           | -           | -           |
| Ba, Yb, Gd, Al             | -                                      | -           | [200]         | -           | -           | -           |
| Ca, Yb, Al, Ga, In         | -                                      | -           | [200,269]     | -           | -           | -           |
| Ba, Yb, Al, La, Gd, Ga, In | -                                      | -           | [200]         | -           | -           | -           |
| Ba, Yb, Al, La, Eu Ga, In  | [269]                                  | -           | [200,268,269] | -           | -           | -           |

Whereas for the single-filled p-type, independent of the composition, only some reach a  $ZT > 1$  (Figure 9a), many n-type single-filled skutterudites have  $ZT$ s between 1 and 1.4, and even a  $ZT \geq 1.4$ , such as Yb<sub>0.35</sub>Co<sub>4</sub>Sb<sub>12</sub> in Dahal et al. [144], Yb<sub>0.15</sub>Co<sub>4</sub>Sb<sub>12</sub> in Allen et al. [258], Yb<sub>0.35</sub>Co<sub>4</sub>Sb<sub>12</sub> in Li et al. [171] or InCo<sub>4</sub>Sb<sub>12</sub> in Khovaylo et al. [214].

In most publications of n-type single-filled M<sub>y</sub>Co<sub>4</sub>Sb<sub>12</sub> skutterudites the authors try to enhance  $ZT$  by varying the filler amount, by trying out different preparation methods and/or annealing temperatures and times. In some cases, however, M<sub>y</sub>Co<sub>4</sub>Sb<sub>12</sub> is the reference sample for Fe/Co, Ni/Co or Fe/Ni substitutions [37,54,188,243], for substitutions at the antimony site [63,119], to compare the single-filled with a double-or multi-filled compound, [67,74,75,77,79,84,91–93,98,108,216,236] or to compare pure M<sub>y</sub>Co<sub>4</sub>Sb<sub>12</sub> with samples with various additives (see Table 3).

**Table 3.** Additions and substitutions, respective references for p-type and for n-type skutterudites.

| Additives                                              | P-Type Refs.              | N-Type Refs.                      |
|--------------------------------------------------------|---------------------------|-----------------------------------|
| TiO <sub>2</sub>                                       | -                         | [88,158]                          |
| Cu <sub>2</sub> O                                      | -                         | [159,220]                         |
| ZnO                                                    | -                         | [143]                             |
| MoO <sub>2</sub>                                       | [64]                      | -                                 |
| WO                                                     | [64]                      | -                                 |
| Al <sub>2</sub> O <sub>3</sub>                         | -                         | [220]                             |
| Yb <sub>2</sub> O <sub>3</sub>                         | -                         | [61,128,145]                      |
| La <sub>1.85</sub> Sr <sub>0.15</sub> CuO <sub>4</sub> | [220]                     | [220]                             |
| Ni core shells                                         | -                         | [165]                             |
| Ag                                                     | -                         | [126,172]                         |
| Al                                                     | -                         | [211]                             |
| CoSb <sub>3</sub>                                      | -                         | [71]                              |
| GaSb                                                   | -                         | [100,270]                         |
| InSb                                                   | -                         | [191,260,261,271]                 |
| Fe <sub>3</sub> Si                                     | [200]                     | -                                 |
| CoSi                                                   | -                         | [255]                             |
| PbTe                                                   | -                         | [143]                             |
| AgSbTe <sub>2</sub>                                    | -                         | [129,149]                         |
| InCo <sub>4</sub> Sb <sub>12</sub>                     | -                         | [175]                             |
| Fe <sub>2.25</sub> Co <sub>0.075</sub> B               | [220]                     | [220]                             |
| Ta <sub>0.8</sub> Zr <sub>0.2</sub> B                  | [220,238]                 | [220,238]                         |
| SiC                                                    | -                         | [257]                             |
| fullerene C <sub>60</sub>                              | -                         | [66]                              |
| graphene                                               | [237]                     | -                                 |
| carbon fiber                                           | [183]                     | -                                 |
| MWCNT                                                  | [221]                     | [210]                             |
| <b>Substitutions</b>                                   |                           |                                   |
| Sb/Ga                                                  | -                         | [100,132]                         |
| Sb/Ge                                                  | [119,139,140,174,203,241] | [119]                             |
| Sb/Te                                                  | [189,190]                 | [56,63,70,78,188,235,245,252,273] |
| Sb/Sn                                                  | [164,174]                 | [41,201]                          |
| Sb/Se                                                  | -                         | [227,248]                         |
| Sb/TeGe                                                | -                         | [179]                             |

For double-filled n-type skutterudites (Figure 11b) the most popular filler combinations are Ba-Yb, Ba-In and In-Yb (Table 2). ZTs are mainly in the range of 1 to 1.4, but there are some with  $ZT \geq 1.4$ : Ba<sub>0.08</sub>Yb<sub>0.09</sub>Co<sub>4</sub>Sb<sub>12</sub> (Shi et al. [74]), Ce<sub>0.1</sub>In<sub>0.05</sub>Co<sub>4</sub>Sb<sub>12</sub> (Graff et al. [146]), In<sub>0.2</sub>Ce<sub>0.15</sub>Co<sub>4</sub>Sb<sub>12</sub> (Li et al. [81]) and In<sub>0.2</sub>Yb<sub>0.2</sub>Co<sub>4</sub>Sb<sub>12</sub> (Ballikaya et al. [114]).

The multi-filled skutterudites present even higher values of the figure of merit (Figure 11c); 40% of all multi-filled Co<sub>4</sub>Sb<sub>12</sub>-based skutterudites have a  $ZT \geq 1.4$ , showing that multi-filling is a perfect method for high ZT skutterudites. The highlights in this group are Sr<sub>0.09</sub>Ba<sub>0.11</sub>Yb<sub>0.05</sub>Co<sub>4</sub>Sb<sub>12</sub> with  $ZT = 1.6$ , with an enhancement after severe plastic deformation to  $ZT = 1.9$ , and after annealing for the thermally stable sample,  $ZT = 1.7$

(Rogl et al. [150]);  $\text{Ba}_{0.08}\text{La}_{0.05}\text{Yb}_{0.08}\text{Co}_4\text{Sb}_{12}$  (Shi et al. [111]) and  $\text{Sr}_{0.07}\text{Ba}_{0.07}\text{Yb}_{0.07}\text{Co}_4\text{Sb}_{12}$  (Rogl et al. [120]) both with  $\text{ZT} = 1.7$  or  $\text{Sr}_{0.07}\text{Ba}_{0.10}\text{Yb}_{0.06}\text{Co}_4\text{Sb}_{12}$  and  $(\text{Sm},\text{Mm})_y\text{Co}_4\text{Sb}_{12}$  with  $\text{ZT} = 1.6$  (Rogl et al. [120,151]). The highest value of  $\text{ZT} \sim 2.2$  at 883 K was reached for commercial  $(\text{Sm},\text{Mm})_{0.15}\text{Co}_4\text{Sb}_{12}$  powder, densified via high pressure torsion for a sample with a diameter of 30 mm and a height of about 1 mm [275].

### 3.3.2. N-Type Skutterudites with Co/Cr, Fe/Co, Ni/Co, Co/Pd and Fe/Ni Substitution

As already explained in the introduction, T-metal substitutions help to enhance ZT. For single-filled n-type skutterudites Co/Cr, Fe/Co, Ni/Co, Co/Pd substitutions were used (Table 2, Figure 11a). Wang et al. [186] were the only ones to substitute Co by Cr; they noticed not only a lower thermal conductivity but also a higher Seebeck coefficient and obtained  $\text{ZT} = 1.3$  for  $\text{Ce}_{0.5}\text{Co}_{3.9}\text{Cr}_{0.1}\text{Sb}_{12}$ , which is 30% higher than without Cr. Ni/Co is the most-used substitution for n-type single-filled skutterudites, followed by Fe/Co and Co/Pd substitution (see Table 2). The highest  $\text{ZT} = 1.4$  was for  $\text{Dy}_{0.4}\text{Ni}_{0.8}\text{Co}_{3.2}\text{Sb}_{12}$  (Trivedi [243]), which is almost three times higher than for  $\text{Dy}_{0.4}\text{Co}_4\text{Sb}_{12}$ .

Comparing Figures 9a and 11a it is obvious that for the p-type, the T-metal substitution is applied more often than in the case of the n-type and as a consequence, as shown in Figure 11a, there are many single-filled n-type skutterudites without any substitution but with a  $\text{ZT} \geq 1.2$ .

More n-type single-filled skutterudites have  $\text{ZTs} > 1$  than their p-type counterparts, Yb and In turned out to be excellent fillers. From Figure 11b,c it is obvious that multi-filling is beneficial (Sr, Ba, Yb or Sm, Mm) as well as substituting Co by Ni.

## 3.4. Substitutions and Additives

### 3.4.1. Sb Substituted by Ga, Ge, Sn, Se, Te, Ge + Te

The benefit of substituting at the Sb-site was used by many research groups. As can be seen in Table 3, most of them published substitutions of Sb by Ge or Sb by Te, but also by Ga, Sn, Se as well as Ge together with Te were applied for both p- and n-type skutterudites. In all cases a series of substituted skutterudites was investigated and ZT was always more or less enhanced, usually for smaller amounts of Ga, Ge, Sn or Se, Te more than for larger amounts.

In the p-type series the highest enhancement with Sb/Te substitution was 67% for  $\text{CeFe}_4\text{Sb}_{11.9}\text{Te}_{0.1}$  (Fu et al. [189]) and even 150 % for  $\text{Ce}_{0.9}\text{Fe}_{3.75}\text{Ni}_{0.25}\text{Sb}_{11.9}\text{Te}_{0.1}$  (Fu et al. [190]). From all Sb/Ge substituted samples the highest ZT enhancement, 53%, was published by Zhang et al. [140] for  $\text{Nd}_{0.5}\text{Fe}_2\text{Co}_2\text{Sb}_{11.7}\text{Ge}_{0.3}$ . Rogl et al. [174] processed  $\text{DD}_{0.59}\text{Fe}_{2.7}\text{Co}_{1.3}\text{Sb}_{11.8}\text{Sn}_{0.2}$  ( $\text{ZT} = 1.28$ ) and  $\text{DD}_{0.54}\text{Fe}_{2.7}\text{Co}_{1.3}\text{Sb}_{11.8}\text{Ge}_{0.1}$  via high-pressure torsion and could enhance ZT from  $\text{ZT} = 1$  to 1.45 and even to  $\text{ZT} = 1.8$  with the thermally stable values of 1.32 and 1.4, in any case outstanding high ZTs for a p-type skutterudite. For the Sb/Sn substitution, the enhancement of ZT is in the range of 14–30% ([164,174]).

For n-type skutterudites almost all research groups worked with Sb/Te substitutions. Jin et al. [273] and Wang et al. [245] both published  $\text{S}_y\text{Co}_4\text{Sb}_{12-x}\text{Te}_x$  and had  $\text{ZT} = 1.6$  for  $\text{S}_{0.4}\text{Co}_4\text{Sb}_{11.2}\text{Te}_{0.8}$  and  $\text{ZT} = 1.5$  for  $\text{S}_{0.3}\text{Co}_4\text{Sb}_{11.2}\text{Te}_{0.8}$ , respectively, as the highest values in their series; the latter was confirmed by Duan et al. [188]. For the series of Sn-filled skutterudites [56,70,78],  $\text{Sn}_{0.25}\text{Co}_8\text{Sb}_{23.25}\text{Te}_{0.75}$  of Mallik et al. [70] with  $\text{ZT} = 0.6$  was the best. For Se-filled and Sb/Se substituted samples, the change in ZT with the changing Se amount is marginal ( $\text{ZT} \sim 0.4$  [227] and  $\text{ZT} \sim 0.85$  [248]), however, for  $\text{Se}_{0.17}\text{Co}_4\text{Sb}_{11.31}\text{Te}_{0.53}$ ,  $\text{ZT} = 1.2$  [188]. Mallik et al. [119] used Sb/Ge for In-filled skutterudites. The only one who used a “double” substitution (TeGe) on the Sb-site was Sun et al. [179]; for  $\text{In}_{0.1}\text{Co}_4\text{Sb}_{11}\text{Te}_{0.8}\text{Ge}_{0.2}$  they reached  $\text{ZT} = 1.2$ .

### 3.4.2. Additives

It is a fact that in almost all cases the introduction of all kinds of sub-micro or nanoparticles (see Table 3) in the bulk material reduces the thermal conductivity without disturbing

the charge carriers, but it turned out that the added amount of such additives in order to enhance ZT should be rather small (in the range of <2 vol.%) [22].

For the p-type  $\text{DD}_{0.6}\text{Fe}_3\text{CoSb}_{12}$ , Rogl et al. [220] added in various small quantities  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ ,  $\text{Fe}_{2.25}\text{Co}_{0.75}\text{B}$  and  $\text{Ta}_{0.8}\text{Zr}_{0.2}\text{B}$ : ZT was enhanced more or less, most successfully for  $\text{Ta}_{0.8}\text{Zr}_{0.2}\text{B}$  with an increase from  $\text{ZT} = 1.2$  to  $\text{ZT} = 1.32$  at 823 K. The same strategy was used by Peng et al. [218], who added n-type  $\text{Fe}_3\text{Si}$  to p-type  $\text{La}_{0.8}\text{Ti}_{0.1}\text{Ga}_{0.1}\text{Fe}_3\text{CoSb}_{12}$  and enhanced ZT slightly to  $\text{ZT} = 1.2$  at 700 K. Qin et al. [237] added graphene to the same compound by plasma-enhanced chemical vapor deposition but could raise ZT only to  $\text{ZT} = 1$  at 723 K. Wan et al. [183] added carbon fibers to  $\text{CeFe}_4\text{Sb}_{12}$  but the highest ZT was within the error bar—the same as without additive; however, for amounts > 1 vol.% ZT was even lower. Schmitz et al. [221] was more successful by adding multi-walled carbon nano tubes (MWCNTs) to  $\text{Ce}_{0.1}\text{La}_{0.08}\text{Co}_2\text{Fe}_2\text{Sb}_{12}$  and almost doubled ZT to  $\text{ZT} = 0.46$ ; however, it was measured only up to 450 K.

Whereas for the p-type filled skutterudites only some papers with additives are published, for the n-type a manifold is known (Table 3), namely, many oxides ( $\text{TiO}_2$ ,  $\text{Cu}_2\text{O}$ ,  $\text{ZnO}$ ,  $\text{MoO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ ), some transition metals and metals (Ni, Ag, Al), antimonides ( $\text{CoSb}_3$ ,  $\text{GaSb}$ ,  $\text{InSb}$ ), tellurides ( $\text{PbTe}$ ,  $\text{AgSbTe}_2$ ), a boride ( $\text{Ta}_{0.8}\text{Zr}_{0.2}\text{B}$ ), a carbide ( $\text{SiC}$ ), fullerene and MWCNTs.

The enhancements in ZT are mainly in the range of 10% to 50% but there are negative and positive exceptions.

For  $\text{PbTe}$  added to  $\text{In}_{0.2}\text{Co}_4\text{Sb}_{12}$ , ZT was lower. Addition of  $\text{ZnO}$  resulted in the same ZT as without an additive (Chubilleau et al. [143]). Lower ZTs also turned out for  $(\text{Mm}, \text{Sm})_y\text{Co}_4\text{Sb}_{12}$  plus  $\text{Al}_2\text{O}_3$  and  $\text{Cu}_2\text{O}$ , however, plus  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ , ZT was about the same as without any additive (Rogl et al. [220]).

Fu et al. could almost double the ZT of  $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$  by adding  $\text{AgSbTe}_2$  [129] or Ni core shells [165]. Battabyal et al. [159] dispersed  $\text{Cu}_2\text{O}$  in  $\text{Sn}_{0.4}\text{Ba}_{0.2}\text{Co}_4\text{Sb}_{12}$  and in  $\text{Ba}_{0.2}\text{Co}_4\text{Sb}_{12}$  and doubled and tripled ZT, respectively. Peng et al. [149] introduced  $\text{AgSbTe}_2$  into  $\text{Yb}_{0.2}\text{Co}_4\text{Sb}_{12}$  and gained a  $\text{ZT} = 0.51$  at 300 K (no measurements above 300 K were performed), which is more than six times higher than without  $\text{AgSbTe}_2$ . Elsheikh et al. [211] added Al to  $\text{Yb}_{0.25}\text{Co}_4\text{Sb}_{12}$ , but the Al atoms formed  $\text{AlSb}$  nano-inclusions at the grain boundaries instead of entering the voids, which, as they acted as a potential barrier, simultaneously reduced the resistivity and enhanced the Seebeck coefficient reaching  $\text{ZT} = 1.36$  at 850.

As summary one can conclude that in almost all cases, additions of any kind of nano particles enhance the thermoelectric performance of the respective skutterudite. Substitution on the Sb-site should be tried out for even more elements, as the benefit from one element to another presently ranges between 3% and 150%. The same statement applies for additives.

#### 4. Conclusions

The present review attempts to cover all thermoelectric research on filled skutterudites of the last 25 years, starting with one of the first high ZTs of Fleurial et al. for Ce-filled p-type skutterudites. In various plots the paper displays the dependency of ZTs, grouped for single-filled, double-filled and multi-filled compounds, as a function of time, temperature, composition, and substitution in the three sublattices. Particularly the dependencies of ZTs on the Seebeck coefficient, electrical resistivity and thermal conductivity may be of help in the understanding of the interrelations among these three key-parameters, and in due course, in designing efficient modules for thermoelectric generators suitable for a given thermal gradient. In addition, from all the evaluations in this review one can see that, generally, double- and multi-filled skutterudites, especially with the natural double-filler didymium, provide higher ZTs than single-filled ones. Especially in case of n-type skutterudites, multi-filling is important. Substituting Fe by Co (especially  $\text{Fe}_3\text{Co}$ ) in p-type skutterudites is a good strategy to enhance ZT. Additions, as well as substituting at the Sb-site, represent a further step towards an enhancement of ZT. Equally important is



the proper adjustment of the microstructure (grain size and dislocation density, defects, precipitates etc.) by employing the sustainable method of producing bulk skutterudites via severe plastic deformation techniques such as HPT.

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