## Supporting Information: Structure, Phase Composition, and Thermoelectric Properties of Yb<sub>x</sub>Co<sub>4</sub>Sb<sub>12</sub> and Their Dependence on Synthesis Method

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## Neutron powder diffraction

Neutron powder diffraction measurements were performed on the time-of-flight instrument POWGEN (SNS, Oak Ridge National Laboratory, Oak Ridge, TN, USA) using a 1Å wavelength band centered at  $\lambda = 1.066$  Å and on the powder diffractometer E9 (Helmholtz-Zentrum Berlin, Germany) using a monochromatic beam with a wavelength of  $\lambda = 1.798$  Å. The  $Yb_xCo_4Sb_{12}$  skutterudite powder was filled into vanadium cans with a diameter of 8 and 6 mm for the diffraction experiments on POWGEN and E9, respectively. The samples were loaded into standard cryostats for both experiments. The cryostat at POWGEN was equipped with an automatic sample changer. Data were taken on both instruments at temperatures of 10 K and 300 K. Additional measurements at T = 50 K, 100 K, 150 K, and 225 K have been performed on POWGEN. Samples with nominal Yb filling fractions  $x_{\text{nom}} = 0.15, 0.25, \text{ and } 0.35 \text{ (ampoule method) as well as } x_{\text{nom}} = 0.15 \text{ and } 0.35 \text{ (ball mill)}$ method) were studied on POWGEN and the data were analyzed with the Rietveld refinement software packages GSAS and EXPGUI,<sup>1,2</sup> which provide an optimized background model for POWGEN. Samples with  $x_{\text{nom}} = 0.45$  (ampoule method) as well as  $x_{\text{nom}} = 0.55$  and 0.75 (ball mill method) were investigated on E9 and the data were refined with the FullProf program suite.<sup>3</sup> For both analyses, the bound coherent neutron scattering lengths used were  $b_c(\text{Co}) = 2.49(2) \text{ fm}, b_c(\text{Sb}) = 5.57(3) \text{ fm}, \text{ and } b_c(\text{Yb}) = 12.43(3) \text{ fm}, \text{ as tabulated by Sears.}^4$ 

For the crystal structure refinement, the nominal Yb content on the 2a site was used as the starting value. The Co and Sb sites at 8c and 24g were assumed to be fully occupied. For the absorption correction of the data collected with a monochromatic incident wavelength on E9, the absorption coefficient  $\mu$  was calculated by using the neutron incoherent scattering absorption cross sections published by Sears<sup>4</sup> and kept as a fixed parameter for the refinement. For the refinement of the data obtained on POWGEN with time-of-flight powder diffraction covering a large wavelength band, the absorption coefficient was refined. Since POWGEN accesses much lower *d*-spacings due to its increased wavevector coverage as compared to E9, the isotropic atomic displacement parameters (ADP) can be determined with a higher accuracy from these data sets. The ADPs of two samples with the highest Yb content on the 2a site,  $x_{nom} = 0.25$  and 0.35 (ampoule route), were refined for data sets collected at 10 K, 50 K, 100 K, 150 K, 225 K and 300 K, constraining the absorption and the occupancy of Yb atoms on the 2a site to be identical for all temperatures. Further, the parameter correcting for a sample displacement relative to the ideal, centered sample position was constrained to be identical for the diffraction patterns of consecutive runs without sample change, for which the position of the automatic sample changer cell remained fixed. For data sets obtained after moving to another sample with the sample changer, the parameter was refined without constraint. From these analyses, the temperature-dependent isotropic ADPs shown in Fig. 2 (main text) were obtained.

For the following analysis, we focussed on the powder patterns obtained at 10 and 300 K. The patterns were individually refined by constraining the isotropic ADPs  $U_{iso}$  at the individual crystallographic sites as follows:  $2U_{iso}(\text{Co on } 8c) = 2U_{iso}(\text{Sb on } 24g) = U_{iso}(\text{Yb on } 2a)$ for the data at 10 K, and  $4U_{iso}(\text{Co on } 8c) = 4U_{iso}(\text{Sb on } 24g) = U_{iso}(\text{Yb on } 2a)$  for the data at 300 K. These constraints are in agreement with the refined ADPs of the time-of-flight data obtained at POWGEN for high Yb contents and allow for a consistent data treatment across both neutron instruments and respective data sets. The results of the refinements at 10 K are given in Tables S1 and S2. Based on these refinements, the  $R_{wp}$  values range from 0.0375 to 0.0590, while the  $\chi^2$  values range from 3.74 to 7.29 (POWGEN) and 1.25 to 1.60 (E9).

We find that the refinements, in particular those for the samples synthesized by the ball mill routine, can be improved by allowing for an additional, finite site-occupancy of Yb on the Co 8c site, assuming that the 8c site remains overall fully occupied (see Table S3). The  $R_{wp}$  and  $\chi^2$  values are seen to improve, especially for the case of  $x_{nom} = 0.75$ , for which  $R_{wp}$  reduces from 0.0420 to 0.0386, while  $\chi^2$  reduces from 1.62 to 1.37. Identical agreement factors were obtained in a refinement based on an alternative scenario in which Sb vacancies exist on the Sb 24g site, while the 8c site remains fully occupied by Co, and Yb only enters the 2a site. This scenario leads to smaller Yb occupancies on the 2a site and smaller fractions of secondary phases but to identical lattice parameters, ADPs and fractional coordinates of Sb. These two extreme cases allow to extract the range of site occupancies compatible with the diffraction data. Possible Yb occupancy on the 8c site with a simultaneous presence of Sb vacancies cannot be extracted from the data.

Distinct secondary phases are observed for the two different synthesis methods. The diffraction patterns of samples with  $x_{nom} \ge 0.25$  synthesized by the ampoule route show additional Bragg peaks attributed to secondary phases of YbSb<sub>2</sub> (orthorhombic) and CoSb<sub>2</sub> (monoclinic). The corresponding refined weight fractions are given in Tables S1-S3. For the sample  $x_{nom} = 0.25$ , which roughly corresponds to the theoretically proposed FFL, orthorhombic YbSb<sub>2</sub> (space group  $Cmcm^5$ ) is identified as secondary phase with a small weight fraction of 0.66(9) %. On increasing  $x_{nom}$ , an additional monoclinic CoSb<sub>2</sub> phase (space group P12<sub>1</sub>/c1<sup>6</sup>) is observed and the weight fractions of both secondary phases increase with increasing nominal Yb content.

The samples synthesized by the ball mill routine show a qualitatively different behavior. The diffraction patterns of samples with  $x_{nom} \ge 0.55$  show additional Bragg peaks associated with monoclinic CoSb<sub>2</sub> only. In fact, for a nominal Yb content of  $x_{nom} = 0.75$ , a secondary phase weight fraction of up to 22.4 % (depending on refinement scenario) is obtained. For the sample with  $x_{nom} = 0.55$ , weak additional reflections corresponding to cubic Yb<sub>2</sub>O<sub>3</sub> with a weight fraction of 0.45(5) wt% are observed. A YbSb<sub>2</sub> secondary phase was not observed in any of the samples synthesized by the ball mill route. This places the samples synthesized by the ball mill routine in the two-phase region of the Yb-Co-Sb phase diagram proposed by Tang *et al.*,<sup>7</sup> while samples synthesized by the melt-quench-anneal or ampoule method are located in the three-phase region of the same phase diagram. Both these regions reside in the Co-rich part of the phase diagram. This observation is somewhat surprising, since our sample synthesis is based on stoichiometric ratios of the starting elements Yb, Co and Sb.

The seconday phase  $\text{CoSb}_2$  was investigated in more detail.  $\text{CoSb}_2$  crystallizes in two different crystal structures, in a monoclinic structure with space group  $P12_1/c1$  and in an

orthorhombic structure with *Pnnm* space group.<sup>6,8</sup> Both structures can satisfactorily explain the additional reflections in the diffraction patterns. While the refined monoclinic angle is  $\beta = 118.100(12)^{\circ}$  and  $\beta = 118.383(5)^{\circ}$  for the samples  $x_{nom} = 0.55$  and  $x_{nom} = 0.75$ , respectively, which is slightly larger than the literature value of  $\beta_{lit.} = 117.65^{\circ}$ ,<sup>6</sup> we assume the monoclinic CoSb<sub>2</sub> crystal structure for the refinements because this corresponds to the low-temperature modification of CoSb<sub>2</sub> formed in the Co-Sb phase diagram,<sup>9</sup> appropriate for our synthesis conditions.

Representative Rietveld refinement results of the powder diffraction data obtained on POWGEN and E9 are shown in Fig. S1 and S2, respectively.



Figure S1: Time-of-flight neutron powder diffraction pattern for  $Yb_{0.25}Co_4Sb_{12}$  (ampoule) at T = 10 K. The diffraction pattern was analyzed with the Rietveld refinement software packages GSAS and EXPGUI.



Figure S2: Constant wavelength ( $\lambda = 1.798 \text{ Å}$ ) neutron powder diffraction pattern for Yb<sub>0.55</sub>Co<sub>4</sub>Sb<sub>12</sub> (ball mill) at T = 10 K. The diffraction pattern was analyzed with the Full-Prof program suite. For the refinement it was assumed that Yb atoms also occupy a fraction of the 8*c* site (Co site).

Table S1: Results of the Rietveld refinements of T = 10 K neutron powder diffraction data of the samples synthesized by the ampoule route. The agreement factors  $R_p$  and  $R_{wp}$  are not background-corrected. The values of  $R_F$  and  $R_{F^2}$  indicate the global *R*-factors. For the data analyzed by GSAS and EXGUI (POWGEN data)  $R_{F^2} = \sum |F_{obs}^2 - F_{cal}^2| / \sum F_{obs}^2$  is given while for the data analyzed with FullProf (E9 data)  $R_F = \sum |F_{obs} - F_{cal}| / \sum |F_{obs}|$  is given.

$x_{ m nom}$	0.15	0.25	0.35	0.45	
instrument	POWGEN	POWGEN	POWGEN	E9	
a (Å)	9.02880(2)	9.03463(2)	9.03883(3)	9.04604(7)	
$y(\mathrm{Sb})$	0.33532(5)	0.33539(6)	0.33527(7)	0.33621(18)	
$z(\mathrm{Sb})$	0.15821(5)	0.15836(5)	0.15844(7)	0.15851(18)	
$U_{iso}(\text{Co, Sb}) (\text{\AA}^2)$	0.00102(4)	0.00096(4)	0.00095(6)	0.0034(3)	
$U_{iso}(Yb)$ (Å <sup>2</sup> )	0.00204(9)	0.00193(9)	0.00189(12)	0.0067(6)	
occ(Yb-2a)	0.099(3)	0.159(3)	0.201(4)	0.290(6)	
$\operatorname{CoSb}_2(\operatorname{wt}\%)$	-	-	3.3(3)	5.7(3)	
$YbSb_2 (wt \%)$	-	0.66(9)	1.83(12)	2.61(10)	
$R_p$	0.1114	0.1010	0.1059	0.0319	
$R_{wp}$	0.0508	0.0462	0.0590	0.0408	
$R_F/R_{F^2}$	0.0503	0.0636	0.0552	0.0437	
$\chi^2$	5.85	5.41	7.29	1.50	

Table S2: Results of the Rietveld refinements of T = 10 K neutron powder diffraction data of the samples synthesized by the ball mill route where only the Yb occupancy of the 2asite was refined. The Co and Sb sites were constrained to be fully occupied by Co and Sb, respectively. The agreement factors are defined as in Table S1.

$\overline{x_{\text{nom}}}$	0.15	0.35	0.55	0.75	
instrument	POWGEN	POWGEN	E9	E9	
a (Å)	9.02293(8)	9.02589(3)	9.04984(7)	9.06361(8)	
$y(\mathrm{Sb})$	0.33527(5)	0.33530(6)	0.33621(19)	0.3363(2)	
$z(\mathrm{Sb})$	0.15814(5)	0.15825(5)	0.15904(19)	0.1598(3)	
$U_{iso}(\text{Co,Sb})$ (Å <sup>2</sup> )	0.00048(4)	0.00062(5)	0.0032(3)	0.0041(3)	
$U_{iso}(Yb)$ (Å <sup>2</sup> )	0.00098(9)	0.00124(10)	0.0063(6)	0.0081(7)	
occ(Yb-2a)	0.002(3)	0.050(3)	0.362(6)	0.493(8)	
$\operatorname{CoSb}_2(\operatorname{wt}\%)$	-	-	9.2(3)	22.4(4)	
$Yb_2O_3 (wt \%)$	-	-	0.55(5)	-	
$R_p$	0.0998	0.0958	0.0295	0.0329	
$R_{wp}$	0.0420	0.0409	0.0375	0.0420	
$R_F/R_{F^2}$	0.0354	0.0488	0.0399	0.05.45	
$\chi^2$	3.74	3.77	1.25	1.62	

Table S3: Results of the Rietveld refinements of T = 10 K neutron powder diffraction data of the samples synthesized by the ball mill route. The refined parameters are tabulated for the two different scenarios: an additional partial Yb occupation of the 8*c* site assuming a fully occupied 8*c* site (Yb-8*c* and Co-8*c*) wherein full occupancy of the 8*c* site is taken as 1 (not including the multiplicity of the site) and Sb vacancies of the Sb 24*g* site (Sb-vac.). The agreement factors are defined as in Table S1.

$x_{ m nom}$	0.15		0.35		0.55		0.75	
instrument	POWGEN		POWGEN		E9		${ m E9}$	
assumption	Yb-8c	Sb-vac.	Yb-8c	Sb-vac.	Yb-8c	Sb-vac.	Yb-8c	Sb-vac.
a (Å)	9.02295(8)		9.02590(3)		9.04984(7)		9.06360(8)	9.06359(8)
$y(\mathrm{Sb})$	0.33525(5)		0.33527(6)		0.33624(18)		0.3364(2)	
$z(\mathrm{Sb})$	0.15814(5)		0.15824(5)		0.15899(19)		0.1597(3)	
$U_{iso}(\text{Co,Sb})$ (Å <sup>2</sup> )	0.00050(4)		0.00064(5)		0.0034(3)		0.0045(3)	
$U_{iso}(Yb)$ (Å <sup>2</sup> )	0.00100(9)		0.00128(10)		0.0067(5)		0.0091(6)	0.0090(6)
occ(Yb-2a)	0.006(3)		0.057(3)	0.054(3)	0.384(7)	0.345(6)	0.548(9)	0.439(7)
occ(Yb-8c)	0.008(1)	-	0.011(1)	-	0.028(3)	-	0.063(4)	-
$\operatorname{occ}(\operatorname{Sb-24}g)$	-	0.971(5)	-	0.959(5)	-	0.900(10)	-	0.802(9)
$\operatorname{CoSb}_2(\operatorname{wt}\%)$	-	-	-	-	9.3(3)	8.3(3)	22.3(4)	18.4(4)
$Yb_2O_3 (wt\%)$	-	-	-	-	0.45(5)	0.40(4)	-	-
$R_p$	0.1002		0.0958		0.0289		0.0300	0.0301
$R_{wp}$	0.0418		0.0406		0.0366		0.0386	
$R_F/R_{F^2}$	0.0356		0.0482		0.0367	0.0366	0.0390	0.0388
$\chi^2$	3.70		3.71		1.19		1.37	

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