Electronic Supplementary Information for:

Low thermal conductivity and promising thermoelectric performance in A_xCoSb (A = V, Nb or Ta) half-Heuslers with inherent vacancies

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Table S1. Lattice parameters (*a*), fractional site occupancies (*Occ*), thermal displacement parameters (U_{iso} / Å^2), weight percentages (*wt%*) of the phases present, and fit statistics for selected A_xCoSb samples from Rietveld fits against neutron powder diffraction data.

	$V_{0.87}CoSb$	**$Nb_{0.83}CoSb$**	**$Ta_{0.81}CoSb$**
a (Å)	5.8058(1)	5.9022(1)	5.8910(1)
X Occ	V: 0.838(2) Co: 0.032(2)	Nb: 0.85(1)	Ta: 0.83(1)
U_{iso} (Å^2)	0.003(1)	0.0049(2)	0.0129(2)
Y Occ	Co: 0.968(2) V: 0.032(2)	Co: 1	Co: 1
U_{iso} (Å^2)	0.0084(3)	0.0120(3)	0.0125(2)
Z Occ	Sb: 1	Sb: 1	Sb: 1
U_{iso} (Å^2)	0.0107(1)	0.0123(3)	0.0041(1)
Main Phase (wt.%)	98.9(1)	94.2(1)	93.9(1)
Impurities (wt.%)			
V_2O_3	1.1(1)	-	-
Nb_3Sb	-	5.8(1)	-
$TaCo_2$	-	-	6.1(2)
Fit Statistics			
x^2	1.6	12.12	2.0
x^2 / x^2_{LeBail}	1.0	1.0	1.0
wR_p (%)			
Bank 4	2.8	4.0	1.9
Bank 5	3.6	4.8	2.3
R_p (%)			
Bank 4	4.4	4.5	2.9
Bank 5	5.2	6.2	3.8

Space group: $F\bar{4}3m$. X: (0,0,0) Y: (¼, ¼, ¼) Z: (½, ½, ½).

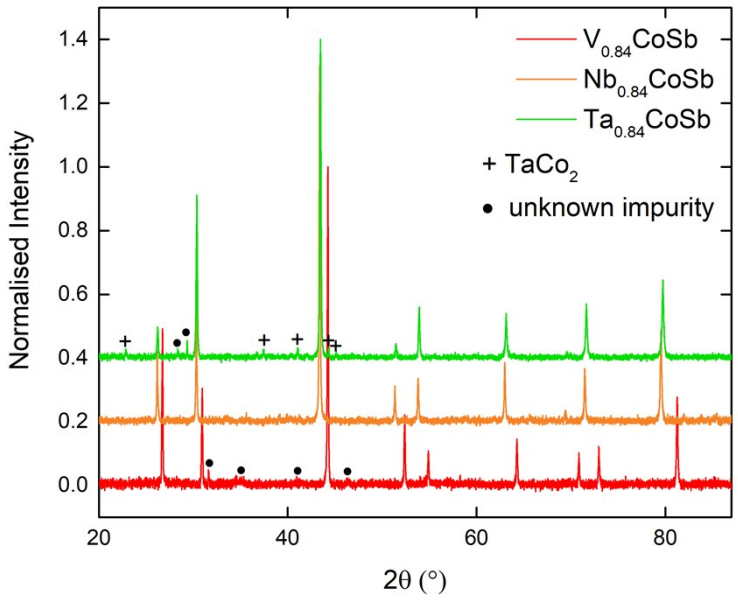

Figure S1. Laboratory X-ray powder diffraction data for the $A_{0.84}CoSb$ (A = V, Nb, Ta) trial series.

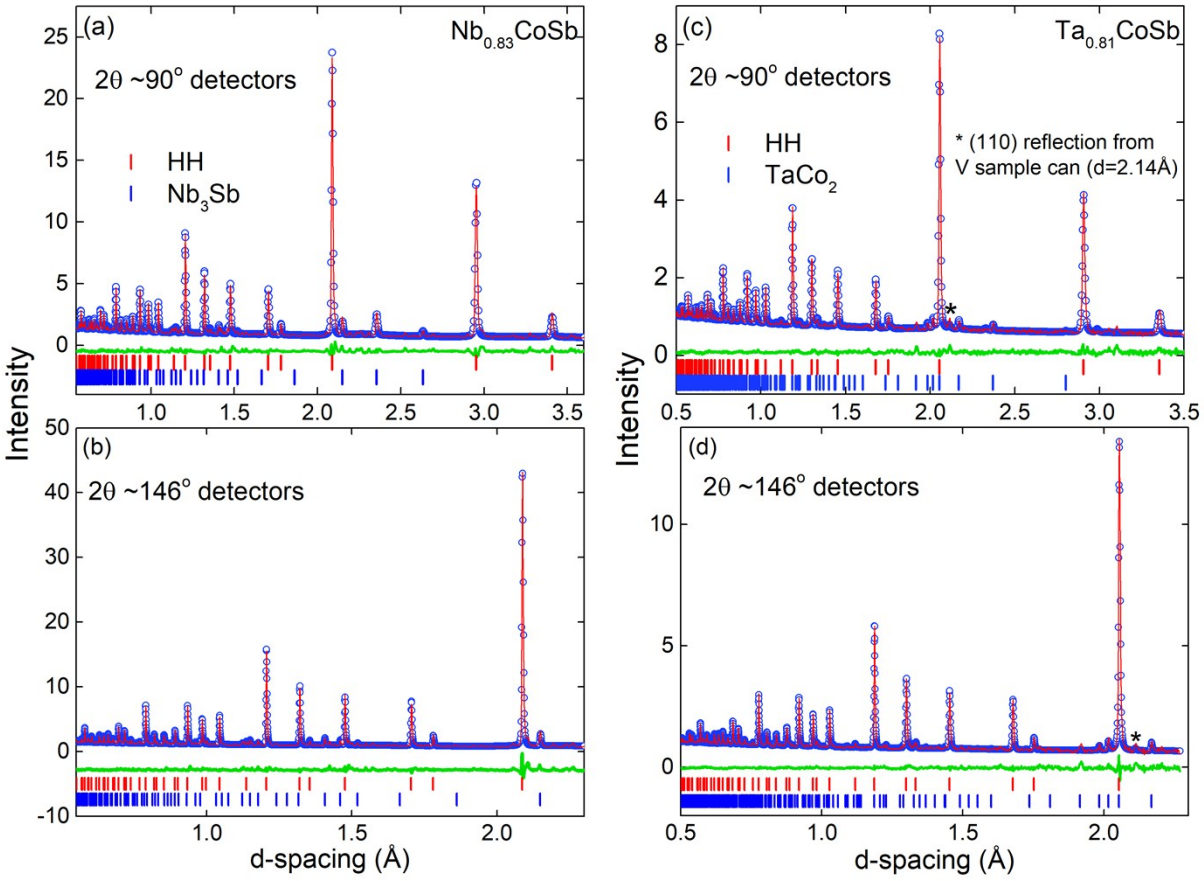

Figure S2. Fitted powder neutron diffraction profiles for **(a-b)** $Nb_{0.83}CoSb$ and **(c-d)** $Ta_{0.81}CoSb$. Blue circles are observed data, red lines are the calculated profiles, green lines are difference curves (obs-calc). Vertical lines indicate Bragg reflection positions (phases indicated in figures).

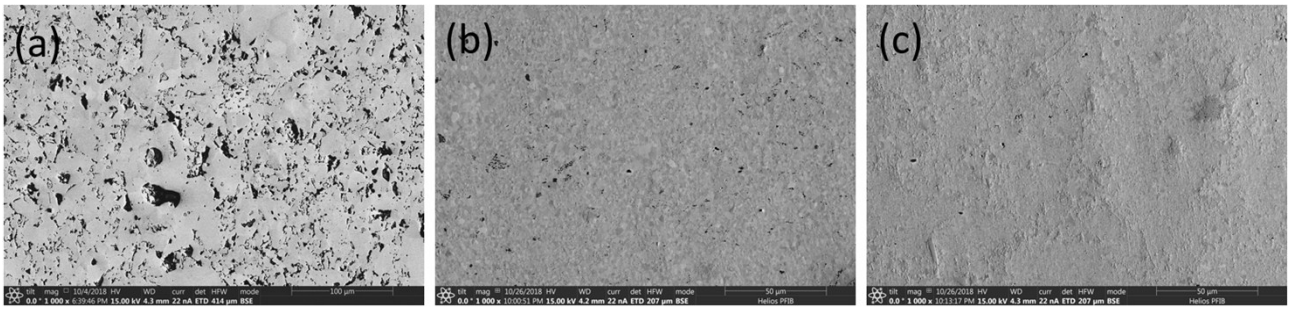

Figure S3. Large area backscattered electron images for polished internal surfaces of **(a)** $V_{0.87}CoSb$, **(b)** $Nb_{0.85}CoSb$ and **(c)** $Ta_{0.81}CoSb$ samples.

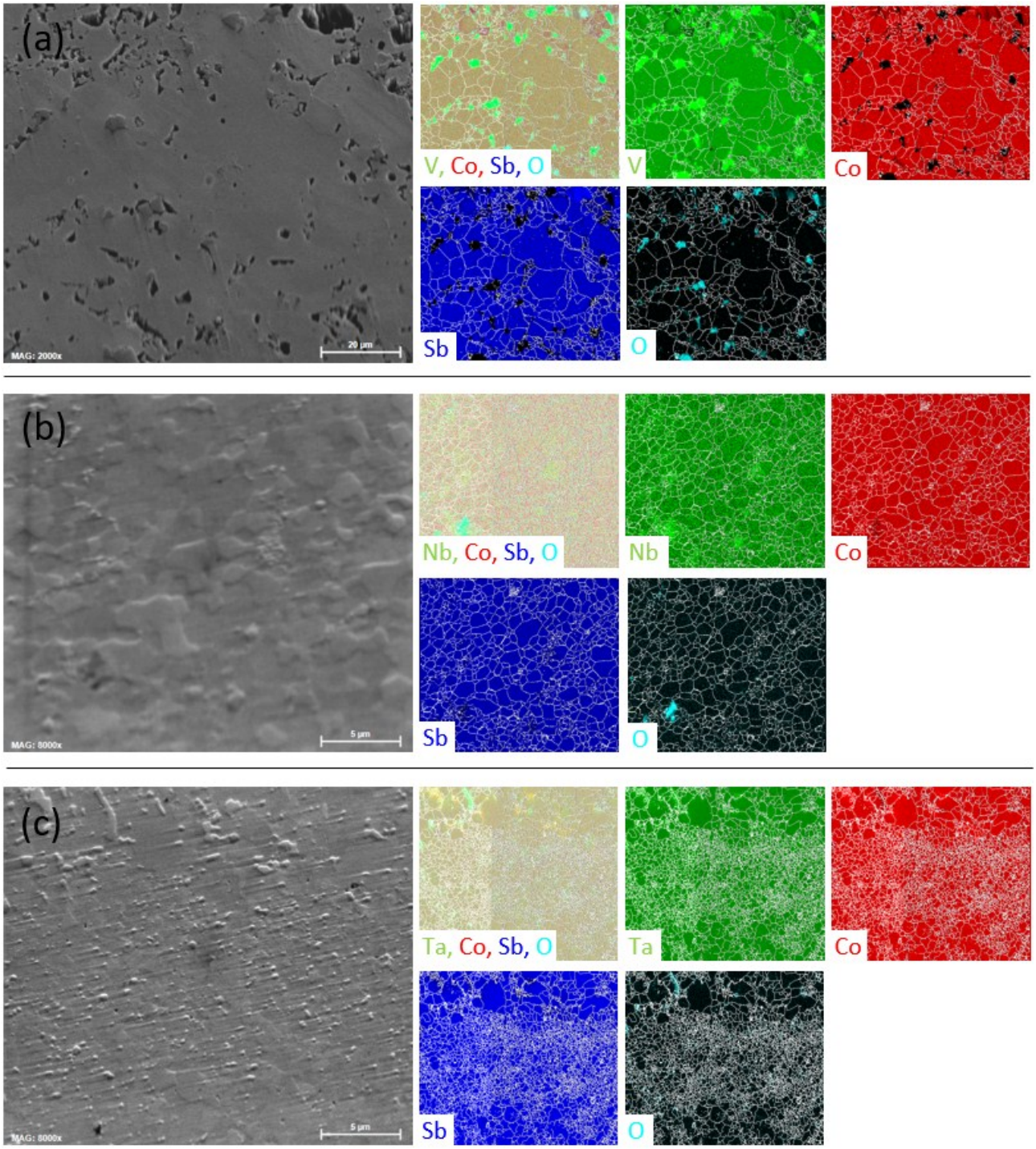

Figure S4. (Left) Back-scattered electron and (right) elemental maps derived from EDS and showing the distribution of main elements, and O, in **(a)** $V_{0.87}CoSb$, **(b)** $Nb_{0.85}CoSb$ and **(c)** $Ta_{0.81}CoSb$ samples. The areas correspond to the EBSD images shown in the main manuscript and each elemental map is over-layed with a grain boundary map derived from EBSD.

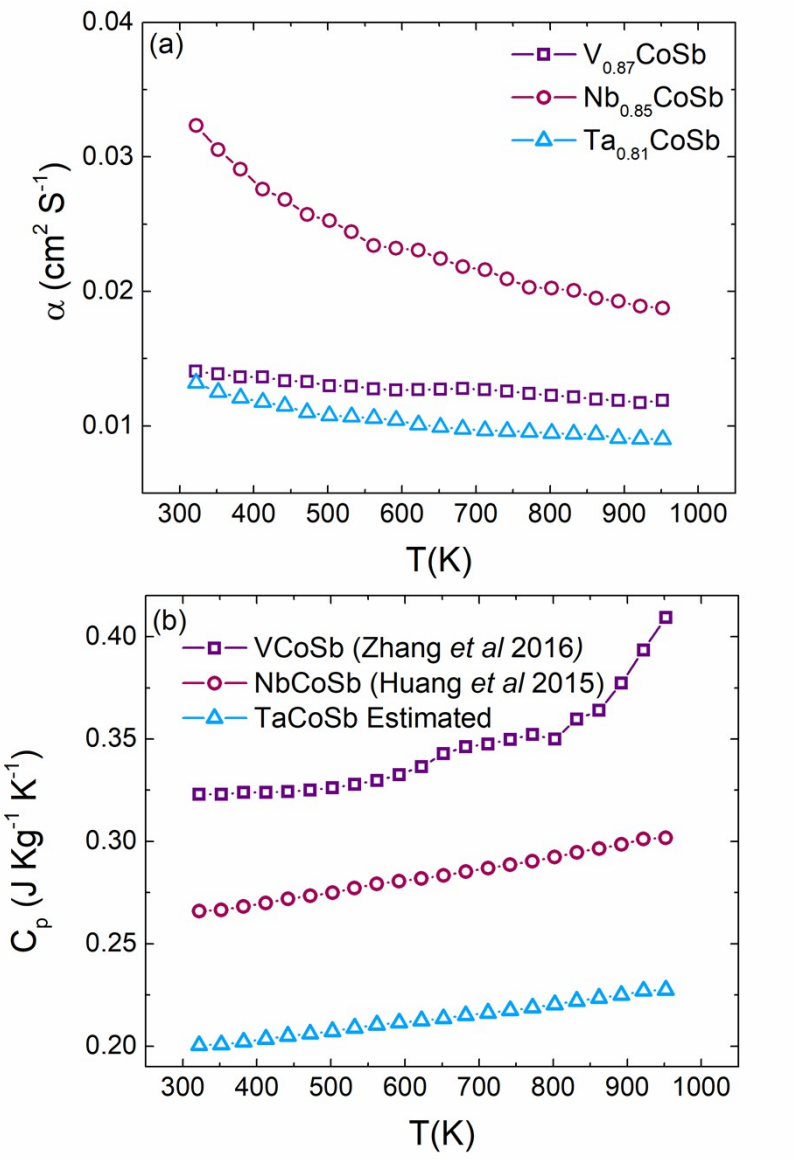

Figure S5. Temperature dependence of **(a)** thermal diffusivity (α) and **(b)** heat capacity (C_p) values for the A_xCoSb samples. C_p values for VCoSb and NbCoSb were taken from Zhang *et al*[1] and Huang *et al*.[2], respectively.

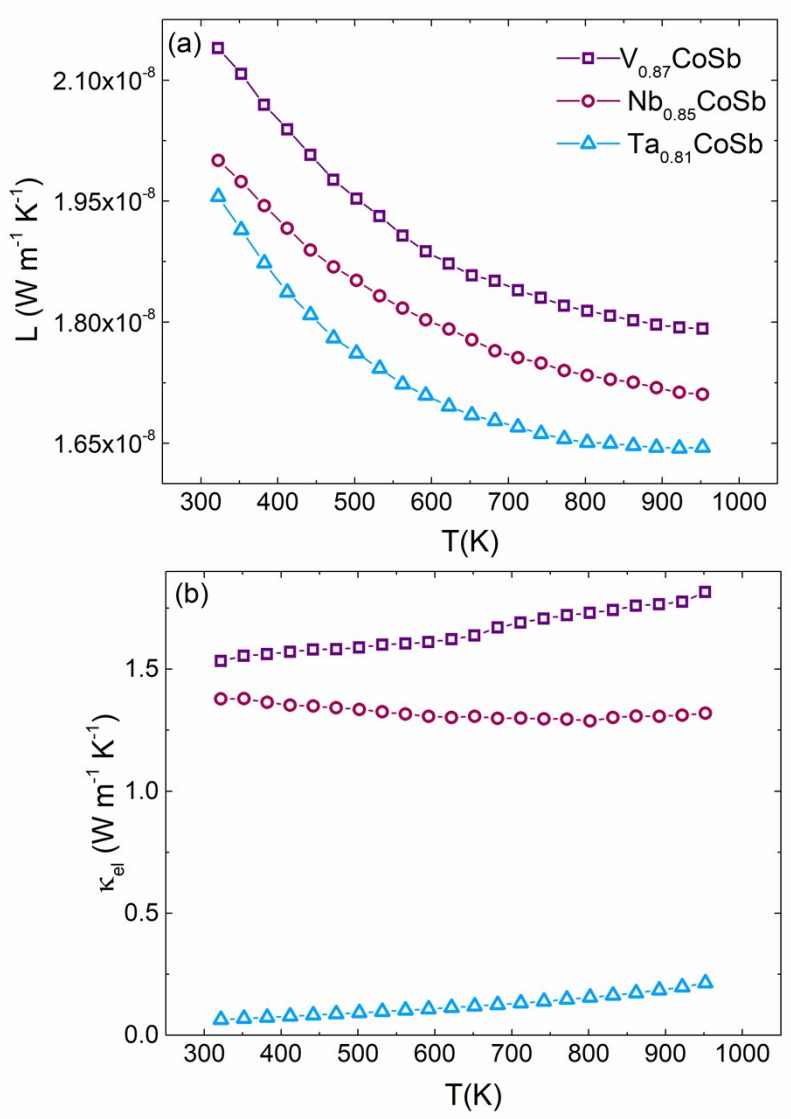

Figure S6. Temperature dependence of **(a)** the Lorenz number (L) and **(b)** the electronic thermal conductivity (κ_{el}) for the A_xCoSb samples.

References

1. H. Zhang, Y. Wang, L. Huang, S. Chen, H. Dahal, D. Wang and Z. Ren, *Journal of Alloys and Compounds*, 2016, **654**, 321-326.
2. L. H. Huang, R. He, S. Chen, H. Zhang, K. Dahal, H. Q. Zhou, H. Wang, Q. Y. Zhang and Z. F. Ren, *Materials Research Bulletin*, 2015, **70**, 773-778.