

# Journal of Materials Chemistry C

Materials for optical, magnetic and electronic devices

rsc.li/materials-c



ISSN 2050-7526



ROYAL SOCIETY  
OF CHEMISTRY

Celebrating  
IYPT 2019

## PAPER

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



Cite this: *J. Mater. Chem. C*, 2019, 7, 6539

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

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Half-Heuslers with vacancies that are stabilised by a semiconducting electron count offer new opportunities for discovering good thermoelectric performance. Here, we present a comparative study of  $A_xCoSb$  half-Heuslers ( $A = V$ , Nb or Ta) with intrinsic vacancies. Structural analysis reveals an increasing vacancy concentration from V (13%) to Nb (15%) to Ta (19%) with evidence for  $\sim 3\%$  V/Co inversion. This decrease in ability to n-type dope these materials is caused by an increase in conduction band dispersion, evident from a decreasing density of states mass from Hall data, leading to a higher cost of populating these antibonding states.  $V_{0.87}CoSb$  has an ultralow lattice thermal conductivity,  $\kappa_{lat} \sim 2.2 \text{ W m}^{-1} \text{ K}^{-1}$ , which cannot be explained within the Callaway framework. Coupled to a promising power factor,  $S^2/\rho = 2.25 \text{ mW m}^{-1} \text{ K}^{-2}$ , this results in  $ZT = 0.6$  at 950 K.  $Nb_{0.85}CoSb$  has a power factor of  $S^2/\rho = 2.75 \text{ mW m}^{-1} \text{ K}^{-2}$  with  $\kappa \sim 4.75 \text{ W m}^{-1} \text{ K}^{-1}$ , yielding a similar  $ZT = 0.5$  at 950 K.  $Ta_{0.81}CoSb$  has a microstructure consisting of smaller grains than the other samples, impacting both the carrier and thermal transport, yielding a power factor  $S^2/\rho = 0.75 \text{ mW m}^{-1} \text{ K}^{-2}$  and  $ZT = 0.3$  at 950 K. The ultralow  $\kappa_{lat}$  for  $V_{0.87}CoSb$  may be linked to porosity effects that do not strongly impact on the charge transport, thus affording a new route towards improved performance.

Received 8th February 2019,  
Accepted 8th March 2019

DOI: 10.1039/c9tc00743a

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## Introduction

Thermoelectric waste heat recovery is one of a range of renewable energy strategies that are currently being developed to reduce reliance on fossil fuels and to mitigate climate change.<sup>1,2</sup> Half-Heuslers (HHs) are leading candidates for commercialisation due to their unique combination of good thermoelectric performance, abundance of constituent elements, good mechanical properties and thermal stability.<sup>3–5</sup> HHs are ternary XYZ compounds typically comprising two transition metals (X and Y) and a main

group element (Z) that crystallise in the cubic space group  $F\bar{4}3m$  with the electropositive X metals occupying octahedral sites and the Y metals occupying half the tetrahedral sites in a face centred cubic Z lattice.<sup>6</sup> Recently, HH compositions with a nominal 19 valence electron count (VEC), including  $VCoSb$  and  $NbCoSb$ ,<sup>7,8</sup> have attracted attention due to their apparent violation of the long-established 18-electron requirement for semiconducting properties.<sup>6</sup> This was resolved through studies of  $NbCoSb$  that demonstrated the formation of Nb vacancies, leading to  $Nb_xCoSb$  ( $x \sim 0.85$ ) compositions with  $VEC \sim 18.25$ .<sup>9–11</sup> Varying the nominal Nb content between  $x = 0.8$  ( $VEC = 18$ ) and  $x = 1$  ( $VEC = 19$ ) affords a systematic change in carrier concentration ( $n_H$ ) and a means of optimising the thermoelectric power factor,  $S^2/\rho$ , where  $S$  is the Seebeck coefficient and  $\rho$  is the electrical resistivity.<sup>11</sup> The optimised power factor of  $S^2/\rho = 2.4 \text{ mW m}^{-1} \text{ K}^{-2}$  and low thermal conductivity ( $\kappa$ ) resulted in a highly promising thermoelectric figure of merit,  $ZT = (S^2/\rho\kappa)T = 0.9$  at 1123 K, demonstrating that vacancies are a new, useful route to tune the individual thermoelectric parameters and achieve good performance. Here,  $\kappa$  is the sum of  $\kappa_{lat}$  and an electronic component ( $\kappa_{el}$ ) and  $T$  is the absolute temperature. Up to this point optimisation of HHs has been achieved chiefly via doping and alloying,<sup>12–14</sup>

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† Electronic supplementary information (ESI) available: Structural parameters and fit statistics from Rietveld analysis of polaris neutron powder diffraction data; XRD data for the preliminary series of samples, Rietveld fits to polaris NPD data for the  $A_xCoSb$  ( $A = Nb$ , Ta) samples; complementary larger area SEM images and EDX elemental maps; temperature dependence of the thermal diffusivity, heat capacity, Lorenz number and electronic thermal conductivity. See DOI: 10.1039/c9tc00743a



use of interstitial metals<sup>15</sup> or nanostructuring.<sup>16–19</sup> The vacancy approach is therefore a new route in the portfolio that is not well explored.

We have investigated the concentration of X-site vacancies and thermoelectric properties of the  $A_xCoSb$  ( $A = V, Nb$  and  $Ta$ ) compositions allowing for the impact of the  $A$  metal to be assessed. A recent study has investigated the structural stability of a range of vacancy HHs.<sup>20</sup> This revealed an increasing cost for filling the X-site from  $V$  to  $Nb$  to  $Ta$ . We confirm the existence of preferred  $x$  compositions for the  $V$  and  $Nb$  compositions and show that  $A = Ta$  fits with the proposed trend.<sup>20</sup> The thermoelectric properties of stoichiometric  $VCoSb$  have been reported (ref. 8) but the properties of the  $A_xCoSb$  ( $A = V, Ta$ ) compositions with targeted vacancies remain unexplored.

## Experimental

### Synthesis

A preliminary series of polycrystalline  $A_{0.84}CoSb$  ( $A = V, Nb$  and  $Ta$ ) samples was prepared on a 1 gram scale from powdered elements purchased from Alfa Aesar;  $V$ : 325-mesh, 99.5% purity;  $Nb$ : 325-mesh, 99.8%;  $Ta$ : 325-mesh, 99.9%;  $Co$ : 1.6  $\mu m$ , 99.8% and  $Sb$ : 1–5 mm shots, 99.99%. This was followed by a 5 gram scale-up of the optimised compositions (see below) to produce  $V_{0.87}CoSb$ ,  $Nb_{0.85}CoSb$  and  $Ta_{0.81}CoSb$ . The initial choice for the  $A_{0.84}CoSb$  compositions was based on a survey of the literature for  $A = Nb$ , where  $0.83 \leq x \leq 0.85$  based on diffraction results.<sup>9,10</sup> In all reactions, stoichiometric amounts of elemental precursors were mixed using an agate pestle and mortar and cold-pressed into 13 mm diameter pellets using a 10 tonne press. Samples were wrapped in  $Nb$  ( $V, Nb$  samples) or  $Ta$  ( $Ta$  samples) foil and sintered in vacuum sealed quartz tubes for 24 hours at 1073 K, then cooled at 20 K min<sup>-1</sup>. The samples were then re-ground, re-sealed and subjected to a further 7 days of sintering at 1123 K before being air-quenched. As a final step, the samples were powdered using mortar and pestle then hot-pressed into two 13 mm disks under an argon atmosphere at 1273 K ( $Nb$  and  $Ta$  samples) or 1123 K ( $V$  sample) and 80 MPa for 30 minutes.

### Characterisation

Laboratory X-ray powder diffraction (XRD) data was collected using a D8 Bruker Advance diffractometer with monochromated

$Cu K\alpha_1$  radiation. High-quality datasets suitable for Rietveld analysis were collected in the  $5^\circ \leq 2\theta \leq 100^\circ$  range over seven hours. Time-of-flight neutron powder diffraction (NPD) patterns were collected on the POLARIS instrument at the ISIS neutron and muon source, Rutherford Appleton Laboratory, UK. Data were collected at room temperature for between 200 and 300  $\mu A$  proton beam current to the ISIS target, with 1–2 g of powdered sample loaded into cylindrical vanadium cans. This corresponds to an exposure of approximately 1.5–2 hours for each sample. Note that a different  $A = Nb$  sample was used for the NPD and Hall study, with nominal  $Nb_{0.83}CoSb$  composition. This was due to the timings of these experiments, which were not done in-house. All other data in this manuscript were collected on the  $A_xCoSb$  samples with optimised compositions. Rietveld analysis of both XRD and NPD datasets were done using the GSAS and EXPGUI software programs.<sup>21,22</sup>

### Microscopy

Scanning electron microscopy (SEM) employing both secondary electron (SE) and backscattered electron (BSE) imaging was performed on samples that were first cut from a hot-pressed disk with a low speed diamond saw to expose an internal face, then mechanically polished (SiC paper followed by alumina, colloidal silica and diamond paste to achieve a flat surface finish). A Thermo Fischer Helios Dualbeam instrument equipped with a Bruker XFlash 100 mm<sup>2</sup> detector was used for energy dispersive X-ray spectroscopy (EDS) analysis of composition and a Bruker eFlash FS Electron back-scattered diffraction (EBSD) detector was used for assessment of crystallography and granularity. EDS analysis was performed using Bruker's Esprit 2.1 software package and a standard-less quantification method to derive compositions that are accurate to 2–3 atomic percent. EBSD images were processed using ATOM,<sup>23</sup> whereby EBSD patterns were fitted to HH structures and pixels were false-coloured to indicate the crystallographic orientation, producing vivid mosaic-like images that clearly discriminate grains and which were then used to assess grain size distributions.

### Thermoelectric property measurements

The Seebeck coefficient ( $S$ ) and electrical resistivity ( $\rho$ ) were measured on rectangular bars cut from the hot-pressed disks using a Linseis LSR 3 instrument between 320–970 K. Thermal diffusivities ( $\alpha$ ) were measured on whole hot-pressed disks ( $\sim 2$  mm thickness) using a Linseis LFA 1000 Laser Flash

**Table 1** Half-Heusler lattice parameters ( $a$ ) from X-ray powder diffraction, gravimetric densities ( $d$ ), percentage densities ( $d\%$ ), chemical compositions from EDX elemental mapping and from Rietveld analysis of X-ray and neutron powder diffraction data for the  $A_xCoSb$  ( $A = V, Nb, Ta$ ) samples investigated in this study

Sample	$x$	$a$ (Å)	$d$ (g cm <sup>-3</sup> )	$d\%$	EDX composition	Rietveld composition
$V_xCoSb$	0.84	5.8039(1)	7.2	95	0.87(1):0.99(1):1.00	$V_{0.87(1)}CoSb$ [ $V_{0.838(2)}Co_{0.032(2)}$ ][ $Co_{0.968(2)}V_{0.032(2)}$ ]Sb <sup>a</sup>
	0.87	5.8058(1)				
$Nb_xCoSb$	0.84	5.9024(1)	8.4	100	0.86(1):0.99(1):1.00	$Nb_{0.85(1)}CoSb$ $Nb_{0.85(1)}CoSb$
	0.85	5.9023(1)				
$Ta_xCoSb$	0.84	5.8888(1)	10.7	100	0.89(2):1.02(1):1.00	$Ta_{0.81(1)}CoSb$ $Ta_{0.81(1)}CoSb$
	0.81	5.8910(1)				

<sup>a</sup> Compositions from Rietveld analysis of neutron powder diffraction data.



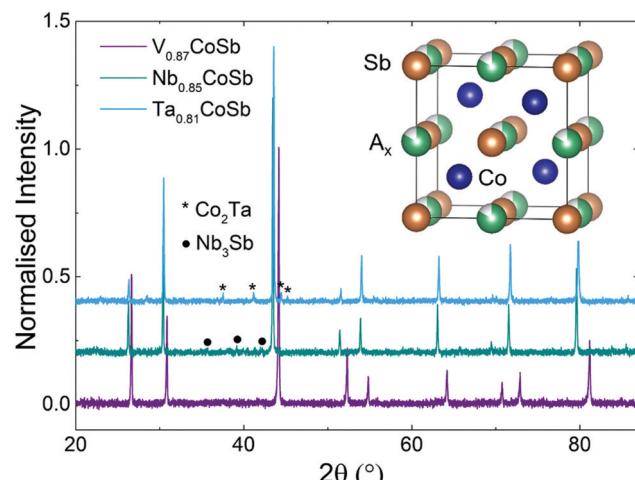


Fig. 1 Laboratory X-ray powder diffraction patterns for  $V_{0.87}\text{CoSb}$ ,  $\text{Nb}_{0.85}\text{CoSb}$  and  $\text{Ta}_{0.81}\text{CoSb}$ , showing the presence of a major half-Heusler (HH) phase and small  $\text{Nb}_3\text{Sb}$  and  $\text{Co}_2\text{Ta}$  impurity phases. The inset shows a schematic of a HH structure with X-site vacancies.

instrument. The samples were coated with graphite spray to avoid emissivity errors. The densities ( $d$ ) of the samples were calculated from the dimensions and mass of the pellets and are given in Table 1. The thermal conductivity  $\kappa = \alpha C_p d$  was calculated using experimental  $\alpha$  and  $d$  values, with heat capacity ( $C_p$ ) values taken from the literature.<sup>8,24</sup> A porosity correction,  $\kappa_m/\kappa = (1 - \phi)/(1 + \phi/2)$ , where  $\kappa_m$  is the uncorrected measured value and  $\phi$  is the porosity taken from the percentage density, was applied for the V sample. Hall measurements were undertaken on  $5 \times 5 \text{ mm}^2$  square slices in applied fields of  $\pm 1 \text{ T}$  using an AC Field Hall system from SemiMetrics, Ltd. Silver paint was used to achieve good electrical contacts on the corners of the samples.

## Results

### XRD

A preliminary series of  $A_{0.84}\text{CoSb}$  ( $A = \text{V}, \text{Nb}, \text{Ta}$ ) samples was prepared to check for phase purity and analysis of the crystallographic site occupancies of the HH phase through Rietveld fitting. The XRD patterns for these samples are shown in Fig. S1 in the ESI.† Rietveld analysis of the X-site occupancy suggested a systematic decrease from 0.87(1) for  $A = \text{V}$  to 0.85(1) for  $A = \text{Nb}$  and 0.81(1) for  $A = \text{Ta}$ . In response to these initial results, synthesis of  $V_{0.87}\text{CoSb}$ ,  $\text{Nb}_{0.85}\text{CoSb}$  and  $\text{Ta}_{0.81}\text{CoSb}$  was undertaken on a 5 gram scale so that full structural and thermoelectric characterisation could be undertaken. Rietveld analysis of XRD data collected from these samples (the patterns are shown in Fig. 1) confirmed the targeted X-site occupancies. The V and Nb samples have good purity from XRD with only a small  $\text{Nb}_3\text{Sb}$  phase (<1 wt%) observed. The lattice parameter for the  $\text{Nb}_{0.85}\text{CoSb}$  sample ( $a = 5.902 \text{ \AA}$ ) is in good agreement with the near-constant values reported for  $\text{Nb}_x\text{CoSb}$  ( $a = 5.903 \text{ \AA}$ ;  $0 \leq x \leq 0.2$ ).<sup>11</sup> The Ta sample contains a 5.3(1) wt%  $\text{Co}_2\text{Ta}$  intermetallic impurity.

### NPD

Neutron diffraction is highly complementary to XRD as it offers good scattering contrast between first row transition metals, which is important as V/Co inversion has been suggested to occur.<sup>8</sup> The full results of the Rietveld fits are summarised in Table S1 (ESI†) with the experimental HH compositions given in Table 1. The final fits are shown in Fig. 2 (V sample) and Fig. S2 in the ESI† (Nb and Ta samples). The main result is that the  $V_{0.87}\text{CoSb}$  sample does indeed have a degree of V/Co inversion with an experimental composition of  $[\text{V}_{0.839(2)}\text{Co}_{0.032(2)}][\text{Co}_{0.968(2)}\text{V}_{0.032(2)}]\text{Sb}$ . Free refinement of the X-site occupancy yielded an unrealistic composition of  $V_{0.58(1)}\text{CoSb}$ , which corresponds to a 17-electron HH. HHs with this valence electron count are predicted to be metallic,<sup>6,25</sup> which is not in keeping with the observed semiconducting behaviour. We note that this result is robust against variations in atomic displacement parameter (ADP). For example, fixing the X-site site occupancy at 0.87 leads to ADP values for that

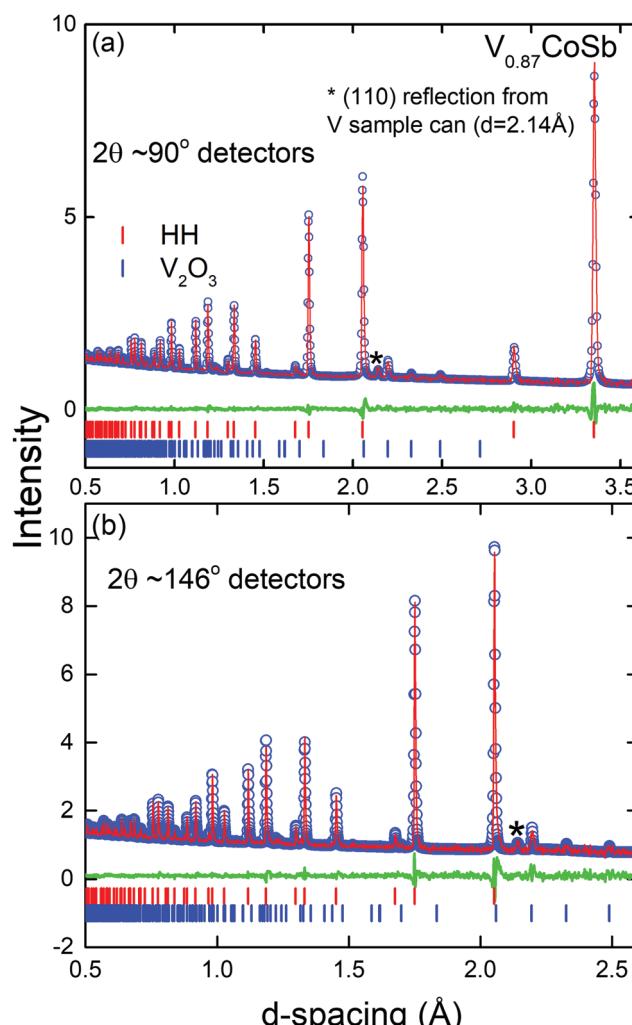


Fig. 2 Fitted Polaris neutron powder diffraction profiles for  $V_{0.87}\text{CoSb}$  (a)  $2\theta \sim 90^\circ$  detectors and (b)  $2\theta \sim 146^\circ$  detectors. Blue circles are observed data, red lines are the calculated profile, green lines are the difference profiles (obs-calc). Vertical lines indicate Bragg reflection positions.

site that are unphysically large with respect to those of the other sites. The best way to reconcile the XRD and NPD fits is to assume that the overall  $V_{0.87}\text{CoSb}$  composition from XRD is maintained and allow for V/Co inversion over the X and Y sites. This yields near identical goodness of fit statistics (see Table S1, ESI<sup>†</sup>) and indicates the presence of  $\sim 3\%$  V/Co inversion. Analysis of the site occupancies for the Nb and Ta samples confirms the XRD results with refined compositions of  $\text{Nb}_{0.85(1)}\text{CoSb}$  and  $\text{Ta}_{0.83(1)}\text{CoSb}$  that are within 1–2 estimated standard deviations of the starting values. The indexed impurity phases include a small  $\text{V}_2\text{O}_3$  phase (1.1(1) wt%) that had not been noted by XRD and the  $\text{Nb}_3\text{Sb}$  and  $\text{Co}_2\text{Ta}$  phases that were already observed in XRD. The final fits for all samples were compared against a model-less LeBail fit and found to be close to the best possible value for all compositions (Table S1, ESI<sup>†</sup>).

### Scanning electron microscopy

SEM imaging, EBSD and EDX mapping were used to investigate the microstructure and compositions of all three  $\text{A}_x\text{CoSb}$  compositions. Large area ( $> 200 \times 200 \mu\text{m}^2$ ) SEM images are shown in Fig. S3 (ESI<sup>†</sup>); higher magnification images and EBSD data are presented in Fig. 3 with the EDX maps for these areas given in Fig. S4 (ESI<sup>†</sup>). Several striking trends are discernible in the SEM and EBSD data. First, the  $V_{0.87}\text{CoSb}$  sample has notable micron-scale porosity, despite having a gravimetric density of 95%. The Nb and Ta samples by contrast appear fully dense, in keeping with the 100% gravimetric densities (Table 1). Secondly, the EBSD data show a gradual decrease of the average grain size diameter from  $\sim 3.2 \mu\text{m}$  (V) to  $\sim 0.80 \mu\text{m}$  (Nb) and  $\sim 0.43 \mu\text{m}$  (Ta). This trend is in keeping with the increasing refractory nature of the A-elements. The EDS mapping reveals that all

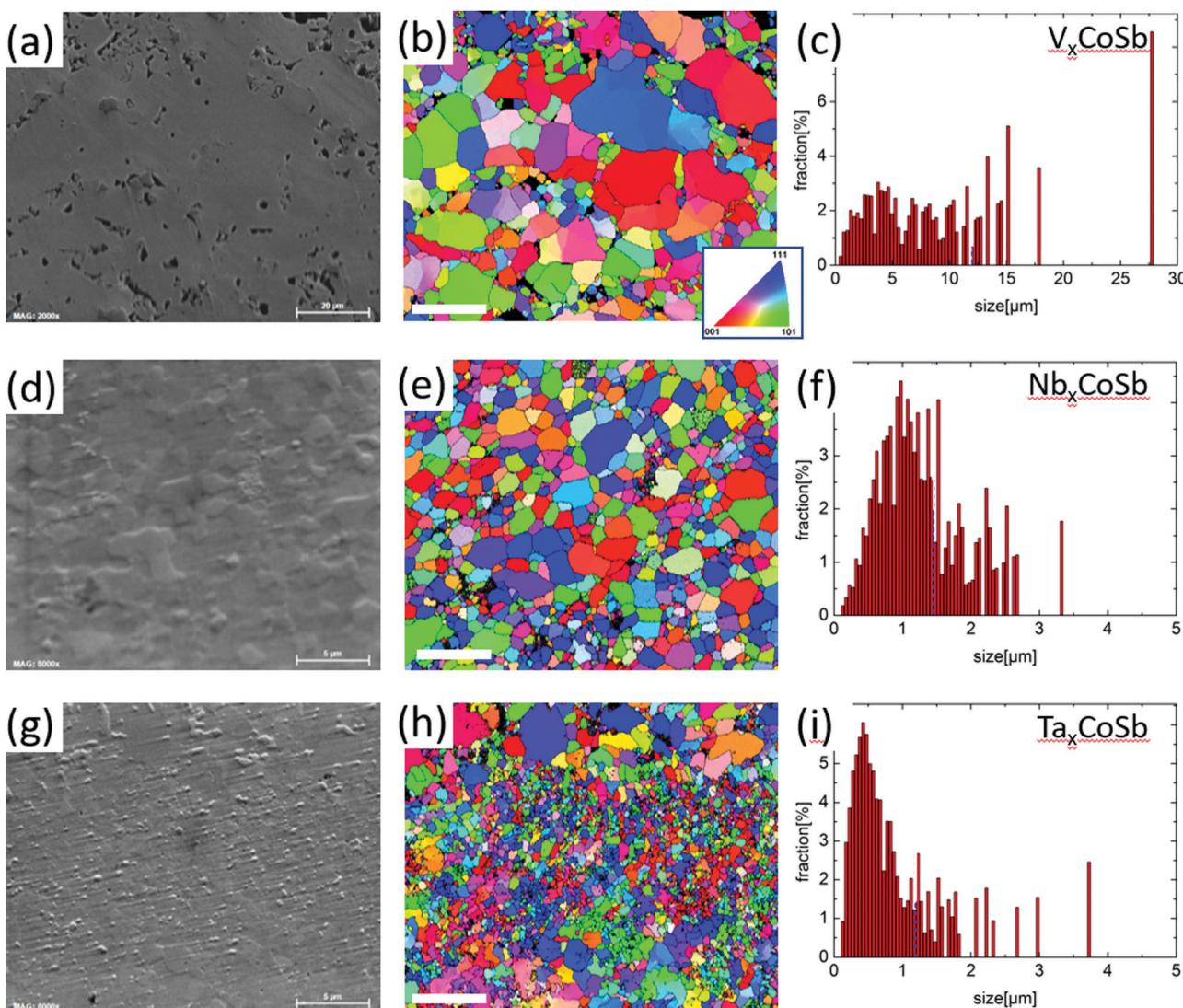


Fig. 3 (Left) Scanning electron microscopy, (middle) false-coloured electron backscatter diffraction (EBSD) images and (right) measured grain size distributions of (a–c)  $V_{0.87}\text{CoSb}$ , (d–f)  $\text{Nb}_{0.85}\text{CoSb}$  and (g–i)  $\text{Ta}_{0.81}\text{CoSb}$ , illustrating the internal structure and granularity. The scale-bars in the SEM images are the same as those in the EBSD and are, respectively,  $20 \mu\text{m}$ ,  $5 \mu\text{m}$  and  $5 \mu\text{m}$  in length. Colours in the EBSD images relate to the orientation of crystallographic grains, as indicated in the key in panel (b); the random distribution of orientations enables rapid discrimination of grain sizes. A mean diameter was calculated for each grain picked out by black lines in the EBSD and used to construct the distributions in panels (c, f and i).



$A_xCoSb$  samples are largely phase pure HHs with no obvious variation in composition. The elemental maps for  $V_{0.87}CoSb$  indicate fractionally more oxide formation than for the other two samples. The obtained HH compositions, averaged across all HH grains measured in the samples, are given in Table 1.

### Electrical properties

All samples exhibit negative  $S(T)$  values, indicating n-type conduction (Fig. 4a). There is a clear increase in  $S(T)$  as the A site element becomes heavier; in addition, the Ta sample has a much steeper increase. The V and Nb samples have a similar metal-like  $\rho(T)$  that increases across the temperature range whilst the Ta sample, by contrast, is much less conductive and has a gradually decreasing convex temperature dependence. This non-standard temperature dependence is not typical of either degenerate or non-degenerately doped semiconductors and is likely linked to its microstructure, consisting of many nanoscale grains. The highest power factor,  $S^2/\rho = 2.7 \text{ mW m}^{-1} \text{ K}^{-2}$ , is observed for the  $Nb_{0.85}CoSb$  composition, while  $V_{0.87}CoSb$  has  $S^2/\rho = 2.2 \text{ mW m}^{-1} \text{ K}^{-2}$  (Fig. 4c). Both compositions are characterised by a  $S^2/\rho$  plateau above  $\sim 800 \text{ K}$  (V) and  $\sim 700 \text{ K}$  (Nb), reflecting the saturation of  $S$  and increasing  $\rho$ . Increasing the temperature above  $950 \text{ K}$  is expected to lead to a reduction in  $S^2/\rho$ . The Ta sample with its high  $\rho$  values has a  $S^2/\rho$  that increases linearly from  $\sim 0.1 \text{ mW m}^{-1} \text{ K}^{-2}$  at  $323 \text{ K}$  to a maximum  $\sim 0.7 \text{ mW m}^{-1} \text{ K}^{-2}$  at  $950 \text{ K}$ . However, it is worth emphasising that this might not reflect its intrinsic behaviour but instead be a result of microstructure effects.

Hall measurements were undertaken to gain further insight in the electrical properties of these materials. The  $n_H$ , Hall mobilities ( $\mu_H$ ) and  $S$  and  $\rho$  for these samples are summarised in Table 2. Significantly,  $n_H$  has a linear dependence on the nominal free electron count (VEC-18) from the Rietveld compositions (see inset to Fig. 4b), confirming the validity of our structural analysis, and the tendency for a reduced occupation of the X-site from V to Nb to Ta.<sup>20</sup> To gain insight into possible changes in the electronic structure of these materials, Single Parabolic Band analysis was undertaken, following approaches outlined in the literature (e.g. ref. 26). This led to a significant result, namely the gradual decrease of the electronic density of states band masses from  $m^* = 12.8m_e$  (V), to  $m^* = 9.6m_e$  (Nb) and  $m^* = 5.9m_e$  (Ta), demonstrating that the A-metal impacts on the electronic bandstructure. The value for the Nb sample is in good agreement with  $m^* = 8\text{--}10m_e$  from the literature.<sup>11,27</sup> The decrease of  $m^* = N_v^{2/3}m_b$  signals either a decrease in valley degeneracy ( $N_v$ ) or increasingly dispersive electronic bands (reduced  $m_b$ ) for the pockets that contribute the electrical transport. The more diffuse 4d and 5d orbitals for the heavier A elements are known to afford better orbital overlap and increased bandwidths, which is in keeping with the observed trend. The carrier mobility for the Nb sample is largest at  $\mu_H = 4.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is comparable to the highest literature values.<sup>11,27</sup> The mobility is lower for the V sample with  $\mu_H = 1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is partially due to its higher  $m^*$  and  $n_H$  but is also likely to be linked to the observed porosity. The magnitude is in keeping with reported data for nominally

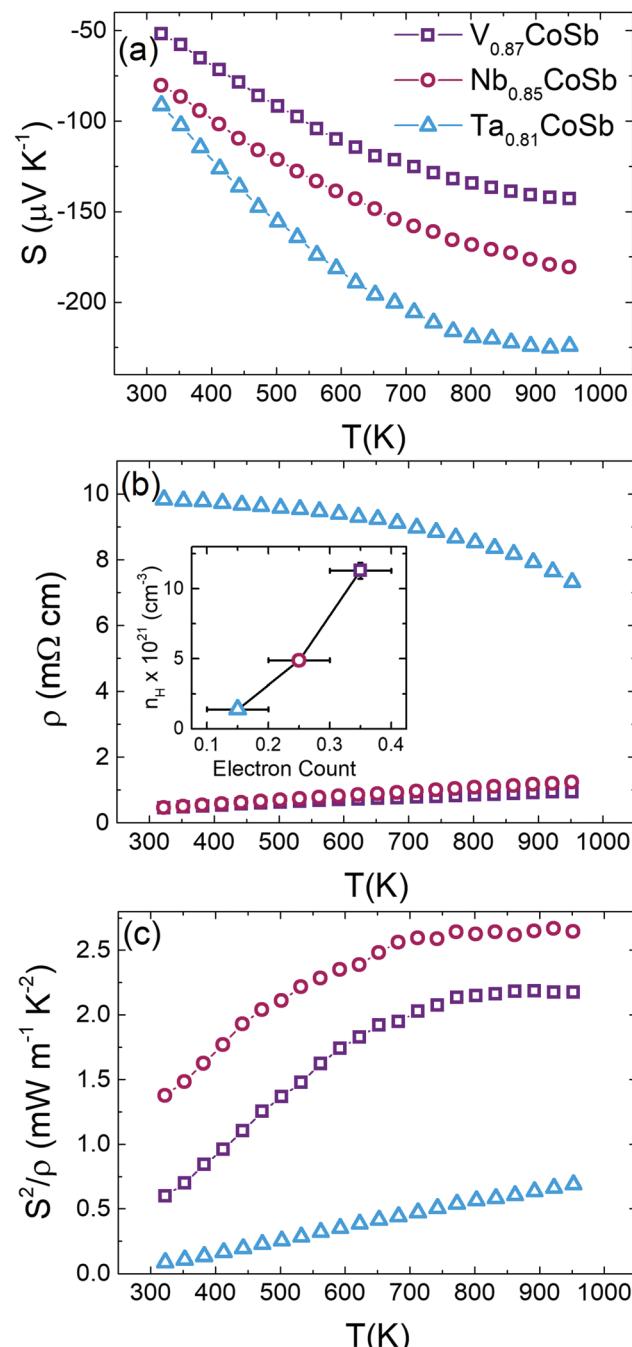


Fig. 4 Temperature dependence of (a) the Seebeck coefficient ( $S$ ), (b) the electrical resistivity ( $\rho$ ), and (c) the power factor ( $S^2/\rho$ ) for  $V_{0.87}CoSb$ ,  $Nb_{0.85}CoSb$  and  $Ta_{0.81}CoSb$ . The inset to panel (b) shows the linear dependence of the Hall carrier concentration ( $n_H$ ) on formal electron count (VEC – 18).

stoichiometric  $VCoSb$ .<sup>27</sup> The A = Ta sample has  $\mu_H = 0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , despite its lower  $m^*$  and  $n_H$ , which reflects its microstructure consisting of many very small grains.

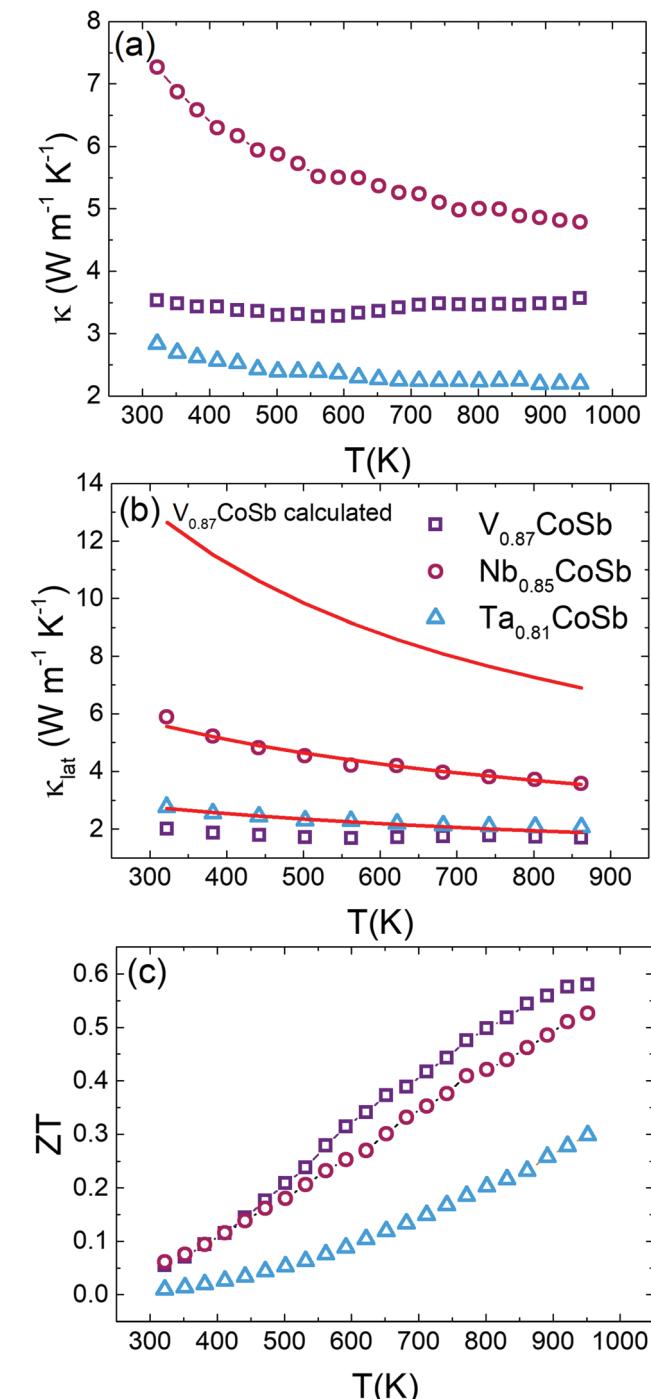
### Thermal conductivity

Fig. 5a shows the total thermal conductivity ( $\kappa$ ) for all samples. The measured thermal diffusivities ( $\alpha$ ) and heat capacities ( $C_p$ )



**Table 2** Nominal electron count, Seebeck coefficient ( $S$ ), electrical resistivity ( $\rho$ ), Hall carrier concentration ( $n_H$ ), Hall mobility ( $\mu_H$ ) and density of states effective mass ( $m^*$ ) for the  $A_xCoSb$  samples. Data collected at room temperature

Composition	Electron count	$S$ ( $\mu\text{V K}^{-1}$ )	$\rho$ ( $\text{m}\Omega \text{cm}$ )	$n_H$ ( $\times 10^{21} \text{ cm}^{-3}$ )	$\mu_H$ ( $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	$m^*(m_e)$
$V_{0.87}\text{CoSb}$	0.35(5)	-53	0.44	11.3	1.2	12.8
$Nb_{0.85}\text{CoSb}$	0.25(5)	-68	0.31	4.9	4.2	9.6
$Ta_{0.81}\text{CoSb}$	0.15(5)	-93	15.3	1.4	0.3	5.9



**Fig. 5** Temperature dependence of (a) the total thermal conductivity ( $\kappa$ ), (b) the lattice thermal conductivity ( $\kappa_{\text{lat}}$ ) and (c) the dimensionless figure of merit ( $ZT$ ) for  $V_{0.87}\text{CoSb}$ ,  $Nb_{0.85}\text{CoSb}$  and  $Ta_{0.81}\text{CoSb}$ . The solid red lines in panel (b) are calculated using the Callaway model, see manuscript text.

are shown in Fig. S5 (ESI†).  $Nb_{0.85}\text{CoSb}$  has the highest  $\kappa$  and the value for  $Ta_{0.81}\text{CoSb}$  is much reduced by comparison.  $V_{0.87}\text{CoSb}$  has an unusual, nearly temperature independent,  $\kappa(T)$  between 323–950 K, which is not in line with the observed decreasing  $\kappa(T)$  trends for the Nb and Ta samples. Subtraction of  $\kappa_{\text{el}}$  using the Wiedemann–Franz law yields the lattice thermal conductivities ( $\kappa_{\text{lat}}$ ) that are plotted in Fig. 5b. The temperature dependence of the Lorenz number ( $L$ ) and  $\kappa_{\text{el}}$  are shown in Fig. S6 (ESI†). The  $\kappa_{\text{lat}}(T)$  values confirm the gradual decreasing temperature dependence for the Nb and Ta samples.  $\kappa_{\text{el}} \sim 1.5 \text{ W m}^{-1} \text{ K}^{-1}$  for the V sample, leading to  $\kappa_{\text{lat}}$  values of  $2.0 \text{ W m}^{-1} \text{ K}^{-1}$  at 323 K and  $1.8 \text{ W m}^{-1} \text{ K}^{-1}$  at 950 K. These values are lower than those for  $Ta_{0.81}\text{CoSb}$ , and around three times lower than the Nb sample. The ultralow  $\kappa_{\text{lat}}$  for the V sample goes against the usual dependence on average atomic mass, where lower sound velocities ( $v_s$ ) for heavier elements tend to favour lower  $\kappa_{\text{lat}}$ .

To gain a better understanding of the thermal transport in these three samples,  $\kappa_{\text{lat}}(T)$  was modelled using the Callaway model. As a first step the Debye temperatures ( $\theta_D$ ) and  $v_s$  were estimated from the average room temperature ADPs listed in Table S1 (ESI†) using the procedure from ref. 28 as followed in our earlier work.<sup>10</sup> The resulting  $\theta_D$  and  $v_s$  for the  $A_x\text{CoSb}$  samples are listed in Table 3 and follow the expected trends based on increasing average atomic mass.  $\theta_D$  values decrease from V (279(6) K) to Nb (221(3) K) and Ta (192(2) K), signalling a softening of the lattice for the heavier A atoms. This is reflected in  $v_s$ , which gradually reduces. For comparison,  $\theta_D = 361(3)$  K for  $\text{NbCoSn}$ ,<sup>10</sup> demonstrating that the X-site vacancies lead to a softening of the lattice, as expected when removing a fraction of the chemical bonds in the structure. The low  $\kappa_{\text{lat}}$  of the V sample is therefore not explained by an anomalous  $\theta_D$  or  $v_s$  value, which both fit in with the behaviour of the Nb and Ta samples.

The Callaway model is based on the Debye approximation for  $C_p$  for a monoatomic cubic lattice and allows for phonon scattering from boundaries between grains, point-defects and other phonons through the Umklapp mechanism. This leads to the following expressions:<sup>29–31</sup>

$$\kappa_{\text{lat}} = \frac{k_B}{2\pi^2 v_s} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D} \frac{x^4 e^x}{\tau_{\text{ph}}^{-1} (e^x - 1)^2} dx \quad (1)$$

where  $x = \hbar\omega/k_B T$  is the reduced phonon energy,  $k_B$  is Boltzmann's constant,  $\hbar$  is the reduced Planck's constant, and  $\tau_{\text{ph}}$  is the total phonon relaxation rate defined as

$$\tau_{\text{ph}}^{-1} = \frac{v_s}{D} + A_{\text{PD}} \omega^4 + B_{\text{U}} T \omega^2, \quad (2)$$



**Table 3** Lattice thermal conductivity ( $\kappa_{\text{lat}}$ ) at 322 K, Debye temperature ( $\theta_D$ ), velocity of sound ( $v_s$ ), calculated mass fluctuation disorder parameter ( $\Gamma_M$ ), theoretical and fitted Umklapp scattering factors ( $B_U$ ) for the  $A_x\text{CoSb}$  compositions

Composition	$\kappa_{\text{lat},322\text{K}}$ (W m $^{-1}$ K $^{-1}$ )	$\theta_D$ (K)	$v_s$ (m s $^{-1}$ )	$\Gamma_M$	$L$ ( $\mu\text{m}$ )	$B_{U,\text{calc}}^a$ (10 $^{-18}$ s K $^{-1}$ )	$B_{U,\text{fit}}$ (s K $^{-1}$ )
$\text{V}_{0.87}\text{CoSb}$	2.0	270(6)	2339(50)	0.016	3.2	1.10	—
$\text{Nb}_{0.85}\text{CoSb}$	5.9	221(3)	1951(25)	0.044	0.80	1.65	1.45
$\text{Ta}_{0.81}\text{CoSb}$	3.0	192(2)	1696(20)	0.099	0.43	2.07	2.06

<sup>a</sup> The Grüneisen parameter was set to 1.0 for all three compositions.

where  $D$  is the average grain size,  $A_{\text{PD}}$  and  $B_U$  are the strengths of point-defect and Umklapp scattering, respectively.  $A_{\text{PD}}$  can be estimated using

$$A_{\text{PD}} = \frac{V}{4\pi v_s^3} \Gamma. \quad (3)$$

Here,  $V$  is the volume per atom and  $\Gamma$  is the disorder scattering parameter, which was calculated from the mass fluctuations caused by introduction of vacancies using:<sup>32</sup>

$$\Gamma = \frac{1}{3}q(1-q) \left( \frac{m_A}{m_{\text{av}}} \right)^2. \quad (4)$$

Here,  $q$  is the fraction of X-site vacancies and  $m_A$  is the mass of the A atoms occupying the X-site. We note that the site inversion of V and Co could contribute to point-defect scattering but the similarity in mass and size of V and Co atoms suggest this contribution to be small. Strain fluctuations due to size differences were also excluded as this leads to unphysically large values for vacancy compositions.<sup>32</sup> Finally,  $B_U$  was calculated from:

$$B_U = \left( \frac{V}{6\pi^2} \right)^{1/3} \frac{2k_{\text{B}}\gamma^2}{m_{\text{av}}v_s^3}. \quad (5)$$

Here,  $\gamma$  is the Grüneisen parameter and  $m_{\text{av}}$  is average mass.

The magnitude of  $A_{\text{PD}}$  was calculated using eqn (3) and (4) and kept fixed through the fitting.  $D$  was estimated from the average grain size from the EBSD data and was also kept fixed. Values for the disorder parameter  $\Gamma$  and grain size  $D$  are given in Table 3. Starting values of  $B_U$  were calculated and are compared against the fitted values in Table 3. We find that  $\kappa_{\text{lat}}(T)$  for the Nb and Ta samples is well described using the Callaway model (see Fig. 5b, full lines), where  $\gamma = 1$  gives good agreement between predicted and experimental  $B_U$  values (Table 3). The  $\gamma = 1$  value is in keeping with the largely harmonic bonding in HHs. The limited temperature dependence of  $\kappa_{\text{lat}}(T)$  for the Ta sample is linked to the small grains ( $B = 0.44 \mu\text{m}$ ), leading to substantial boundary scattering. Fits with  $B > 1 \mu\text{m}$  could not satisfactorily reproduce the data. In case of the Nb sample, a comparable fit can be obtained with  $B_U$  at the calculated value and  $B = 1.8 \mu\text{m}$ , suggesting that boundary scattering is less important for this composition. The good agreement between experimental and calculated  $\kappa_{\text{lat}}(T)$  for the Nb and Ta samples, from an essentially parameter-less fit, suggests that the behaviour for “ideal”  $\text{V}_{0.87}\text{CoSb}$  can be predicted using the Callaway model. The calculated  $\kappa_{\text{lat}}(T)$  for  $\text{V}_{0.87}\text{CoSb}$  using the input parameters as listed in Table 3 ( $D = 3.2 \mu\text{m}$ ;  $\Gamma = 0.016$ ;  $B_U = 1.12 \times 10^{-18}$  s K $^{-1}$ ) is shown in Fig. 5b and yields  $\kappa_{\text{lat}}$  values that are much greater and with a

stronger temperature dependence than the experimental trends. The discrepancy between the predicted and observed values will be discussed below.

### Figure of merit

The highest  $ZT$  is observed for  $\text{V}_{0.87}\text{CoSb}$  with a maximum of 0.58 at 950 K (Fig. 5c). This value is slightly higher than  $ZT \sim 0.5$  at 973 K for “stoichiometric” VCoSb, which has a comparable  $S^2/\rho = 2.5 \text{ mW m}^{-1} \text{ K}^{-2}$  but slightly larger  $\kappa = 4.4 \text{ W m}^{-1} \text{ K}^{-1}$  at 973 K.<sup>8</sup>  $\text{Nb}_{0.85}\text{CoSb}$  has a maximum  $ZT = 0.52$  at 950 K, which is consistent with previous values from nominally stoichiometric NbCoSb (ref. 7 and 10) and Sn substituted samples ( $ZT \sim 0.5$  at 950 K for  $\text{NbCoSb}_{0.8}\text{Sn}_{0.2}$ );<sup>27</sup> but is  $\sim 33\%$  lower than the best Nb<sub>x</sub>CoSb composition with adjusted stoichiometry ( $ZT = 0.75$  at 950 K for  $x = 0.82$ ).<sup>11</sup> This discrepancy is mostly caused by a lower  $\kappa_{\text{lat}} = 2.25 \text{ W m}^{-1} \text{ K}^{-1}$  at 950 K for those samples that were processed via levitation melting.  $\text{Ta}_{0.81}\text{CoSb}$  reaches  $ZT = 0.3$  at 950 K, which is limited by the high  $\rho$  values.

## Discussion

Structural analysis and Hall measurements both confirm the reported tendency for a reduced occupancy of the X-site from V to Nb to Ta, and thereby lower n-type carrier concentrations. We find values of  $x = 0.87$  (V),  $x = 0.85$  (Nb) and  $x = 0.81$  (Ta), which were observed for both the trial series and when specifically targeted, suggesting that these are “preferred” values under the used synthesis conditions. The reduced X-site occupancy has been linked to the cost of filling antibonding conduction band states.<sup>20</sup> Our Hall data support this with the reduced  $m^*$  from V to Nb to Ta signalling an increase in band dispersion. This results in a higher cost for band filling, leading to reduced X-site occupancies. Whilst our data show that each system has a preferred vacancy concentration, this does not mean that it cannot be controlled, as has indeed been done for the Nb<sub>x</sub>CoSb HHs by varying the nominal composition between  $0.8 \leq x \leq 1$ .<sup>11</sup> The reported  $n_{\text{H}}$  suggests that the actual variation is between  $0.81 \leq x \leq 0.87$ , assuming each Nb beyond  $x = 0.8$  donates 5 electrons. This is in good agreement with the stability window ( $\Delta x \sim 0.05$  at 1073 K) reported by Anand *et al.*<sup>20</sup> It is likely that the V and Ta systems have a similar stability window over which the vacancy concentration can be varied and this should be pursued to optimise  $ZT$ . Using  $n_{\text{H}}$  to estimate the X-site occupancy, leads to  $x = 0.91$  (V),  $x = 0.85$  (Nb) and  $x = 0.81$  (Ta), where the slight overestimate for the V sample may be linked to V/Co inversion.

The second important result pertains to the microstructure, where both porosity and grain-size variations were discovered



between samples. A gradually decreasing average grain size was observed from V to Nb to Ta, a reduction that scales with the increased melting point of the A elements and suggests that much higher sintering and consolidation temperatures are needed for the Ta sample. On the other hand, despite its largest average grain size diameter ( $\sim 3.2$   $\mu\text{m}$ ) and 95% gravimetric density, the V sample has many micron-sized pores that reduce the connectivity of grains.

The other significant result is the unexpectedly low  $\kappa_{\text{lat}}$  for the V sample. Our results demonstrate a gradual decrease in  $\theta_D$  and a softening of the lattice from V to Nb to Ta, consistent with the increased mass of the A atom and the increasing amount of chemical bonds removed from the structure. The observation of the lowest  $\kappa_{\text{lat}}$  for the V sample is therefore highly surprising. The  $\kappa_{\text{lat}}$  for the Nb and Ta samples is explained well within the Callaway framework, but this model substantially over-estimates  $\kappa_{\text{lat}}$  for  $\text{V}_{0.87}\text{CoSb}$ . The two main differences compared to the other samples are the presence of V/Co inversion and the micron-scale porosity and it is tempting to speculate that one of these differences accounts for the failure of the model. The impact of V/Co disordering in terms of mass fluctuations and lattice strain is small and is not expected to explain the low  $\kappa_{\text{lat}}$  values. Literature on nominally stoichiometric  $\text{VCoSb}$  with similar  $\sim 95\%$  gravimetric densities, prepared using arc-melting, ball-milling and hot-pressing, reveals a comparable  $\kappa_{\text{lat}} = 3 \text{ W m}^{-1} \text{ K}^{-1}$ .<sup>8</sup> We therefore surmise that the observed ultralow  $\kappa$  is generic and linked to the microstructure of these samples. The microstructure also affects the electrical properties with a reduced  $\mu_{\text{H}}$  compared to the Nb sample. However, the observed  $S^2/\rho$  remain competitive and the electrical transport is therefore less affected than  $\kappa_{\text{lat}}$ . The surface area porosity based on analysis of Fig. 3a is  $\sim 14\%$ , which is much larger than the  $\sim 5\%$  estimated from density measurements. This pushes this material in the domain where classical porosity corrections no longer hold.<sup>33,34</sup> To fully analyse the low  $\kappa_{\text{lat}}$ , multilength scale modelling considering the nature of the porosity and the phonon spectrum needs to be undertaken.

Finally, the ultralow  $\kappa$  for the  $\text{V}_{0.87}\text{CoSb}$  sample is coupled to a large  $n_{\text{H}}$  and modest  $\mu_{\text{H}} = 1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , enabling  $S^2/\rho = 2.3 \text{ mW m}^{-1} \text{ K}^{-2}$  and  $ZT = 0.6$ . It may be possible to improve  $\mu_{\text{H}}$  through sample processing, while the vacancy concentration could be changed to control  $n_{\text{H}}$  and optimise  $ZT$ . The Nb sample has  $\mu_{\text{H}} = 4.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $S^2/\rho = 2.7 \text{ mW m}^{-1} \text{ K}^{-2}$ , which are amongst the largest values in the literature,<sup>11,27</sup> demonstrating the viability of the powder-based synthesis route for the Nb samples. The performance of the Ta sample is limited by its low  $\mu_{\text{H}}$  and large  $\rho$ , which is caused by the nanoscale grain sizes that also affect  $\kappa_{\text{lat}}$ . For the Ta system, the focus should be on increasing the average grain size, *e.g.* by higher temperature processing, which will afford increases in  $S^2/\rho$ , whereas even for  $B = 5 \mu\text{m}$ ,  $\kappa_{\text{lat}}$  increases by only  $\sim 0.8 \text{ W m}^{-1} \text{ K}^{-1}$  at 323 K from the Callaway analysis. In case of the V system, work should focus on controlling the micron-scale porosity evident in Fig. 3a to explore to what extent it is possible to increase  $\mu_{\text{H}}$  and reduce  $\kappa_{\text{lat}}$ .

## Conclusions

To conclude, the topical  $\text{A}_x\text{CoSb}$  ( $\text{X} = \text{V}, \text{Nb}, \text{Ta}$ ) HHs form with different “preferred” vacancy concentrations, increasing from 13% (V) to 15% (Nb) and 19% (Ta). This is explained by the increased cost of populating antibonding conduction band states, which limits the maximum achievable n-type carrier concentration. The anomalously low  $\kappa_{\text{lat}}$  for  $\text{V}_{0.87}\text{CoSb}$  was modelled using the Callaway approximation but cannot be understood within this framework, whilst the Nb and Ta compositions can. Further work is needed to understand the low  $\kappa_{\text{lat}}$ , which may be linked to porosity, and could offer a route to improved  $ZT$  via microstructure control. Competitive maximum figures of merit of  $ZT = 0.5\text{--}0.6$  were observed for  $\text{A} = \text{V}, \text{Nb}$  at 950 K, whilst  $\text{A} = \text{Ta}$  has  $ZT = 0.3$  at the same temperature, largely due to a higher electrical resistivity linked to smaller grain sizes compared to the other compositions.

## Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

The EPSRC is acknowledged for funding the research on half-Heusler thermoelectrics and instrumentation (EP/N01717X/1, EP/N017218/1 and EP/P001483/1) and for a studentship for DAF. The STFC is acknowledged for allocation of neutron scattering beamtime at the ISIS facility (RB1810470 and Xpress 1890125). Raw data upon with this publication is based can be accessed at <http://dx.doi.org/10.5525/gla.researchdata.753>.

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