Supporting Information

Chains, layers, and twists: structural evolution in the VSn_2-VSb_2 pseudo-binary system

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1. Electron microphotographs of the samples

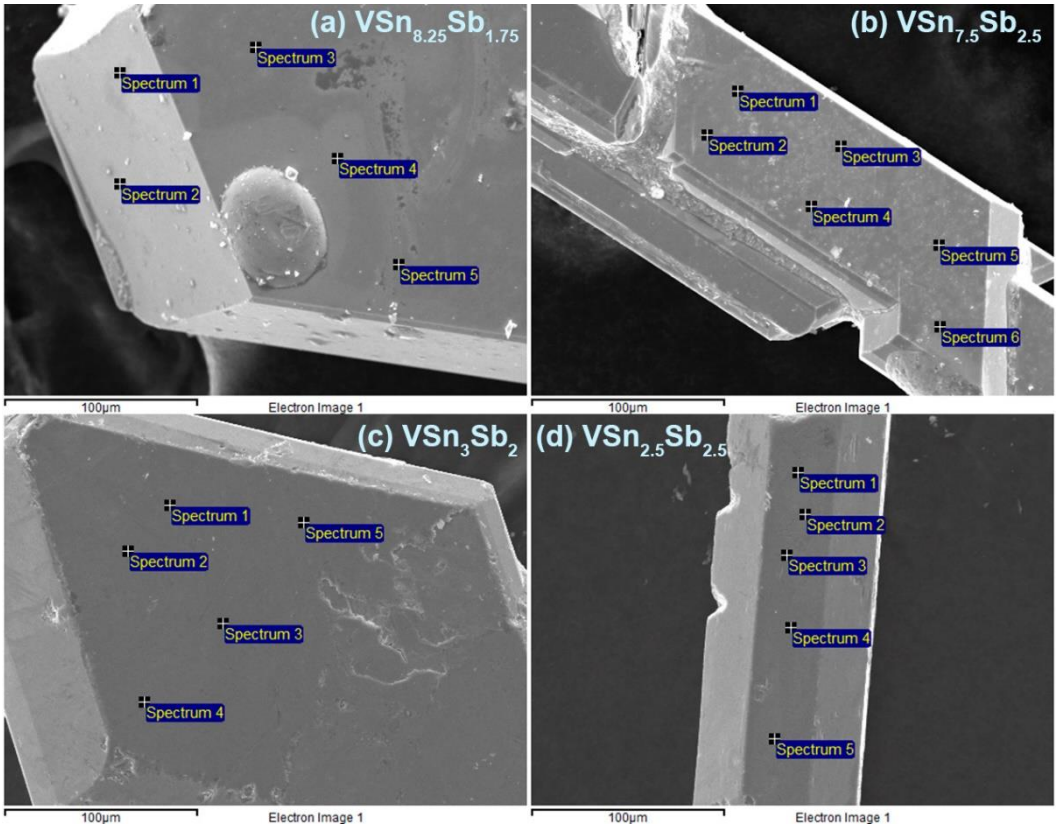


Figure S1. Electron microphotographs (secondary electrons) of the obtained crystals from samples with the following initial compositions: $VSn_{8.75}Sb_{1.25}$ (a), $VSn_{7.5}Sb_{2.5}$ (b), VSn_3Sb_2 (c), and $VSn_{2.5}Sb_{2.5}$ (d).

2. Starting compositions of the samples and results of the phase and elemental analysis

Table S1. Initial composition and results of the powder XRD and EDX analyses. The elemental compositions are normalized to two p-element atoms per formula, since the V concentration was frequently overestimated in our EDX analysis, due to incorrect quantitative corrections owing to the large difference in the atomic number between V and Sn or Sb.

No.	Starting composition	Phase compositions as determined by powder XRD	Elemental composition of the target phase as determined by EDX
1	VSn_{10}	VSn_2, $V_{3+x}Sn_{1-x}$	$V_{1.086(7)}Sn_{2.000(7)}$
2	$VSn_{8.75}Sb_{1.25}$	$VSn_{2-x}Sb_x$, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.09(1)}Sn_{1.43(1)}Sb_{0.567(3)}$
3	$VSn_{7.5}Sb_{2.5}$	τ_1, τ_2, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.059(3)}Sn_{1.03(1)}Sb_{0.97(1)}$
4	VSn_5Sb_5	$VSn_{x'}Sb_{2-x'}$, SnSb, $V_{3+x}Sn_{1-x-y}Sb_y$	$V_{1.047(7)}Sn_{0.517(5)}Sb_{1.482(8)}$
5	$VSn_{1.25}Sb_{8.75}$	$VSn_{x'}Sb_{2-x'}$, $V_{3+x}Sb_{1-x-y}Sn_y$, SnSb, Sb	$V_{0.97(5)}Sn_{0.14(6)}Sb_{1.86(7)}$
6	$VSn_{0.625}Sb_{9.375}$	$VSn_{x'}Sb_{2-x'}$, $V_{3+x}Sb_{1-x-y}Sn_y$, Sb	$V_{1.044(6)}Sn_{0.073(8)}Sb_{1.93(1)}$
7	VSb_{10}	VSb_2, $V_{7+x}Sb_9$	$V_{1.003(6)}Sb_{2.000(6)}$
8	$VSn_{4.5}Sb_{0.5}$	$VSn_{2-x}Sb_x$, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.139(1)}Sn_{1.550(9)}Sb_{0.45(1)}$
9	$VSn_{4.125}Sb_{0.875}$	$VSn_{2-x}Sb_x$, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.09(1)}Sn_{1.35(1)}Sb_{0.65(1)}$
10	VSn_4Sb	$VSn_{2-x}Sb_x$, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.12(2)}Sn_{1.294(7)}Sb_{0.71(1)}$
11	$VSn_{3.875}Sb_{1.125}$	$VSn_{2-x}Sb_x$, $V_{3+x}Sn_{1-x-y}Sb_y$	$V_{1.055(6)}Sn_{1.19(1)}Sb_{0.807(7)}$
12	$VSn_{3.625}Sb_{1.375}$	$VSn_{2-x}Sb_x$, τ_1, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.08(2)}Sn_{1.09(2)}Sb_{0.907(7)}$
13	$VSn_{3.5}Sb_{1.5}$	τ_1, $VSn_{2-x}Sb_x$, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.059(4)}Sn_{1.06(1)}Sb_{0.94(1)}$
14	$VSn_{3.3}Sb_{1.7}$	τ_2, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.03(1)}Sn_{0.95(1)}Sb_{1.053(8)}$
15	$VSn_{3.25}Sb_{1.75}$	τ_2, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{0.945(4)}Sn_{0.929(4)}Sb_{1.071(4)}$
16	$VSn_{3.125}Sb_{1.875}$	τ_2, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.06(2)}Sn_{0.89(1)}Sb_{1.10(2)}$
17	VSn_3Sb_2	τ_2, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.04(2)}Sn_{0.872(6)}Sb_{1.13(2)}$
18	$VSn_{2.75}Sb_{2.25}$	$VSn_{x'}Sb_{2-x'}$, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.082(5)}Sn_{0.72(1)}Sb_{1.28(1)}$
19	$VSn_{2.5}Sb_{2.5}$	$VSn_{x'}Sb_{2-x'}$, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.083(6)}Sn_{0.62(1)}Sb_{1.377(7)}$
20	$VSn_{2.25}Sb_{2.75}$	$VSn_{x'}Sb_{2-x'}$, $V_{3+x}Sn_{1-x-y}Sb_y$, SnSb	$V_{1.04(1)}Sn_{0.568(7)}Sb_{1.43(1)}$

3. Explanation of the chosen Sn/Sb ratios at the crystallographic sites

Sb and Sn are very close in terms of their X-ray scattering factors making it almost impossible to discern these atoms from the X-ray diffraction experiments. The analysis of the interatomic distances in the $VSn_{2-x}Sb_x$, τ_1, and τ_2, however, clearly shows that the Sb and Sn atoms are distributed unequally within these structures. Thus, we set different Sb/Sn ratios for different p-element sites.

Since the VSn_x,Sb_{2-x}, solid solution features only one p-element site, it can serve as a reference point to compare distances in the E-E dumbbells commonly present in all other obtained $V(Sn,Sb)_2$ phases. The E-E distance of 2.9014(6) in Sn-enriched $VSn_{0.7}Sb_{1.3}$ is particularly useful reference, since the distances in E-E dumbbells in the other compounds with higher Sn content are longer, meaning that the Sb/Sn ratios in these dumbbells should not exceed 0.65/0.35.

In the case of $VSn_{2-x}Sb_x$, there are two p-element sites: E1 and E2. The environment of the E1 site differs only slightly compared to that in the undoped compounds. The E1 atoms have a distinct twisted coordination of 4 V atoms (Figure 2 in main text) and thus support the 60° twists between the layers. Upon transformation from to $VSn_{2-x}Sb_x$, the τ_1, τ_2, and VSn_xSb_{2-x} phases, the number of twists gradually reduces from 1 to 0. Therefore, we believe that only a marginal amount of Sb atoms can be present at this site, which causes the observed structural transformations upon the increasing Sb concentration.

At the same time, coordination of the E2 site experiences more dramatic changes, with the E2-E2 distances becoming more similar to the distances between Sb-Sb atoms in VSb_2 rather than Sn2-Sn2 distances in VSn_2 (Tables S2 and S3). Thus, we set the E2 site to the higher Sb/Sn ratios, compared to the those of the E1 site. Given that the E2-E2 bond in $VSn_{1.1}Sb_{0.9}$ is slightly longer than the length of the E-E dumbbell in $VSn_{0.7}Sb_{1.3}$, we set this site to the Sb/Sn ratio of 0.6/0.4, while the E1 site is defined as Sb/Sn = 0.3/0.7 to match the EDX analysis results. The $VSn_{1.35}Sb_{0.65}$ compound is treated similarly, but with lower Sb/Sn at both E1 and E2 sites.

The p-element sites in the τ_1, τ_2 phases were also treated similarly, with the E1 sites located in the twists being set to Sb/Sn ratio of 0.3/0.7, which we assume is the limit for this type of positions, while the rest of the E sites set to fixed Sb/Sn ratio. For the phase τ_2, the rest of the E3 and E4 sites were set to the same Sb/Sn ratio of 0.6/0.4, while the E2 site was defined as Sb/Sn = 0.65/0.35 due to the shorter E2-E2 distances. In the case of the τ_1 phase the E2 site was set to the Sb/Sn ratio of 0.55/0.45, while the E3-E5 sites were set to the Sb/Sn ratio of 0.6/0.4. The slightly higher Sn concentration for the E2 site was chosen due to the noticeably larger E-E distances in the E2-E2 dumbbells.

4. Cell parameters of $VSn_{x'}Sb_{2-x'}$

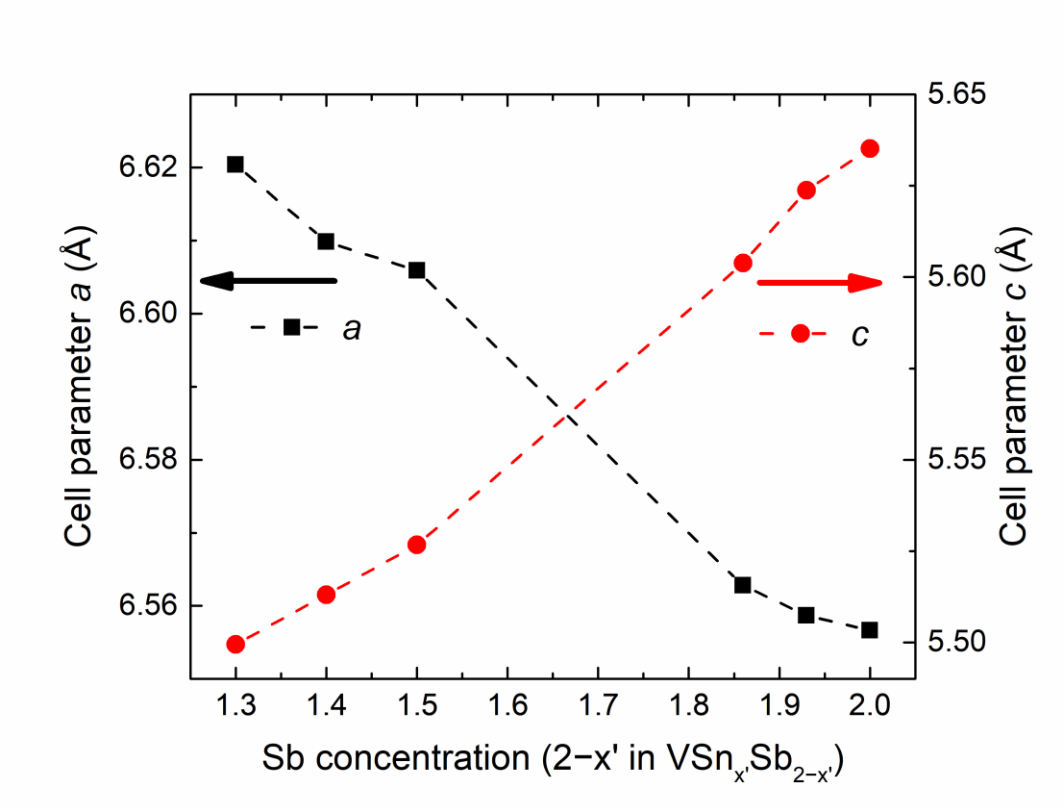


Figure S2. Cell parameters of $VSn_{x'}Sb_{2-x'}$ versus Sb content (2–x') at room temperature as determined from powder XRD. The lines are drawn to guide the eye.

5. Interatomic distances

Table S2. Most important interatomic distances in VSn_2, VSb_2, and their solid solutions.

Atom	Atom	Distance, Å	Atom	Atom	Distance, Å	Atom	Atom	Distance, Å
VSn_2			$VSn_{1.35}Sb_{0.65}$			$VSn_{1.1}Sb_{0.9}$		
V1	V1×2	2.7310(3)	V1	V1×2	2.7253(3)	V1	V1×2	2.72322(18)
	Sn1×2	2.7665(12)		E1×2	2.7936(13)		E1×2	2.7955(10)
	Sn2×2	2.8236(5)		E2×2	2.8475(6)		E2×2	2.8458(5)
	Sn1×2	2.8485(13)		E1×2	2.8489(13)		E1×2	2.8470(11)
	Sn2×2	2.8560(5)		E2×2	2.8535(5)		E2×2	2.8564(4)
Sn1	Sn1	3.1470(9)	E1	E1	3.1551(9)	E1	E1	3.1573(8)
	Sn1×2	3.1562(5)		E1×2	3.1275(5)		E1×2	3.1214(4)
Sn2	Sn2	3.0963(9)	E2	E2	2.9351(8)	E2	E2	2.9114(7)
	Sn2×2	3.1388(5)		E2×2	3.2395(5)		E2×2	3.2514(4)
Atom	Atom	Distance, Å	Atom	Atom	Distance, Å	Atom	Atom	Distance, Å
VSb_2			$VSn_{0.6}Sb_{1.4}$			$VSn_{0.7}Sb_{1.3}$		
V	V1×2	2.8031(5)	V×2		2.7485(4)	V×2		2.7360(3)
V	Sb1×8	2.8389(4)	V	E×8	2.8464(4)	V	E×8	2.8434(4)
Sb	Sb1	2.8708(5)	E	E	2.8999(6)	E1	E	2.9014(6)
	Sb1×2	3.3030(5)		E×2	3.2655(4)		E×2	3.2544(4)

Table S3. Most important interatomic distances in τ_1 and τ_2.

Atom	Atom	Distance, Å	Atom	Atom	Distance, Å
τ_1 ($VSn_{1.033}Sb_{0.967}$)			τ_2 ($VSn_{0.9}Sb_{1.1}$)		
V1	V1×2	2.7143(6)	V1	V2	2.71930(14)
	E1×2	2.7992(15)	V1	E1×2	2.8349(9)
	E5×2	2.8538(10)		E3×2	2.8385(9)
	E5×2	2.8466(8)		E2×2	2.8467(4)
	E1×2	2.8534(15)		E4×2	2.8551(4)
V2	V3	2.7209(9)	V2	E1×2	2.8073(9)
	E1×2	2.8351(15)		E4×2	2.8551(4)
	E3×2	2.8397(15)		E2×2	2.8597(9)
	E4×2	2.8447(8)		E2×2	2.8580(4)
	E2×2	2.8492(8)			
V3	E1×2	2.8074(15)			
	E2×2	2.8390(8)			
	E4×2	2.8548(8)			
	E3×2	2.8583(15)			
E1	E1	3.1172(9)	E1	E1	3.1508(6)
	E1	3.1209(12)		E1×2	3.1227(3)
	E1	3.1493(12)			
E2	E2	2.9254(11)	E2	E2	2.9054(6)
	E4×2	3.2502(9)		E4×2	3.2471(3)
E3	E3	2.9114(13)	E3	E3	2.9145(5)
	E3	3.2405(13)		E3×2	3.2428(5)
	E3	3.2443(13)			
E4	E5	2.9115(11)	E4	E4	2.9181(6)
E5	E5	3.2438(7)			

6. Calculated electron density in VSn_2

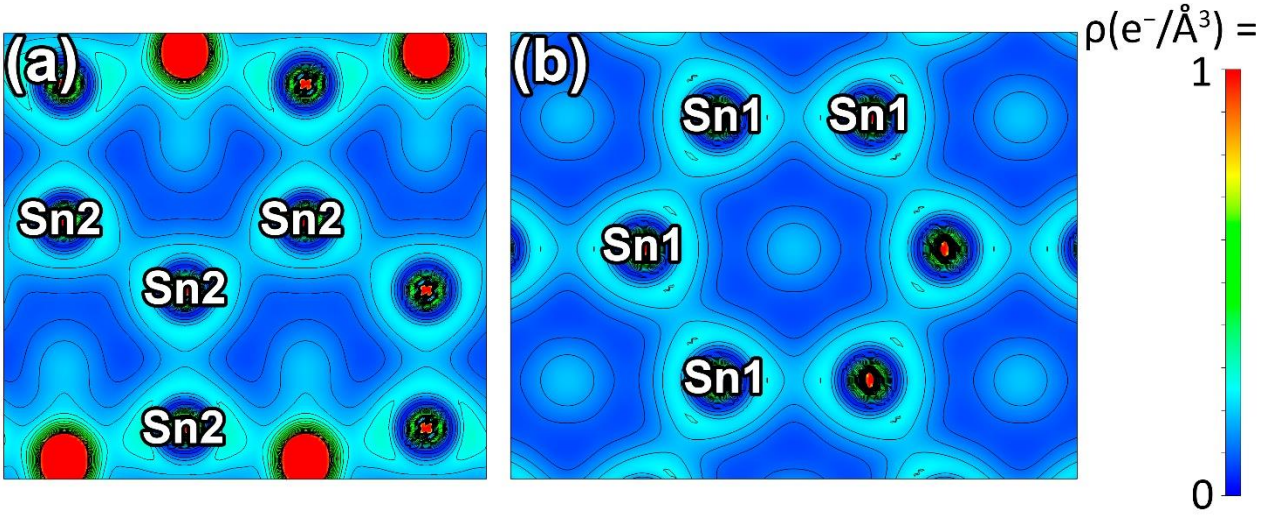


Figure S3. Cross-sections of the electron density distribution near the Sn2-Sn2 dumbbells (a) and the Sn1 honeycomb nets (b) in VSn_2.