

Supporting Information for

Fast Direct Synthesis and Compaction of Phase Pure

Thermoelectric ZnSb

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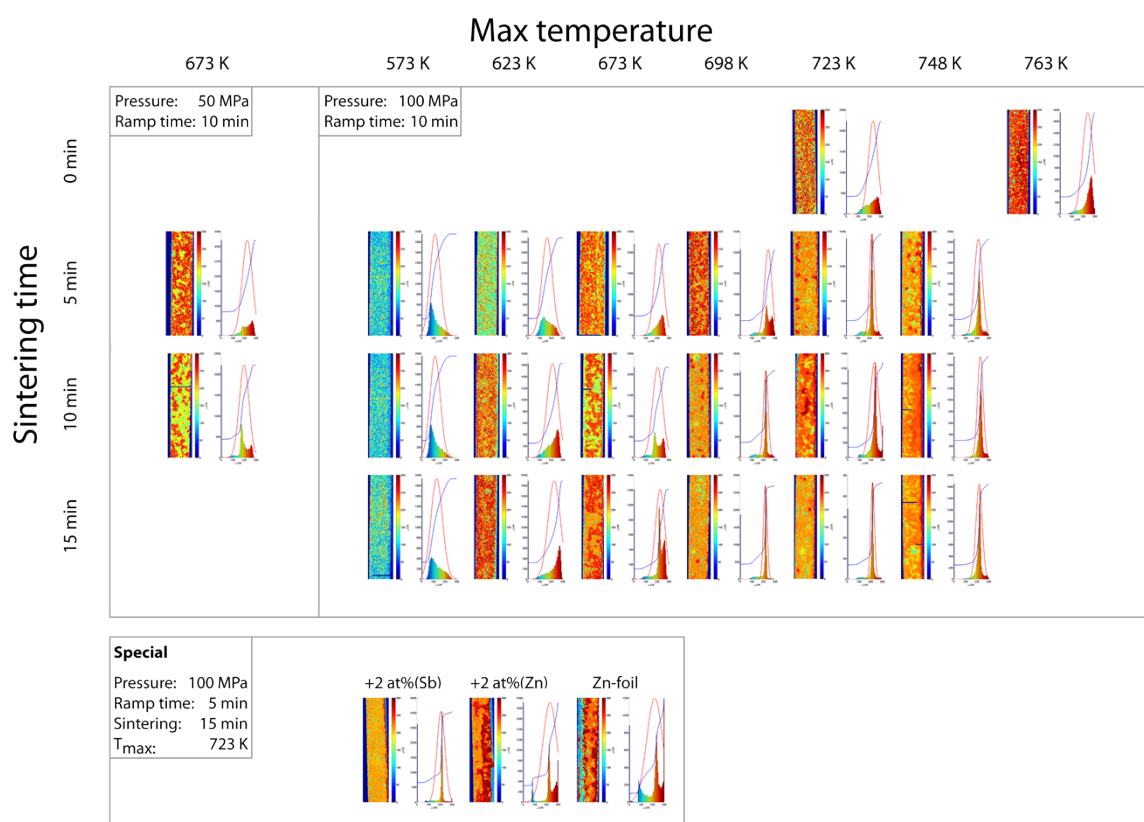


Figure S1: An overview of all PSM scans for the samples made for this study.

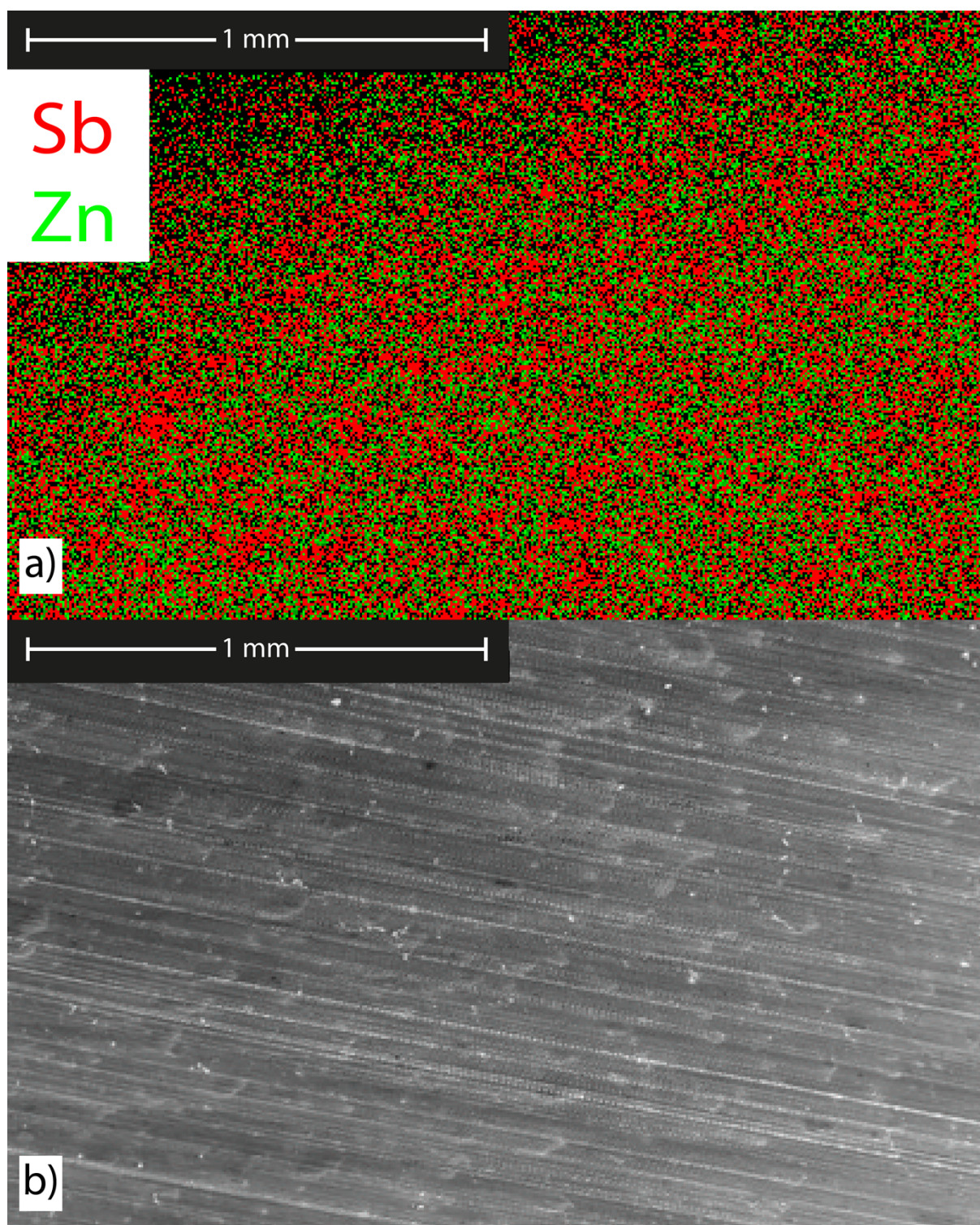


Figure S2: a) EDX map of the surface of a pellet made at 573 K, an applied pressure of 100 MPa, a ramping time of 10 minutes and reaction time of 5 minutes. b) Backscattered electron SEM picture of the same area as in a).

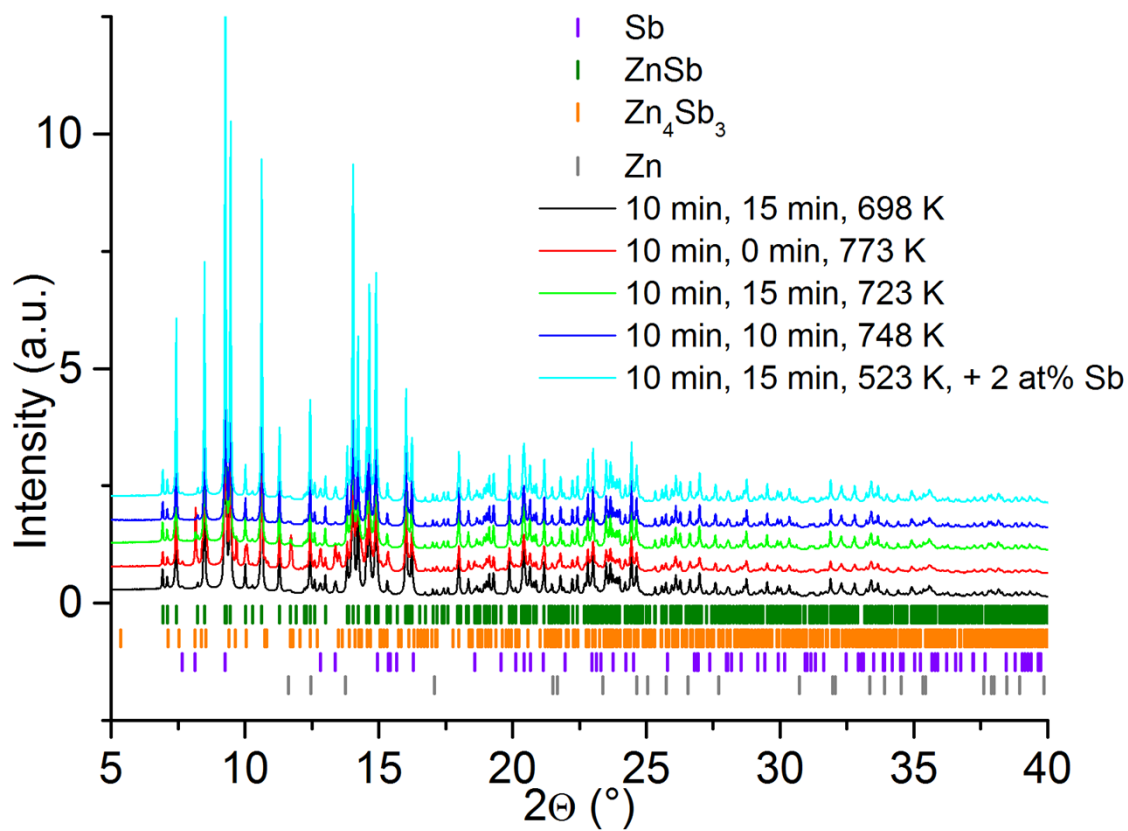


Figure S3: Synchrotron PXRD data on selected samples. The data was collected up to $2\theta = 77^\circ$, but a smaller range is shown here, to be able to distinguish the different peaks.

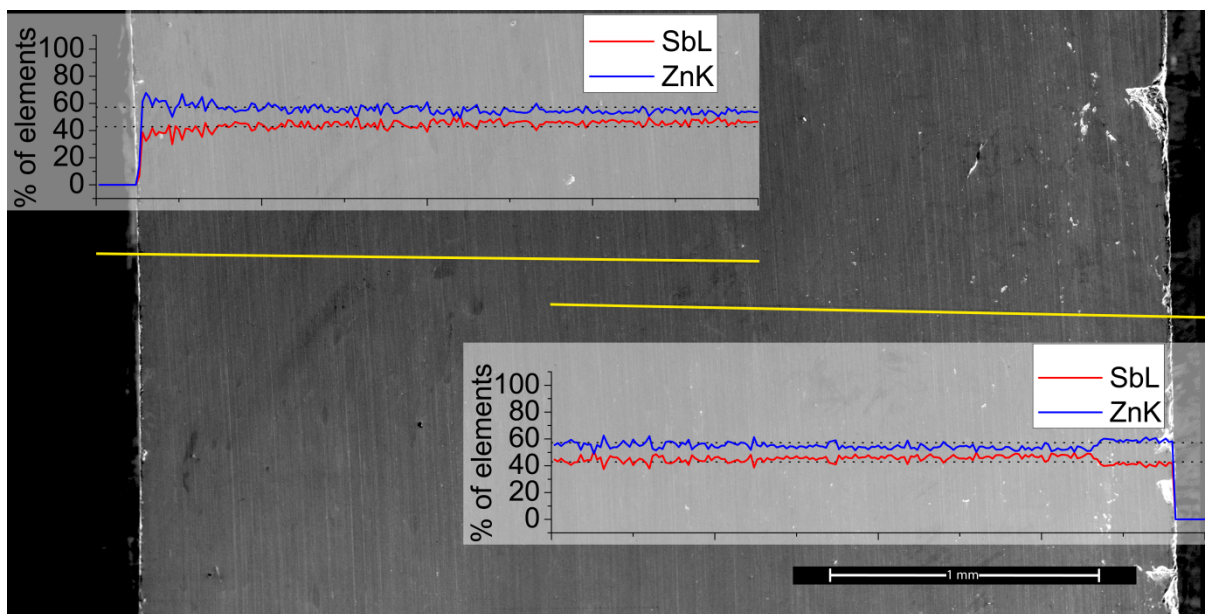


Figure S4: Two EDX line scans show that the composition of the SPS pressed ZnSb pellets with 2 at% extra Zn. The dashed lines in the graphs correspond to a composition of Zn:Sb = 4:3. The secondary electron SEM picture is a merge of two individual pictures. The uncertainties of the measurements are on the order of $\pm 5\%$.

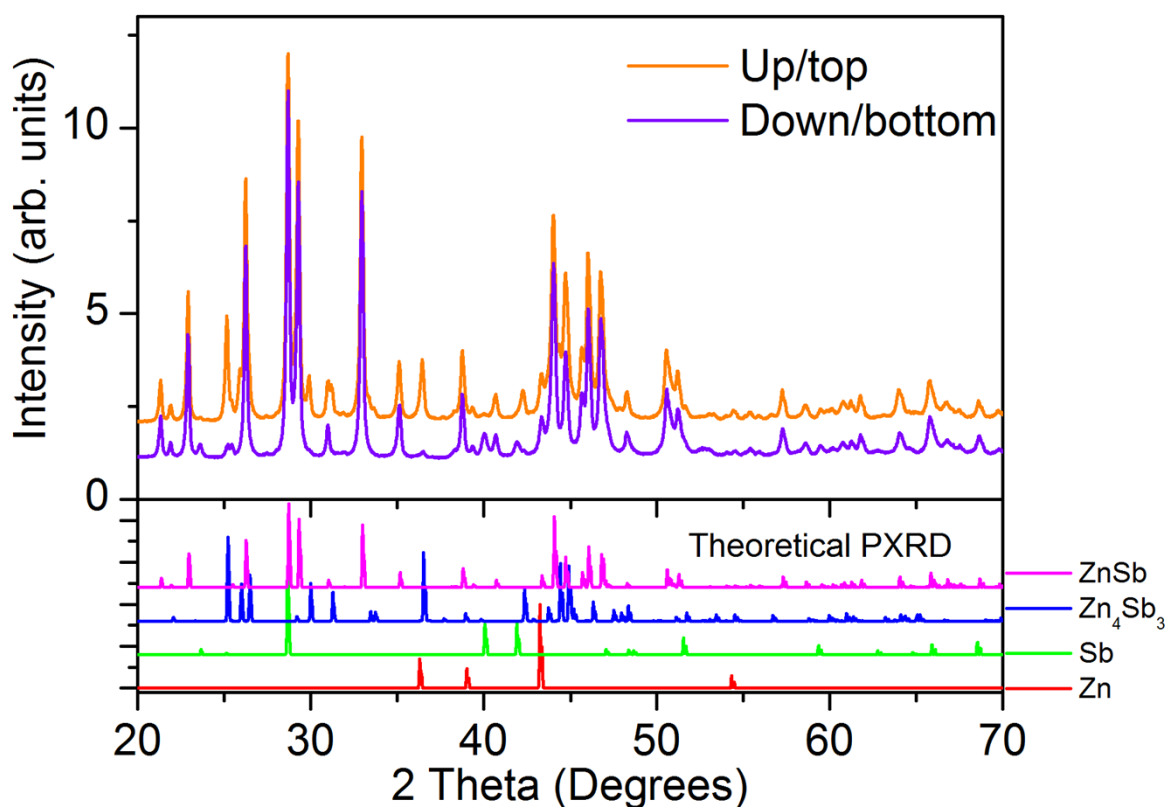


Figure S5: XRD patterns ($20^\circ < 2\theta < 70^\circ$ Cu- K_α) on the top and bottom sides of pellets made at an applied pressure of 100 MPa, a ramping time of 10 minutes, a sintering time of 15 minutes, and a maximum temperature of 698 K. The current enters from the bottom. The migration of Zn-ions results in excess Zn at the top(right side in PSM scans), forming Zn_4Sb_3 .

Ramp (min)	10	10	10	10	10	10	10	10	10	10
Hold time (min)	5	5	10	10	15	15	10	10	10	10
Max temp.(K)	673	673	673	673	673	673	623	623	698	698
Side	top	bottom	top	bottom	top	bottom	top	bottom	top	bottom
# parametre	27	16	27	16	22	17	19	17	18	18
# phases	4	2	4	2	3	2	3	2	2	2
χ^2	6.91	10.9	14.2	24.6	17.7	26.7	15.9	27.8	8.12	12.2
R_{Bragg}(ZnSb)	3.81	4.38	3.44	4.3	3.89	8.46	3.96	5.05	4.26	8.85
R_{Bragg} Zn₄Sb₃	4.45	-	4.09	-	4.39	-	4.43	-	3.87	-
R_{Bragg}(Sb)	4.69	7.97	3.58	12.8	-	14.2	5.62	15.1	-	17.3
R_{Bragg}(Zn)	2.42	-	3.27	-	5.35	-	-	-	-	-
wt % (ZnSb)	37.8(4)	94.6(8)	66.8(4)	95.6(7)	9.5(4)	94.8(6)	49.4(2)	94.4(7)	72.0(4)	96.7(6)
wt %(Zn₄Sb₃)	59.5(4)	-	31.8(2)	-	40.3(2)	-	48.4(3)	-	28.0(2)	-
wt %(Sb)	1.75(9)	5.4(2)	1.02(8)	4.43(7)	-	5.17(8)	2.19(5)	5.6(1)	-	3.33(7)
wt %(Zn)	0.9(1)	-	0.40(8)	-	0.16(5)	-	-	-	-	-
ZnSb	Zn/Sb B_{iso}	0.14(9)	-	0.691(4)	-	0.75(5)	-	-	0.42(4)	-
	Zn-B_{iso}	-	0.85(8)	-	0.44(5)	-	0.23(5)	-	0.07(5)	-
	Sb-B_{iso}	-	0.06(6)	-	1.5(8)	-	1.1(7)	-	0.99(8)	-
	a	6.2067(2)	6.2098(2)	6.2066(1)	6.2078(2)	6.2051(2)	6.2063(1)	6.2084(2)	6.2077(2)	6.2079(1)
	b	7.7509(3)	7.7538(2)	7.7479(2)	7.7485(2)	7.7457(2)	7.7462(2)	7.7504(2)	7.7487(2)	7.7506(1)
	c	8.1007(3)	8.0993(2)	8.0969(2)	8.0944(2)	8.0953(2)	8.0936(2)	8.1002(3)	8.0964(2)	8.1003(1)
Zn₄Sb₃	a	12.2439(4)	-	12.2402(3)	-	12.2379(3)	-	12.2424(4)	-	12.2427(3)
	c	12.4443(4)	-	12.4425(4)	-	12.4382(3)	-	12.4421(4)	-	12.4448(3)
Sb	a	4.3021(5)	4.3074(3)	4.2997(6)	4.3062(2)	-	4.3057(2)	4.3038(4)	4.3071(2)	-
	c	11.261(2)	11.287(1)	11.255(3)	11.2789(9)	-	11.2747(9)	11.279(2)	11.281(1)	-
Zn	a	2.6909(6)	-	2.6742(9)	-	2.6690(8)	-	-	-	-
	c	4.964(2)	-	4.966(3)	-	4.970(3)	-	-	-	-

Tabel S1: Parameters from Rietveld analysis on data recorded on an in-house Rigaku Smartlab

diffractometer. The data have been recorded on both sides of the pellets, to check for homogeneity.

Ramp (min)		10	10	10	10	10
Hold time (min)		15	10	0	10	15
Maximum temp. (K)		698	573	773	748	723
Comments		2 at% (Sb) added				
# in the article		iv	i	ii	iii	v
# parametre		36	44	41	33	37
# phases		2	3	3	2	2
χ^2		2.74	1.9	2.13	2.05	3.57
$R_{\text{Bragg}}(\text{ZnSb})$		1.7	1.59	1.53	1.62	1.71
$R_{\text{Bragg}}(\text{Sb})$		2.1	1.78	3.1	1.96	2.37
$R_{\text{Bragg}}(\text{Zn}_4\text{Sb}_3)$		-	3.11	5.35	-	-
wt % (ZnSb)		95.8(3)	67.8(2)	94.7(2)	99.1(2)	96.4(2)
wt % (Sb)		4.25(8)	8.47(6)	1.01(5)	0.89(5)	3.61(8)
wt % (Zn ₄ Sb ₃)		-	23.7(2)	4.3(1)	-	-
ZnSb	Sb-x	0.14295(6)	0.14327(7)	0.14306(5)	0.14294(5)	0.14295(6)
	Sb-y	0.08198(5)	0.08201(6)	0.08205(4)	0.08211(4)	0.08206(5)
	Sb-z	0.10832(5)	0.10826(6)	0.10829(4)	0.10839(4)	0.10839(5)
	Sb-B _{iso}	0.0030(2)	0.0022(2)	0.0030(2)	0.0029(2)	0.0028(2)
	Sb-occ.	1	1	1	1	1
	B11	0.0003(1)	-0.0002(1)	0.00015(8)	0.00039(8)	0.00044(9)
	B22	0.00146(7)	0.00115(8)	0.00161(6)	0.00154(6)	0.00134(7)
	B33	0.00124(6)	0.00106(7)	0.00118(5)	0.00099(5)	0.00102(6)
	B12	0.00020(1)	0.00040(1)	0.00017(9)	0.00020(9)	0.00010(1)
	B13	-0.00010(1)	0.00040(1)	0.00022(8)	0.00004(8)	0.00008(9)
	B23	0.00008(9)	-0.00010(1)	-0.00003(8)	-0.00006(8)	0.00006(8)
	Zn-x	0.45790(1)	0.4575(1)	0.45774(9)	0.45794(9)	0.4578(1)
	Zn-y	0.10971(9)	0.1099(1)	0.10985(7)	0.10970(7)	0.10977(8)
	Zn-z	0.8701(1)	0.8700(1)	0.87034(9)	0.87019(9)	0.8701(1)
	Zn-B _{iso}	0.0060(5)	0.0044(5)	0.0057(4)	0.0056(4)	0.0059(4)
	Zn-occ.	0.992(1)	0.993(2)	0.991(2)	0.992(1)	0.995(1)
	B11	0.0024(2)	0.0003(2)	0.0021(2)	0.0021(2)	0.0026(2)
	B22	0.0027(2)	0.0022(2)	0.0026(1)	0.0026(1)	0.0025(2)
	B33	0.0016(1)	0.0018(2)	0.0016(1)	0.0015(1)	0.0015(1)
	B12	-0.0000(2)	-0.0000(2)	0.0000(1)	-0.0000(1)	-0.0000(1)
	B13	0.0002(1)	0.0002(2)	0.0002(1)	0.0002(1)	0.0001(1)
	B23	-0.0008(1)	-0.0009(2)	-0.0005(1)	-0.0006(1)	-0.0007(1)
	a (Å)	6.17850(3)	6.18022(3)	6.17869(2)	6.17817(2)	6.17844(3)
	b (Å)	7.72714(4)	7.72744(5)	7.72820(3)	7.72773(3)	7.72701(4)
	c (Å)	8.08947(4)	8.08962(5)	8.09124(3)	8.09120(3)	8.08995(4)
Sb	B _{iso}	0.3(1)	-	-	0.05(4)	0.6(1)
	a (Å)	4.2977(3)	4.29949(9)	4.2964(7)	4.2970(4)	4.2983(3)
	c (Å)	11.2369(9)	11.2395(3)	11.248(3)	11.255(2)	11.2415(9)
Zn ₄ Sb ₃	a (Å)	-	12.2007(2)	12.1988(6)	-	-
	c (Å)	-	12.3727(2)	12.369(1)	-	-

Tabel S2: Parameters from Rietveld analysis of five selected samples on synchrotron PXRD data recorded at 100 K.

Temperatur (K)		100	125	150	175	200	225
# parametre		27	27	27	27	27	27
# phases		2	2	2	2	2	2
χ^2		2.98	2.84	2.72	2.69	2.82	2.66
R _{Bragg} (ZnSb)		1.89	1.81	1.86	1.86	1.93	1.86
R _{Bragg} (Sb)		2.07	2.22	2.25	2.35	2.54	2.32
R _{Bragg} (ZnO)		-	-	-	-	-	-
R _{Bragg} (ZnSb ₂ O ₄)		-	-	-	-	-	-
wt % (ZnSb)		95.7(3)	95.5(3)	95.6(3)	95.6(3)	95.4(3)	95.5(3)
wt % (Sb)		4.30(8)	4.46(8)	4.42(8)	4.36(8)	4.56(9)	4.50(9)
wt % (ZnO)		-	-	-	-	-	-
wt % (ZnSb ₂ O ₄)		-	-	-	-	-	-
ZnSb	Sb-x	0.14293(6)	0.14295(6)	0.14290(6)	0.14294(6)	0.14286(6)	0.14285(6)
	Sb-y	0.08193(5)	0.08192(5)	0.08199(5)	0.08196(5)	0.08203(5)	0.08207(5)
	Sb-z	0.10828(5)	0.10836(5)	0.10833(5)	0.10836(5)	0.10844(5)	0.10840(5)
	Sb-B _{iso}	0.208(8)	0.268(9)	0.346(9)	0.420(9)	0.50(1)	0.56(1)
	Sb-occ.	1	1	1	1	1	1
	Zn-x	0.4579(1)	0.4580(1)	0.4580(1)	0.4570(1)	0.4571(1)	0.4569(1)
	Zn-y	0.10982(8)	0.10986(8)	0.10995(8)	0.1101(8)	0.11025(9)	0.11036(9)
	Zn-z	0.8701(1)	0.8701(1)	0.87(1)	0.87(1)	0.87(1)	0.87(1)
	Zn-B _{iso}	0.41(2)	0.50(2)	0.64(2)	0.76(2)	0.89(2)	0.98(2)
	Zn-occ.	0.991(1)	0.988(1)	0.991(1)	0.991(1)	0.988(1)	0.987(1)
	a (Å)	6.17850(3)	6.18093(3)	6.18357(3)	6.18637(3)	6.18931(3)	6.19217(3)
	b (Å)	7.72716(4)	7.72858(4)	7.73023(4)	7.73201(4)	7.73402(4)	7.73588(4)
	c (Å)	8.08947(4)	8.09019(4)	8.09107(4)	8.09202(4)	8.09304(4)	8.09388(4)
Sb	z	0.2338(4)	0.2338(4)	0.2345(4)	0.2342(4)	0.2340(4)	0.2342(4)
	B _{iso}	0.4(1)	0.4(1)	0.5(1)	0.6(1)	0.9(1)	0.9(1)
	a (Å)	4.2981(3)	4.2991(3)	4.2994(3)	4.3000(3)	4.3009(3)	4.3022(3)
	b (Å)	4.2981(3)	4.2991(3)	4.2994(3)	4.3000(3)	4.3009(3)	4.3022(3)
	c (Å)	11.2381(9)	11.2433(9)	11.2471(9)	11.2496(9)	11.2530(9)	11.2599(9)
ZnO	Zn/O B _{iso}	-	-	-	-	-	-
	a (Å)	-	-	-	-	-	-
	b (Å)	-	-	-	-	-	-
	c (Å)	-	-	-	-	-	-
ZnSb ₂ O ₄	a (Å)	-	-	-	-	-	-
	b (Å)	-	-	-	-	-	-
	c (Å)	-	-	-	-	-	-

Tabel S3: Parameters from Rietveld analysis on multi-temperature synchrotron PXRD data measured on powder from the main body of the pellet synthesized at 100 MPa, a ramping time of 10 minutes, a sintering time of 15 minutes, and a maximum temperature of 698 K. The standard error of estimate is specified in parenthesis after a number. If no standard error of estimate is given, then the parameter has not been refined.

Temperatur (K)		250	275	300	400 - Low	400 - high	500
# parametre			27	27	27	18	21
# phases		2	2	2	2	2	3
χ^2		2.45	2.36	2.36	2.14	1.77	1.37
R_{Bragg} (ZnSb)			1.89	2	1.92	7.38	3.22
R_{Bragg} (Sb)			2.32	2.34	2.26	9.37	4.1
R_{Bragg} (ZnO)			-	-	-	-	-
R_{Bragg} (ZnSb ₂ O ₄)			-	-	-	-	-
wt % (ZnSb)			95.7(3)	95.7(3)	95.7(3)	95.3(3)	86.2(5)
wt % (Sb)		4.36(8)	4.28(8)	4.28(8)	4.31(8)	4.7(2)	7.47(9)
wt % (ZnO)			-	-	-	-	6.3(5)
wt % (ZnSb ₂ O ₄)			-	-	-	-	-
ZnSb	Sb-x	0.14290(6)	0.14287(6)	0.14288(6)	0.14280(6)	0.14295	0.14295
	Sb-y	0.08204(5)	0.08212(5)	0.08212(5)	0.08214(5)	0.08198	0.08198
	Sb-z	0.10837(5)	0.10833(5)	0.10833(5)	0.10831(5)	0.10832	0.10832
	Sb-B _{iso}	0.63(1)	0.72(1)	0.79(1)	1.07(1)	1.55(1)	1.24(2)
	Sb-occ.	1	1	1	1	1	1
	Zn-x	0.4568(1)	0.4566(1)	0.4565(1)	0.4557(1)	0.45786	0.45786
	Zn-y	0.11056(8)	0.11067(8)	0.11076(9)	0.11126(9)	0.10971	0.10971
	Zn-z	0.8699(1)	0.8699(1)	0.8698(1)	0.8695(1)	0.87013	0.87013
	Zn-B _{iso}	1.09(2)	1.25(2)	1.39(2)	1.88(3)	2.47(3)	2.58(3)
	Zn-occ.	0.989(1)	0.99(1)	0.991(1)	0.99(1)	1	1
	a (Å)	6.19509(3)	6.19813(3)	6.20115(3)	6.21370(3)	6.21529(5)	6.22879(3)
	b (Å)	7.73780(4)	7.73975(4)	7.74167(4)	7.74945(4)	7.75083(6)	7.75877(4)
	c (Å)	8.09474(4)	8.09564(4)	8.09637(4)	8.09930(4)	8.10033(6)	8.10356(4)
Sb	z	0.2343(4)	0.2343(4)	0.2343(4)	0.2343(4)	0.23246	0.23246
	B _{iso}	0.9(1)	0.9(1)	1(1)	1.277(1)	6.2(4)	1.68(9)
	a (Å)	4.3031(3)	4.3037(3)	4.3043(3)	4.3070(2)	4.3087(2)	4.31286(8)
	b (Å)	4.3031(3)	4.3037(3)	4.3043(3)	4.3070(2)	4.3087(2)	4.31286(8)
	c (Å)	11.2669(8)	11.2689(8)	11.2720(9)	11.2862(8)	11.2958(8)	11.3273(4)
ZnO	Zn/O B _{iso}	-	-	-	-	-	0
	a (Å)	-	-	-	-	-	3.2583(6)
	b (Å)	-	-	-	-	-	3.2583(6)
	c (Å)	-	-	-	-	-	5.2010(2)
ZnSb ₂ O ₄	a (Å)	-	-	-	-	-	-
	b (Å)	-	-	-	-	-	-
	c (Å)	-	-	-	-	-	-

Tabel S3 (continued): Parameters from Rietveld analysis on multi-temperature synchrotron PXRD data measured on powder from the main body of the pellet synthesized at 100 MPa, a ramping time of 10 minutes, a sintering time of 15 minutes, and a maximum temperature of 698 K. The standard error of estimate is specified in parenthesis after a number. If no standard error of estimate is given, then the parameter has not been refined.

Temperatur (K)		600	700	800	900	1000	300 - After
# parametre			26	25	22	15	25
# phases		3	3	3	3	2	3
χ^2		2.18	1.92	1.18	1.47	0.435	10.8
R _{Bragg} (ZnSb)			4	6.34	-	-	-
R _{Bragg} (Sb)			2.27	2.62	2.63	-	14.1
R _{Bragg} (ZnO)			1.83	3.3	7.99	7.61	7.01
R _{Bragg} (ZnSb ₂ O ₄)			-	-	32.6	60.5	21.1
wt % (ZnSb)			51.5(4)	6.79(8)	-	-	-
wt % (Sb)		17.9(1)	28.9(2)	59.6(2)	61.2(2)	-	63.7(4)
wt % (ZnO)			19.6(6)	33.6(3)	34.8(2)	99.2(6)	31.8(4)
wt % (ZnSb ₂ O ₄)			-	-	3.97(5)	0.83(7)	4.6(1)
ZnSb	Sb-x	0.14295	0.14295	0.14295	-	-	-
	Sb-y	0.08198	0.08198	0.08198	-	-	-
	Sb-z	0.10832	0.10832	0.10832	-	-	-
	Sb-B _{iso}	1.39(2)	1.56(3)	2.1(1)	-	-	-
	Sb-occ.	1	1	1	-	-	-
	Zn-x	0.45786	0.45786	0.45786	-	-	-
	Zn-y	0.10971	0.10971	0.10971	-	-	-
	Zn-z	0.87013	0.87013	0.87013	-	-	-
	Zn-B _{iso}	3.10(4)	3.79(6)	5.0(2)	-	-	-
	Zn-occ.	1	1	1	-	-	-
	a (Å)	6.24228(4)	6.25751(4)	6.2716(1)	-	-	-
	b (Å)	7.76680(5)	7.77695(5)	7.7855(1)	-	-	-
	c (Å)	8.10576(5)	8.10921(5)	8.1094(1)	-	-	-
Sb	z	0.23246	0.23246	0.23246	0.23377(3)	-	0.23383(6)
	B _{iso}	1.42(4)	2.04(3)	2.51(1)	3.06(2)	-	1.02(2)
	a (Å)	4.31762(5)	4.32132(3)	4.32476(2)	4.32796(2)	-	4.30726(4)
	b (Å)	4.31762(5)	4.32132(3)	4.32476(2)	4.32796(2)	-	4.30726(4)
	c (Å)	11.3422(2)	11.35722(9)	11.36766(7)	11.38047(7)	-	11.2882(1)
ZnO	Zn/O B _{iso}	0	0.2(2)	0.53(4)	1.67(3)	1.73(2)	0.566(5)
	a (Å)	3.2580(3)	3.2602(2)	3.26050(7)	3.26283(6)	3.26555(9)	3.24978(9)
	b (Å)	3.2580(3)	3.2602(2)	3.26050(7)	3.26283(6)	3.26555(9)	3.24978(9)
	c (Å)	5.2140(1)	5.2180(7)	5.2217(2)	5.2222(1)	5.2231(2)	5.2057(2)
ZnSb ₂ O ₄	a (Å)	-	-	-	8.5890(2)	8.6025(8)	8.5203(3)
	b (Å)	-	-	-	8.5890(2)	8.6025(8)	8.5203(3)
	c (Å)	-	-	-	5.9493(3)	5.9537(7)	5.9317(3)

Tabel S3 (continued): Parameters from Rietveld analysis on multi-temperature synchrotron PXRD data measured on powder from the main body of the pellet synthesized at 100 MPa, a ramping time of 10 minutes, a sintering time of 15 minutes, and a maximum temperature of 698 K. The standard error of estimate is specified in parenthesis after a number. If no standard error of estimate is given, then the parameter has not been refined.