# From $NaZn_4Sb_3$ to *HT*-$Na_{1-x}Zn_{4-y}Sb_3$: panoramic hydride synthesis, structure diversity, and thermoelectric properties

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# Supporting Information

**Table S1.** Experimental details and crystallographic data for the $NaZn_4Sb_3$ and *HT*-$Na_{1-x}Zn_{4-y}Sb_3$ compounds. Rietveld refinement was done using high resolution synchrotron X-ray powder diffraction data (11-BM APS).

| Empirical formula | $NaZn_4Sb_3$* | *HT*-$Na_{1-x}Zn_{4-y}Sb_3$ |
|---|---|---|
| Formula weight, g/mol | 649.76 | 641.58 |
| Space group, *Z* | $P6_3/mmc$, 2 | $P2_1/c$, 32 |
| Cell parameters: *a*, Å | 4.43579(4) | 19.5366(7) |
| *b*, Å | | 14.7410(5) |
| *c*, Å | 23.41553(9) | 20.7808(7) |
| *β*, ° | | 90.317(2) |
| *V*, Å$^3$ | 399.003(5) | 5984.6(5) |
| Temperature, K | 298 | 298 |
| Wavelength, Å | $\lambda$ = 0.412804 | $\lambda$ = 0.412804 |
| Step scan increment | 0.001 | 0.001 |
| 2$\theta$° range | 0.5-50 | 1.5-34 |
| Program | GSAS II | GSAS II |
| $R_B$ | 0.12 | 0.12 |
| $R_P$ | 0.10 | 0.10 |
| *Goof* | 3.20 | 4.26 |

* Further details of the crystal structure refinement can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD 1919786.

**Table S2.** Atomic coordinates and isotropic displacement parameters of *HT*-$Na_{1-x}Zn_{4-y}Sb_3$ ($P2_1/c$, *mP*252, $a$ = 19.508(3) Å, $b$ = 14.708(3) Å, $c$ = 20.736(4) Å, $\beta$ = 90.402(5)°) from the refinement of single crystal X-ray diffraction data at 100 K. The split Zn/Sb are *italicized*.

| Site | Wyckoff site | *occ.* | *x* | *y* | *z* | $U_{eq}$, Å$^{2*}$ |
|---|---|---|---|---|---|---|
| Sb(1) | 4*e* | 1 | 0.04289(3) | 0.11780(5) | 0.15935(3) | 0.0116(1) |
| Sb(2) | 4*e* | 1 | 0.04446(3) | 0.62057(5) | 0.15950(3) | 0.0119(1) |
| Sb(3) | 4*e* | 1 | 0.67521(3) | 0.37728(5) | 0.15270(3) | 0.0117(1) |
| Sb(4) | 4*e* | 1 | 0.17585(3) | 0.12730(5) | 0.35154(3) | 0.0116(1) |
| Sb(5) | 4*e* | 1 | 0.54409(3) | 0.38534(5) | 0.33886(3) | 0.0121(1) |
| Sb(6) | 4*e* | 1 | 0.45995(3) | 0.38033(5) | 0.15738(3) | 0.0116(1) |
| Sb(7) | 4*e* | 1 | 0.32664(3) | 0.37886(5) | 0.35140(3) | 0.0119(1) |
| Sb(8) | 4*e* | 1 | 0.08942(3) | 0.37194(5) | 0.28427(3) | 0.0118(1) |
| Sb(9) | 4*e* | 1 | 0.08608(3) | 0.87472(5) | 0.29380(3) | 0.0119(1) |
| Sb(10) | 4*e* | 1 | 0.59286(3) | 0.13000(4) | 0.21091(3) | 0.0118(1) |
| Sb(11) | 4*e* | 1 | 0.40464(3) | 0.13339(5) | 0.28479(3) | 0.0124(1) |
| Sb(12) | 4*e* | 1 | 0.17274(3) | 0.62361(5) | 0.35254(3) | 0.0123(1) |
| Sb(13) | 4*e* | 1 | 0.68440(3) | 0.11946(5) | 0.01137(3) | 0.0122(1) |
| Sb(14) | 4*e* | 1 | 0.08031(3) | 0.62205(5) | 0.55689(3) | 0.0126(1) |
| Sb(15) | 4*e* | 1 | 0.81084(4) | 0.37283(5) | 0.01142(3) | 0.0127(1) |
| Sb(16) | 4*e* | 1 | 0.42514(3) | 0.13140(5) | 0.05826(3) | 0.0128(1) |
| Sb(17) | 4*e* | 0.955(3) | 0.24854(4) | 0.01667(7) | 0.16924(4) | 0.0120(2) |
| *Sb(25)* | 4*e* | 0.045(3) | 0.2525(10) | 0.5149(16) | 0.6669(10) | 0.0120(2) |
| Sb(18) | 4*e* | 1 | 0.07598(3) | 0.37190(5) | 0.04981(3) | 0.0123(1) |
| Sb(19) | 4*e* | 1 | 0.19085(4) | 0.37104(5) | 0.48126(3) | 0.0132(1) |
| Sb(20) | 4*e* | 1 | 0.31418(3) | 0.11471(5) | 0.48770(3) | 0.0122(1) |
| Sb(21) | 4*e* | 0.967(2) | 0.24732(4) | 0.27765(5) | 0.16596(3) | 0.0120(2) |
| *Sb(26)* | 4*e* | 0.033(2) | 0.2507(11) | 0.2256(18) | 0.1663(10) | 0.0120(2) |
| Sb(22) | 4*e* | 1 | 0.57057(4) | 0.12705(5) | 0.43936(3) | 0.0135(1) |
| Sb(23) | 4*e* | 1 | 0.24746(4) | 0.73713(5) | 0.16767(3) | 0.0141(1) |
| Sb(24) | 4*e* | 0.870(4) | 0.24886(7) | 0.47406(8) | 0.16525(7) | 0.0101(2) |
| *Sb(27)* | 4*e* | 0.130(4) | 0.2488(6) | 0.4969(6) | 0.1660(6) | 0.0101(2) |
| Zn(1) | 4*e* | 1 | 0.56647(6) | 0.30735(8) | 0.22265(6) | 0.0138(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Zn(2) | 4*e* | 1 | 0.06902(6) | 0.19350(8) | 0.27629(6) | 0.0144(2) |
| Zn(3) | 4*e* | 1 | 0.13810(6) | 0.03588(9) | 0.23905(6) | 0.0155(2) |
| Zn(4) | 4*e* | 1 | 0.43640(6) | 0.30727(8) | 0.27783(6) | 0.0143(2) |
| Zn(5) | 4*e* | 1 | 0.36860(6) | 0.29314(8) | 0.08465(6) | 0.0149(2) |
| Zn(6) | 4*e* | 1 | 0.06634(6) | 0.69584(8) | 0.27633(6) | 0.0151(2) |
| Zn(7) | 4*e* | 1 | 0.46878(7) | 0.06214(9) | 0.17633(6) | 0.0169(3) |
| Zn(8) | 4*e* | 1 | 0.36269(6) | 0.45190(9) | 0.23651(6) | 0.0166(2) |
| Zn(9) | 4*e* | 1 | 0.80778(6) | 0.44175(9) | 0.13358(6) | 0.0155(2) |
| Zn(10) | 4*e* | 1 | 0.03578(6) | 0.57613(9) | 0.67443(6) | 0.0160(2) |
| Zn(11) | 4*e* | 1 | 0.30896(7) | 0.06555(9) | 0.36045(6) | 0.0176(3) |
| Zn(12) | 4*e* | 1 | 0.13172(6) | 0.71414(9) | 0.08796(6) | 0.0151(2) |
| Zn(13) | 4*e* | 1 | 0.19131(6) | 0.43353(9) | 0.35707(6) | 0.0169(3) |
| Zn(14) | 4*e* | 1 | 0.74347(7) | 0.24834(9) | 0.08130(6) | 0.0177(2) |
| Zn(15) | 4*e* | 1 | 0.69623(7) | 0.06254(9) | 0.14360(7) | 0.0179(3) |
| Zn(16) | 4*e* | 0.812(10) | 0.5227(2) | 0.0584(2) | 0.3210(2) | 0.0162(5) |
| *Zn(32)* | 4*e* | 0.188(10) | 0.5100(7) | 0.0527(9) | 0.3383(7) | 0.0162(5) |
| Zn(17) | 4*e* | 0.955(3) | 0.22183(6) | 0.62419(9) | 0.58147(6) | 0.0142(3) |
| Zn(18) | 4*e* | 1 | 0.78659(6) | 0.28889(9) | 0.21414(6) | 0.0169(3) |
| Zn(19) | 4*e* | 1 | 0.19391(7) | 0.46310(9) | 0.04620(6) | 0.0176(3) |
| Zn(20) | 4*e* | 0.955(3) | 0.67448(7) | 0.38248(9) | 0.28737(6) | 0.0156(3) |
| *Zn(33)* | 4*e* | 0.045(3) | 0.642(1) | 0.458(2) | 0.266(2) | 0.0156(3) |
| Zn(21) | 4*e* | 1 | 0.06084(9) | 0.43862(10) | 0.16934(7) | 0.0261(3) |
| Zn(22) | 4*e* | 1 | 0.60769(7) | 0.29698(9) | 0.42781(7) | 0.0219(3) |
| Zn(23) | 4*e* | 0.967(2) | 0.34351(7) | 0.14237(9) | 0.16430(7) | 0.0163(3) |
| Zn(24) | 4*e* | 1 | 0.14493(7) | 0.03569(9) | 0.07938(6) | 0.0183(3) |
| Zn(25) | 4*e* | 1 | 0.13449(7) | 0.22726(9) | 0.10138(7) | 0.0194(3) |
| Zn(26) | 4*e* | 1 | 0.19335(7) | 0.19321(9) | 0.47627(6) | 0.0180(3) |
| Zn(27) | 4*e* | 0.812(10) | 0.3090(1) | 0.5543(2) | 0.0355(2) | 0.0206(6) |
| *Zn(34)* | 4*e* | 0.188(10) | 0.3155(6) | 0.5614(8) | 0.0113(8) | 0.0206(6) |
| Zn(28) | 4*e* | 1 | 0.34885(7) | 0.62322(10) | 0.16586(7) | 0.0209(3) |
| Zn(29) | 4*e* | 0.955(4) | 0.23981(10) | 0.2642(1) | 0.29186(7) | 0.0290(5) |
| *Zn(35)* | 4*e* | 0.045(4) | 0.277(2) | 0.219(3) | 0.291(2) | 0.0290(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Zn(30) | 4*e* | 0.870(4) | 0.16757(8) | 0.59399(12) | 0.22346(8) | 0.0193(4) |
| *Zn(36)* | 4*e* | 0.130(4) | 0.1459(5) | 0.5446(9) | 0.2342(5) | 0.0193(4) |
| Zn(31) | 4*e* | 0.813(9) | 0.30788(13) | 0.0601(2) | 0.0197(2) | 0.0321(8) |
| *Zn(37)* | 4*e* | 0.187(9) | 0.3206(6) | 0.4323(7) | 0.4895(9) | 0.0321(8) |
| Na(1) | 4*e* | 1 | 0.5636(2) | 0.2488(3) | 0.0731(2) | 0.0217(10) |
| Na(2) | 4*e* | 1 | 0.0520(2) | 0.2595(3) | 0.4222(2) | 0.0192(9) |
| Na(3) | 4*e* | 1 | 0.4294(2) | 0.2455(3) | 0.4277(2) | 0.0197(9) |
| Na(4) | 4*e* | 1 | 0.0577(2) | 0.0009(3) | 0.4310(2) | 0.0201(9) |
| Na(5) | 4*e* | 0.813(9) | 0.4420(3) | 0.4971(4) | 0.4354(3) | 0.022(1) |
| Na(6) | 4*e* | 1 | 0.0620(2) | 0.7507(3) | 0.4309(2) | 0.0187(9) |
| Na(7) | 4*e* | 1 | 0.0635(2) | 0.5035(3) | 0.4325(2) | 0.0191(9) |
| Na(8) | 4*e* | 0.812(10) | 0.5609(3) | 0.4926(4) | 0.0623(3) | 0.028(2) |

*$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

$U_{eq}$ parameters for the split Zn/Sb sites were constrained to be the same.

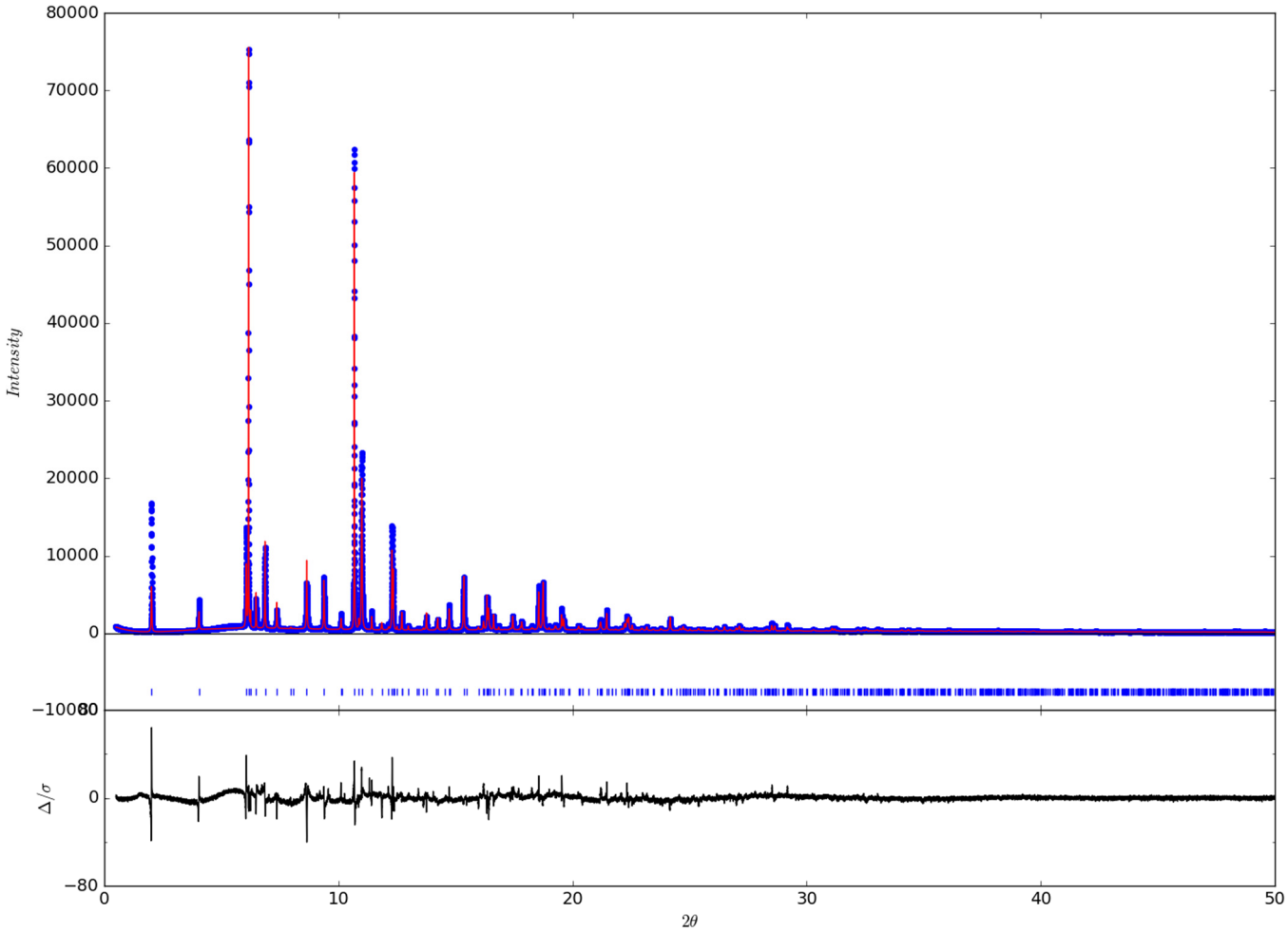


**Figure S1.** Rietveld refinement of **s**ynchrotron X-ray powder diffractogram of $NaZn_4Sb_3$ compound (experimental powder pattern is in blue, calculated – in red, difference – in black, $R_B$= 0.12, $R_p$ = 0.10, *Goof* = 3.20).

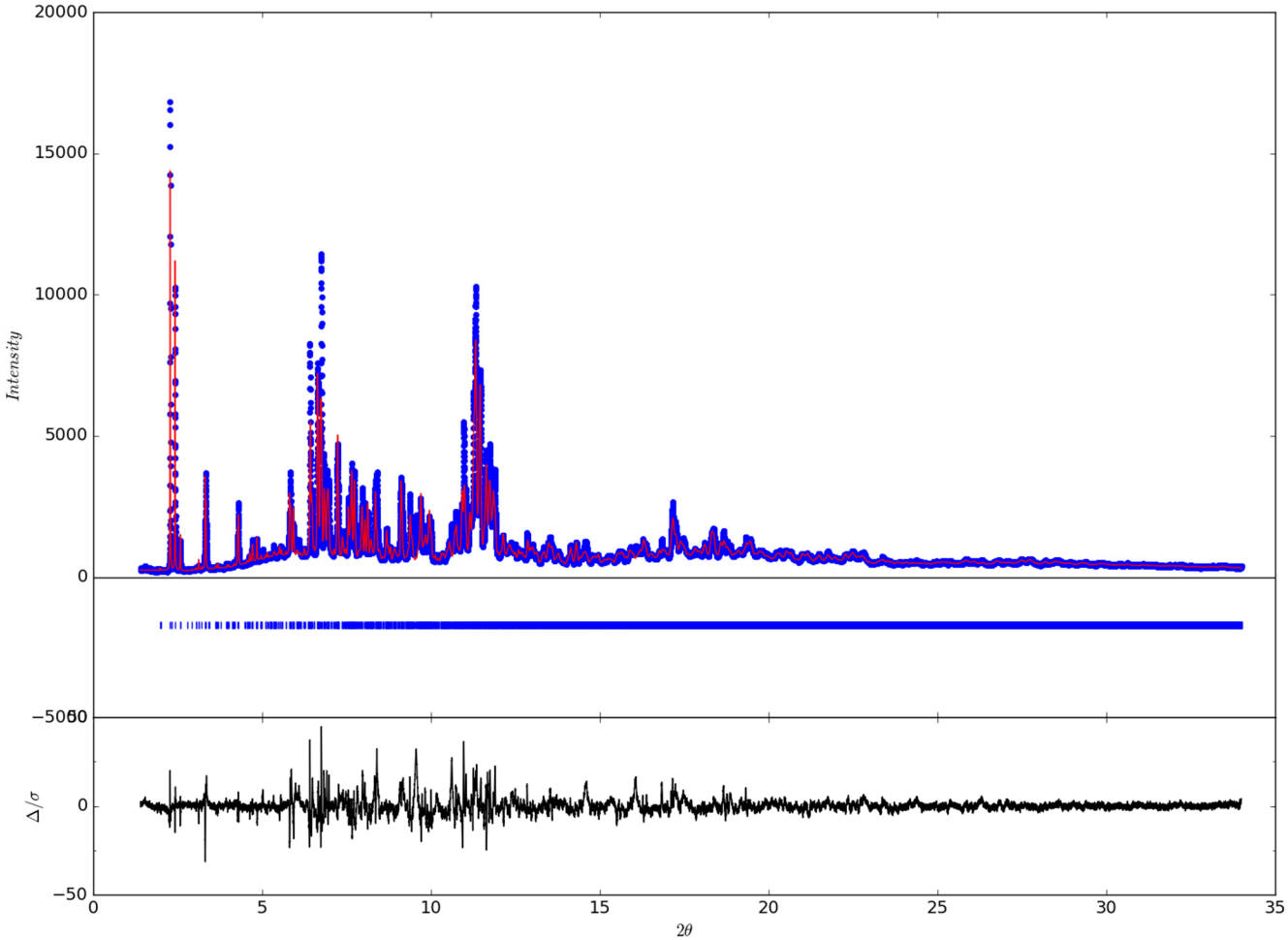


**Figure S2.** Fitting of the structure model of compound *HT*-$Na_{1-x}Zn_{4-y}Sb_3$ (determined from single crystal data) with synchrotron X-ray powder diffraction data (experimental powder pattern is in blue color, calculated – in red, difference – in black, $R_B = 0.12$, $R_p = 0.10$, $GOF = 4.26$).

**Table S3.** Selected interatomic distances in the structure of *HT*-$Na_{1-x}Zn_{4-y}Sb_3$ compound. The split Zn/Sb sites or Na/Zn sites with partial occupancy are *italicized*. The unrealistically short distances due to the split sites are not shown.

| Atom | Atom | *d*, Å | Atom | Atom | *d*, Å | Atom | Atom | *d*, Å |
|---|---|---|---|---|---|---|---|---|
| Sb1 | Zn6 | 2.695(2) | Sb2 | Zn12 | 2.651(1) | Sb3 | *Zn33* | 2.71(3) |
| | Zn2 | 2.713(2) | | Zn6 | 2.695(2) | | Zn14 | 2.755(2) |
| | Zn3 | 2.755(1) | | Zn21 | 2.703(2) | | Zn1 | 2.776(2) |
| | Zn6 | 2.771(2) | | *Zn36* | 2.74(2) | | Zn9 | 2.785(2) |
| | Zn24 | 2.867(2) | | Zn30 | 2.763(2) | | Zn20 | 2.794(2) |
| | Zn10 | 2.873(2) | | Zn2 | 2.805(2) | | Zn11 | 2.8000(2) |
| | Na7 | 3.385(5) | | Na4 | 3.246(5) | | Zn18 | 2.828(2) |
| | Na6 | 3.385(6) | | Na2 | 3.246(5) | | Na1 | 3.314(5) |
| | | | | | | | *Na8* | 3.363(7) |
| Sb4 | Zn29 | 2.677(2) | Sb5 | Zn22 | 2.569(2) | Sb6 | *Zn32* | 2.60(1) |
| | *Zn35* | 2.71(3) | | Zn7 | 2.631(2) | | Zn5 | 2.657(1) |
| | Zn11 | 2.756(2) | | *Zn33* | 2.67(3) | | Zn16 | 2.678(3) |
| | Zn9 | 2.765(2) | | Zn4 | 2.701(1) | | Zn1 | 2.695(1) |
| | Zn2 | 2.771(1) | | Zn1 | 2.707(1) | | Zn8 | 2.728(2) |
| | Zn26 | 2.781(2) | | Zn20 | 2.766(2) | | Zn4 | 2.760(2) |
| | Zn3 | 2.787(2) | | *Na5* | 3.277(6) | | *Na8* | 3.247(6) |
| | Na4 | 3.396(5) | | Na3 | 3.562(5) | | Na1 | 3.307(5) |
| | Na2 | 3.438(5) | | | | | | |
| Sb7 | Zn29 | 2.685(2) | Sb8 | Zn21 | 2.633(2) | Sb9 | Zn6 | 2.683(2) |
| | Zn8 | 2.711(2) | | Zn13 | 2.647(2) | | Zn9 | 2.736(1) |
| | Zn15 | 2.741(2) | | Zn2 | 2.660(2) | | Zn10 | 2.753(2) |
| | Zn13 | 2.763(2) | | Zn10 | 2.704(2) | | Zn18 | 2.792(2) |
| | *Zn35* | 2.83(3) | | *Zn36* | 2.96(2) | | Zn3 | 2.820(2) |
| | Zn4 | 2.840(1) | | Na2 | 3.388(5) | | Zn21 | 3.117(2) |
| | *Zn37* | 2.97(2) | | Na7 | 3.669(5) | | Na6 | 3.414(5) |
| | Na3 | 3.214(5) | | | | | Na4 | 3.444(5) |
| | *Na5* | 3.327(6) | | | | | | |
| Sb10 | Zn15 | 2.653(2) | Sb11 | *Zn32* | 2.61(1) | Sb12 | Zn15 | 2.710(2) |
| | Zn1 | 2.671(2) | | Zn4 | 2.636(2) | | Zn30 | 2.713(2) |
| | Zn7 | 2.710(2) | | Zn11 | 2.642(2) | | *Zn36* | 2.76(1) |
| | Zn28 | 2.792(2) | | Zn16 | 2.656(3) | | Zn14 | 2.809(2) |
| | Zn16 | 2.870(4) | | Zn23 | 2.764(2) | | Zn6 | 2.809(1) |
| | Zn8 | 2.965(2) | | Zn7 | 2.786(2) | | Zn13 | 2.821(2) |
| | Na1 | 3.395(5) | | *Zn35* | 2.79(5) | | Zn18 | 2.910(2) |
| | *Na5* | 3.669(6) | | *Zn33* | 2.92(3) | | Na7 | 3.235(5) |
| | | | | Na3 | 3.423(5) | | Na6 | 3.294(5) |
| Sb13 | Zn22 | 2.591(2) | Sb14 | Zn10 | 2.680(2) | Sb15 | Zn12 | 2.678(1) |
| | Zn14 | 2.646(2) | | Zn24 | 2.680(2) | | Zn14 | 2.685(2) |
| | *Zn17* | 2.666(2) | | Zn12 | 2.686(2) | | *Zn34* | 2.69(1) |
| | Zn31 | 2.723(2) | | *Zn17* | 2.804(2) | | Zn19 | 2.694(2) |
| | *Zn37* | 2.76(1) | | Na7 | 3.130(5) | | Zn9 | 2.729(2) |
| | Zn15 | 2.875(2) | | Na2 | 3.146(5) | | Zn27 | 2.742(2) |
| | *Na5* | 3.251(6) | | Na6 | 3.243(5) | | Na6 | 3.282(5) |
| | Na1 | 3.294(5) | | Na7 | 3.366(5) | | Na4 | 3.393(5) |
| Sb16 | Zn31 | 2.636(2) | Sb17 | Zn3 | 2.619(2) | *Sb25* | *Zn33* | 2.52(3) |
| | *Zn37* | 2.65(1) | | Zn23 | 2.620(2) | | Zn3 | 2.80(2) |
| | Zn5 | 2.680(2) | | Zn20 | 2.635(2) | | Zn24 | 2.86(2) |
| | Zn23 | 2.729(2) | | *Zn33* | 2.67(3) | | Zn23 | 2.92(2) |
| | Zn7 | 2.780(2) | | Zn24 | 2.754(2) | | | |
| | *Na5* | 3.191(6) | | *Zn17* | 2.804(2) | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Na1 | 3.219(5) | | *Sb26* | 3.07(3) | | | |
| | Na3 | 3.258(5) | | | | | | |
| | *Na5* | 3.261(6) | | | | | | |
| Sb18 | Zn25 | 2.637(2) | Sb19 | Zn31 | 2.617(2) | Sb20 | Zn26 | 2.634(2) |
| | Zn19 | 2.665(2) | | Zn24 | 2.617(2) | | *Zn34* | 2.64(1) |
| | Zn21 | 2.684(2) | | Zn26 | 2.618(2) | | Zn5 | 2.641(1) |
| | Zn26 | 2.921(2) | | *Zn37* | 2.69(1) | | Zn27 | 2.678(2) |
| | Na4 | 3.113(5) | | Zn13 | 2.734(2) | | Zn11 | 2.737(2) |
| | Na4 | 3.252(5) | | Zn25 | 3.089(2) | | Zn19 | 2.885(2) |
| | Na6 | 3.256(5) | | Na7 | 3.311(5) | | *Na8* | 3.206(6) |
| | Na2 | 3.307(5) | | Na2 | 3.389(5) | | Na3 | 3.216(5) |
| Sb21 | Zn29 | 2.623(2) | *Sb26* | Zn25 | 2.63(2) | Sb22 | Zn22 | 2.614(2) |
| | Zn25 | 2.673(2) | | *Zn35* | 2.63(4) | | *Zn34* | 2.63(1) |
| | Zn23 | 2.735(2) | | Zn29 | 2.67(2) | | Zn27 | 2.632(3) |
| | *Zn35* | 2.79(4) | | Zn5 | 3.03(2) | | *Zn32* | 2.64(1) |
| | Sb24 | 2.889(2) | | Sb17 | 3.07(3) | | Zn28 | 2.699(2) |
| | Zn5 | 2.924(2) | | | | | Zn16 | 2.809(3) |
| | *Sb27* | 3.225(9) | | | | | *Na8* | 3.105(7) |
| | | | | | | | *Na8* | 3.238(7) |
| | | | | | | | Na3 | 3.266(5) |
| | | | | | | | Na1 | 3.323(5) |
| Sb23 | Zn28 | 2.593(2) | Sb24 | Zn30 | 2.666(2) | *Sb27* | *Zn36* | 2.56(2) |
| | Zn18 | 2.655(2) | | Zn8 | 2.679(2) | | Zn28 | 2.69(1) |
| | *Zn17* | 2.756(2) | | *Zn36* | 2.69(1) | | Zn8 | 2.73(1) |
| | Zn20 | 2.782(2) | | Zn19 | 2.689(2) | | Zn19 | 2.74(1) |
| | Zn12 | 2.809(2) | | Sb21 | 2.889(2) | | Zn27 | 3.08(1) |
| | Zn30 | 2.868(2) | | Zn28 | 2.936(2) | | Sb21 | 3.225(9) |
| | | | | Zn27 | 3.171(5) | | | |
| Zn1 | Sb10 | 2.671(2) | Zn2 | Sb8 | 2.660(2) | Zn3 | Sb17 | 2.619(2) |
| | Sb6 | 2.695(2) | | Sb1 | 2.713(2) | | Sb1 | 2.755(1) |
| | Sb5 | 2.707(1) | | Sb4 | 2.771(1) | | Sb4 | 2.787(2) |
| | Zn20 | 2.724(2) | | Zn3 | 2.793(2) | | Zn2 | 2.793(2) |
| | Sb03 | 2.776(1) | | Sb02 | 2.805(1) | | *Sb25* | 2.80(2) |
| | Zn4 | 2.791 (2) | | Zn6 | 2.850(2) | | Sb9 | 2.820(2) |
| | *Zn33* | 2.80(3) | | Na2 | 3.197(5) | | Zn10 | 2.908(2) |
| | Na1 | 3.219(5) | | | | | Zn9 | 3.157(2) |
| Zn4 | Sb11 | 2.636(2) | Zn5 | Sb20 | 2.641(1) | Zn6 | Sb9 | 2.683(2) |
| | Sb5 | 2.701(2) | | Sb6 | 2.657(1) | | Sb2 | 2.695(2) |
| | Zn8 | 2.704(2) | | Sb16 | 2.680(2) | | Zn30 | 2.716(2) |
| | Sb6 | 2.760(2) | | Zn23 | 2.810(2) | | Sb1 | 2.771(2) |
| | Zn1 | 2.791(2) | | Sb21 | 2.924(2) | | Sb12 | 2.809(1) |
| | Sb7 | 2.840(1) | | *Sb26* | 3.03(2) | | Zn2 | 2.850(2) |
| | Na3 | 3.242(5) | | Na3 | 3.518(5) | | *Zn36* | 2.85(1) |
| | | | | | | | Na6 | 3.307(5) |
| Zn7 | Sb5 | 2.631(2) | Zn8 | Sb24 | 2.679(2) | Zn9 | Sb15 | 2.729(2) |
| | Sb10 | 2.710(2) | | Zn4 | 2.704(2) | | Sb9 | 2.736(1) |
| | Zn23 | 2.724(2) | | Sb7 | 2.711(2) | | Sb4 | 2.765(2) |
| | Sb16 | 2.880(2) | | Sb6 | 2.728(2) | | Sb3 | 2.785(2) |
| | Sb11 | 2.786(2) | | *Sb27* | 2.733(1) | | Zn18 | 2.833(2) |
| | *Zn33* | 2.91(3) | | Zn28 | 2.926(2) | | Zn11 | 2.919(2) |
| | *Na5* | 3.062(6) | | Sb10 | 2.965(2) | | Na4 | 3.080(5) |
| | | | | Zn16 | 2.985(3) | | Zn3 | 3.157(2) |
| Zn10 | Sb14 | 2.680(2) | Zn11 | Sb11 | 2.643(2) | Zn12 | Sb2 | 2.651(1) |
| | Sb8 | 2.704(2) | | Sb20 | 2.737(2) | | Sb15 | 2.678(1) |
| | Sb9 | 2.753(2) | | *Zn35* | 2.75(4) | | Sb14 | 2.687(2) |
| | Sb1 | 2.873(2) | | Sb4 | 2.756(2) | | Sb23 | 2.809(2) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Zn3 | 2.908(2) | | Sb3 | 2.800(2) | | *Zn17* | 2.961(2) |
| | Na7 | 3.158(5) | | Zn9 | 2.919(2) | | Na6 | 3.558(5) |
| | Na2 | 3.570(5) | | *Na8* | 3.180(7) | | Na2 | 3.650(5) |
| Zn13 | Sb8 | 2.647(2) | Zn14 | Sb13 | 2.646(2) | Zn15 | Sb10 | 2.653(2) |
| | Sb19 | 2.734(2) | | Sb15 | 2.685(2) | | Sb12 | 2.710(2) |
| | Sb7 | 2.763(2) | | Sb3 | 2.755(2) | | Sb7 | 2.741(2) |
| | Sb12 | 2.821(2) | | Sb12 | 2.809(2) | | Sb13 | 2.875(2) |
| | Zn15 | 2.901(2) | | Zn18 | 2.936(2) | | Zn13 | 2.901(2) |
| | Zn29 | 2.991(2) | | Na1 | 3.511(5) | | *Na5* | 3.289(6) |
| | Na7 | 3.127(5) | | | | | | |
| Zn16 | Sb11 | 2.656(3) | *Zn32* | Sb06 | 2.60(1) | *Zn17* | Sb13 | 2.666(2) |
| | Sb6 | 2.678(3) | | Sb11 | 2.61(1) | | Sb23 | 2.756(2) |
| | Zn28 | 2.694(3) | | Sb22 | 2.64(1) | | Zn24 | 2.790(2) |
| | Sb22 | 2.809(3) | | *Na8* | 2.64(2) | | Sb14 | 2.804(2) |
| | Sb10 | 2.870(4) | | Zn28 | 2.94(2) | | Sb17 | 2.804(2) |
| | Zn8 | 2.985(3) | | | | | Zn12 | 2.961(2) |
| | *Na8* | 3.083(7) | | | | | | |
| Zn18 | Sb23 | 2.655(2) | Zn19 | Zn27 | 2.625(3) | Zn20 | Sb17 | 2.635(2) |
| | Sb9 | 2.792(2) | | Sb18 | 2.665(2) | | Zn1 | 2.724(2) |
| | Sb3 | 2.828(2) | | Sb24 | 2.689(2) | | Sb5 | 2.766(2) |
| | Zn9 | 2.833(2) | | Sb15 | 2.694(2) | | Sb23 | 2.782(2) |
| | Sb12 | 2.910(2) | | Zn26 | 2.718(2) | | Sb3 | 2.794(2) |
| | Zn14 | 2.936(2) | | *Sb27* | 2.74(1) | | Zn18 | 3.005(2) |
| | Zn20 | 3.005(2) | | *Zn34* | 2.87(1) | | | |
| | | | | Sb20 | 2.885(2) | | | |
| | | | | Na4 | 3.600(5) | | | |
| *Zn33* | *Sb25* | 2.52(3) | Zn21 | Sb8 | 2.633(2) | Zn22 | Sb5 | 2.569(2) |
| | Sb17 | 2.67(3) | | *Zn36* | 2.64(1) | | Sb13 | 2.591(2) |
| | Sb5 | 2.67(3) | | Sb18 | 2.684(2) | | Sb22 | 2.614(2) |
| | Sb3 | 2.71(3) | | Sb2 | 2.703(2) | | Na1 | 3.210(5) |
| | Zn1 | 2.80(3) | | Sb9 | 3.117(2) | | Na3 | 3.559(5) |
| | Zn7 | 2.91(3) | | Na4 | 3.232(5) | | | |
| | Sb11 | 2.92(3) | | | | | | |
| Zn23 | Sb17 | 2.620(2) | Zn24 | Sb19 | 2.617(2) | Zn25 | *Sb26* | 2.63(2) |
| | Zn7 | 2.724(2) | | Sb14 | 2.680(2) | | Sb18 | 2.637(2) |
| | Sb16 | 2.729(2) | | Sb17 | 2.754(2) | | Sb21 | 2.673(2) |
| | Sb21 | 2.735(2) | | *Zn17* | 2.790(2) | | Sb1 | 2.695(2) |
| | Sb11 | 2.764(2) | | Zn25 | 2.862(2) | | Zn24 | 2.862(2) |
| | Zn5 | 2.810(2) | | *Sb25* | 2.86(2) | | Sb19 | 3.089(2) |
| | *Sb25* | 2.92(2) | | Sb01 | 2.867(2) | | | |
| | | | | Na7 | 3.475(5) | | | |
| Zn26 | Sb19 | 2.618(2) | Zn27 | Zn19 | 2.625(3) | *Zn34* | Sb22 | 2.63(1) |
| | Sb20 | 2.634(2) | | Sb22 | 2.632(3) | | Sb20 | 2.64(1) |
| | Zn19 | 2.718(2) | | Sb20 | 2.678(2) | | Sb15 | 2.69(1) |
| | Sb04 | 2.781(2) | | Sb15 | 2.742(2) | | Zn19 | 2.87(1) |
| | Sb18 | 2.921(2) | | Zn28 | 2.985(4) | | *Na8* | 2.97(1) |
| | Zn25 | 3.076(2) | | *Sb27* | 3.08(1) | | | |
| | Na2 | 3.126(5) | | Sb24 | 3.1701(5) | | | |
| | | | | *Na8* | 3.333(7) | | | |
| Zn28 | Sb23 | 2.593(2) | Zn29 | Sb21 | 2.623(2) | *Zn35* | *Sb26* | 2.63(4) |
| | Zn16 | 2.694(3) | | *Sb26* | 2.67(2) | | Sb4 | 2.71(3) |
| | *Sb27* | 2.69(1) | | Sb4 | 2.677(2) | | Zn11 | 2.75(4) |
| | Sb22 | 2.699(2) | | Sb7 | 2.685(2) | | Sb11 | 2.79(5) |
| | Sb10 | 2.792(2) | | | | | Sb21 | 2.79(4) |
| | Zn8 | 2.926(2) | | | | | Sb07 | 2.83(3) |
| | Sb24 | 2.936(2) | | | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *Zn32* | 2.94(1) | | | | | | |
| | Zn27 | 2.986(4) | | | | | | |
| Zn30 | Sb24 | 2.666(2) | *Zn36* | *Sb27* | 2.56(2) | Zn31 | Sb19 | 2.617(2) |
| | Sb12 | 2.713(2) | | Zn21 | 2.64(1) | | Sb16 | 2.636(2) |
| | Zn6 | 2.716(2) | | Sb24 | 2.68(1) | | Sb13 | 2.723(2) |
| | Sb2 | 2.763(2) | | Sb2 | 2.74(1) | | *Na5* | 3.266(6) |
| | Sb23 | 2.868(2) | | Sb12 | 2.76(1) | | | |
| | | | | Zn6 | 2.85(1) | | | |
| | | | | Sb08 | 2.96(1) | | | |
| *Zn37* | Sb16 | 2.65(1) | | | | | | |
| | Sb19 | 2.69(1) | | | | | | |
| | Sb13 | 2.75(1) | | | | | | |
| | Sb7 | 2.97(2) | | | | | | |
| Na1 | Sb16 | 3.219(5) | Na2 | Sb14 | 3.146(5) | Na3 | Sb07 | 3.214(5) |
| | Sb13 | 3.294(5) | | Sb2 | 3.247(5) | | Sb20 | 3.216(5) |
| | Sb6 | 3.307(5) | | Sb18 | 3.307(5) | | Sb16 | 3.258(5) |
| | Sb3 | 3.314(5) | | Sb08 | 3.388(5) | | Sb22 | 3.266(5) |
| | Sb22 | 3.323(5) | | Sb19 | 3.389(5) | | Sb11 | 3.423(5) |
| | Sb10 | 3.395(5) | | Sb4 | 3.438(5) | | Sb5 | 3.562(5) |
| | *Na8* | 3.593(8) | | Na7 | 3.602(7) | | *Na5* | 3.712(7) |
| | *Na5* | 3.707(8) | | Na6 | 3.786(7) | | *Na8* | 3.731(8) |
| Na4 | Sb18 | 3.113(5) | *Na5* | Sb16 | 3.191(6) | Na6 | Sb14 | 3.243(5) |
| | Sb2 | 3.246(5) | | Sb13 | 3.251(6) | | Sb18 | 3.255(5) |
| | Sb18 | 3.252(5) | | Sb16 | 3.261(6) | | Sb15 | 3.282(5) |
| | Sb15 | 3.392(5) | | Sb05 | 3.277(6) | | Sb12 | 3.294(5) |
| | Sb4 | 3.396(5) | | Sb07 | 3.327(6) | | Sb1 | 3.385(5) |
| | Sb9 | 3.444(5) | | *Na5* | 3.50(1) | | Sb9 | 3.414(5) |
| | Na4 | 3.655(9) | | Sb10 | 3.669(6) | | Na7 | 3.636(6) |
| | Na6 | 3.681(6) | | Na1 | 3.708(8) | | Na4 | 3.681(6) |
| Na7 | Sb14 | 3.130(5) | *Na8* | Sb22 | 3.104(7) | | | |
| | Sb12 | 3.235(5) | | Sb20 | 3.206(6) | | | |
| | Sb19 | 3.311(5) | | Sb22 | 3.238(6) | | | |
| | Sb14 | 3.366(5) | | Sb06 | 3.247(6) | | | |
| | Na2 | 3.602(7) | | Sb03 | 3.362(7) | | | |
| | Na6 | 3.636(6) | | *Na8* | 3.50(1) | | | |
| | Sb08 | 3.669(5) | | Na1 | 3.593(8) | | | |

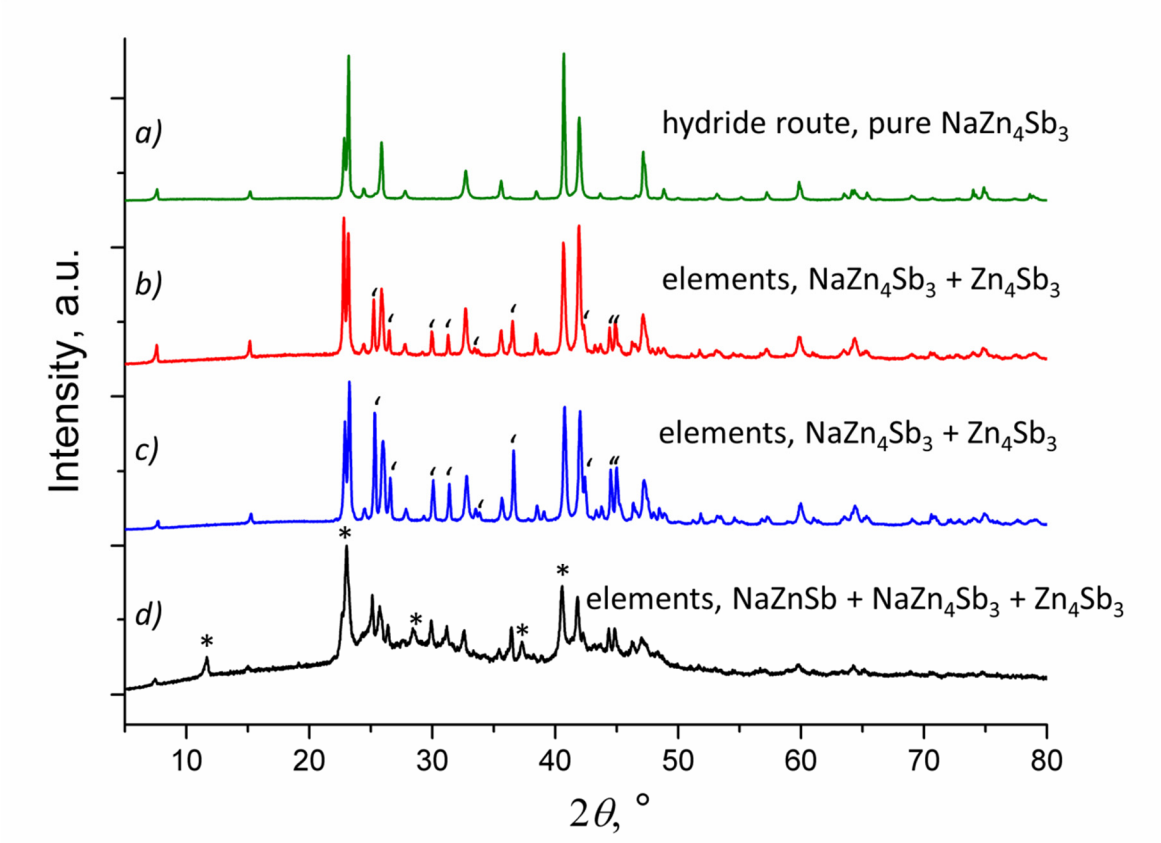


**Figure S3**. Comparison of X-ray powder diffraction patterns of *a)* $NaZn_4Sb_3$ sample synthesized via hydride route (NaH:Zn:Sb = 1:0.3:4:3 molar ratio); *b)* and *c)* chunks selected from inhomogeneous samples synthesized from elements with nominal Na:Zn:Sb molar ratio = of 1.7:4.7:3 and 1.3:4.3:3. With decreasing of Na and Zn content (moving to 1:4:3 ratio) fraction of binary zinc antimonide $Zn_4Sb_3$ impurity (peaks are marked with ´) increases; *d)* PXRD pattern of an inhomogeneous sample with nominal Na:Zn:Sb molar 1.3:4.3:3 indicates presence of considerable amount of NaZnSb phase in powdery form (peaks marked with *) together with $NaZn_4Sb_3$ and $Zn_4Sb_3$ phases present as chunks (in *c*).

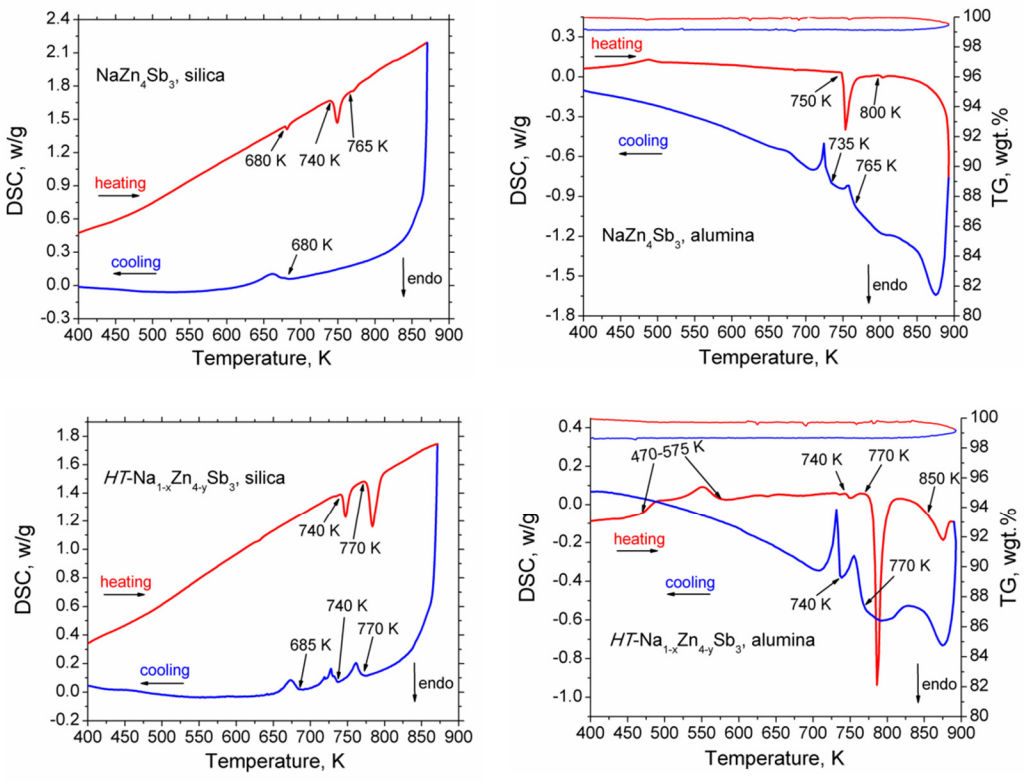


**Figure S4**. DSC showing the transformation of powdered sample $NaZn_4Sb_3$ (top) and *HT*-$Na_{1-x}Zn_{4-y}Sb_3$ (bottom) sealed into evacuated silica tube (left) or measured in alumina crucible under Ar flow (right).

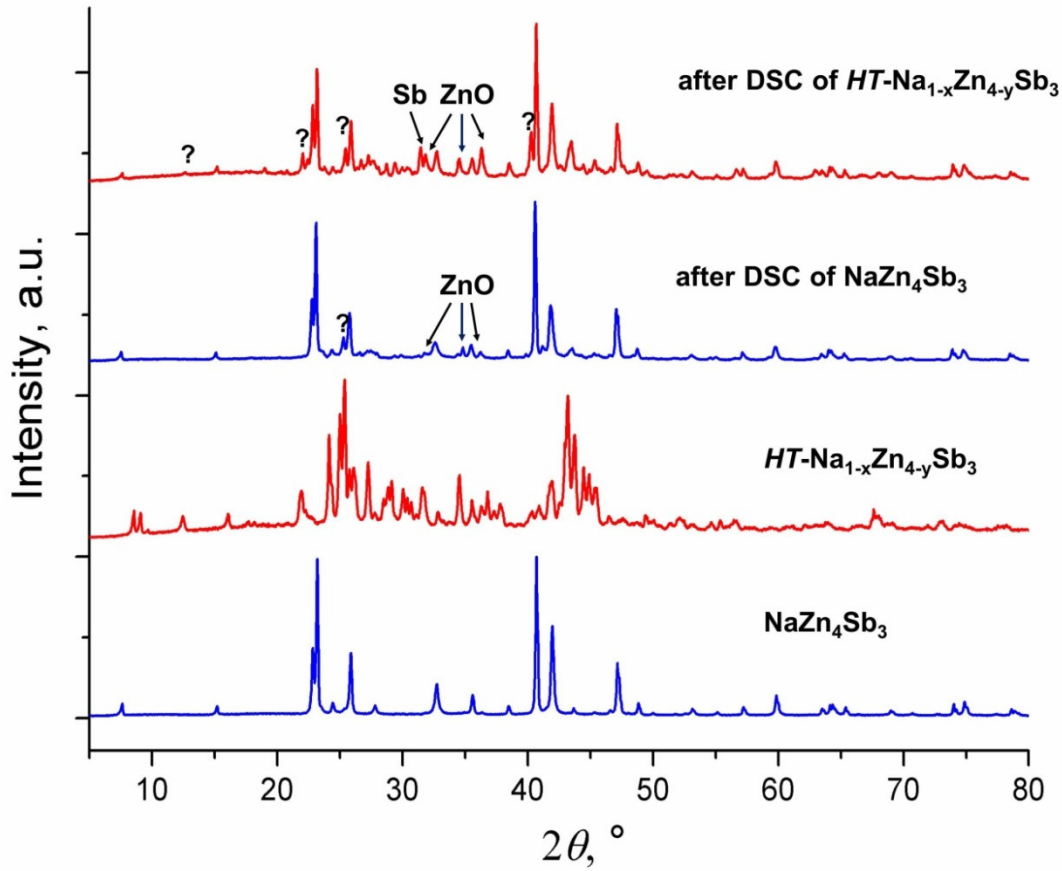


**Figure S5**. Comparison of X-ray powder diffraction patterns of $NaZn_4Sb_3$ and *HT*-$Na_{1-x}Zn_{4-y}Sb_3$ compounds before and after DSC measurement (in a evacuated and sealed silica crucible). Due to side reactions and/or Na/Zn elimination the sample after DSC contains $NaZn_4Sb_3$ together with traces of ZnO, Sb and another unknown compound(s) (peaks are labeled with ? marks).

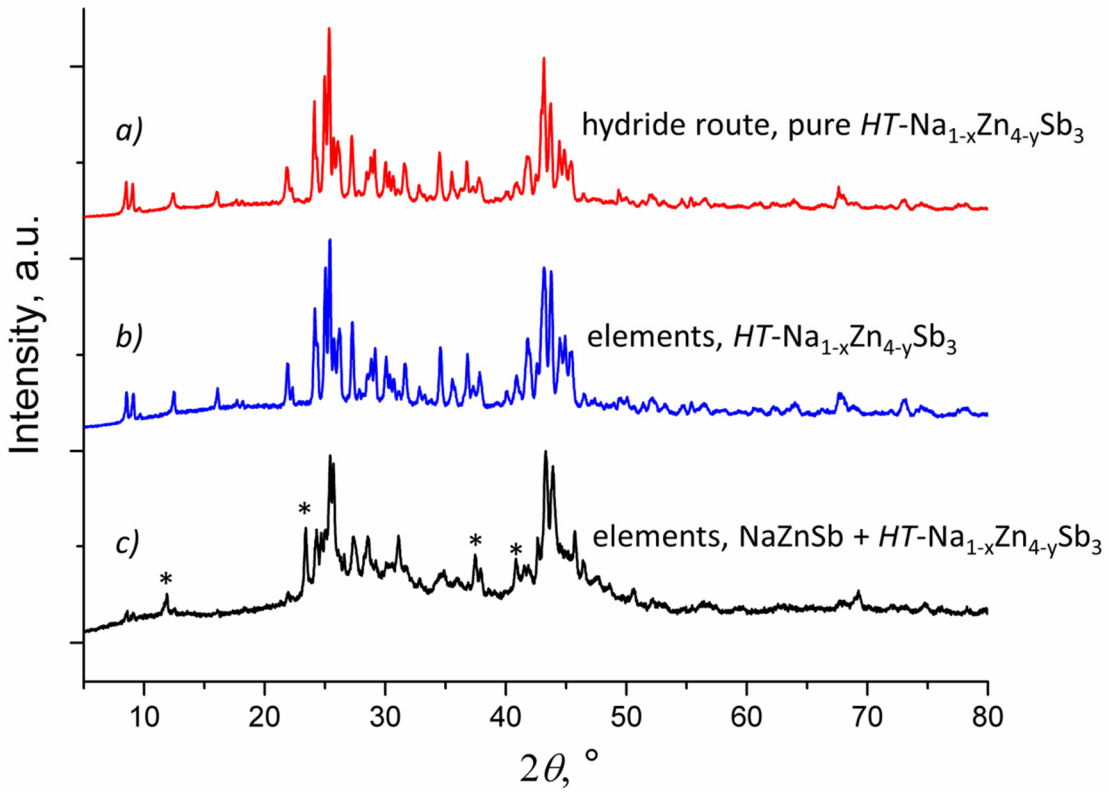


**Figure S6**. Comparison of X-ray powder diffraction patterns of *a)* *HT*-$Na_{1-x}Zn_{4-y}Sb_3$ phase synthesized via hydride route; *b)* chunks selected from inhomogeneous sample synthesized from elements with nominal compositions Na1.7:Zn4.7:Sb3; and *c)* diffractogram of initial sample Na1.7:Zn4.7:Sb3 shows on presence of considerable amount of NaZnSb phase (marked with *) together with *HT*-$Na_{1-x}Zn_{4-y}Sb_3$ phase present in chunks (*c)*).