Supporting Information

The First Ambient-Pressure Tin Borate $Sn_3B_4O_9$ and $Sn_2[B_7O_{12}]F$

Table S1: Crystal data and details oft he structure refinement of $Sn_3B_4O_9$ and $Sn_2[B_7O_{12}]F$.

Sum formula	**$Sn_3B_4O_9$**	**$Sn_2[B_7O_{12}]F$**
Molar mass / g·mol-1	543.65	524.05
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a / pm	768.07(3)	1037.99(2)
b / pm	1206.78(4)	859.78(2)
c / pm	924.96(3)	2370.71(8)
β /°	101.8470(10)	93.5650(10)
cell volume / $\cdot 10^6$ pm^3	839.08(5)	2111.63(10)
Z	4	8
$\rho_{X\text{-}ray}$ / g·cm^{-3}	4.301	3.297
Crystal dimensions / mm^3	0.110 × 0.060 × 0.030	0.080 × 0.025 × 0.010
Crystal shape	rod	block
Colour	colourless	colourless
Absorption coefficient μ / mm^{-1}	8.890	4.814
F(000)	968	1920
Used diffractometer	Bruker D8 Venture	Bruker D8 Venture
Radiation | λ / nm	Mo-K_α | 0.071073	Mo-K_α | 0.071073
Temperature / K	298(2)	297(2)
Index range $h_{min.}\|k_{min.}\|l_{min.}$; $h_{max.}\|k_{max.}\|l_{max.}$	-15|0|0; 14|24|18	-14|-12|-33; 14|12|33
Measured angle / °	$2.813 \le \theta \le 44.996$	$3.079 \le \theta \le 30.000$
Measured peak intensities	13906	36715
Symmetry independent peaks	13906	3084
Observed peaks (I>2σ)	10550	2674
Absorption correction	Multi-Scan	Multi-Scan
Transmission factor (min. / max.)	0.441 / 0.776	0.6858 / 0.7479
R_{int}		0.054
Refined parameters | restraints	147 | 0	199 | 0
R_σ	0.0356	0.024
R_1 (all data)	0.0276	0.045
wR_2 (all data)	0.0704	0.069
Weighing scheme	$\omega^{-1} = \sigma 2F_o^2 + (0.0237P)^2 + 1.1434P$; $P = (F_o^2 + 2F_c^2)/3$	$\omega^{-1} = \sigma 2F_o^2 + (0.0210P)^2 + 27.7161P$; $P = (F_o^2 + 2F_c^2)/3$
GooF	1.098	1.158

Table S2: Results of the MAPLE calculations, regarding the ligands of the tin and boron atoms in $Sn_3B_4O_9$.

#	atom	*x*	*y*	*z*	distance / pm	e-ECoN(1)	e-ECoN(3)
ZT	**Sn1**	0.3419	0.8544	0.3671			
1	O4	0.1670	0.7521	0.4679	217.087	1.065	1.067
2	O3	0.5457	0.7316	0.4508	217.862	1.037	1.039
3	O1	0.2408	0.7409	0.1919	214.211	1.010	1.011
4	O6	0.0691	0.9046	0.1494	266.083	0.059	0.060
next ligand:							
5	O8	0.4244	0.7712	0.6633	286.446	0.017	0.017
last ligand:							
21	O8	0.5756	1.2288	0.3367	489.159	0.000	0.000
coordination number: 4							

#	atom	*x*	*y*	*z*	distance / pm	e-ECoN(1)	e-ECoN(5)
ZT	**Sn2**	0.8995	0.8336	0.5486			
1	O1	0.7408	0.7591	0.6919	217.128	1.116	1.137
2	O5	1.1196	0.7609	0.7118	220.399	1.115	1.136
3	O2	0.8354	0.6761	0.4327	218.796	1.047	1.068
4	O4	1.167	0.7521	0.4679	252.452	0.395	0.411
next ligand:							
5	O9	1.0762	0.9326	0.8102	278.853	0.0380	0.042
last ligand:							
22	O7	1.2449	1.0987	0.8682	477.370	0.000	0.000
coordination number: 4							

#	atom	*x*	*y*	*z*	distance / pm	e-ECoN(1)	e-ECoN(3)
ZT	**Sn3**	0.9562	0.3890	0.6572			
1	O2	1.1646	0.3239	0.5673	210.132	1.089	1.097
2	O4	0.8330	0.2479	0.5321	216.455	1.071	1.079
3	O8	1.0756	0.2712	0.8367	223.46	0.855	0.863
next ligand:							
4	O1	0.7592	0.2591	0.8081	275.010	0.031	0.032
last ligand:							
24	O1	0.7408	0.7591	0.6919	479.685	0.000	0.000
coordination number: 3							

#	atom	*x*	*y*	*z*	distance / pm	e-ECoN(1)	e-ECoN(2)
ZT	**B1**	0.5714	0.7119	0.6115			
1	O3	0.5457	0.7316	0.4508	147.790	1.102	1.102
2	O8	0.4244	0.7712	0.6633	149.586	1.002	1.002
3	O6	0.5691	0.5954	0.6494	145.036	0.953	0.953
4	O1	0.7408	0.7591	0.6919	147.433	0.928	0.928
next ligand:							
9	O7	0.2551	0.5987	0.6318	282.670	0.000	0.000
last ligand:							
19	O9	1.0762	0.9326	0.8102	475.188	0.000	0.000
coordination number: 4							

#	atom	*x*	*y*	*z*	distance / pm	e-ECoN(1)	e-ECoN(2)
ZT	**B2**	0.4126	0.5410	0.6532			
1	O9	0.4238	0.4326	0.6898	134.944	1.068	1.068
2	O6	0.5691	0.5954	0.6494	137.643	0.976	0.977
3	O7	0.2551	0.5987	0.6318	137.426	0.948	0.948
next ligand:							
4	O8	0.4244	0.7712	0.6633	277.996	0.000	0.000
last ligand:							
22	O1	0.2408	0.7409	0.1919	484.305	0.000	0.000
coordination number: 3							

#	atom	*x*	*y*	*z*	distance / pm	e-ECoN(1)	e-ECoN(2)
ZT	**B3**	0.2458	0.7197	0.6235			
1	O8	0.4244	0.7712	0.6633	148.175	1.048	1.047
2	O5	0.1196	0.7609	0.7118	147.590	1.044	1.044
3	O4	0.1670	0.7521	0.4679	149.415	1.035	1.034
4	O7	0.2551	0.5987	0.6318	146.356	0.851	0.850
next ligand:							
5	O6	0.5691	0.5954	0.6494	286.919	0.000	0.000
last ligand:							
20	O6	0.4309	0.4046	0.3506	493.167	0.000	0.000
coordination number: 4							

#	atom	*x*	*y*	*z*	distance / pm	e-ECoN(1)	e-ECoN(2)
ZT	**B4**	0.3417	0.3259	0.6452			
1	O2	0.1646	0.3239	0.5673	140.257	1.196	1.200
2	O3	0.4543	0.2684	0.5492	152.759	0.913	0.916
3	O5	0.3804	0.2609	0.7882	151.413	0.910	0.914
4	O9	0.4238	0.4326	0.6898	145.578	0.909	0.913
next ligand:							
5	O8	0.0756	0.2712	0.8367	303.920	0.000	0.000
last ligand:							
21	O6	-0.0691	0.0954	0.8506	487.537	0.000	0.000
coordination number: 4							

Table S3: Results for the MAPLE calculations for all atoms in $Sn_3B_4O_9$, regarding charge, distance, obtained charge, partial maple factor (PMF) and MAPLE energies (*MAPLE: MAPLE / charge).

	charge	distance / pm	obtained charge	PMF	MAPLE	*MAPLE
Sn1	+2.0000	145.04	-3.15413	6.38445	1569.8554	174.4284
Sn2	+2.0000	134.94	-2.97120	6.01417	1478.8092	164.3121
Sn3	+2.0000	146.36	-3.16339	6.40320	1574.4661	174.9407
B1	+3.0000	140.26	-3.25799	6.59469	1621.5514	180.1724
B2	+3.0000	214.21	-1.37102	1.85011	454.9175	113.7294
B3	+3.0000	217.13	-1.42032	1.91664	471.2765	117.8191
B4	+3.0000	210.13	-1.43949	1.94250	477.6362	119.409
O1	-2.0000	147.43	1.57584	2.12650	522.8806	130.7202
O2	-2.0000	140.26	1.66291	2.24400	551.7707	137.9427
O3	-2.0000	147.79	1.88752	2.54709	626.2976	156.5744
O4	-2.0000	149.42	1.59677	2.15474	529.8244	132.4561
O5	-2.0000	147.59	1.83635	2.47804	609.3196	152.3299
O6	-2.0000	137.64	2.17114	2.92982	720.4067	180.1017
O7	-2.0000	137.43	2.14852	2.89930	712.9019	178.2255
O8	-2.0000	148.17	2.00892	2.71091	666.5792	166.6448
O9	-2.0000	134.94	2.12913	2.87313	706.4671	176.6168
			Madelung constant:	54.0693 ± 0.000002		
			Coulomb portion of the lattice energy:	13294.96000 ± 0.000597 kcal·mol^{-1}		
			Coulomb portion of the lattice energy:	55652.7162 ± 0.002500 kJ·mol^{-1}		

Table S4:Results of the MAPLE calculations, regarding the ligands of the tin atoms in $Sn_2[B_7O_{12}]F$.

#	atom	*x*	*y*	*z*	distance / pm	e-ECoN(1)	e-ECoN(3)
ZT	Sn1	0.4041	0.6683	0.0053			
1	O7	0.5917	0.5800	0.0273	212.397	1.163	1.185
2	F1	0.3465	0.5729	0.0792	205.653	1.147	1.170
3	O7	0.4083	0.4200	-0.0273	227.175	0.762	0.784
4	O46	0.4940	0.8828	0.0704	254.351	0.240	0.253
next ligand:							
5	O67	0.1922	0.4657	-0.0500	303.878	0.002	0.002
last ligand:							
26	O23	0.4070	0.9385	0.1850	485.025	0.000	0.000
coordination number: 4							

#	atom	*x*	*y*	*z*	distance / pm	e-ECoN(1)	e-ECoN(1)
ZT	**Sn2**	0.3654	0.4301	0.1622			
1	O45	0.1517	0.4751	0.1431	226.890	1.283	1.354
2	O13	0.3492	0.677	0.2038	235.164	1.071	1.146
3	F1	0.3465	0.5729	0.0792	231.556	0.933	1.008
4	O12	0.2643	0.3967	0.2559	253.278	0.636	0.706
5	O47	0.2044	0.2539	0.0918	274.322	0.260	0.308
6	O21	0.3261	0.1487	0.2324	297.903	0.051	0.069
next ligand:							
7	O34	0.5348	0.7312	0.1543	314.162	0.012	0.017
last ligand:							
30	O45	0.6517	-0.0249	0.1431	495.068	0.000	0.000
coordination number: 3							

Table S5: Results for the MAPLE calculations for all atoms in $Sn_2[B_7O_{12}]F$, regarding charge, distance, obtained charge, partial maple factor (PMF) and MAPLE energies (*MAPLE: MAPLE / charge).

	charge	distance / pm	obtained charge	PMF	MAPLE	*MAPLE
Sn1	+2.0000	205.65	-1.39494	1.86056	462.8564	115.7141
Sn2	+2.0000	226.89	-1.40853	1.87868	467.3642	116.8410
B1	+3.0000	142.58	-3.01372	6.02950	1499.9758	166.6640
B2	+3.0000	133.60	-2.91160	5.82519	1449.1479	161.0164
B3	+3.0000	135.56	-2.81866	5.63925	1402.8917	155.8769
B4	+3.0000	145.53	-2.99659	5.99522	1491.4468	165.7163
B5	+3.0000	133.38	-2.89111	5.78418	1438.9467	159.8830
B6	+3.0000	136.42	-2.85777	5.71750	1422.3572	158.0397
B7	+3.0000	135.38	-3.07488	6.15186	1530.4156	170.0462
F1	-1.0000	205.65	0.62123	0.41430	103.0658	103.0658
O12	-2.0000	135.45	2.20655	2.94308	732.1569	183.0392
O13	-2.0000	137.05	2.23817	2.98525	742.6476	185.6619
O15	-2.0000	133.38	2.23210	2.97714	740.6319	185.1580
O21	-2.0000	133.60	2.20433	2.94010	731.4175	182.8544
O23	-2.0000	137.58	2.47381	3.29954	820.8359	205.2090
O34	-2.0000	135.56	2.17716	2.90386	722.4019	180.6005
O45	-2.0000	138.70	2.21228	2.95072	734.0580	183.5145
O46	-2.0000	137.23	2.26916	3.02657	752.9289	188.2322
O47	-2.0000	135.38	2.10851	2.81230	699.6245	174.9061
O56	-2.0000	136.42	2.35477	3.14077	781.3377	195.3344
O67	-2.0000	136.66	2.28826	3.05205	759.2663	189.8166
O7	-2.0000	136.01	1.74826	2.33180	580.0892	145.0223
			Madelung constant:	80.6594 ± 0.000003		
			Coulomb portion of the lattice energy:	20065.8645 ± 0.00083 kcal·mol^{-1}		
			Coulomb portion of the lattice energy:	83995.7292 ± 0.003472 kJ·mol^{-1}		

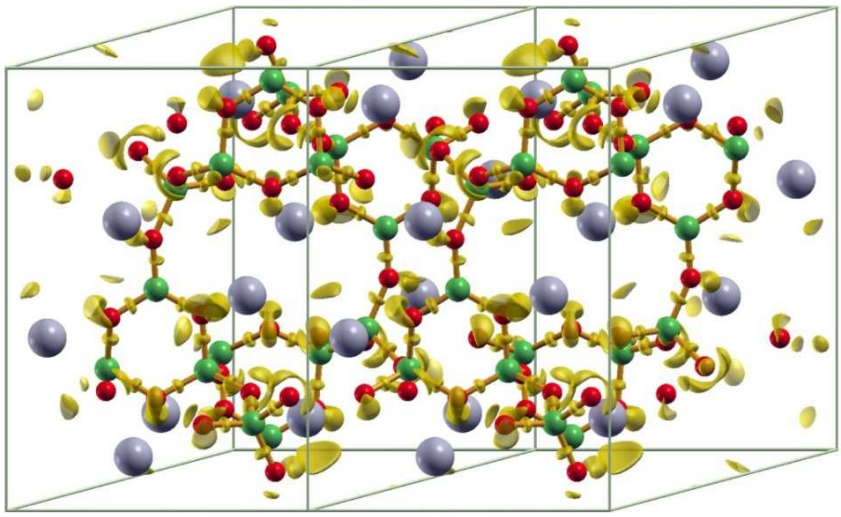

Figure S1: Electron localization function (ELF) (isosurface at 0.86) showing the attractors of the B-O bonds and the lone pairs of the oxygen anions and the tin cations.

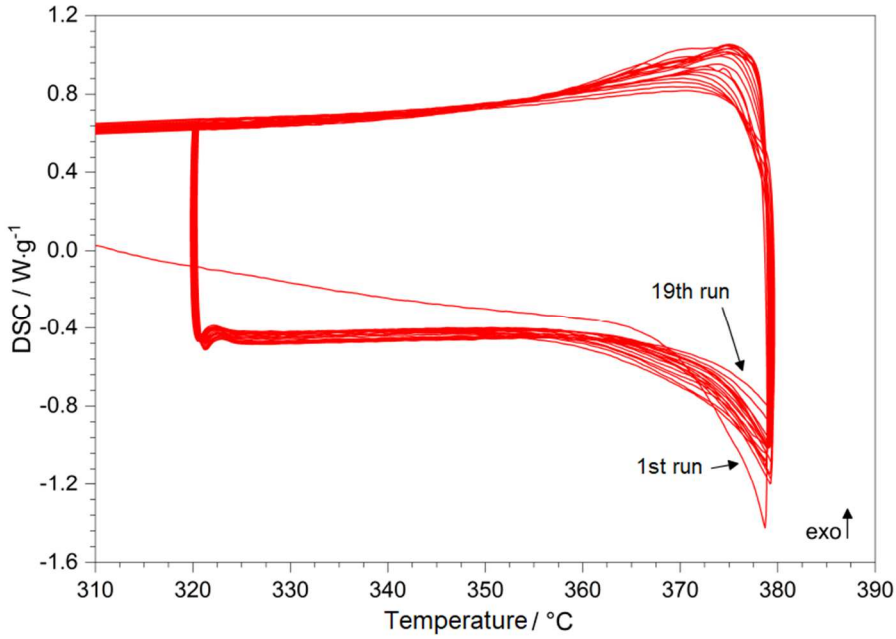

Figure S2: DSC measurement that led to the synthesis of a single crystal of $Sn_2[B_7O_{12}]F$; the sample was heated to a temperature within the endothermic peak of the original DSC measurement (Fig. 4) and then cooled again. After 18 repetitions of this cycle, the crucible was opened and a large crystal was found.

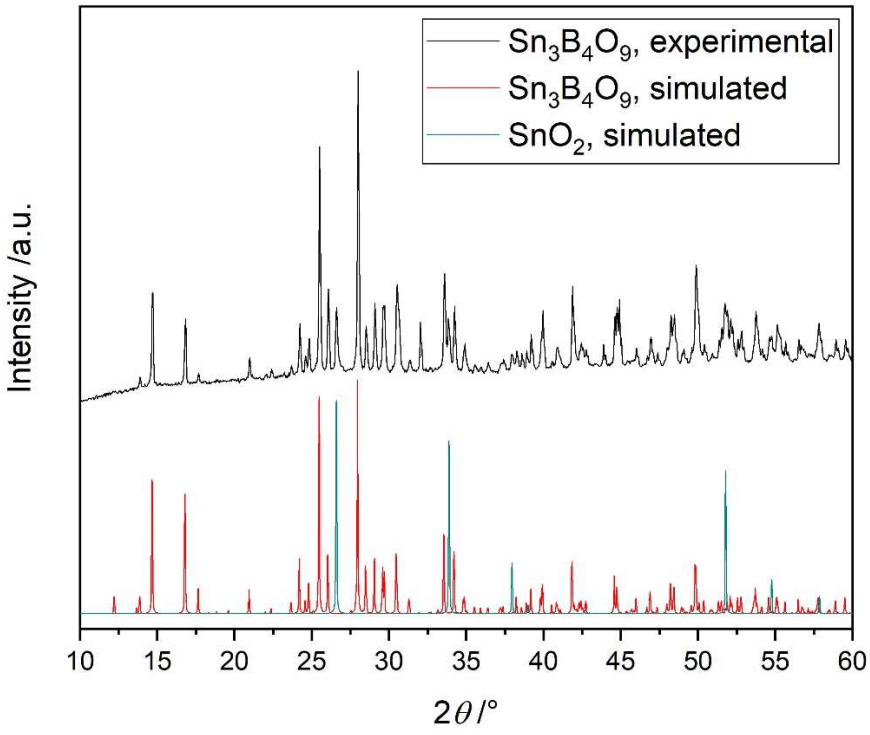

Figure S3: Powder diffraction pattern of the final product tin borate; shown are the calculated patterns of SnO_2 and tin borate.