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Electronic Supplementary Information

$Sn_2B_7O_{12}F$ with a $^{2}_{\infty}[B_{14}O_{24}]^{6-}$ layer constructed from the unprecedented $[B_7O_{16}]^{11-}$ fundamental building block

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Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Sn_2B_7O_{12}F$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	*x*	*y*	*z*	*U*(eq)
Sn (1)	958(1)	3317(1)	9947(1)	12(1)
Sn (2)	1345(1)	5698(1)	8379(1)	13(1)
B (1)	4052(3)	6665(4)	8858(2)	10(1)
B (2)	706(3)	9788(4)	9248(2)	11(1)
B (3)	4076(3)	3799(4)	8594(2)	12(1)
B (4)	2783(3)	2632(4)	7777(2)	11(1)
B (5)	2999(3)	8727(4)	9424(2)	11(1)
B (6)	5678(4)	7194(4)	8192(2)	13(1)
B (7)	3198(4)	5043(4)	7214(2)	13(1)
O (1)	3484(2)	5249(3)	8570(1)	10(1)
O (2)	4655(2)	7684(3)	8458(1)	12(1)
O (3)	60(2)	1177(3)	9296(1)	12(1)
O (4)	1919(2)	9656(3)	9500(1)	15(1)
O (5)	3678(2)	2602(3)	8272(1)	17(1)
O (6)	122(2)	8553(3)	8975(1)	13(1)
O (7)	5928(3)	5627(3)	8148(1)	26(1)
O (8)	2958(2)	7461(3)	9082(1)	12(1)
O (9)	-916(2)	4207(3)	9727(1)	18(1)
O (10)	6503(2)	8238(2)	7962(1)	10(1)
O (11)	3259(2)	3518(3)	7324(1)	16(1)
O (12)	2357(2)	6037(2)	7441(1)	9(1)
F (1)	1533(2)	4266(2)	9206(1)	26(1)

Table S2. Selected bond lengths (Å) and angles (°) for $Sn_2B_7O_{12}F$.

Sn(1)-F(1)	2.063(2)	B(3)-O(5)	1.335(5)
Sn(1)-O(9)	2.132(3)	B(3)-O(6)#5	1.389(4)
Sn(1)-O(9)#1	2.273(3)	B(3)-O(1)	1.395(4)
Sn(1)-O(3)	2.549(3)	B(4)-O(11)	1.432(4)
Sn(2)-O(1)	2.279(3)	B(4)-O(5)	1.456(4)
Sn(2)-F(1)	2.318(3)	B(4)-O(12)#6	1.475(4)
Sn(2)-O(10)#2	2.352(3)	B(4)-O(10)#2	1.522(4)
Sn(2)-O(12)	2.539(3)	B(5)-O(8)	1.361(4)
B(1)-O(2)	1.464(4)	B(5)-O(9)#3	1.366(4)
B(1)-O(3)#3	1.493(4)	B(5)-O(4)	1.402(4)
B(1)-O(1)	1.503(4)	B(6)-O(2)	1.339(4)
B(1)-O(8)	1.458(4)	B(6)-O(10)	1.382(4)
B(2)-O(4)	1.369(4)	B(6)-O(7)	1.383(5)
B(2)-O(6)	1.370(4)	B(7)-O(11)	1.342(4)
B(2)-O(3)#4	1.383(4)	B(7)-O(12)	1.361(4)
		B(7)-O(7)#7	1.385(4)
F(1)-Sn(1)-O(9)	87.57(10)	O(6)-B(2)-O(3)#4	120.6(3)
F(1)-Sn(1)-O(9)#1	86.00(10)	O(5)-B(3)-O(6)#5	117.3(3)
O(9)-Sn(1)-O(9)#1	73.03(10)	O(5)-B(3)-O(1)	123.3(3)
F(1)-Sn(1)-O(3)	83.40(10)	O(6)#5-B(3)-O(1)	119.4(3)
O(9)-Sn(1)-O(3)	79.41(9)	O(11)-B(4)-O(5)	112.5(3)
O(9)#1-Sn(1)-O(3)	150.82(8)	O(11)-B(4)-O(12)#6	105.5(3)
O(1)-Sn(2)-F(1)	73.19(8)	O(5)-B(4)-O(12)#6	108.1(3)
O(1)-Sn(2)-O(10)#2	80.66(8)	O(11)-B(4)-O(10)#2	112.5(3)
F(1)-Sn(2)-O(10)#2	82.64(10)	O(5)-B(4)-O(10)#2	107.6(3)
O(1)-Sn(2)-O(12)	74.97(8)	O(12)#6-B(4)-O(10)#2	110.6(3)
F(1)-Sn(2)-O(12)	141.90(8)	O(8)-B(5)-O(9)#3	123.5(3)
O(10)#2-Sn(2)-O(12)	71.99(8)	O(8)-B(5)-O(4)	122.7(3)
O(8)-B(1)-O(2)	109.3(3)	O(9)#3-B(5)-O(4)	113.7(3)
O(8)-B(1)-O(3)#3	114.2(3)	O(2)-B(6)-O(10)	120.9(3)
O(2)-B(1)-O(3)#3	108.1(3)	O(2)-B(6)-O(7)	120.3(3)
O(8)-B(1)-O(1)	104.8(3)	O(10)-B(6)-O(7)	118.8(3)
O(2)-B(1)-O(1)	111.4(3)	O(11)-B(7)-O(12)	124.4(3)
O(3)#3-B(1)-O(1)	109.1(3)	O(11)-B(7)-O(7)#7	116.9(3)
O(4)-B(2)-O(6)	120.9(3)	O(12)-B(7)-O(7)#7	118.7(3
O(4)-B(2)-O(3)#4	118.5(3)		

Symmetry transformations used to generate equivalent atoms:

#1 – x, – y + 1, – z + 2 # 2 x – 1/2, y – 1/2, z #3 x + 1/2, y + 1/2, z #4 x, y + 1, z #5 x + 1/2, y – 1/2, z #6 – x + 1/2, y – 1/2, – z + 3/2 #7 – x + 1, y, – z + 3/2 #8 x, y – 1, z #9 x – 1/2, y + 1/2, z #10 – x + 1/2, y + 1/2, – z + 3/2

Table S3. Configurations and the degree of the polymerization (R) of the FBBs with seven boron atoms.

FBB Configurations	R	Representative examples
7: $_{\infty}^{3}$[<2ΔT> + <Δ2T> + Δ]	3	$Li_3B_7O_{12}$[1]
7: $_{\infty}^{3}$[<6T>^{B} + Δ]	3	$Fe_3B_7O_{13}Cl$[2]
7: $_{\infty}^{3}$[<3Δ3T>^{B} + Δ]	3	$Co_3B_7O_{13}F(OH)$[3]
7: $_{\infty}^{2}$[Δ + <2ΔT> + 2ΔT]	**2**	**$Sn_2B_7O_{12}F$**
7: $_{\infty}^{2}$[<T2Δ> + TΔ + TΔ]	**2**	**$AgSrB_7O_{12}$**
7: [|Δ|Δ| + <Δ2T> + |Δ|Δ|]	0	$K_3PtB_7O_{11}(OH)_6(H_2O)_3$[4]
7: [T + <2Δ3T>^{8} + T]	0	$NaBa_3Si_2B_7O_{16}(OH)_4$[5]
7: [5Δ2T]$^{2\text{-}8}$	0	$NaMg_2Ba_7B_{14}O_{28}F_5$[6]

Table S4. Bonding electron density difference ($\Delta\rho$) of different units calculated by the REDA method and the density of different groups in the unit cell.

Units	$\Delta\rho$	($\times 10^{-3}$/ Å^3)
$[BO_3]^{3-}$	12.6566	18.7793
$[BO_4]^{5-}$	0.0007	7.5117
$[SnO_3F]^{5-}$	0.0012	5.6338
$[SnO_4F]^{7-}$	0.0099	3.7559
$[B_{14}O_{24}]^{6-}$ layer	12.6573	/
$[Sn_4O_{12}F_2]^{18-}$ cluster	0.0111	/

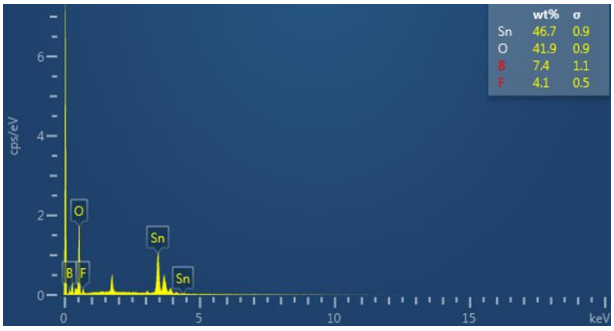

Figure S1. EDS of the $Sn_2B_7O_{12}F$ crystal.

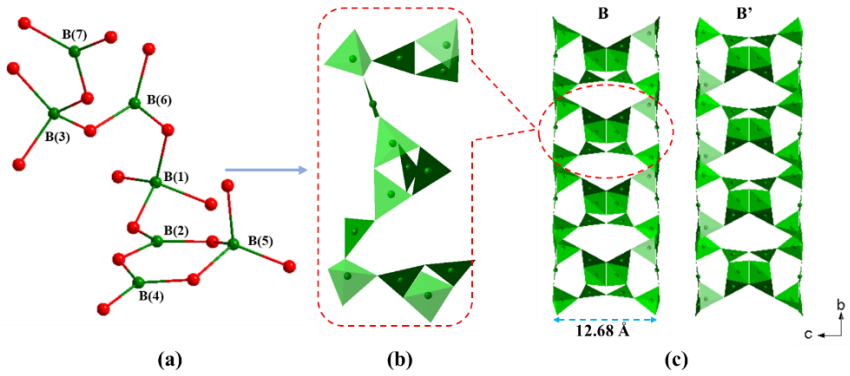

Figure S2. (a) $[B_7O_{17}]^{13-}$ FBB of $AgSrB_7O_{12}$. (b) Chain-like cluster $[B_{14}O_{31}]^{20-}$ in $AgSrB_7O_{12}$. (c) $^{2}_{\infty}[B_{14}O_{24}]^{6-}$ layer of $AgSrB_7O_{12}$.

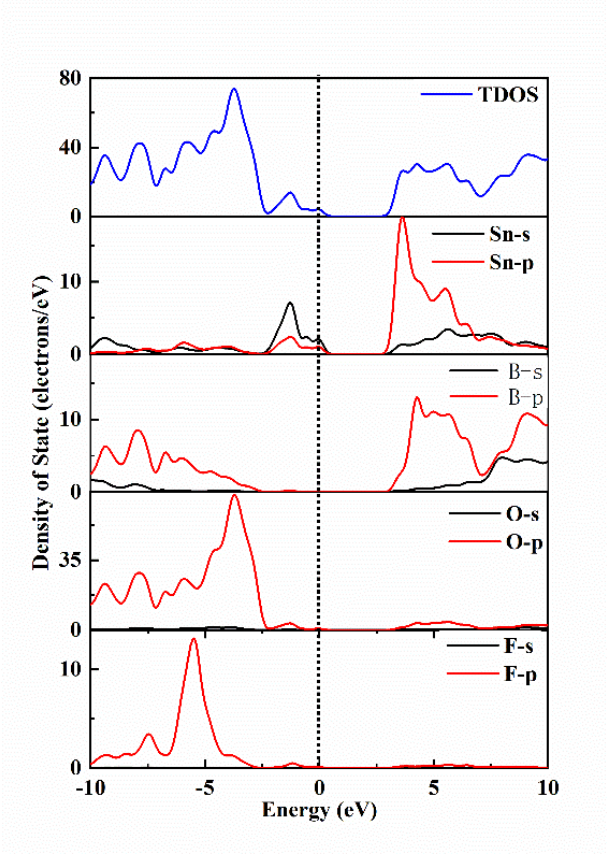

Figure S3. PDOS of $Sn_2B_7O_{12}F$

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