Supporting Information

$Pb_3B_6O_{11}F_2$: A First Noncentrocentric Lead Fluoroborate with Large Second Harmonic Generation Response

Hongyi Li,[a] Hongping Wu,[a]* Xin Su,[a] Hongwei Yu,[a,b] Shilie Pan,[a]* Zhihua Yang,[a]* Yi Lu,[c] Jian Han,[a] Kenneth R. Poeppelmeier[d]

[a] Key Laboratory of Functional Materials and Devices for Special Environments of CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices, Xinjiang Technical Institute of Physics & Chemistry of CAS, 40-1 South Beijing Road, Urumqi 830011, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

[c] Xinjiang Products Quality Supervision & Inspection Institute of Technology, Urumqi 830011, China

[d]Deparment of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston IL 60208-3113, USA

*Corresponding author. E–mail: slpan@ms.xjb.ac.cn. Tel: (86)991-3674558. Fax: (86)991-3838957.

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Pb_3B_6O_{11}F_2$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U(eq)	BVS
Pb1	4628(1)	8130(1)	9531(1)	14(1)	2.157
Pb2	5479(1)	8344(1)	5274(1)	13(1)	2.224
Pb3	214(1)	9879(1)	2269(1)	12(1)	2.315
B1	-720(50)	8370(30)	8590(30)	16(6)	2.998
B2	1020(40)	1080(30)	9300(30)	4(5)	3.001
B3	3250(40)	1180(30)	7330(30)	7(5)	2.989
B4	7280(40)	860(30)	7950(30)	7(5)	2.996
B5	0(50)	6530(40)	4450(30)	20(6)	3.012
B6	1010(40)	8710(30)	6300(30)	11(5)	3.007
F1	6670(20)	247(18)	931(18)	27(4)	1.102
F2	3790(20)	575(18)	3789(18)	26(4)	1.087
O1	-470(20)	9940(20)	5638(16)	10(3)	2.008
O2	7290(20)	9287(19)	8088(17)	9(3)	2.013
O3	5490(30)	1730(20)	7298(17)	12(4)	2.079
O4	660(20)	9373(18)	9584(18)	13(3)	1.986
O5	3000(20)	9434(19)	6890(16)	7(3)	1.976
O6	1510(30)	7518(19)	5229(19)	14(4)	2.185
O7	1340(20)	1892(17)	764(17)	7(3)	2.098
O8	130(20)	7810(20)	7375(17)	12(4)	2.067
O9	2860(20)	1472(18)	8759(16)	9(3)	2.089
O10	9090(20)	1740(17)	8387(17)	7(3)	1.985
O(11)	8150(20)	7132(18)	3779(17)	9(3)	1.994

Table S2(a). Selected bond lengths (Å) for $Pb_3B_6O_{11}F_2$

Atoms	Distance	Atoms	Distance
Pb1-O(9)#1	2.469(15)	B1-O(7)#2	1.46(3)
Pb1-O2	2.574(16)	B1-O2#7	1.48(3)
Pb1-O(5)	2.738(15)	B2-O(9)	1.42(3)
Pb1-O(4)	2.758(16)	B2-O(4)#6	1.47(3)
Pb1-F(1)	2.426(16)	B2-O(10)	1.47(3)
Pb1-F(1)#2	2.545(15)	B2-O(7)	1.52(3)
Pb2-O(5)	2.575(15)	B3-O(9)#7	1.44(3)
Pb2-O(6)	2.628(16)	B3-O(11)#8	1.47(3)
Pb2-O(11)	2.628(15)	B3-O(5)	1.51(3)
Pb2-O(3)#3	2.742(16)	B3-O(3)	1.51(3)
Pb2-F2	2.447(15)	B4-O2	1.31(3)
Pb2-F2#3	2.478(15)	B4-O(10)	1.37(3)
Pb3-O(7)	2.399(15)	B4-O(3)	1.40(3)
Pb3-O(8)#4	2.471(19)	B5-O(1)#3	1.36(4)
Pb3-O(4)#6	2.647(16)	B5-O(11)	1.33(3)
Pb3-O(10)#1	2.739(15)	B5-O(6)#6	1.37(4)
Pb3-F(1)	2.397(16)	B6-O(5)	1.42(3)
Pb3-F2#5	2.526(17)	B6-O(1)	1.45(3)
B(1)-O(4)	1.43(3)	B6-O(8)	1.46(3)
B(1)-O(8)	1.45(3)	B6-O(6)	1.50(3)

Table S2(b). Selected bond angles (deg) for $Pb_3B_6O_{11}F_2$

Atoms	Angles	Atoms	Angles
F1-Pb1-O9#1	80.4(5)	O8#4-Pb3-O4#6	108.5(5)
F1-Pb1-F1#2	154.1(3)	F2#5-Pb3-O4#6	109.1(5)
O9#1-Pb1-F1#2	74.7(5)	F1-Pb3-O10#1	100.5(5)
F1-Pb1-O2	71.1(5)	O7-Pb3-O10#1	116.6(4)
O9#1-Pb1-O2	98.1(5)	O8#4-Pb3-O10#1	172.4(5)
F1#2-Pb1-O2	119.3(5)	F2#5-Pb3-O10#1	100.1(5)
F1-Pb1-O5	106.3(5)	O4#6-Pb3-O10#1	65.0(5)
O9#1-Pb1-O5	154.6(5)	O4-B1-O8	1162
F1#2-Pb1-O5	99.4(5)	O4-B1-O7#2	1142
O2-Pb1-O5	62.7(5)	O8-B1-O7#2	1042
F1-Pb1-O4	96.9(5)	O4-B1-O2#7	1072
O9#1-Pb1-O4	133.1(5)	O8-B1-O2#7	1102
F1#2-Pb1-O4	94.8(5)	O7#2-B1-O2#7	106.2(19)
O2-Pb1-O4	125.5(5)	O9-B2-O4#6	117.5(18)
O5-Pb1-O4	71.4(5)	O9-B2-O10	111.6(17)
F2-Pb2-F2#3	160.1(4)	O4#6-B2-O10	108.9(17)
F2-Pb2-O5	79.7(5)	O9-B2-O7	104.6(17)
F2#3-Pb2-O5	102.1(5)	O4#6-B2-O7	105.1(17)
F2-Pb2-O6	82.6(5)	O10-B2-O7	108.6(16)
F2#3-Pb2-O6	83.0(5)	O9#7-B3-O11#8	112.6(18)
O5-Pb2-O6	52.7(5)	O9#7-B3-O5	113.2(18)
F2-Pb2-O11	104.0(5)	O11#8-B3-O5	107.7(18)
F2#3-Pb2-O11	74.9(5)	O9#7-B3-O3	107.8(18)
O5-Pb2-O11	176.1(5)	O11#8-B3-O3	105.7(17)
O6-Pb2-O11	128.5(5)	O5-B3-O3	109.6(17)
F2-Pb2-O3#3	82.0(5)	O2-B4-O10	1212
F2#3-Pb2-O3#3	81.9(5)	O2-B4-O3	1242

O5-Pb2-O3#3	129.9(5)	O10-B4-O3	1162
O6-Pb2-O3#3	79.0(5)	O11-B5-F2#3	122(3)
O11-Pb2-O3#3	52.5(5)	O11-B5-O6#6	120(3)
F1-Pb3-O7	87.9(5)	F2#3-B5-O6#6	118(2)
F1-Pb3-O8#4	81.2(5)	O5-B6-F2	109.4(19)
O7-Pb3-O8#4	56.0(5)	O5-B6-O8	112.7(19)
F1-Pb3-F2#5	159.2(5)	F2-B6-O8	110.7(19)
O7-Pb3-F2#5	80.4(5)	O5-B6-O6	104.5(19)
O8#4-Pb3-F2#5	78.0(5)	F2-B6-O6	112(2)
F1-Pb3-O4#6	77.4(5)	O8-B6-O6	107.1(19)
O7-Pb3-O4#6	55.9(5)		

Note. Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y-1/2,-z+2 #2 -x+1,y-1/2,-z+2

#3 -x+1,y-1/2,-z+1 #4 -x+1,y+1/2,-z+2

#5 x+1,y,z+1 #6 x+1,y,z #7 x-1,y,z

#8 -x+1,y+1/2,-z+1 #9 x-1,y,z-1 #10 -x+2,y+1/2,-z+2

Table S3. The direction and magnitude of the dipole moments in the PbO_xF_2 (x=4, 5, 6) polyhedra, BO_4 tetrahedra and BO_3 triangle groups, and their contributions to the polarization in the unit cell.

Species	x(a)	y(b)	z(c)	Debye	10^{-4}esu cmA^{-3}
$Pb2O_4F_2$	-3.6834	6.6122	-2.4553	7.7316	312
$Pb1O_4F_2$	0.1221	-0.063	2.9225	2.9018	117
$Pb3O_4F_2$	-0.4166	4.2873	-2.2822	4.8364	195
$B1O_4$	-2.3931	-1.049	-0.7105	2.5820	104
$B2O_4$	-0.6380	1.3337	2.5717	3.0728	124
$B3O_4$	1.0767	0.5589	-1.2475	1.8851	76
$B4O_3$	0.3748	1.1583	-0.6854	1.4327	58
$B5O_3$	0.6876	0.0506	0.0709	0.6792	27
$B6O_4$	1.0259	-0.9679	-0.5033	1.5636	63
B-O in unit cell	0	2.2230	0	2.2230	91
Pb-O in unit cell	0	21.6688	0	21.6688	438

Table S4. The refractive indices and birefringence of $Pb_3B_6O_{11}F_2$.

λ(nm)	n^x	n^y	n^z	$\Delta n=n^y-n^z$
1036.7	2.00619	2.03599	1.96609	0.06991
938.8	2.01533	2.04523	1.97506	0.07017
822.2	2.02629	2.05630	1.98585	0.07046
731.4	2.03932	2.06944	1.99869	0.07075
658.6	2.05471	2.08494	2.01392	0.07102
534.6	2.10255	2.13302	2.06167	0.07134
449.8	2.17677	2.20752	2.13747	0.07005

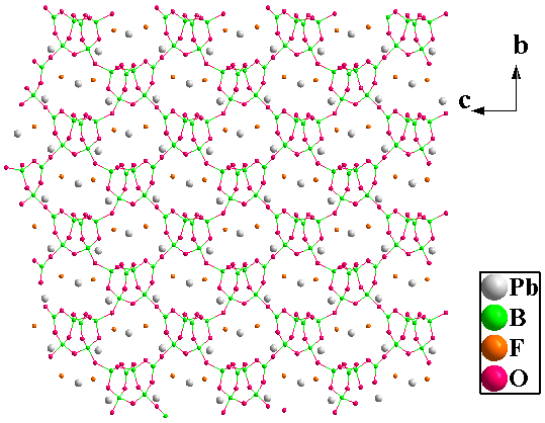

Figure S1 The 3D framework of $Pb_3B_6O_{11}F_2$ with 18-member tunnels viewing along the *a*-axis where the Pb and F atoms were located (Pb-O bonds are omitted for the clarity).

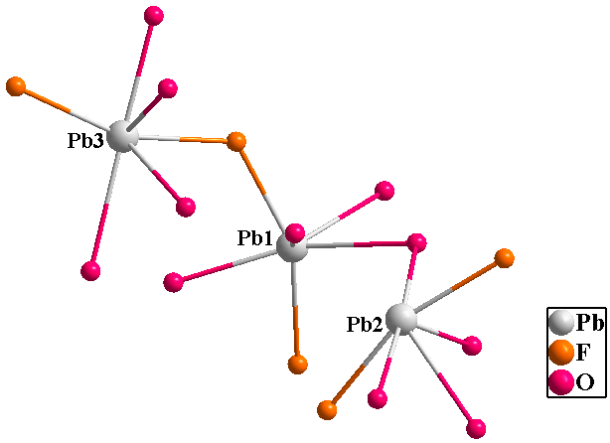

Figure S2 The coordinated environments of lead atoms in the structure.

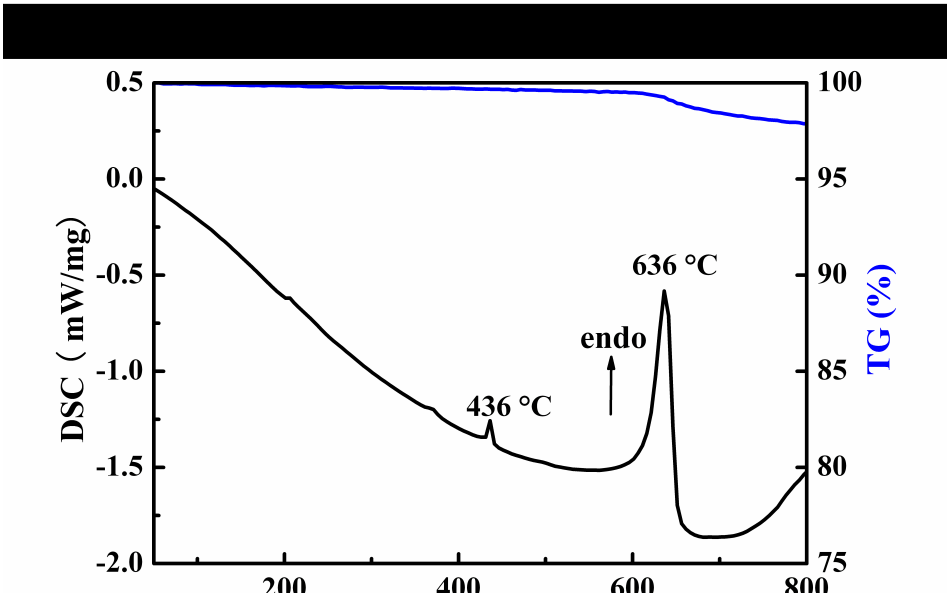

Figure S3 TG-DSC curves of $Pb_3B_6O_{11}F_2$.

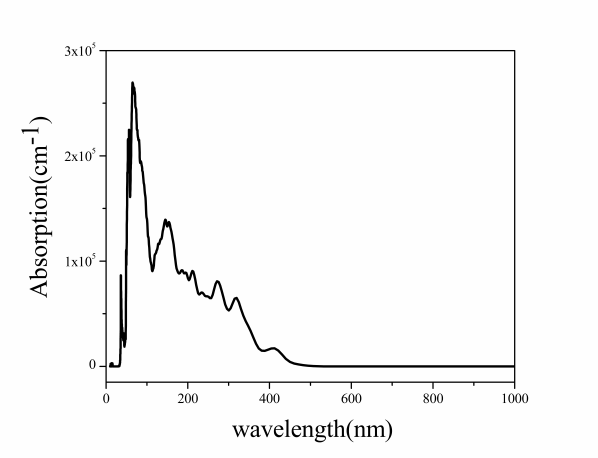

Figure S4 Absorption spectrum of $Pb_3B_6O_{11}F_2$.