

Supporting Information

Ba₁₀LuB₁₈O₃₂F₁₃: the First Example of Borate in Lu-B-O-F System with the Unprecedented FBB [B₉O₂₂] Group

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Table S1. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) and bond valence sums (BVS) for $\text{Ba}_{10}\text{LuB}_{18}\text{O}_{32}\text{F}_{13}$. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x/a	y/b	z/c	U(eq)	BVS
Ba(1)	6235(1)	6177(1)	9340(1)	12(1)	1.926
Ba(2)	5000	5000	4788(1)	11(1)	2.279
Ba(3)	2870(1)	5000	6391(1)	12(1)	2.049
Ba(4)	5000	2230(1)	1420(1)	15(1)	1.879
Ba(5)	5000	5000	1867(1)	18(1)	1.233
Lu(1)	5000	5000	7387(1)	10(1)	2.872
B(1)	2500	2500	6131(9)	7(2)	3.102
B(2)	3426(6)	3008(5)	4816(6)	11(2)	3.075
B(3)	3217(6)	4244(5)	3861(6)	9(2)	3.057
B(4)	4232(6)	3299(5)	3369(7)	10(2)	3.091
B(5)	2944(6)	3412(5)	2449(7)	11(2)	3.047
O(1)	2553(4)	3230(3)	6695(4)	11(1)	1.996
O(2)	3236(3)	2449(3)	5515(4)	11(1)	2.056
O(3)	2965(3)	3654(3)	4637(4)	11(1)	1.941
O(4)	3030(5)	5000	4295(6)	9(1)	1.903
O(6)	4114(3)	2836(3)	4307(4)	13(1)	2.005
O(7)	3632(4)	2993(3)	2650(4)	14(1)	2.050
O(8)	4063(3)	4140(3)	3587(4)	8(1)	1.853
O(9)	5000	3185(4)	2946(5)	9(2)	1.994
O(10)	2711(4)	4068(3)	2987(4)	13(1)	2.200
F(1)	5000	5000	9213(7)	19(2)	0.864
F(2)	5000	6249(4)	8038(5)	16(2)	1.047
F(3)	6211(4)	5000	8025(5)	14(1)	1.234
F(4)	4241(3)	4221(2)	6299(3)	15(1)	1.037
F(5)	1358(5)	5000	5722(5)	18(2)	1.085
F(6)	5000	3683(4)	627(5)	16(2)	1.086

Table S2. Selected bond distances (Å) and angles (deg) for Ba₁₀LuB₁₈O₃₂F₁₃.

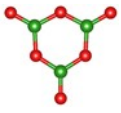
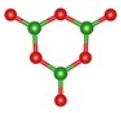
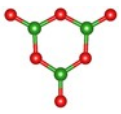
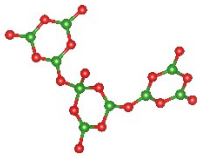
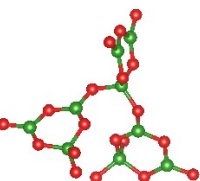
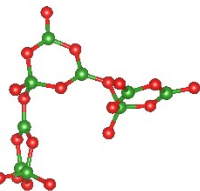
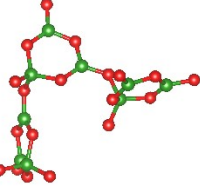
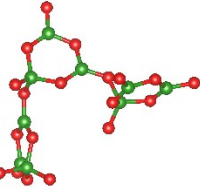
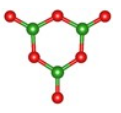
Lu(1)-F(1)	2.487(10)	Ba(4)-O(2)#13	3.218(6)
Lu(1)-F(2)	2.273(6)	Ba(4)-O(2)#12	3.218(6)
Lu(1)-F(2)#1	2.273(6)	Ba(4)-O(6)#12	3.233(6)
Lu(1)-F(3)	2.187(7)	Ba(4)-O(6)#13	3.233(6)
Lu(1)-F(3)#1	2.187(7)	Ba(4)-O(7)#2	3.095(6)
Lu(1)-F(4)	2.342(4)	Ba(4)-O(7)	3.095(6)
Lu(1)-F(4)#2	2.342(4)	Ba(4)-O(9)	2.624(7)
Lu(1)-F(4)#3	2.342(4)	Ba(4)-F(2)#14	2.749(7)
Lu(1)-F(4)#1	2.342(4)	Ba(4)-F(4)#12	2.743(4)
Ba(1)-O(3)#7	2.909(6)	Ba(4)-F(4)#13	2.743(4)
Ba(1)-O(10)#7	3.091(6)	Ba(4)-F(6)	2.665(6)
Ba(1)-O(6)#9	2.841(5)	Ba(5)-O(8)	3.159(5)
Ba(1)-O(2)#9	2.807(5)	Ba(5)-O(8)#1	3.159(5)
Ba(1)-F(1)	2.8483(8)	Ba(5)-O(8)#3	3.159(5)
Ba(1)-F(2)	2.711(4)	Ba(5)-O(8)#2	3.159(5)
Ba(1)-F(3)	2.666(4)	Ba(5)-F(5)#10	2.739(8)
Ba(1)-F(5)#6	2.735(5)	Ba(5)-F(5)#11	2.739(8)
Ba(1)-F(6)#8	2.705(4)	Ba(5)-F(6)	2.780(6)
Ba(2)-O(8)#3	2.677(5)	Ba(5)-F(6)#1	2.780(6)
Ba(2)-O(8)	2.677(5)	B(1)-O(1)	1.446(8)
Ba(2)-O(8)#2	2.677(5)	B(1)-O(2)#15	1.483(8)
Ba(2)-O(8)#1	2.677(5)	B(1)-O(2)	1.483(8)
Ba(2)-F(4)	2.742(5)	B(2)-O(2)	1.373(10)
Ba(2)-F(4)#2	2.742(5)	B(2)-O(3)	1.348(10)
Ba(2)-F(4)#1	2.742(5)	B(2)-O(6)	1.365(11)
Ba(2)-F(4)#3	2.742(5)	B(3)-O(3)	1.507(9)
Ba(3)-O(1)	3.042(5)	B(3)-O(4)	1.432(8)
Ba(3)-O(1)#3	3.042(5)	B(3)-O(4)#3	1.432(9)
Ba(3)-O(3)	3.291(5)	B(4)-O(6)	1.508(10)
Ba(3)-O(3)#3	3.291(5)	B(4)-O(7)	1.487(10)
Ba(3)-O(4)	2.868(7)	B(4)-O(9)	1.411(10)
Ba(3)-F(3)#1	2.697(7)	B(4)-O(9)#2	1.411(10)
Ba(3)-F(4)	2.625(5)	B(5)-O(1)#5	1.352(10)
Ba(3)-F(4)#3	2.625(5)	B(5)-O(7)	1.367(10)
Ba(3)-F(5)	2.666(8)	B(5)-O(10)	1.377(10)
O(1)#15-B(1)-O(1)	115.9(9)	O(4)-B(3)-O(3)	103.4(6)
O(1)-B(1)-O(2)#15	107.5(3)	O(4)-B(3)-O(10)	112.6(7)
O(1)-B(1)-O(2)	107.4(3)	O(10)-B(3)-O(3)	105.9(6)
O(1)#15-B(1)-O(2)#15	107.4(3)	O(8)-B(4)-O(6)	107.4(6)
O(1)#15-B(1)-O(2)	107.5(3)	O(8)-B(4)-O(7)	109.7(6)
O(2)#15-B(1)-O(2)	111.1(9)	O(9)-B(4)-O(8)	112.6(7)
O(3)-B(2)-O(6)	123.5(7)	O(9)-B(4)-O(6)	113.2(7)
O(3)-B(2)-O(2)	123.0(8)	O(9)-B(4)-O(7)	106.7(7)

O(6)-B(2)-O(2)	113.5(7)	O(7)-B(4)-O(6)	107.1(6)
B(2)-O(2)-B(1)	122.8(6)	O(1)#25-B(5)-O(10)	114.5(7)
O(8)-B(3)-O(3)	111.5(6)	O(1)#25-B(5)-O(7)	123.0(7)
O(8)-B(3)-O(10)	108.2(6)	O(7)-B(5)-O(10)	122.5(7)
O(4)-B(3)-O(8)	114.8(7)		

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y+1, z$	#2 $-x+1, y, z$	#3 $x, -y+1, z$	#4 $-x+1/2, -y+1, z+1/2$
#5 $-x+1/2, y, z+1/2$	#6 $x+1/2, y, z+1/2$	#7 $x+1/2, -y+1, z+1/2$	#8 $-x+1, -y+1, z+1$
#9 $-x+1, y+1/2, z+1/2$	#10 $x+1/2, y, z-1/2$	#11 $-x+1/2, -y+1, z-1/2$	#12 $-x+1, -y+1/2, z-1/2$
#13 $x, -y+1/2, z-1/2$	#14 $x, y-1/2, z-1/2$	#15 $-x+1/2, -y+1/2, z$	#16 $-x+1, y, z-1$
#17 $x, -y+1, z-1$	#18 $-x+1, -y+1, z-1$	#19 $x-1/2, -y+1, z-1/2$	#20 $x-1/2, y, z-1/2$
#21 $x-1/2, y, z+1/2$	#22 $-x+1, -y+1/2, z+1/2$	#23 $x, y+1/2, z+1/2$	#24 $-x+1, y-1/2, z-1/2$
#25 $-x+1/2, y, z-1/2$			

Table S3. The fundamental building blocks (FBBs) of the anhydrous borates with 18 compositions of Boron in chemical formula.

Compound	Space Group	FBB		ICSD Code
$\text{Ba}_{8.35}\text{Pb}_{0.65}(\text{B}_3\text{O}_6)_6$	$R\bar{3}$	$[\text{B}_3\text{O}_6]$ $3:[(3\Delta)]$		243527
$\text{Ba}_{8.019}\text{Pb}_{0.981}\text{B}_{18}\text{O}_{36}$	$P3m1$	$[\text{B}_3\text{O}_6]$ $3:[(3\Delta)]$		432451
$\text{Pb}_{1.13}\text{Ba}_{7.87}\text{B}_{18}\text{O}_{36}$	$R32$	$[\text{B}_3\text{O}_6]$ $3:[(3\Delta)]$		189013
$\text{Cs}_2\text{O}(\text{B}_2\text{O}_3)_9$	$P2_1$	$[\text{B}_9\text{O}_{17}]$ $9: [(3:2\Delta + \text{T}) + 2(3:3\Delta)]$		15331
$\text{Na}_2\text{Cs}_2\text{Sr}(\text{B}_9\text{O}_{15})_2$	$P2_1/c$	$[\text{B}_9\text{O}_{19}]$ $9:[3(3:2\Delta+\text{T})]$		193498
$\text{Na}_2\text{Cs}_2\text{BaB}_{18}\text{O}_{30}$	$P2_1/c$	$[\text{B}_9\text{O}_{19}]$ $9:[3(3:2\Delta+\text{T})]$		433333
$\text{Na}_2\text{Cs}_2\text{PbB}_{18}\text{O}_{30}$	$P2_1/c$	$[\text{B}_9\text{O}_{19}]$ $9:[3(3:2\Delta+\text{T})]$		433334
$\text{Na}_2\text{Rb}_2\text{PbB}_{18}\text{O}_{30}$	$P2_1/c$	$[\text{B}_9\text{O}_{19}]$ $9:[3(3:2\Delta+\text{T})]$		433335
$\text{Ba}_4\text{K}_2\text{Zn}_5(\text{B}_3\text{O}_6)_3(\text{B}_9\text{O}_{19})$	$P2_1/n$	$[\text{B}_3\text{O}_6]+[\text{B}_9\text{O}_{19}]$ $3:[(3\Delta)]+ 9:[3(3:2\Delta + \text{T}) + 3\Delta + 3(3:2\Delta +$		193185

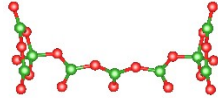
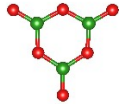
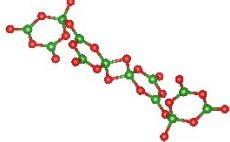
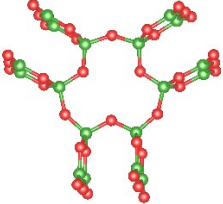
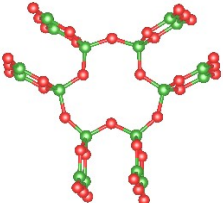
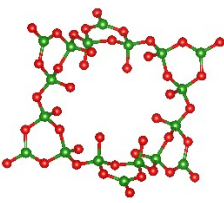
		T)]		
$\text{Ba}_4\text{Na}_2\text{Zn}_4(\text{B}_3\text{O}_6)_2(\text{B}_{12}\text{O}_{24})$	$P\bar{1}$	$[\text{B}_3\text{O}_6]+[\text{B}_{12}\text{O}_{24}]$ 3:[(3 Δ)]+12:[4(3:2 Δ + T)]	 	188636
$\text{Sr}_8\text{MgB}_{18}\text{O}_{36}$	$R\bar{3}c$	$[\text{B}_{18}\text{O}_{36}]$ 18:[6(3:2 Δ +T)]		250745
$\text{NaSr}_7\text{AlB}_{18}\text{O}_{36}$	$R\bar{3}c$	$[\text{B}_{18}\text{O}_{36}]$ 36:[6(3:2 Δ +T)]		427849
$\text{ZnV}_{12}\text{B}_{18}\text{O}_{63}$	$P\bar{1}$	$[\text{B}_{18}\text{O}_{42}]$ 18:[6(3:2 Δ + T)]		248355

Fig. S1. (a) The coordination environment of Lu^{3+} in $\text{Ba}_2\text{Lu}(\text{BO}_3)_2\text{Cl}$. (b) The coordination environment of Lu^{3+} in $\text{Ba}_{10}\text{LuB}_{18}\text{O}_{32}\text{F}_{13}$.

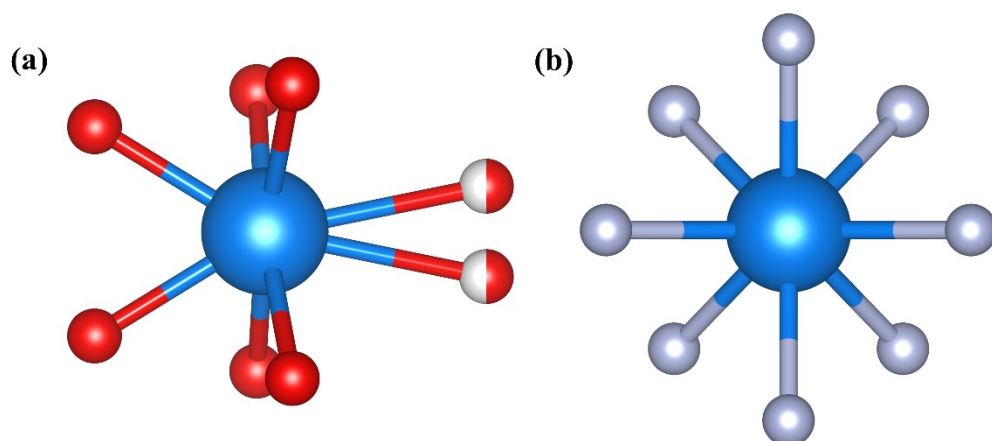


Fig. S2. The crystal of $\text{Ba}_{10}\text{LuB}_{18}\text{O}_{32}\text{F}_{13}$ for EDS measurement.

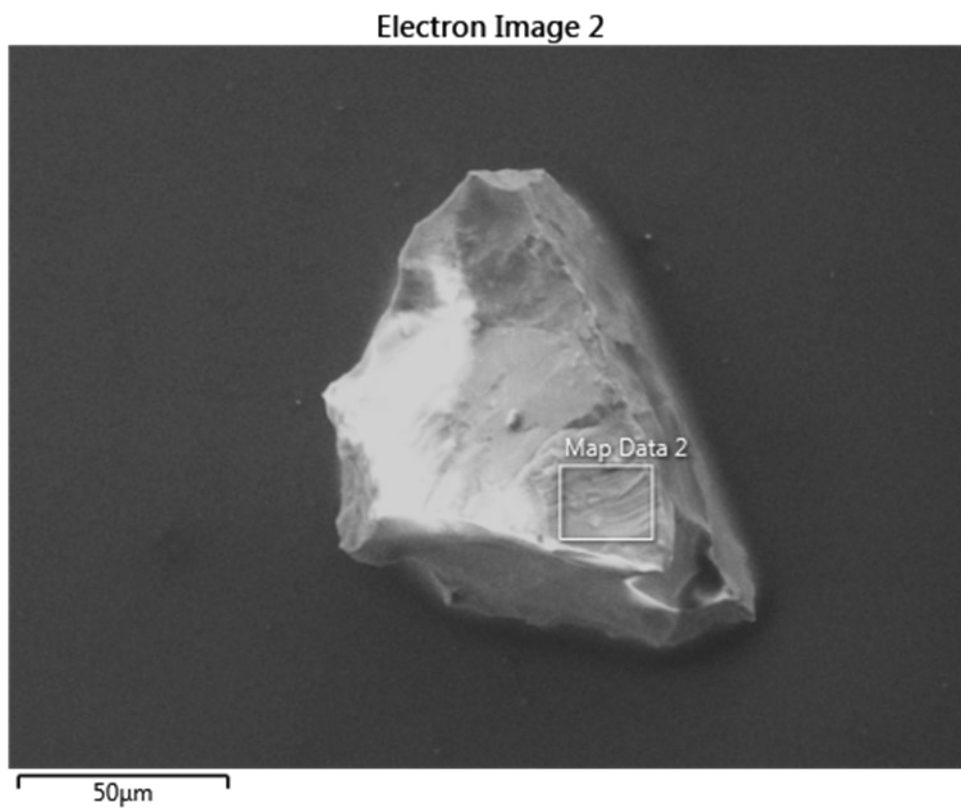


Fig. S3. The result of EDS for $\text{Ba}_{10}\text{LuB}_{18}\text{O}_{13}\text{F}_{13}$.

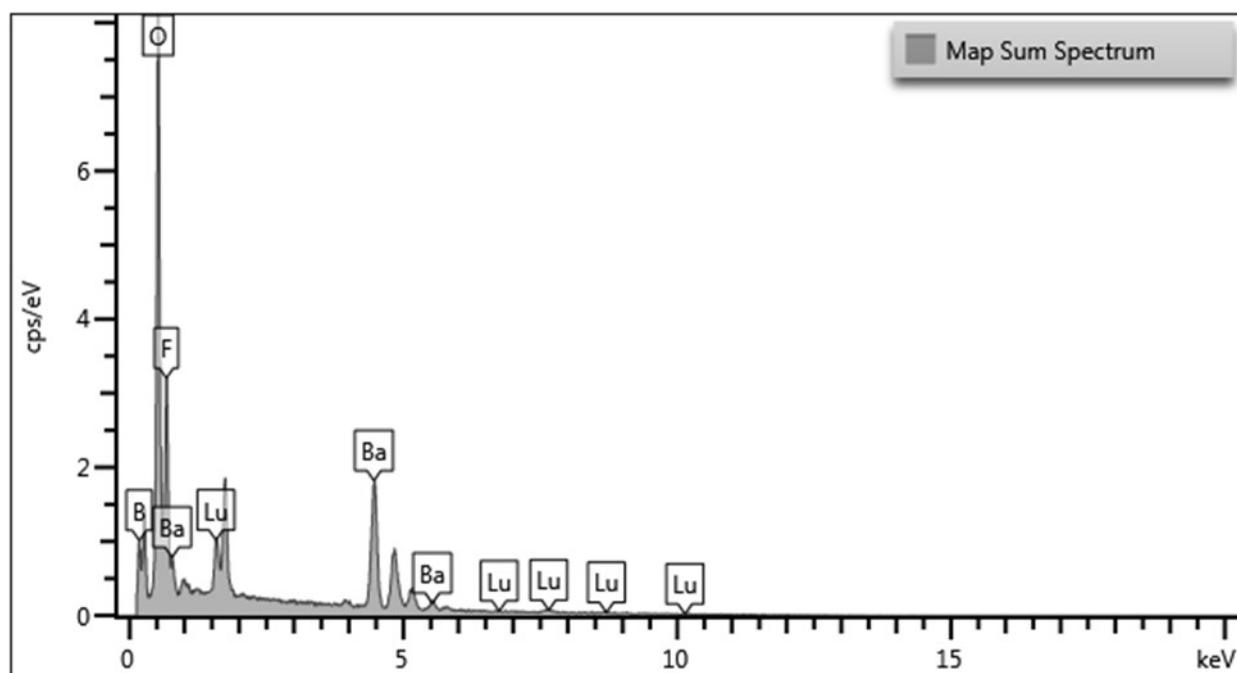


Fig. S4. Powder XRD patterns of $\text{Ba}_{10}\text{LuB}_{18}\text{O}_{32}\text{F}_{13}$.

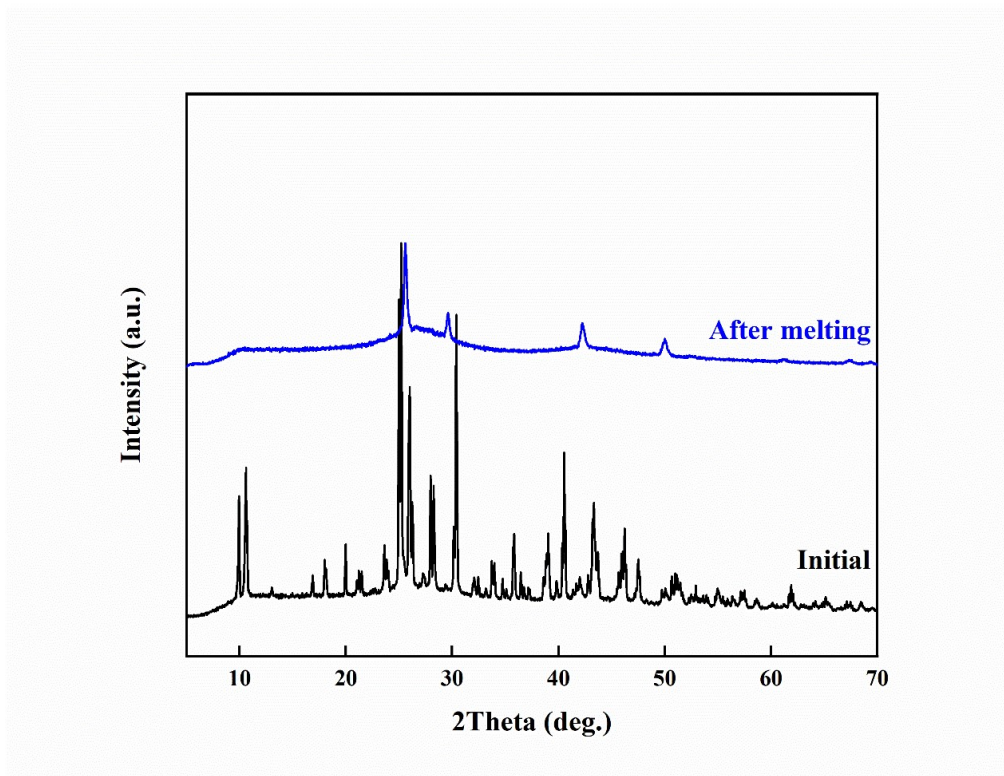


Fig. S5. The IR spectrum of $\text{Ba}_{10}\text{LuB}_{18}\text{O}_{32}\text{F}_{13}$.

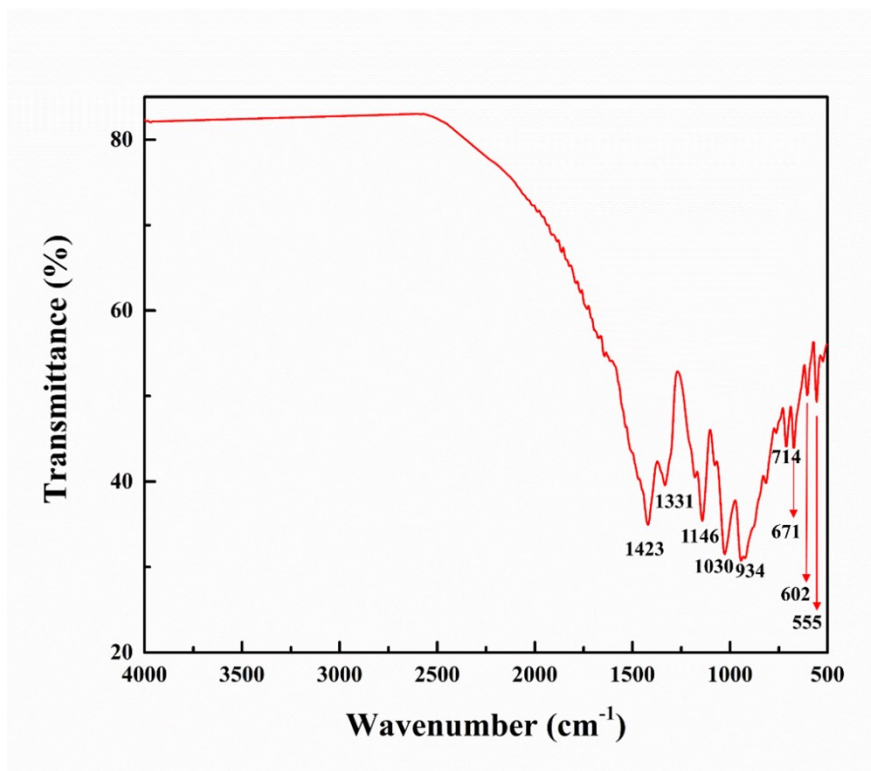


Fig. S6. The band gap of $\text{Ba}_{10}\text{LuB}_{18}\text{O}_{32}\text{F}_{13}$ calculated by using GGA.

