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Electronic Supplementary Information

Two Barium Fluoroiodate Crystals with Large Band Gap and Birefringence

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Table S1. Fractional atomic coordinates (×10^4), equivalent isotropic displacement parameters (Å^2×10^3) and bond valence sum (BVS) calculations for $BaI_2O_5F_2$. *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	*U*(*eq*)	BVS
Ba(1)	4045(1)	1622(1)	2601(1)	10(1)	2.04
I(1)	7258(1)	1746(1)	1469(1)	8(1)	5.19
I(2)	654(1)	1200(1)	3368(1)	11(1)	5.06
O(1)	6280(4)	112(5)	2006(5)	16(1)	2.33
O(2)	963(4)	-949(6)	4264(6)	22(1)	1.78
O(3)	1253(4)	968(7)	1695(5)	23(1)	2.07
O(4)	6721(4)	1455(5)	-714(5)	15(1)	2.17
O(5)	8816(4)	331(5)	1976(5)	16(1)	2.18
F(1)	2592(3)	1902(5)	4734(4)	19(1)	0.98
F(2)	5389(3)	3425(4)	897(4)	14(1)	1.00

Table S2. Selected Bond lengths (Å) and angles (deg.) for $BaI_2O_5F_2$.

$BaI_2O_5F_2$			
Ba(1)-F(1)	2.790(4)	Ba(1)-O(1)	2.861(4)
Ba(1)-F(1)#1	2.678(3)	Ba(1)-O(1)#3	2.711(4)
Ba(1)-F(2)	2.746(3)	Ba(1)-O(3)	2.878(4)
Ba(1)-F(2)#2	2.711(3)	Ba(1)-O(4)#2	3.114(4)
Ba(1)-F(2)#4	2.723(3)	Ba(1)-O(4)#5	2.807(4)
I(1)-O(1)	1.785(4)	I(2)-O(3)	1.772(4)
I(1)-O(4)	1.781(4)	I(2)-O(5)#6	2.043(4)
I(1)-O(5)	1.913(4)	I(1)-F(2)	2.289(3)
I(2)-O(2)	1.789(4)	I(2)-F(1)	2.085(3)
F(1)#1-Ba(1)-F(2)#2	155.04(11)	F(1)#1-Ba(1)-O(1)#3	69.24(12)
F(2)#2-Ba(1)-O(1)#3	85.88(11)	F(1)#1-Ba(1)-F(2)#4	141.05(10)
F(2)#2-Ba(1)-F(2)#4	62.46(11)	O(1)#3-Ba(1)-F(2)#4	146.26(11)
F(1)#1-Ba(1)-F(2)	63.15(10)	F(2)#2-Ba(1)-F(2)	111.95(11)
O(1)#3-Ba(1)-F(2)	72.06(12)	F(2)#4-Ba(1)-F(2)	128.67(7)
F(1)#1-Ba(1)-F(1)	106.92(11)	F(2)#2-Ba(1)-F(1)	62.16(10)
O(1)#3-Ba(1)-F(1)	73.68(12)	F(2)#4-Ba(1)-F(1)	80.87(10)
F(2)-Ba(1)-F(1)	145.59(10)	F(1)#1-Ba(1)-O(4)#5	81.41(11)
F(2)#2-Ba(1)-O(4)#5	122.81(10)	O(1)#3-Ba(1)-O(4)#5	149.56(12)
F(2)#4-Ba(1)-O(4)#5	60.36(11)	F(2)-Ba(1)-O(4)#5	102.22(11)
F(1)-Ba(1)-O(4)#5	108.86(11)	F(1)#1-Ba(1)-O(1)	105.50(12)
F(2)#2-Ba(1)-O(1)	89.92(11)	O(1)#3-Ba(1)-O(1)	124.50(11)
F(2)#4-Ba(1)-O(1)	70.13(11)	F(2)-Ba(1)-O(1)	58.64(11)
F(1)-Ba(1)-O(1)	147.02(11)	O(4)#5-Ba(1)-O(1)	70.28(12)
F(1)#1-Ba(1)-O(3)	65.96(12)	F(2)#2-Ba(1)-O(3)	114.78(11)
O(1)#3-Ba(1)-O(3)	92.06(13)	F(2)#4-Ba(1)-O(3)	91.13(12)
F(2)-Ba(1)-O(3)	129.07(11)	F(1)-Ba(1)-O(3)	55.02(11)
O(4)#5-Ba(1)-O(3)	67.92(13)	O(1)-Ba(1)-O(3)	138.12(12)
F(1)#1-Ba(1)-O(4)#2	113.07(11)	F(2)#2-Ba(1)-O(4)#2	55.78(10)
O(1)#3-Ba(1)-O(4)#2	67.72(11)	F(2)#4-Ba(1)-O(4)#2	100.07(10)
F(2)-Ba(1)-O(4)#2	56.24(10)	F(1)-Ba(1)-O(4)#2	107.03(10)
O(4)#5-Ba(1)-O(4)#2	134.80(8)	O(1)-Ba(1)-O(4)#2	64.63(11)
O(3)-Ba(1)-O(4)#2	157.25(12)	O(4)-I(1)-O(5)	96.71(18)
O(4)-I(1)-O(1)	100.17(19)	O(4)-I(1)-F(2)	83.93(16)
O(1)-I(1)-O(5)	95.57(19)	O(5)-I(1)-F(2)	179.19(16)
O(1)-I(1)-F(2)	83.82(15)	O(3)-I(2)-O(5)#6	92.10(19)
O(3)-I(2)-O(2)	101.1(2)	O(3)-I(2)-F(1)	85.12(17)
O(2)-I(2)-O(5)#6	87.66(18)	O(5)#6-I(2)-F(1)	175.35(15)

Symmetry transformations used to generate equivalent atoms:

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

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

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

#7 x+1,y,z

Table S3. Fractional atomic coordinates (×10^4), equivalent isotropic displacement parameters (Å^2×10^3) and bond valence sum (BVS) calculations for $BaIO_2F_3$. *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(*eq*)	BVS
Ba1	5000	2606(1)	608(1)	11(1)	2.01
I1	0	3050(1)	1677(1)	10(1)	4.98
O1	2161(5)	4644(4)	1454(1)	21(1)	2.12
F1	7602(5)	5000	0	13(1)	1.14
F2	0	1974(5)	842(1)	20(1)	1.15
F3	0	4321(6)	2427(2)	36(1)	1.24

Table S4. Selected Bond lengths (Å) and angles (deg.) for $BaIO_2F_3$.

$BaIO_2F_3$			
Ba(1)-F(1)	2.6512(19)	Ba(1)-O(1)	2.965(3)
Ba(1)-F(1)#1	2.6512(19)	Ba(1)-O(1)#5	2.965(3)
Ba(1)-F(1)#2	2.6545(17)	Ba(1)-O(1)#6	3.048(3)
Ba(1)-F(1)#3	2.6545(17)	Ba(1)-O(1)#7	3.048(3)
Ba(1)-F(2)	3.2384(9)	Ba(1)-F(2)#4	2.824(3)
Ba(1)-F(2)#8	3.2384(9)	I(1)-O(1)	1.779(3)
I(1)-F(2)	2.060(3)	I(1)-O(1)#9	1.779(3)
I(1)-F(3)	1.924(4)	F(1)#1-Ba(1)-F(1)	76.86(10)
F(1)#1-Ba(1)-F(1)#2	73.486(14)	F(1)-Ba(1)-F(1)#2	115.283(17)
F(1)#1-Ba(1)-F(1)#3	115.283(17)	F(1)-Ba(1)-F(1)#3	73.486(14)
F(1)#2-Ba(1)-F(1)#3	69.81(10)	F(1)#1-Ba(1)-F(2)#4	62.70(5)
F(1)-Ba(1)-F(2)#4	62.70(5)	F(1)#2-Ba(1)-F(2)#4	135.57(5)
F(1)#3-Ba(1)-F(2)#4	135.57(5)	F(1)#1-Ba(1)-O(1)#5	118.85(6)
F(1)-Ba(1)-O(1)#5	74.26(7)	F(1)#2-Ba(1)-O(1)#5	166.75(6)
F(1)#3-Ba(1)-O(1)#5	106.23(7)	F(2)#4-Ba(1)-O(1)#5	56.20(7)
F(1)#1-Ba(1)-O(1)	74.27(7)	F(1)-Ba(1)-O(1)	118.85(6)
F(1)#2-Ba(1)-O(1)	106.23(7)	F(1)#3-Ba(1)-O(1)	166.75(6)
F(2)#4-Ba(1)-O(1)	56.20(7)	O(1)#5-Ba(1)-O(1)	74.65(11)
F(1)#1-Ba(1)-O(1)#6	114.81(7)	F(1)-Ba(1)-O(1)#6	167.92(7)
F(1)#2-Ba(1)-O(1)#6	72.82(6)	F(1)#3-Ba(1)-O(1)#6	102.62(6)
F(2)#4-Ba(1)-O(1)#6	118.66(8)	O(1)#5-Ba(1)-O(1)#6	96.36(9)
O(1)-Ba(1)-O(1)#6	64.29(5)	F(1)#1-Ba(1)-O(1)#7	167.92(7)
F(1)-Ba(1)-O(1)#7	114.81(7)	F(1)#2-Ba(1)-O(1)#7	102.62(6)
F(1)#3-Ba(1)-O(1)#7	72.82(6)	F(2)#4-Ba(1)-O(1)#7	118.66(8)
O(1)#5-Ba(1)-O(1)#7	64.29(5)	O(1)-Ba(1)-O(1)#7	96.36(9)
O(1)#6-Ba(1)-O(1)#7	53.37(11)	F(1)#1-Ba(1)-F(2)#8	140.24(8)
F(1)-Ba(1)-F(2)#8	63.46(8)	F(1)#2-Ba(1)-F(2)#8	124.93(7)
F(1)#3-Ba(1)-F(2)#8	56.87(7)	F(2)#4-Ba(1)-F(2)#8	95.09(5)
O(1)#5-Ba(1)-F(2)#8	49.37(8)	O(1)-Ba(1)-F(2)#8	122.32(8)
O(1)#6-Ba(1)-F(2)#8	104.71(8)	O(1)#7-Ba(1)-F(2)#8	51.36(8)
F(1)#1-Ba(1)-F(2)	63.46(8)	F(1)-Ba(1)-F(2)	140.24(7)
F(1)#2-Ba(1)-F(2)	56.87(7)	F(1)#3-Ba(1)-F(2)	124.93(7)
F(2)#4-Ba(1)-F(2)	95.09(5)	O(1)#5-Ba(1)-F(2)	122.32(8)
O(1)-Ba(1)-F(2)	49.37(8)	O(1)#6-Ba(1)-F(2)	51.36(8)
O(1)#7-Ba(1)-F(2)	104.71(8)	F(2)#8-Ba(1)-F(2)	155.86(11)
O(1)#9-I(1)-F(3)	91.51(12)	O(1)#9-I(1)-O(1)	100.64(19)
O(1)#9-I(1)-F(2)	85.03(11)	O(1)-I(1)-F(3)	91.51(12)
F(3)-I(1)-F(2)	174.57(15)	O(1)-I(1)-F(2)	85.03(11)
Symmetry transformations used to generate equivalent atoms:			
#1 -x+1,-y+1,-z;	#2 x-1/2,y-1/2,z;	#3 -x+3/2,-y+1/2,-z;	#4 x+1/2,y+1/2,z;
#5 -x+1,y,z;	#6 -x+1/2,y-1/2,z;	#7 x+1/2,y-1/2,z;	#8 x+1,y,z;
#9 -x,y,z;	#10 x-1/2,y+1/2,z;	#11 x-1,y,z	

Table S5. The investigation of anionic units in fluoroiodates.

Compounds	Constitutional unit	Birefringence @ 1064 (cal.)	Band gap (cal.)	References
$Cs(IOF_4)$	$(IOF_4)^-$	—	—	1
$SbF_5IF_3O_2$	$(IO_2F_4)^-$	—	—	2
$Cs_3(IO_2F_2)_3 \cdot H_2O$	$(IO_2F_2)^-$	0.093	4.37 eV	3
$[N(CH_3)_4][IO_2F_2]$	$(IO_2F_2)^-$	—	—	4
$(N(CH_3)_4)_2(IO_2F_2)(HF_2)$	$(IO_2F_2)^-$	—	—	4
$(C(NH_2)_3)(IF_2O_2)$	$(IO_2F_2)^-$	—	—	5
$Cs(IO_2F_2)_2 \cdot H_5O_2$	$(IO_2F_2)^-$	0.086	3.77 eV	3
$NaIO_2F_2$	$(IO_2F_2)^-$	—	—	6
KIO_2F_2	$(IO_2F_2)^-$	0.06	—	7
$RbIO_2F_2$	$(IO_2F_2)^-$	0.058	4.28 eV	8
$CsIO_2F_2$	$(IO_2F_2)^-$	0.046	4.15 eV	3
$Ba(IO_2F_2)_2$	$(IO_2F_2)^-$	0.092	3.99 eV	9
$BaIO_2F_3$	**$(IO_2F_2)^-$**	**0.133**	**4.17 eV**	**Title compound**
$SrI_2O_5F_2$	$(IO_3F)^{2-}$	0.180	3.68 eV	9
$BaI_2O_5F_2$	**$(IO_3F)^{2-}$**	**0.164**	**3.95 eV**	**Title compound**

Figure S1. Experimental and calculated powder XRD patterns of $BaI_2O_5F_2$ (a) and $BaIO_2F_3$ (b).

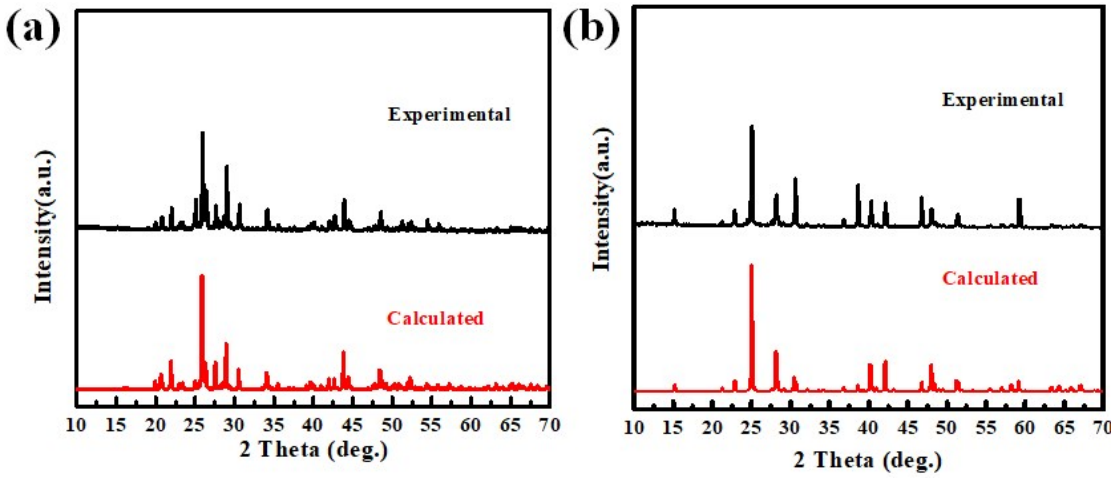


Figure S2. Elemental analysis of $BaI_2O_5F_2$ (a) and $BaIO_2F_3$ (b). Energy dispersive X-ray spectroscope (EDS) was performed to verify the presence of the F and O atoms.

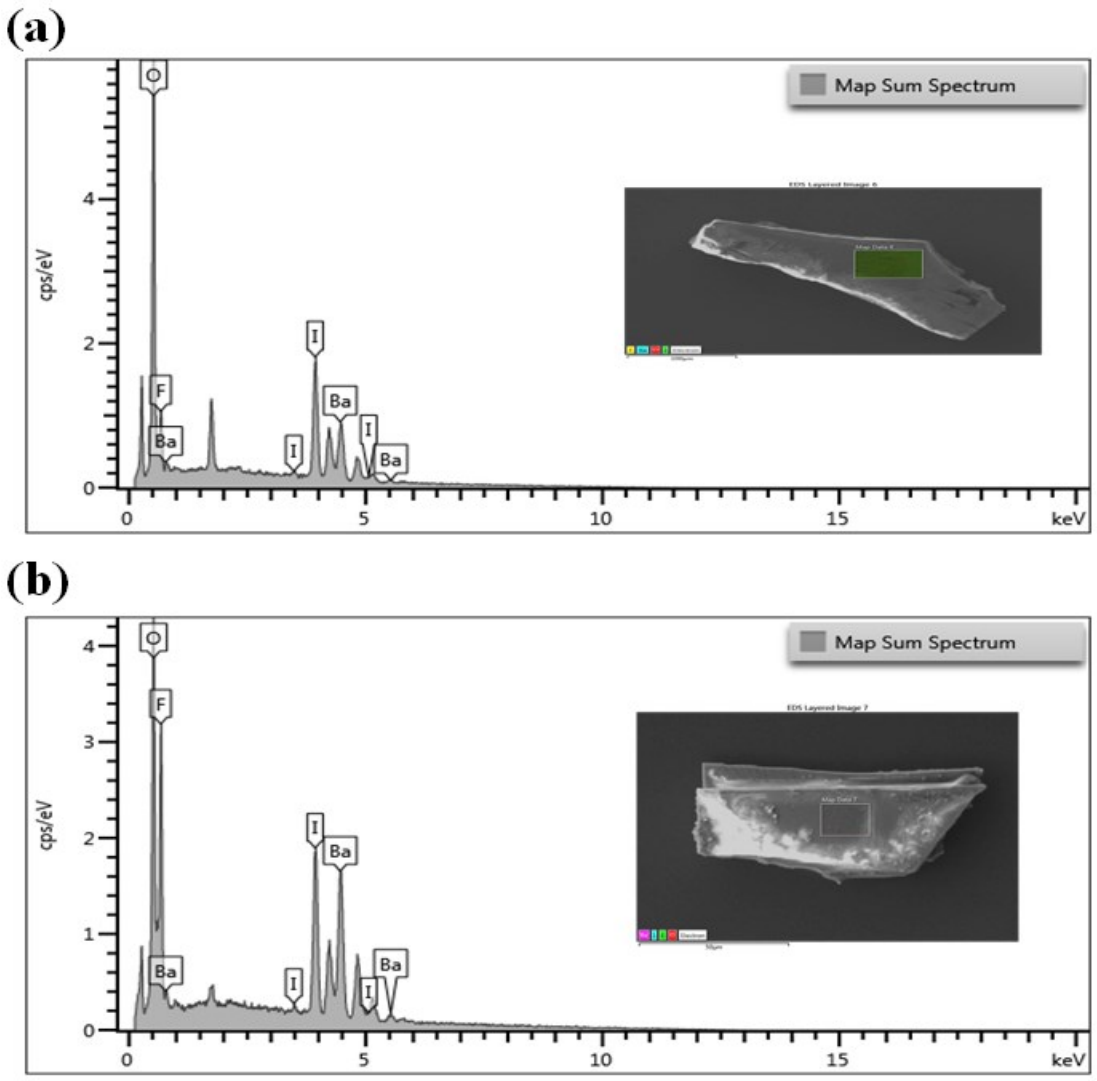


Figure S3. (a) 2D $[BaF]_\infty$ double layers A of $BaI_2O_5F_2$; (b) 2D $[BaF]_\infty$ double layers B of $BaIO_2F_3$; (c) 1D Ba-O-F chains of $Ba(IO_2F_2)_2$.

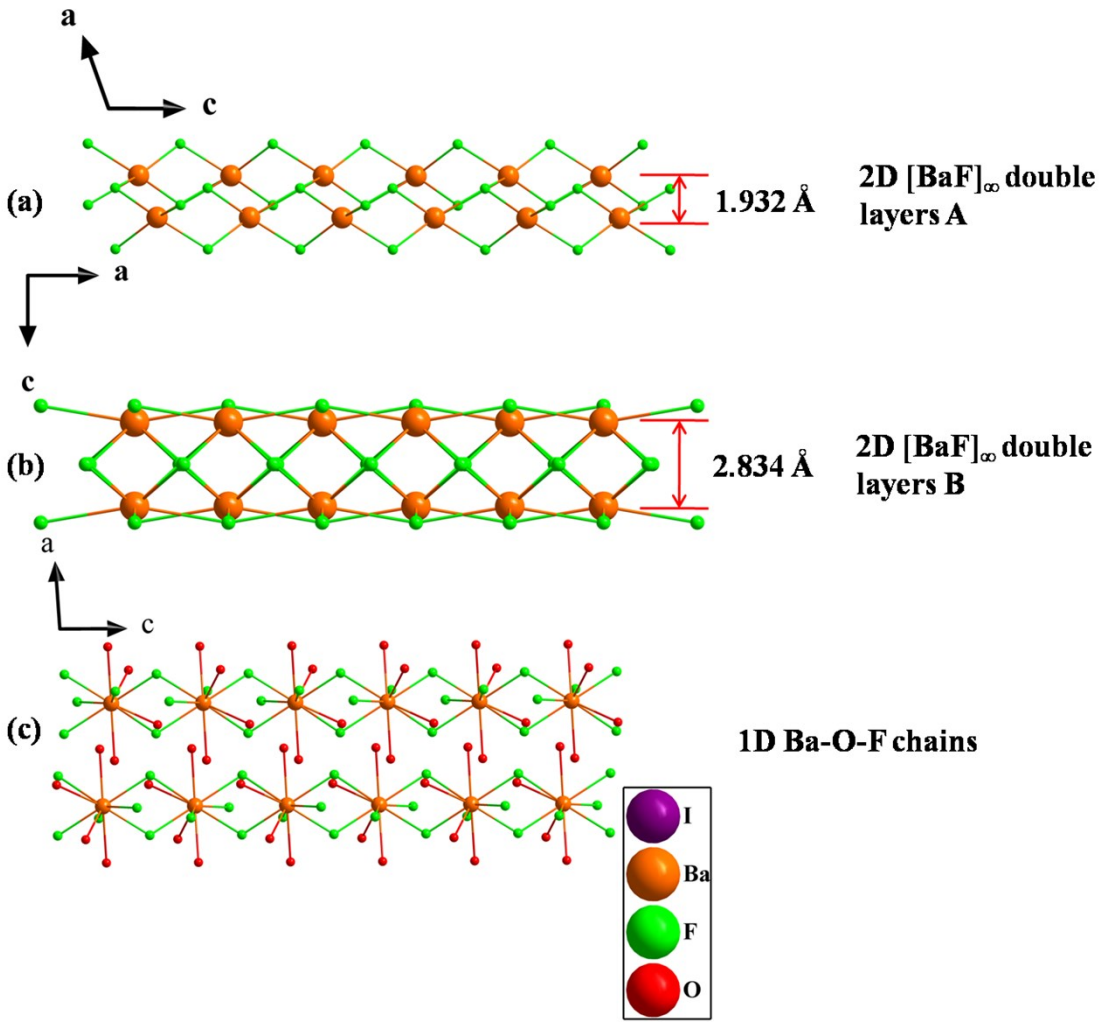


Figure S4. IR diffuse reflectance spectra of $BaI_2O_5F_2$ (a) and $BaIO_2F_3$ (b).

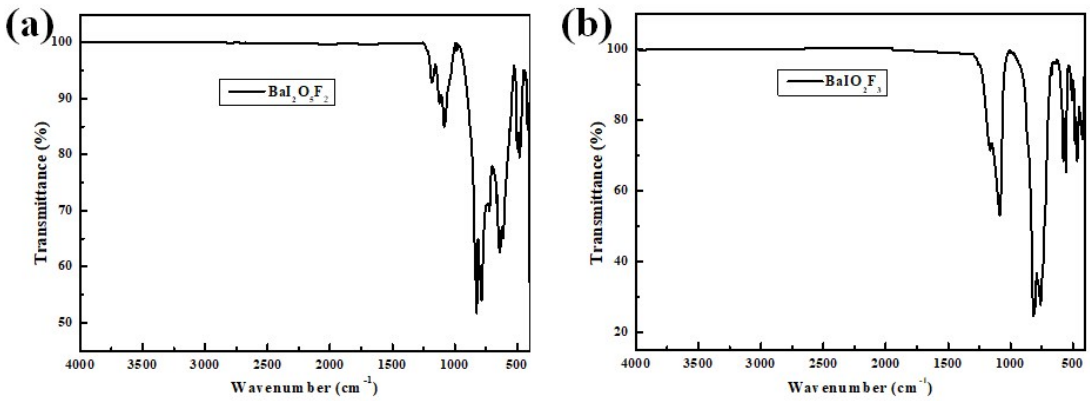


Figure S5. UV−vis−NIR diffuse-reflectance spectra of $BaI_2O_5F_2$ (a) and $BaIO_2F_3$ (b).

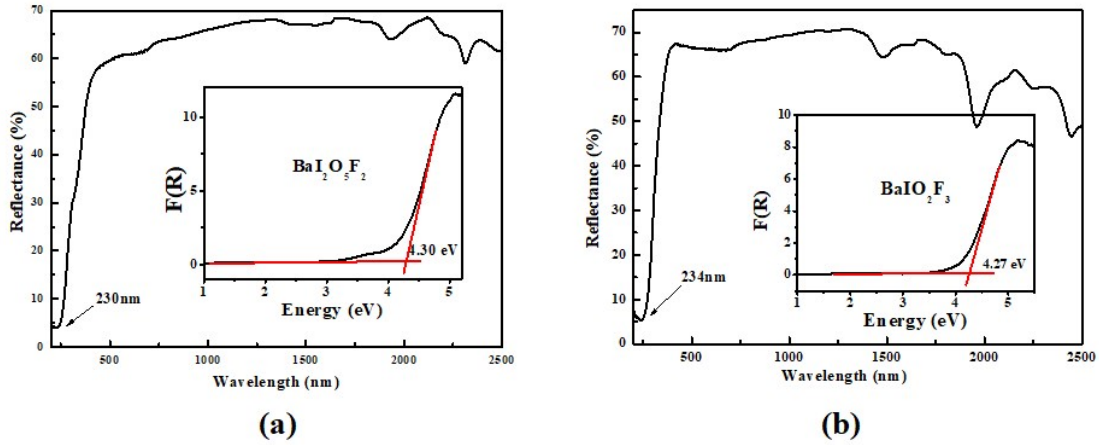


Figure S6. DSC and TG curves of $BaI_2O_5F_2$ (a) and $BaIO_2F_3$ (b).

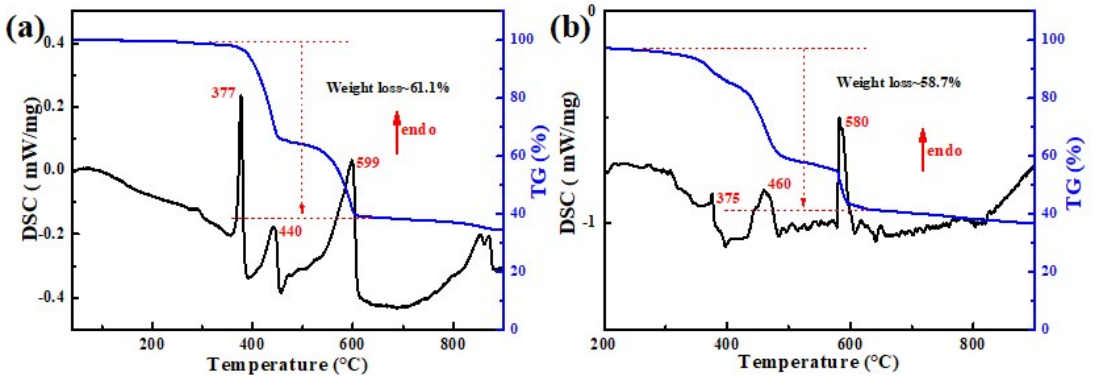


Figure S7. Calculated band structures of $BaI_2O_5F_2$ (a) and $BaIO_2F_3$ (b).

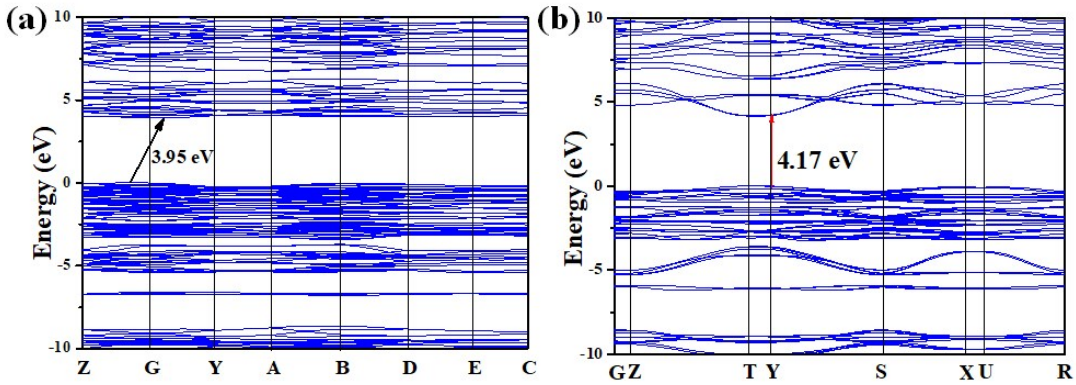


Figure S8. Arrangement of $[IO_2F_2]^{2-}$ anions in $BaIO_2F_3$ (a) and $Ba(IO_2F_2)_2$ (b), the purple arrows indicate the directions of $[IO_2F_2]^{2-}$ polyhedral.

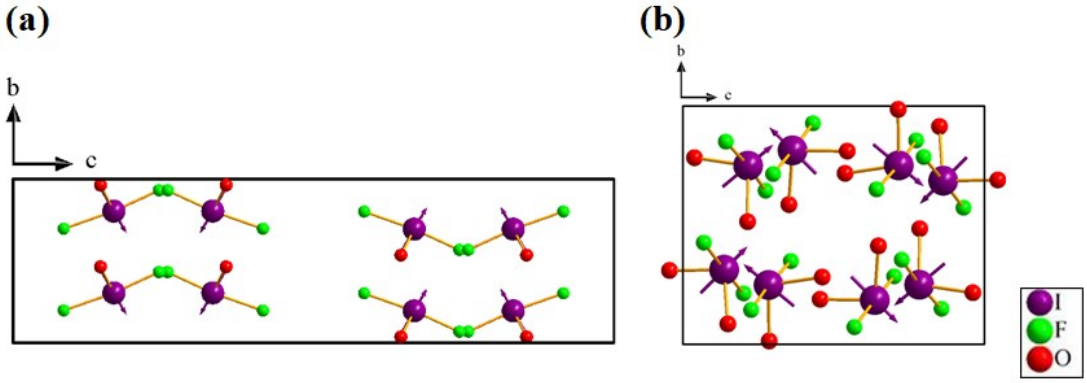
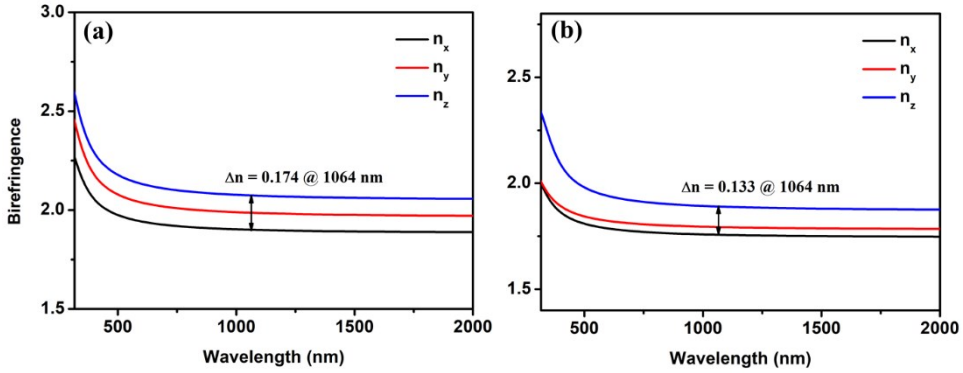


Figure S9. Calculated refractive index dispersion curves of $BaI_2O_5F_2$ and $BaIO_2F_3$.



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