Supporting information

$KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$: From Centrosymmetric Chain to Noncentrosymmetric Double Layer

Ying-Jie Jia,[a] *Yi-Gang Chen*,[*a] *Ting Wang*,[a] *Yao Guo*,[*b] *Xiao-Fang Guan*,[a] *Xian-Ming Zhang*[*a]

[a]Key Laboratory of Magnetic Molecules and Magnetic Information Material of Ministry of Education, School of Chemistry and Material Science, Shanxi Normal University, Linfen 041004, China

[b]Department of Chemical and Environmental Engineering, Anyang Institute of Technology, Anyang 455000, China

Table S1. Crystal data and structure refinement for $NaBi(IO_3)_4$ and $KBi(IO_3)_3(OH)$.

Table S2. Selected bond distances (Å) for $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

Table S3. Energy-Dispersive Spectrometry (EDS) for $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

Table S4. Dipole moments of IO_3 groups BiO_n (n = 7, 8) polyhedra for $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

Table S5. Calculation of dipole moment for $NaM(IO_3)_4$ (M = Ce, Sm, La, Eu, Bi, Y).

Fig. S1. Morphology for $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$..

Fig. S2. Energy-Dispersive Spectrometry (EDS) plot of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

Fig. S3. Experimental and simulated PXRD patterns of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

Fig. S4. (a) Coordinate environments of the K^+ in $KBi(IO_3)_3(OH)$.

Fig. S5. Asymmetric unit of $NaBi(IO_3)_4$.

Fig. S6. Structure of $NaBi(IO_3)_4$ along the *b*-axis.

Fig. S7. TGA and DSC curves of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

Fig. S8. PXRD patterns for the residual of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

Fig. S9. IR spectrum of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

Fig. S10. UV-vis diffuse spectra of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

Fig. S11. Calculated band structures of (a) $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

Fig. S12. Calculated refractive indices and birefringence of $NaBi(IO_3)_4$.

Table S1. Crystal data and structure refinement for $NaBi(IO_3)_4$ and $KBi(IO_3)_3(OH)$.

Empirical formula	$KBi(IO_3)_3(OH)$	$NaBi(IO_3)_4$
Formula weight	789.28	931.57
Crystal system	triclinic	monoclinic
Space group	*P*-1	*Cc*
a/Å	7.2662(4)	31.5437(19)
b/Å	8.1678(5)	5.6122(3)
c/Å	8.8629(5)	12.7289(8)
α/°	101.6212(10)	90
β/°	93.8011(11)	90.7346(12)
γ/°	109.3178(10)	90
Volume/Å^3	481.16(5)	2253.2(2)
Z	2	8
ρ_{calc} g/cm^3	5.448	5.492
μ/mm^{-1}	28.417	26.709
F(000)	683.0	3216.0
Crystal size/mm^3	0.25×0.21×0.15	0.3×0.15×0.08
Goodness-of-fit on F^2	1.180	1.074
R_1, wR_2 [$I>=2\sigma(I)$][a]	0.0170, 0.0488	0.0412, 0.0960
all data [$I>=2\sigma(I)$][a]	0.0171, 0.0489	0.0412, 0.0960
Flack parameter	—	0.4248(14)

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$. $wR_2=[w(F_o^2-F_c^2)^2/w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond distances (Å) and angles (°) for $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

$KBi(IO_3)_3(OH)$

Bi(1)-O(10)	2.137(3)	I(2)-O(9)#2	1.828(4)
Bi(1)-O(9)	2.338(4)	I(3)-O(8)	1.793(4)
Bi(1)-O(1)#1	2.351(4)	I(3)-O(7)	1.820(4)
Bi(1)-O(6)	2.354(4)	I(3)-O(6)	1.831(4)
Bi(1)-O(3)	2.413(4)	K(1)-O(10)#3	2.719(3)
Bi(1)-O(8)#2	2.457(4)	K(1)-O(1)#7	2.758(4)
Bi(1)-O(4)	2.665(4)	K(1)-O(7)#8	2.820(4)
I(1)-O(3)	1.828(4)	K(1)-O(8)#8	2.951(5)
I(1)-O(1)	1.830(4)	K(1)-O(2)#5	2.958(4)
I(1)-O(2)	1.790(4)	K(1)-O(1)#1	3.032(4)
I(2)-O(4)	1.805(4)	K(1)-O(4)#1	3.051(4)
I(2)-O(5)	1.805(4)	K(1)-O(9)#3	3.089(4)
O(2)-I(1)-O(3)	102.15(19)	O(5)-I(2)-O(9)#2	99.25(18)
O(2)-I(1)-O(1)	101.27(18)	O(8)-I(3)-O(7)	96.59(19)
O(3)-I(1)-O(1)	96.23(18)	O(8)-I(3)-O(6)	95.57(19)
O(4)-I(2)-O(5)	100.99(19)	O(7)-I(3)-O(6)	96.62(18)
O(4)-I(2)-O(9)#2	101.45(19)		

Symmetry codes:

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

#5 -x+1, -y+1, -z #6 x+1, y, z #7 x-1, y, z #8 x, y, z-1

$NaBi(IO_3)_4$

Bi(1)-O(9)#1	2.365(5)	Na(2)-O(24)#5	2.539(6)
Bi(1)-O(8)#2	2.388(5)	Na(2)-O(4)#6	2.609(6)
Bi(1)-O(10)#3	2.395(5)	Na(2)-O(13)#5	2.904(6)
Bi(1)-O(5)	2.411(5)	I(1)-O(2)	1.799(5)
Bi(1)-O(3)	2.449(5)	I(1)-O(1)	1.804(5)
Bi(1)-O(12)#3	2.470(5)	I(1)-O(3)	1.825(5)
Bi(1)-O(6)	2.552(5)	I(2)-O(6)	1.812(5)
Bi(1)-O(4)	2.660(5)	I(2)-O(7)	1.813(5)
Bi(2)-O(15)#2	2.319(5)	I(2)-O(8)	1.839(5)
Bi(2)-O(17)	2.350(5)	I(3)-O(9)	1.791(5)
Bi(2)-O(24)#4	2.427(5)	I(3)-O(5)	1.813(5)
Bi(2)-O(19)	2.429(5)	I(3)-O(10)	1.826(5)
Bi(2)-O(18)	2.498(5)	I(4)-O(11)	1.780(5)
Bi(2)-O(21)#5	2.512(5)	I(4)-O(13)	1.798(5)
Bi(2)-O(14)#3	2.523(5)	I(4)-O(4)	1.830(5)
Bi(2)-O(16)	2.549(5)	I(5)-O(24)	1.808(5)
Na(1)-O(11)	2.480(7)	I(5)-O(12)	1.819(5)
Na(1)-O(13)	2.673(6)	I(5)-O(14)	1.822(5)
Na(1)-O(14)	2.496(6)	I(6)-O(17)#6	1.805(5)
Na(1)-O(16)	2.811(7)	I(6)-O(15)	1.820(5)
Na(1)-O(24)	2.836(6)	I(6)-O(16)	1.825(5)

Na(1)-O(15)#2	2.374(6)	I(7)-O(23)	1.785(5)
Na(1)-O(21)#8	2.609(6)	I(7)-O(22)	1.804(5)
Na(1)-O(17)#8	2.744(6)	I(7)-O(18)	1.809(5)
Na(2)-O(10)	2.518(6)	I(8)-O(20)	1.802(5)
Na(2)-O(11)	2.355(6)	I(8)-O(21)	1.818(5)
Na(2)-O(14)	2.463(6)	I(8)-O(19)	1.823(5)
Na(2)-O(12)#5	2.516(5)		
O(2)-I(1)-O(1)	101.3(2)	O(24)-I(5)-O(12)	91.9(2)
O(2)-I(1)-O(3)	97.2(2)	O(24)-I(5)-O(14)	95.8(2)
O(1)-I(1)-O(3)	98.2(2)	O(12)-I(5)-O(14)	99.0(2)
O(6)-I(2)-O(7)	100.3(2)	O(17)#6-I(6)-O(15)	90.2(2)
O(6)-I(2)-O(8)	98.5(3)	O(17)#6-I(6)-O(16)	96.5(2)
O(7)-I(2)-O(8)	96.5(2)	O(15)-I(6)-O(16)	99.3(2)
O(9)-I(3)-O(5)	93.0(2)	O(23)-I(7)-O(22)	101.7(2)
O(9)-I(3)-O(10)	96.6(2)	O(23)-I(7)-O(18)	98.7(3)
O(5)-I(3)-O(10)	97.0(2)	O(22)-I(7)-O(18)	96.6(3)
O(11)-I(4)-O(13)	95.6(3)	O(20)-I(8)-O(21)	97.6(2)
O(11)-I(4)-O(4)	97.9(3)	O(20)-I(8)-O(19)	99.2(2)
O(13)-I(4)-O(4)	102.4(2)	O(21)-I(8)-O(19)	97.4(2)

Symmetry codes:

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

#4 x, -y, z+1/2 #5 x, y-1, z #6 x, -y-1, z-1/2

#7 x, -y-2, z-1/2 #8 x, -y, z-1/2

Table S3. Energy-Dispersive Spectrometry (EDS) for $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

$KBi(IO_3)_3(OH)$

Point 1				Point 2			
Element	Weight	Atomic	Formula	Element	Weight	Atomic	Formul
O K	19.08	65.05		O K	15.71	59.52	
K K	4.82	6.73	1.0	K K	5.06	7.84	1.0
I L	49.43	21.25	3.16	I L	51.53	24.61	3.14
Bi M	26.67	6.96	1.03	Bi M	27.69	8.03	1.02
Totals	100			Totals	100		
Point 3							
Element	Weight	Atomic	Formula				
O K	20.56	67.09					
K K	4.83	6.45	1.0	Average ratio:			
I L	48.41	19.92	3.09	$K_{1.0}Bi_{1.0}I_{3.1}$			
Bi M	26.21	6.55	1.02				
Totals	100						

$NaBi(IO_3)_4$

Point 1				Point 2			
Element	Weight	Atomic	Formula	Element	Weight	Atomic	Formula
O K	22.23	69.28		O K	20.59	66.93	
Na K	2.01	4.96	1.0	Na K	2.14	4.83	1.0
I L	53.74	21.11	4.26	I L	56.04	20.96	4.34
Bi M	22.03	5.26	1.06	Bi M	21.23	5.28	1.09
Totals	100			Totals	100		
Point 3							
Element	Weight	Atomic	Formula				
O K	21.28	67.38					
Na K	2.48	5.47	1.0	Average ratio:			
I L	55.36	22.10	4.04	$Na_{1.0}Bi_{1.03}I_{4.2}$			
Bi M	20.88	5.06	0.93				
Totals	100						

Table S4. Dipole moments of IO_3 groups BiO_n (n = 7, 8) polyhedra units for $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

$KBi(IO_3)_3(OH)$

Species	x-component	y-component	z -component	total magnitude debye $\times 10^{-18}$ esu·cm/Å^3	
I(1)O3	9.0659	7.6012	11.4177	13.2684	
	9.0659	–7.6012	–11.4177	13.2684	
	0	**0**	**0**	**0**	**0**
I(2)O3	–13.1435	–6.6366	3.7756	13.7845	
	13.1435	6.6366	–3.7756	13.7845	
	0	**0**	**0**	**0**	**0**
BiO7	–5.8118	3.0999	–3.1368	8.1638	
	5.8118	–3.0999	3.1368	8.1638	
	0	**0**	**0**	**0**	**0**
Unit cell		**0**	**0**	**0**	**0**

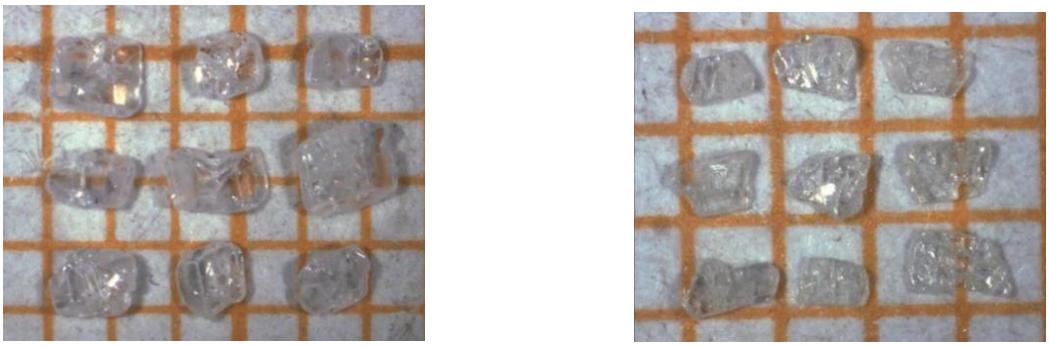
$NaBi(IO_3)_4$

Species	x-component	y-component	z -component	total magnitude debye	$\times 10^{-18}$
I(1)O3	–0.5591	14.3608	0.6727	14.3877	
	–0.5591	14.3608	0.6727	14.3877	
	–0.5591	–14.3608	0.6727	14.3877	
	–0.5591	–14.3608	0.6727	14.3877	
	–2.2364	**0**	**2.6908**	**3.4988**	**0.0016**
I(2)O3	–12.4146	6.3674	–4.5046	14.6614	
	–12.4146	6.3674	–4.5046	14.6614	
	–12.4146	–6.3674	–4.5046	14.6614	
	–12.4146	–6.3674	–4.5046	14.6614	
	–49.6584	**0**	**–18.0184**	**52.8263**	**0.0234**
I(3)O3	–15.5891	5.5097	–0.7776	16.5430	
	–15.5891	–5.5097	–0.7776	16.5430	
	–15.5891	5.5097	–0.7776	16.5430	
	–15.5891	–5.5097	–0.7776	16.5430	
	–62.3564	**0**	**-3.1104**	**62.434**	**0.0277**
I(4)O3	–13.2951	4.0339	5.5183	15.0121	
	–13.2951	–4.0339	5.5183	15.0121	
	–13.2951	–4.0339	5.5183	15.0121	
I(5)O3	–13.2951	4.0339	5.5183	15.0121	
	–53.1804	**0**	**22.0732**	**57.5793**	**0.0256**
	–0.6315	–4.2770	15.4451	16.0466	
	–0.6315	4.2770	15.4451	16.0466	
	–0.6315	4.2770	15.4451	16.0466	
	–0.6315	–4.2770	15.4451	16.0466	

	–2.5260	**0**	**61.7804**	**61.8320**	**0.0274**
I(6)O3	15.3016	–6.0531	–0.5152	16.4695	
	15.3016	6.0531	–0.5152	16.4695	
	15.3016	–6.0531	–0.5152	16.4695	
	15.3016	6.0531	–0.5152	16.4695	
I(7)O3	**61.2064**	**0**	**–2.0608**	**61.2411**	**0.0272**
	2.7175	14.1671	2.5253	14.6387	
	2.7175	14.1671	2.5253	14.6387	
	2.7175	–14.1671	2.5253	14.6387	
	2.7175	–14.1671	2.5253	14.6387	
	10.8700	**0**	**10.1012**	**14.8388**	**0.0066**
I(8)O3	12.8470	6.5269	2.4567	14.5902	
	12.8470	6.5269	2.4567	14.5902	
	12.8470	–6.5269	2.4567	14.5902	
	12.8470	–6.5269	2.4567	14.5902	
	51.3880	**0**	**9.8268**	**52.3191**	**0.0232**
Bi(1)O8	–0.8130	1.3457	1.7533	2.3627	
	–0.8130	–1.3457	1.7533	2.3627	
	–0.8130	1.3457	1.7533	2.3627	
	–0.8130	–1.3457	1.7533	2.3627	
	–3.2520	**0**	**7.0132**	**7.7305**	**0.0034**
Bi(2)O8	1.0198	–1.2673	–0.0191	1.6270	
	1.0198	1.2673	–0.0191	1.6270	
	1.0198	–1.2673	–0.0191	1.6270	
	1.0198	1.2673	–0.0191	1.6270	
	4.0792	**0**	**–0.0764**	**4.0799**	**0.0018**
Unit cell	**–45.6660**	**0**	**90.2196**	**101.1185**	**0.0449**

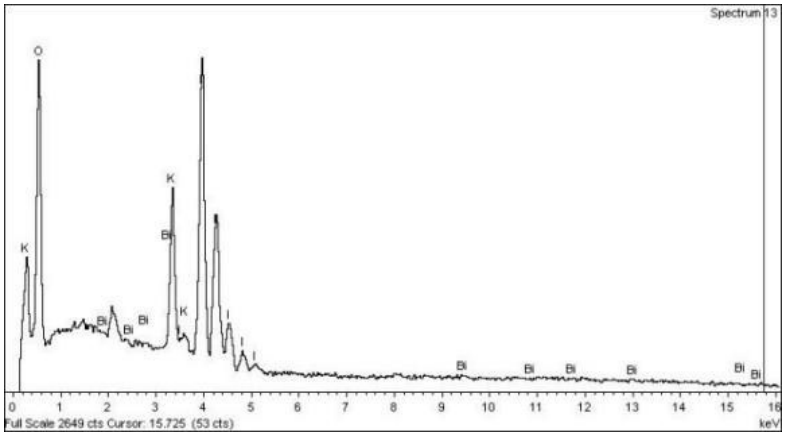
Table S5. Calculation of dipole moment for $NaM(IO_3)_4$ (M = Ce, Sm, La, Eu, Bi, Y).

$NaM(IO_3)_4$	Space group	Ionic Radius (M^{3+})	MO_8 (debye)	Total (debye)	V/Å^3	Total (D·Å $^{-3}$)	SHG
$NaCe(IO_3)_4$	*Cc*	1.14	0.85–1.34	100. 39	2318.58	0.0433	50×α-SiO_2
$NaSm(IO_3)_4$	*Cc*	1.27	0.96–1.60	99. 01	2248.44	0.0440	60×α-SiO_2
$NaLa(IO_3)_4$	*Cc*	1.16	1.19–1.75	98. 38	2316.8	0.0425	120×α-SiO_2
$NaEu(IO_3)_4$	*Cc*	1.25	1.11–1.62	97. 69	2231.4	0.0438	130×α-SiO_2
$NaBi(IO_3)_4$	*Cc*	1.17	1.63–2.33	101. 11	2253.2	0.0449	5.0×KDP
$NaY(IO_3)_4$	*Cc*	1.02	0.84–1.61	100. 46	2181.3	0.0460	400×α-SiO_2

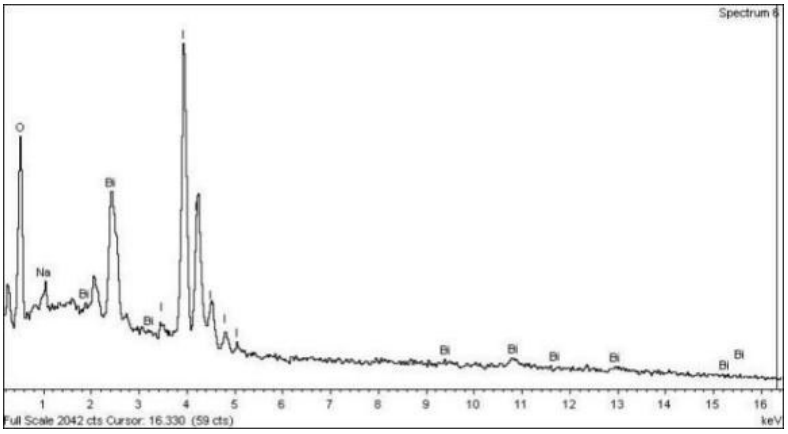


$KBi(IO_3)_3(OH)$ $NaBi(IO_3)_4$

Fig. S1. Morphology for $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.



$KBi(IO_3)_3(OH)$



$NaBi(IO_3)_4$

Fig. S2. Energy-Dispersive Spectrometry (EDS) plot of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

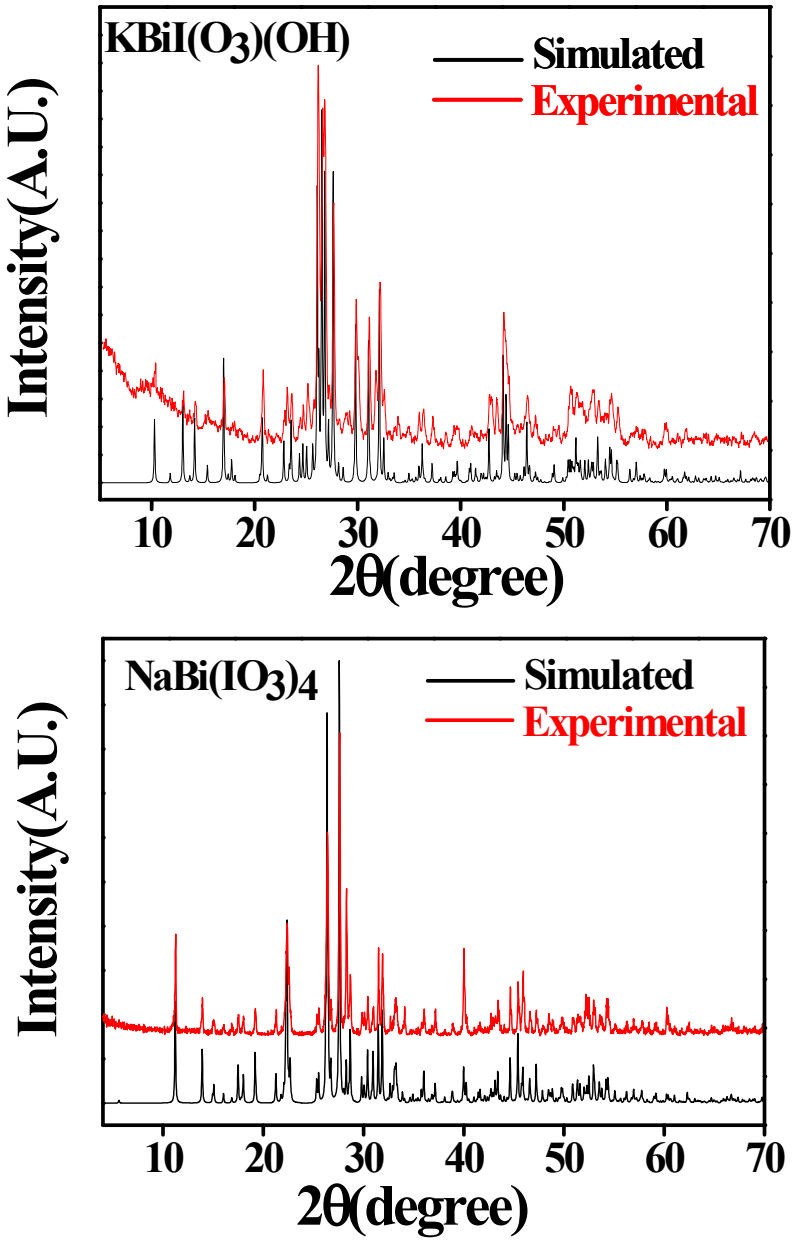


Fig. S3. Experimental and simulated PXRD patterns of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

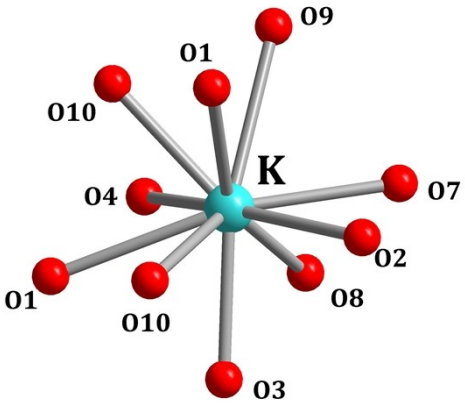


Fig. S4. Coordinate environments of the K^+ in $KBi(IO_3)_3(OH)$.

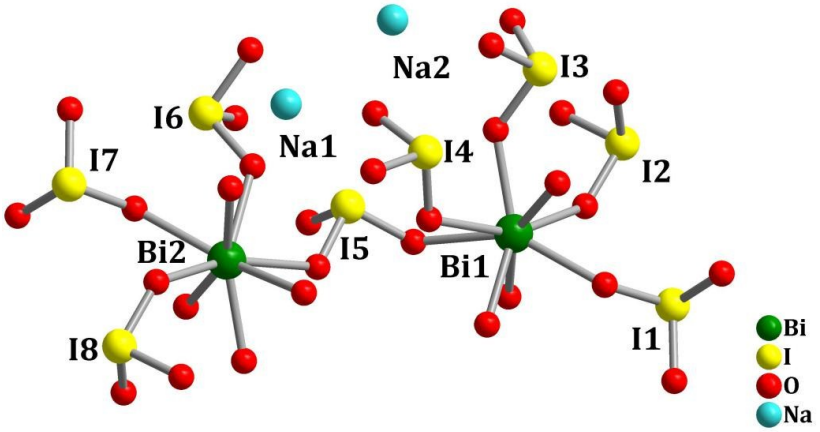


Fig. S5. Asymmetric unit of $NaBi(IO_3)_4$.

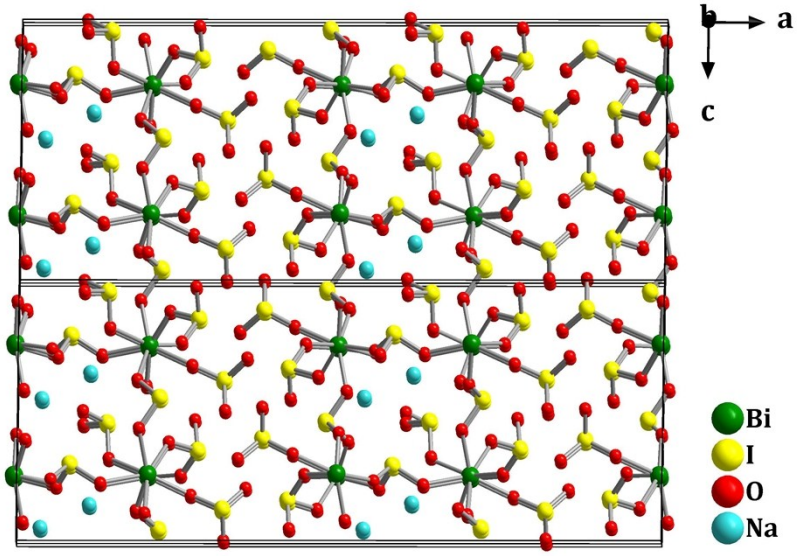


Fig. S6. Structure of $NaBi(IO_3)_4$ along the *b*-axis.

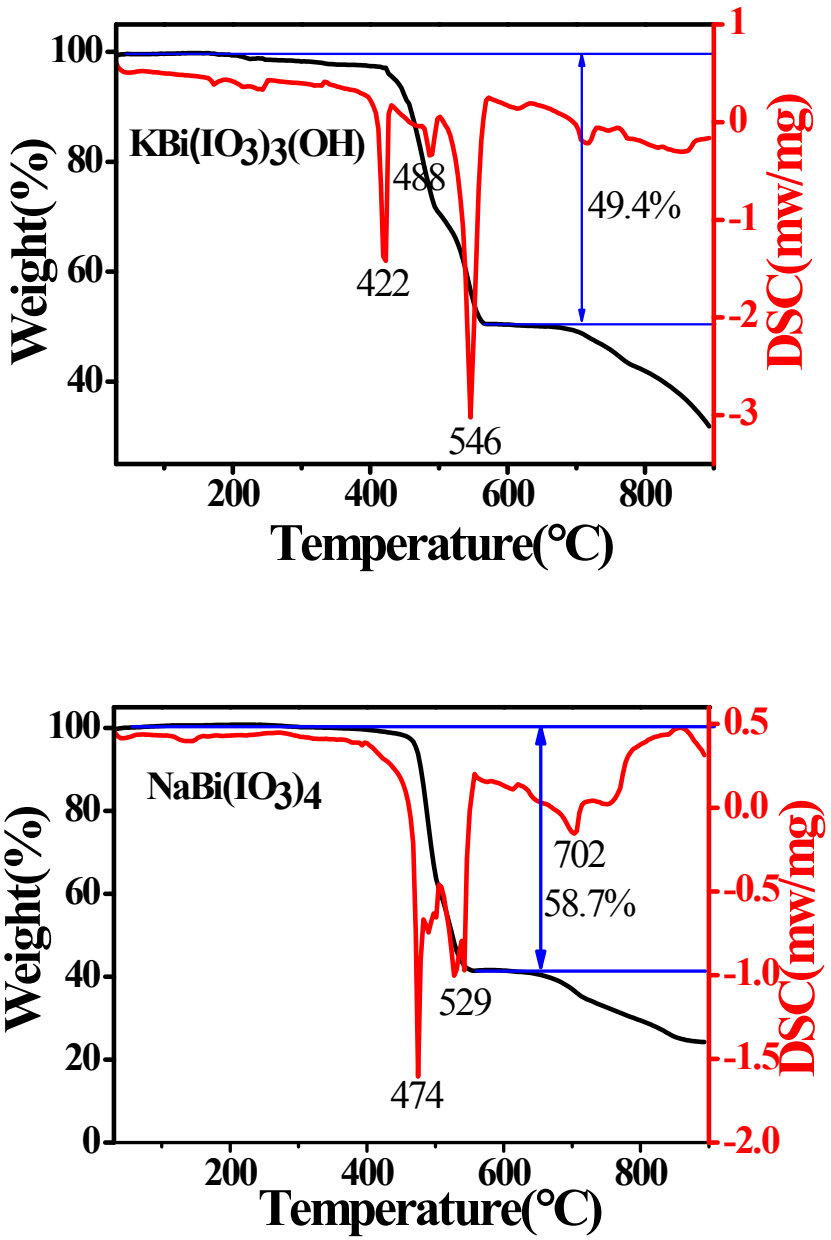


Fig. S7. TGA and DSC curves of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

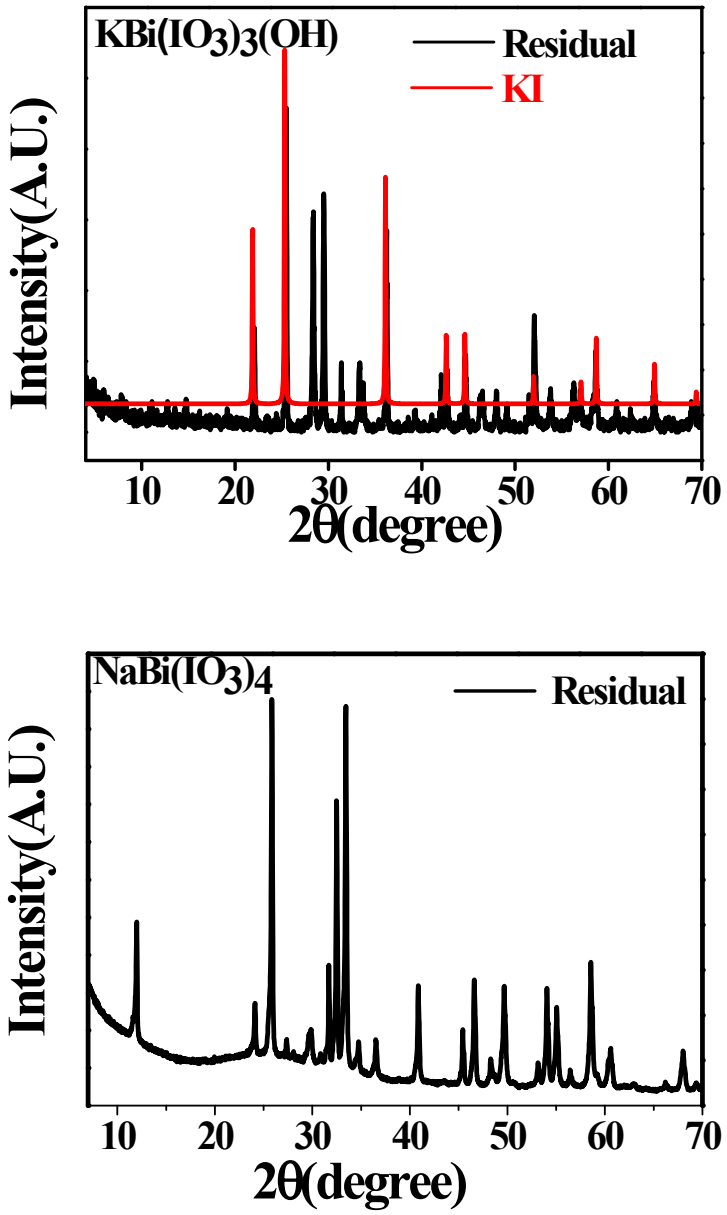


Fig. S8. PXRD patterns for the residual of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

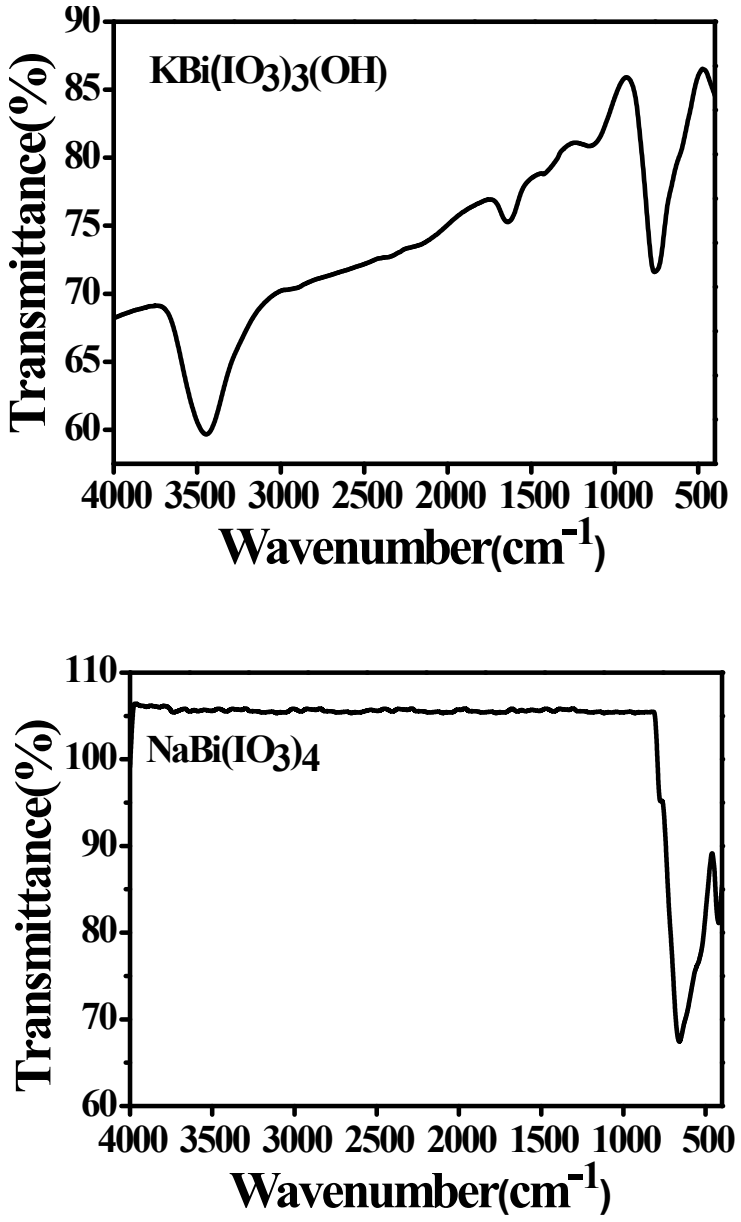


Fig. S9. IR spectrum of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$.

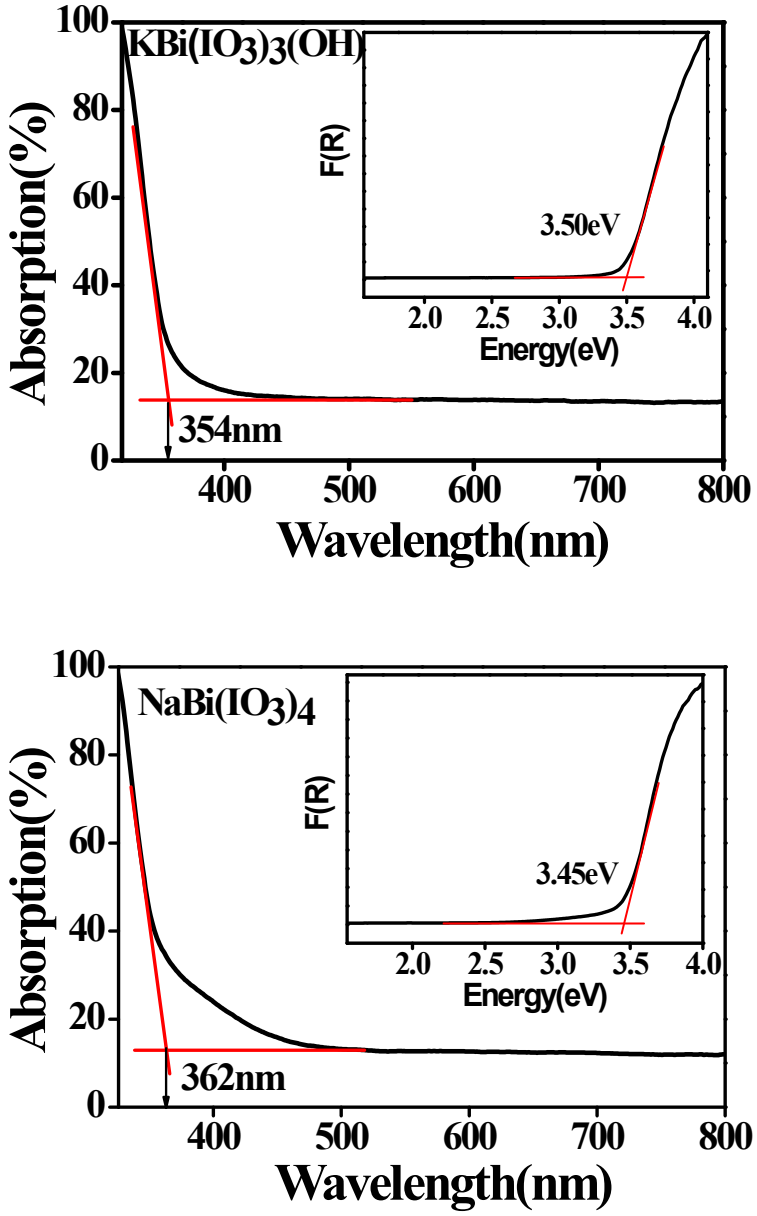


Fig. S10. UV-vis diffuse spectra of $KBi(IO_3)_3(OH)$ and $NaBi(IO_3)_4$

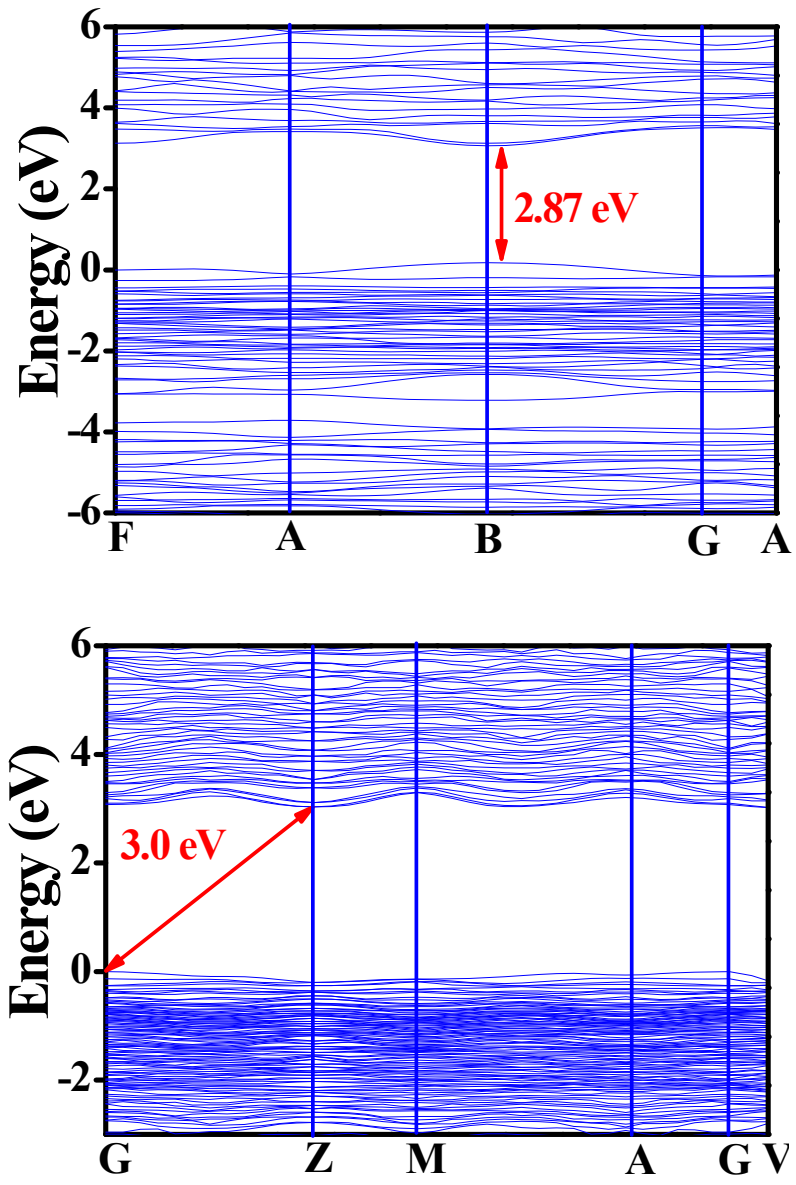


Fig. S11. Calculated band structures of (a) $KBi(IO_3)_3(OH)$ and (b) $NaBi(IO_3)_4$.

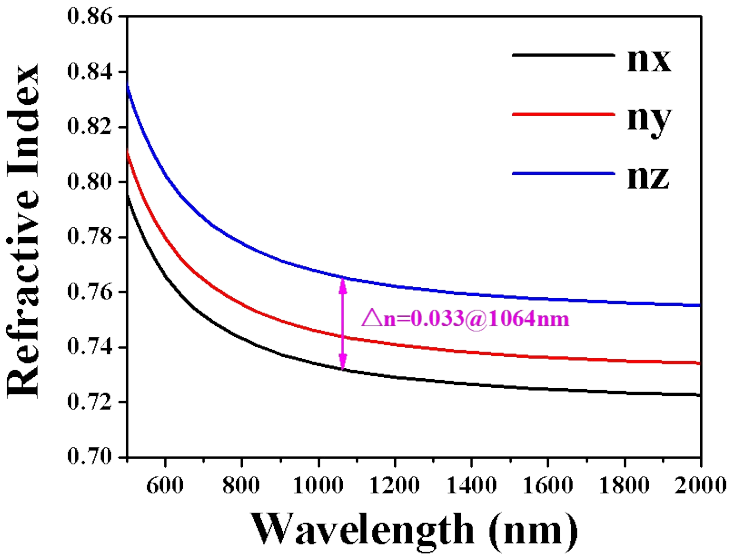


Fig. S12. Calculated refractive indices and birefringence of $NaBi(IO_3)_4$.