Supporting Information

$Pb_6Ba_2(BO_3)_5X$ (X = Cl, Br): new borate halides with strong simulated optical anisotropies derived from Pb^{2+} and $(BO_3)^{3-}$

Lu Liu,[a,b] Bingbing Zhang,[a,b] Fangfang Zhang,[*,a] Shilie Pan,[*,a] Fangyuan Zhang,[a,b] Xingwen Zhang,[a,b] Xiaoyu Dong,[a,b] and Zhihua Yang[*,a]

[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;

*To whom correspondence should be addressed.

E-mail: ffzhang@ms.xjb.ac.cn (Fangfang Zhang); slpan@ms.xjb.ac.cn (Shilie Pan)

Tel: (+86)991-3674558, Fax: (+86)991-3838957

Table S1. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $Pb_6Ba_2(BO_3)_5X$ (X = Cl, Br). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyckoff positions	S.O.F.	*x*	*y*	*z*	U(eq)
Pb(1)	4i	1	6417(1)	0	4361(1)	11(1)
Pb(2)	4i	1	5533(1)	0	1888(1)	17(1)
Pb(3)	4i	1	8551(1)	0	748(1)	29(1)
Ba(1)	4i	1	9241(2)	0	3038(1)	12(1)
Cl(1)	2c	1	0	0	5000	17(2)
B(1)	4i	1	7080(30)	5000	1741(15)	2(5)
B(2)	4i	1	2730(30)	0	3587(18)	13(6)
B(3)	2b	1	0	5000	0	50(17)
O(1)	8j	1	7028(12)	7240(20)	3532(7)	12(3)
O(2)	4i	1	4247(19)	0	3551(10)	14(4)
O(3)	4i	1	5565(19)	5000	1753(10)	16(4)
O(4)	8j	1	7795(14)	7220(20)	1771(7)	20(3)
O(5)	4g	0.5	0	2090(110)	0	55(14)
O(6)	8j	0.5	9820(40)	5900(60)	640(20)	52(10)

Atoms	Wyckoff positions	S.O.F.	*x*	*y*	*z*	U(eq)
Pb(1)	4i	1	6410(1)	0	4347(1)	8(1)
Pb(2)	4i	1	5532(1)	0	1881(1)	17(1)
Pb(3)	4i	1	8547(1)	0	739(1)	21(1)
Ba(1)	4i	1	9226(2)	0	3022(1)	8(1)
Br(1)	2c	1	0	0	5000	66(2)
B(1)	4i	1	6970(30)	5000	1700(18)	5(6)
B(2)	4i	1	2760(30)	0	3561(19)	9(6)
B(3)	2b	1	0	5000	0	28(13)
O(1)	8j	1	7024(13)	7210(20)	3528(7)	10(3)
O(2)	4i	1	4250(20)	0	3554(11)	11(4)
O(3)	4i	1	5531(19)	5000	1728(11)	10(4)
O(4)	8j	1	7778(14)	7230(20)	1764(7)	12(3)
O(5)	4g	0.5	0	2130(80)	0	26(10)
O(6)	8j	0.5	9800(30)	5840(50)	614(16)	23(7)

Table S2(a). Selected bond lengths (Å) and angles (deg.) for $Pb_6Ba_2(BO_3)_5Cl$.

Pb(1)-O(2)	2.250(18)	O(3)#6-Pb(3)-O(4)	74.8(4)
Pb(1)-O(1)	2.255(12)	O(5)#5-Pb(3)-O(4)	161.4(7)
Pb(2)-O(6)#4	2.26(4)	O(5)#7-Pb(3)-O(4)	113.2(12)
Pb(2)-O(4)	2.627(13)	O(6)#1-Pb(3)-O(4)	139.4(9)
Pb(2)-O(3)	2.7094(17)	O(6)-Pb(3)-O(4)	75.1(8)
Pb(3)-O(3)#6	2.339(19)	O(4)#1-Pb(3)-O(4)	71.2(6)
Pb(3)-O(5)#5	2.37(3)	O(3)#6-Ba(1)-O(1)	136.0(4)
Pb(3)-O(6)	2.54(3)	O(3)#6-Ba(1)-O(1)#1	136.0(4)
Pb(3)-O(4)	2.574(13)	O(1)-Ba(1)-O(1)#1	63.7(5)
Ba(1)-O(3)#6	2.821(17)	O(3)#6-Ba(1)-O(4)	63.8(4)
Ba(1)-O(1)	2.822(11)	O(1)-Ba(1)-O(4)	73.3(4)
Ba(1)-O(4)	2.840(14)	O(1)#1-Ba(1)-O(4)	105.6(4)
Ba(1)-O(1)#9	2.846(12)	O(3)#6-Ba(1)-O(4)#1	63.8(4)
Ba(1)-O(2)#8	2.851(6)	O(1)-Ba(1)-O(4)#1	105.6(4)
B(1)-O(4)	1.369(17)	O(1)#1-Ba(1)-O(4)#1	73.3(4)
B(1)-O(3)	1.41(3)	O(4)-Ba(1)-O(4)#1	63.7(5)
B(2)-O(1)#4	1.371(18)	O(3)#6-Ba(1)-O(1)#6	74.8(4)
B(2)-O(2)	1.42(3)	O(1)-Ba(1)-O(1)#6	143.5(5)
B(3)-O(6)	1.29(3)	O(1)#1-Ba(1)-O(1)#6	110.8(2)
B(3)-O(5)	1.57(6)	O(4)-Ba(1)-O(1)#6	137.5(3)
O(2)-Pb(1)-O(1)	83.3(4)	O(4)#1-Ba(1)-O(1)#6	106.8(4)
O(2)-Pb(1)-O(1)#1	83.3(4)	O(3)#6-Ba(1)-O(1)#9	74.8(4)
O(1)-Pb(1)-O(1)#1	82.6(6)	O(1)-Ba(1)-O(1)#9	110.8(2)
O(6)#4-Pb(2)-O(6)#3	24.6(18)	O(1)#1-Ba(1)-O(1)#9	143.5(5)
O(6)#4-Pb(2)-O(4)#1	97.3(9)	O(4)-Ba(1)-O(1)#9	106.8(4)

O(6)#3-Pb(2)-O(4)#1	83.3(9)	O(4)#1-Ba(1)-O(1)#9	137.5(3)
O(6)#4-Pb(2)-O(4)	83.3(9)	O(1)#6-Ba(1)-O(1)#9	50.3(5)
O(6)#3-Pb(2)-O(4)	97.3(9)	O(3)#6-Ba(1)-O(2)#6	106.9(3)
O(4)#1-Pb(2)-O(4)	69.6(6)	O(1)-Ba(1)-O(2)#6	110.7(4)
O(6)#4-Pb(2)-O(3)	72.8(10)	O(1)#1-Ba(1)-O(2)#6	49.8(4)
O(6)#3-Pb(2)-O(3)	97.5(10)	O(4)-Ba(1)-O(2)#6	136.9(5)
O(4)#1-Pb(2)-O(3)	122.6(5)	O(4)#1-Ba(1)-O(2)#6	74.4(4)
O(4)-Pb(2)-O(3)	53.3(5)	O(1)#6-Ba(1)-O(2)#6	63.4(4)
O(6)#4-Pb(2)-O(3)#5	97.5(10)	O(1)#9-Ba(1)-O(2)#6	110.9(4)
O(6)#3-Pb(2)-O(3)#5	72.8(10)	O(3)#6-Ba(1)-O(2)#8	106.9(3)
O(4)#1-Pb(2)-O(3)#5	53.3(5)	O(1)-Ba(1)-O(2)#8	49.8(4)
O(4)-Pb(2)-O(3)#5	122.6(5)	O(1)#1-Ba(1)-O(2)#8	110.7(4)
O(3)-Pb(2)-O(3)#5	169.4(8)	O(4)-Ba(1)-O(2)#8	74.4(4)
O(3)#6-Pb(3)-O(5)#5	88.8(4)	O(4)#1-Ba(1)-O(2)#8	136.9(5)
O(3)#6-Pb(3)-O(5)#7	88.8(4)	O(1)#6-Ba(1)-O(2)#8	110.9(4)
O(5)#5-Pb(3)-O(5)#7	57(2)	O(1)#9-Ba(1)-O(2)#8	63.4(4)
O(3)#6-Pb(3)-O(6)#1	75.1(8)	O(2)#6-Ba(1)-O(2)#8	142.3(7)
O(5)#5-Pb(3)-O(6)#1	38.3(13)	O(4)-B(1)-O(4)#12	122(2)
O(5)#7-Pb(3)-O(6)#1	92.6(14)	O(4)-B(1)-O(3)	118.7(10)
O(6)-Pb(3)-O(4)#1	139.4(9)	O(6)#12-B(3)-O(6)#14	180(3)
O(6)#14-B(3)-O(5)#7	68.0(15)	O(6)#7-B(3)-O(6)#14	44(3)
O(6)-B(3)-O(5)	112.0(15)	O(6)-B(3)-O(5)#7	68.0(15)
O(6)#12-B(3)-O(5)	68.0(15)	O(6)#12-B(3)-O(5)#7	112.0(15)
O(6)#7-B(3)-O(5)	68.0(15)	O(6)#7-B(3)-O(5)#7	112.0(15)
O(6)#14-B(3)-O(5)	112.0(15)	O(5)#7-B(3)-O(5)	180.000(1)

Symmetry transformations used to generate equivalent atoms:

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

#4 x-1/2,-y+3/2,z #5 x,y+1,z #6 x+1/2,y+1/2,z

#7 -x+2,-y+1,-z #8 x+1/2,y-1/2,z #9 x+1/2,-y+3/2,z

#10 x+1,y,z #11 -x+2,-y+2,-z+1 #12 x,-y+1,z

#13 x-1,y,z #14 -x+2,y,-z #15 x,y-1,z

Table S2(b) Selected bond lengths (Å) and angles (deg.) for $Pb_6Ba_2(BO_3)_5Br$.

Pb(1)-O(2)	2.224(18)	O(5)#5-Pb(3)-O(4)	161.8(5)
Pb(1)-O(1)	2.258(13)	O(5)#7-Pb(3)-O(4)	113.0(9)
Pb(2)-O(6)#3	2.29(3)	O(6)#1-Pb(3)-O(4)	139.9(7)
Pb(2)-O(4)	2.610(13)	O(6)-Pb(3)-O(4)	75.6(7)
Pb(2)-O(3)	2.708(2)	O(4)#1-Pb(3)-O(4)	70.6(6)
Pb(3)-O(3)#6	2.295(17)	O(4)-Ba(1)-O(4)#1	63.9(5)
Pb(3)-O(5)#5	2.37(2)	O(4)-Ba(1)-O(3)#6	63.6(4)
Pb(3)-O(6)	2.56(3)	O(4)-Ba(1)-O(1)	73.5(4)
Pb(3)-O(4)	2.583(14)	O(4)#1-Ba(1)-O(1)	106.1(4)
Ba(1)-O(4)#1	2.819(13)	O(3)#6-Ba(1)-O(1)	136.0(3)
Ba(1)-O(3)#6	2.83(2)	O(4)-Ba(1)-O(1)#6	137.7(4)
Ba(1)-O(1)#1	2.835(13)	O(4)#1-Ba(1)-O(1)#6	107.2(4)
Ba(1)-O(1)#6	2.842(12)	O(3)#6-Ba(1)-O(1)#6	75.4(4)
Ba(1)-O(2)#8	2.858(7)	O(1)-Ba(1)-O(1)#6	142.6(5)
B(1)-O(3)	1.35(4)	O(1)#1-Ba(1)-O(1)#6	110.5(2)
B(1)-O(4)	1.41(2)	O(4)-Ba(1)-O(1)#9	107.2(4)
B(2)-O(1)#3	1.370(19)	O(4)#1-Ba(1)-O(1)#9	137.7(4)
B(2)-O(2)	1.38(4)	O(3)#6-Ba(1)-O(1)#9	75.4(4)
B(3)-O(6)	1.24(3)	O(1)-Ba(1)-O(1)#9	110.5(2)
B(3)-O(6)#12	1.24(3)	O(1)#1-Ba(1)-O(1)#9	142.6(5)
B(3)-O(5)	1.54(4)	O(1)#6-Ba(1)-O(1)#9	49.5(5)
O(2)-Pb(1)-O(1)	84.0(5)	O(4)-Ba(1)-O(2)#6	137.6(4)
O(1)-Pb(1)-O(1)#1	83.5(6)	O(4)#1-Ba(1)-O(2)#6	74.9(4)
O(6)#4-Pb(2)-O(6)#3	22.7(13)	O(3)#6-Ba(1)-O(2)#6	107.5(4)

O(6)#4-Pb(2)-O(4)#1	96.7(8)	O(1)-Ba(1)-O(2)#6	110.5(5)
O(6)#3-Pb(2)-O(4)#1	83.8(7)	O(1)#1-Ba(1)-O(2)#6	49.4(4)
O(4)#1-Pb(2)-O(4)	69.7(6)	O(1)#6-Ba(1)-O(2)#6	63.5(4)
O(6)#4-Pb(2)-O(3)#5	95.8(7)	O(1)#9-Ba(1)-O(2)#6	110.1(4)
O(6)#3-Pb(2)-O(3)#5	73.1(7)	O(4)-Ba(1)-O(2)#8	74.9(4)
O(4)#1-Pb(2)-O(3)#5	53.7(5)	O(4)#1-Ba(1)-O(2)#8	137.6(4)
O(4)-Pb(2)-O(3)#5	123.0(5)	O(3)#6-Ba(1)-O(2)#8	107.5(4)
O(3)#5-Pb(2)-O(3)	168.3(8)	O(1)-Ba(1)-O(2)#8	49.4(4)
O(3)#6-Pb(3)-O(5)#5	88.5(4)	O(1)#1-Ba(1)-O(2)#8	110.5(5)
O(5)#5-Pb(3)-O(5)#7	57.9(18)	O(1)#6-Ba(1)-O(2)#8	110.1(4)
O(3)#6-Pb(3)-O(6)#1	76.0(6)	O(1)#9-Ba(1)-O(2)#8	63.5(4)
O(5)#5-Pb(3)-O(6)#1	37.4(10)	O(2)#6-Ba(1)-O(2)#8	141.0(7)
O(5)#7-Pb(3)-O(6)#1	93.2(11)	O(3)-B(1)-O(4)	121.0(12)
O(6)#1-Pb(3)-O(6)	122.5(13)	O(4)-B(1)-O(4)#12	117(2)
O(3)#6-Pb(3)-O(4)#1	75.0(5)	O(1)#3-B(2)-O(2)	119.6(12)
O(5)#5-Pb(3)-O(4)#1	113.0(9)	O(6)#7-B(3)-O(6)	180(3)
O(5)#7-Pb(3)-O(4)#1	161.8(5)	O(6)#7-B(3)-O(6)#14	43(2)
O(6)#1-Pb(3)-O(4)#1	75.6(7)	O(6)-B(3)-O(6)#14	137(2)
O(6)-Pb(3)-O(4)#1	139.9(7)	O(6)-B(3)-O(6)#12	43(2)
O(3)#6-Pb(3)-O(4)	75.0(5)		

Symmetry transformations used to generate equivalent atoms:

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

#4 x-1/2,-y+3/2,z #5 x,y+1,z #6 x+1/2,y+1/2,z

#7 -x+2,-y+1,-z #8 x+1/2,y-1/2,z #9 x+1/2,-y+3/2,z

#10 x+1,y,z #11 -x+2,-y+2,-z+1 #12 x,-y+1,z #13 x-1,y,z #14 -x+2,y,-z #15 x,y-1,z

Table S3. Atom-cutting analysis and calculated birefringence at 532 nm for $Pb_6Ba_2(BO_3)_5Cl$.

Species	n_x	n_y	n_z	Δn
All $(BO_3)^{3-}$	1.7187	1.7325	1.6232	0.1093
Pb^{2+}	1.4675	1.4637	1.4152	0.0523
Ba^{2+}, Cl^-	1.2652	1.2651	1.2334	0.0318
sum				0.1934
Calcd.	2.2592	2.2621	2.1039	0.1582

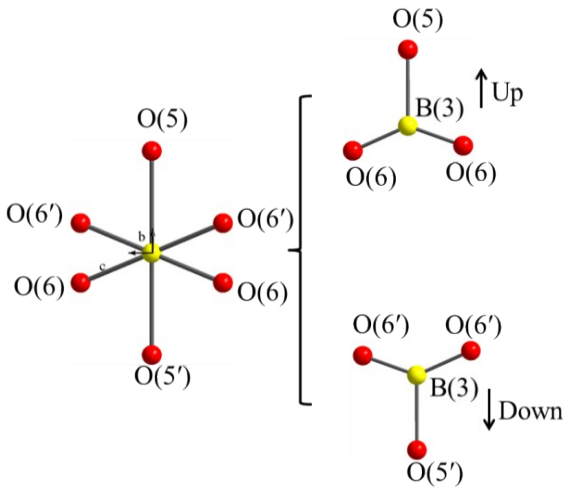
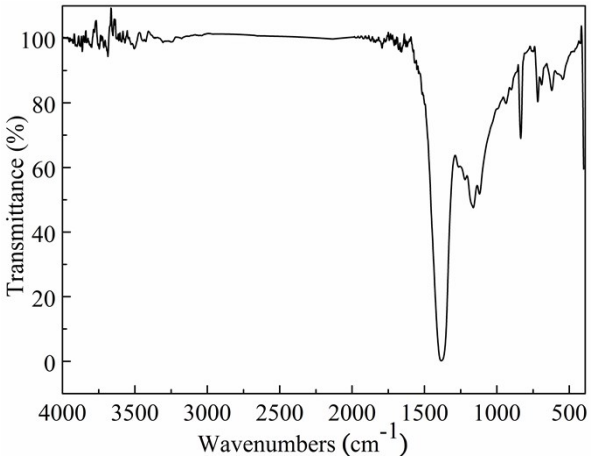
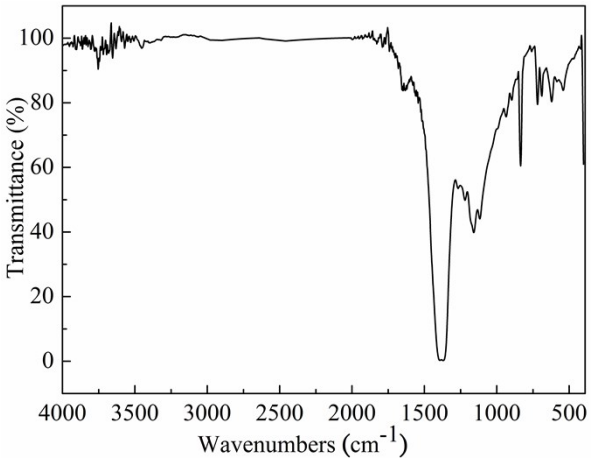


Figure S1. Scheme showing the substructures of $B(3)O_3$ groups.

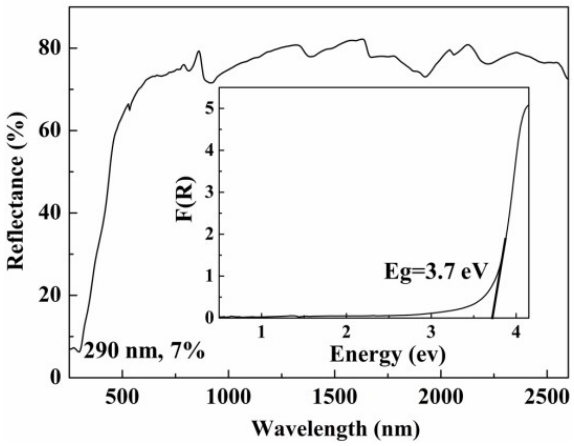


(a)

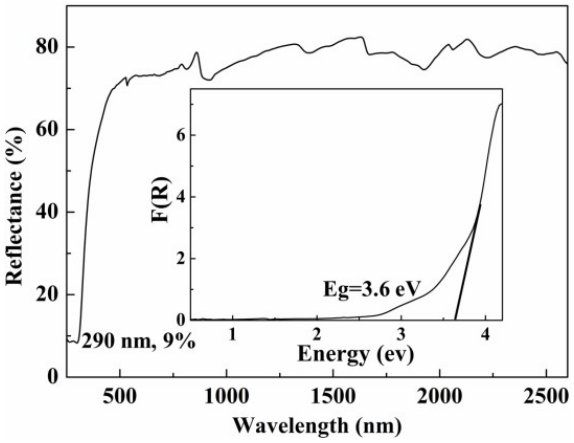


(b)

Figure S2. IR spectra of $Pb_6Ba_2(BO_3)_5Cl$ (a) and $Pb_6Ba_2(BO_3)_5Br$ (b).

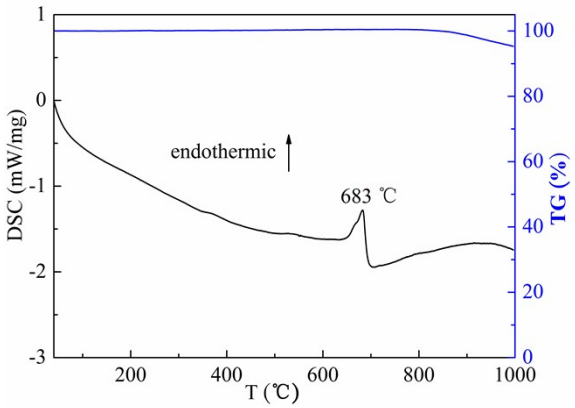


(a)

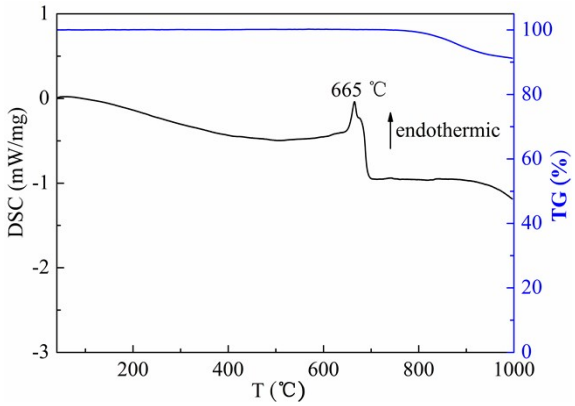


(b)

Figure S3. UV−Vis−NIR diffuse reflectance spectra of $Pb_6Ba_2(BO_3)_5Cl$ (a) and $Pb_6Ba_2(BO_3)_5Br$ (b).

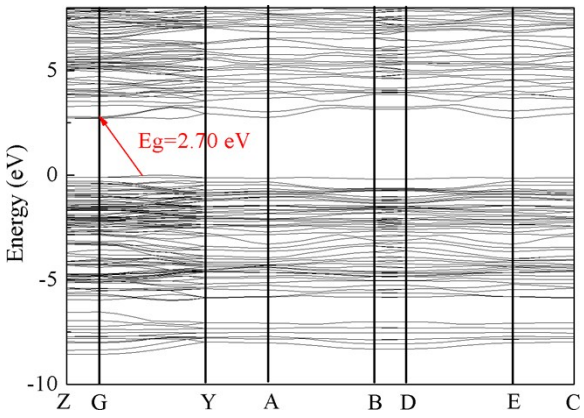


(a)

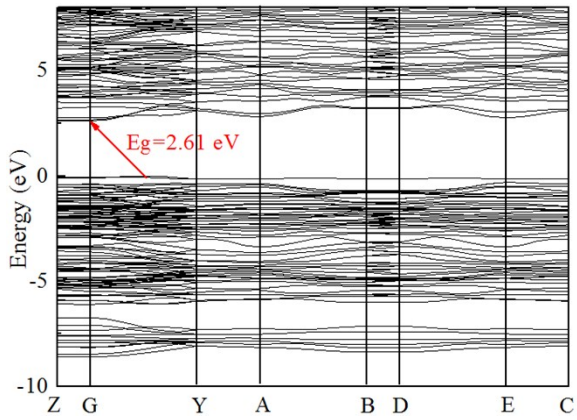


(b)

Figure S4. TG-DSC curves of $Pb_6Ba_2(BO_3)_5Cl$ (a) and $Pb_6Ba_2(BO_3)_5Br$ (b).



(a)



(b)

Figure S5. Band structure of $Pb_6Ba_2(BO_3)_5Cl$ (a) and $Pb_6Ba_2(BO_3)_5Br$ (b).

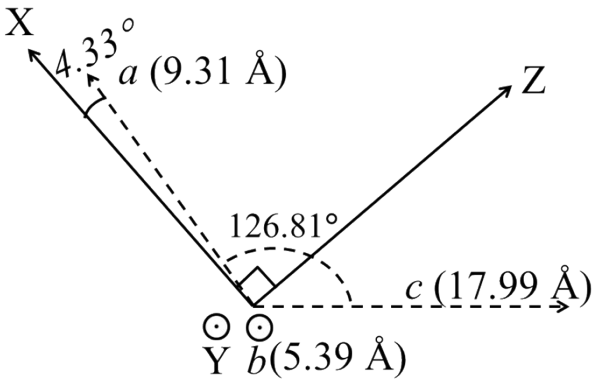


Figure S6. Relative orientation of the indicatrix axes to the crystallographic axes in $Pb_6Ba_2(BO_3)_5Br$.