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Supplementary Information

$Ba_4(BO_3)_3(SiO_4)\cdot Ba_3X$ (X = Cl, Br): New Salt-Inclusion Borosilicate Halides as Potential Deep UV Nonlinear Optical Materials

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Table S1(a) Atomic coordinates and equivalent isotropic displacement parameters for $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff	S.O.F.	x	y	z	U_{eq}
Ba(1)	6*c*	1.00	2829(1)	1414(1)	5277(1)	15(1)
Ba(2)	6*c*	1.00	4738(1)	5263(1)	3731(1)	19(1)
Ba(3)	2*b*	1.00	6667	3333	2412(2)	16(1)
B(1)	6*c*	1.00	8175(8)	6350(16)	860(20)	16(3)
Si(1)	2*b*	1.00	6667	3333	6427(14)	33(2)
O(1)	12*d*	1.00	6965(7)	6017(8)	1723(10)	20(2)
O(2)	2*b*	1.00	6667	3333	– 1340(30)	19(4)
O(3)	6*c*	1.00	3116(11)	1558(6)	9114(16)	25(3)
O(4)	6*c*	1.00	5906(7)	1811(14)	5610(20)	66(4)
Cl(1)	2*a*	1.00	0	0	7459(8)	18(1)

Table S1(b) Atomic coordinates and equivalent isotropic displacement parameters for $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	Wyckoff	S.O.F.	x	y	z	U_{eq}
Ba(1)	2*b*	1.00	3333	6667	1265(3)	11(1)
Ba(2)	6*c*	1.00	7102(1)	8551(1)	– 1690(1)	16(1)
Ba(3)	6*c*	1.00	513(1)	5257(1)	4860(2)	13(1)
Si(1)	2*b*	1.00	3333	6667	– 2822(14)	15(2)
B(1)	6*c*	1.00	1829(10)	3660(20)	2770(30)	13(2)
O(1)	12*d*	1.00	– 930(10)	6028(10)	6880(13)	22(2)
O(2)	6*c*	1.00	1595(8)	3190(16)	4510(20)	31(4)
O(3)	6*c*	1.00	4086(10)	8170(20)	– 1990(30)	59(2)
O(4)	2*b*	1.00	3333	6667	– 5040(40)	14(4)
Br(1)	2*a*	1.00	0	0	1072(5)	19(1)

Table S2(a) Selected bond lengths (Å) and angles (deg.) for $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$.

Ba(1)-O(3)	2.800(12)	O(1)-Ba(2)-O(1)$^{\#8}$	97.6(2)
Ba(1)-O(1)$^{\#1}$	2.960(8)	O(1)$^{\#5}$-Ba(2)-O(1)$^{\#1}$	97.6(2)
Ba(1)-O(1)$^{\#2}$	2.960(8)	O(1)-Ba(2)-O(1)$^{\#1}$	153.55(16)
Ba(1)-O(3)$^{\#3}$	3.013(7)	O(1)$^{\#8}$-Ba(2)-O(1)$^{\#1}$	74.1(3)
Ba(1)-O(3)$^{\#4}$	3.013(7)	O(1)$^{\#1}$-Ba(2)-O(3)$^{\#9}$	116.9(3)
Ba(1)-O(1)$^{\#5}$	3.046(7)	O(1)-Ba(2)-O(3)$^{\#4}$	144.9(2)
Ba(1)-O(1)$^{\#6}$	3.046(7)	O(1)$^{\#5}$-Ba(2)-O(3)$^{\#9}$	144.9(2)
Ba(1)-Cl(1)	3.167(3)	O(1)$^{\#8}$-Ba(2)-O(3)$^{\#4}$	116.9(3)
Ba(1)-O(4)$^{\#7}$	3.255(12)	O(1)$^{\#10}$-Ba(3)-O(1)$^{\#6}$	70.4(3)
Ba(1)-O(4)	3.255(12)	O(1)$^{\#7}$-Ba(3)-O(1)$^{\#6}$	117.08(8)
Ba(2)-O(4)$^{\#4}$	2.587(15)	O(2)$^{\#1}$-Ba(2)-O(3)$^{\#9}$	71.61(16)
Ba(2)-O(1)$^{\#5}$	2.637(7)	O(2)$^{\#1}$-Ba(2)-O(1)$^{\#1}$	82.4(4)
Ba(2)-O(1)	2.637(7)	O(2)#1-Ba(2)-O(3)$^{\#4}$	71.61(16)
Ba(2)-O(4)$^{\#7}$	2.644(14)	O(2)#1-Ba(2)-O(1)$^{\#8}$	82.4(4)
Ba(2)-O(2)$^{\#1}$	2.7233(14)	O(3)$^{\#9}$-Ba(2)-O(3)$^{\#4}$	141.6(3)
Ba(2)-O(1)$^{\#8}$	2.770(7)	O(4)$^{\#4}$-Ba(2)-O(2)$^{\#1}$	60.0(5)
Ba(2)-O(1)$^{\#1}$	2.770(7)	O(4)$^{\#7}$-Ba(2)-O(2)$^{\#1}$	150.1(6)
Ba(2)-O(3)$^{\#9}$	3.157(8)	O(4)$^{\#4}$-Ba(2)-O(1)$^{\#8}$	128.0(2)
Ba(2)-O(3)$^{\#4}$	3.157(8)	O(4)$^{\#7}$-Ba(2)-O(1)$^{\#8}$	73.9(3)
Ba(3)-O(2)	2.73(2)	O(4)$^{\#4}$-Ba(2)-O(1)$^{\#1}$	128.0(2)
Ba(3)-O(4)$^{\#6}$	2.752(15)	O(4)$^{\#7}$-Ba(2)-O(1)$^{\#1}$	73.9(3)
Ba(3)-O(4)	2.752(15)	O(4)$^{\#4}$-Ba(2)-O(3)$^{\#9}$	85.6(2)
Ba(3)-O(4)$^{\#7}$	2.752(15)	O(4)$^{\#7}$-Ba(2)-O(3)$^{\#9}$	103.1(2)
Ba(3)-O(1)$^{\#10}$	2.895(8)	O(4)$^{\#4}$-Ba(2)-O(3)$^{\#4}$	85.6(2)
Ba(3)-O(1)$^{\#7}$	2.895(8)	O(4)$^{\#7}$-Ba(2)-O(3)$^{\#4}$	103.1(2)
Ba(3)-O(1)$^{\#6}$	2.895(8)	O(4)$^{\#4}$-Ba(2)-O(1)$^{\#5}$	77.1(3)
Ba(3)-O(1)$^{\#11}$	2.895(8)	O(4)$^{\#4}$-Ba(2)-O(1)	77.1(3)
Ba(3)-O(1)$^{\#5}$	2.895(8)	O(4)$^{\#4}$-Ba(2)-O(4)$^{\#7}$	149.9(5)
Ba(3)-O(1)	2.895(8)	O(1)$^{\#10}$-Ba(3)-O(1)$^{\#11}$	117.08(8)
B(1)-O(1)$^{\#11}$	1.363(11)	O(1)$^{\#7}$-Ba(3)-O(1)$^{\#11}$	70.4(3)
B(1)-O(1)	1.363(11)	O(1)$^{\#6}$-Ba(3)-O(1)$^{\#11}$	157.0(3)
B(1)-O(3)$^{\#12}$	1.37(2)	O(1)$^{\#10}$-Ba(3)-O(1)$^{\#5}$	117.08(9)
Si(1)-O(4)	1.590(14)	O(1)$^{\#7}$-Ba(3)-O(1)$^{\#5}$	157.0(3)
Si(1)-O(4)$^{\#6}$	1.590(14)	O(1)$^{\#11}$-Ba(3)-O(1)$^{\#5}$	117.08(8)
Si(1)-O(4)$^{\#7}$	1.590(14)	O(1)$^{\#10}$-Ba(3)-O(1)	157.0(3)
Si(1)-O(2)$^{\#13}$	1.62(2)	O(1)$^{\#7}$-Ba(3)-O(1)	117.08(8)
O(1)$^{\#1}$-Ba(1)-O(1)$^{\#2}$	137.6(3)	O(1)$^{\#6}$-Ba(3)-O(1)	117.08(8)
O(1)$^{\#1}$-Ba(1)-O(3)$^{\#3}$	159.6(2)	O(1)$^{\#5}$-Ba(3)-O(1)	70.4(3)
O(1)$^{\#2}$-Ba(1)-O(3)$^{\#4}$	159.6(2)	O(1)$^{\#11}$-B(1)-O(1)	118.0(15)
O(1)$^{\#1}$-Ba(1)-O(1)$^{\#5}$	85.30(17)	O(2)-Ba(3)-O(1)	80.05(15)
O(1)$^{\#2}$-Ba(1)-O(1)$^{\#5}$	129.30(19)	O(2)-Ba(3)-O(1)$^{\#5}$	80.05(15)
O(1)$^{\#1}$-Ba(1)-O(1)$^{\#6}$	129.30(19)	O(2)-Ba(3)-O(4)$^{\#6}$	147.6(3)

O(1)$^{\#2}$-Ba(1)-O(1)$^{\#6}$	85.30(17)	O(2)-Ba(3)-O(4)	147.6(3)
O(1)$^{\#1}$-Ba(1)-Cl(1)	83.17(14)	O(2)-Ba(3)-O(4)$^{\#7}$	147.6(3)
O(1)$^{\#2}$-Ba(1)-Cl(1)	83.17(14)	O(2)-Ba(3)-O(1)$^{\#10}$	80.05(15)
O(1)$^{\#5}$-Ba(1)-Cl(1)	137.92(17)	O(2)-Ba(3)-O(1)$^{\#7}$	80.05(15)
O(1)$^{\#6}$-Ba(1)-Cl(1)	137.92(17)	O(2)-Ba(3)-O(1)$^{\#6}$	80.05(15)
O(1)$^{\#1}$-Ba(1)-O(4)	106.1(3)	O(2)-Ba(3)-O(1)$^{\#11}$	80.05(15)
O(1)$^{\#2}$-Ba(1)-O(4)$^{\#7}$	106.1(3)	O(4)$^{\#6}$-Ba(3)-O(1)$^{\#10}$	95.30(15)
O(1)$^{\#6}$-Ba(1)-O(4)$^{\#7}$	82.9(3)	O(4)-Ba(3)-O(1)$^{\#10}$	73.6(3)
O(1)$^{\#5}$-Ba(1)-O(4)	82.9(3)	O(4)$^{\#7}$-Ba(3)-O(1)$^{\#10}$	128.9(3)
O(3)-Ba(1)-O(3)$^{\#3}$	108.7(2)	O(4)$^{\#6}$-Ba(3)-O(1)$^{\#7}$	73.6(3)
O(3)-Ba(1)-O(3)$^{\#4}$	108.7(2)	O(4)-Ba(3)-O(1)$^{\#7}$	95.30(15)
O(3)$^{\#3}$-Ba(1)-O(3)$^{\#4}$	120.6(4)	O(4)$^{\#7}$-Ba(3)-O(1)$^{\#7}$	128.9(3)
O(3)-Ba(1)-O(1)$^{\#5}$	143.7(2)	O(4)$^{\#6}$-Ba(3)-O(1)$^{\#6}$	128.9(3)
O(3)$^{\#3}$-Ba(1)-O(1)$^{\#5}$	104.2(2)	O(4)-Ba(3)-O(1)$^{\#6}$	73.6(3)
O(3)-Ba(1)-O(1)$^{\#6}$	143.7(2)	O(4)$^{\#7}$-Ba(3)-O(1)$^{\#6}$	95.30(15)
O(3)$^{\#4}$-Ba(1)-O(1)$^{\#6}$	104.2(2)	O(4)$^{\#6}$-Ba(3)-O(1)$^{\#11}$	73.6(3)
O(3)$^{\#3}$-Ba(1)-Cl(1)	77.67(19)	O(4)-Ba(3)-O(1)$^{\#11}$	128.9(3)
O(3)$^{\#4}$-Ba(1)-Cl(1)	77.67(19)	O(4)$^{\#7}$-Ba(3)-O(1)$^{\#11}$	95.30(15)
O(3)-Ba(1)-O(4)$^{\#7}$	80.5(3)	O(4)$^{\#6}$-Ba(3)-O(1)$^{\#5}$	128.9(3)
O(3)$^{\#3}$-Ba(1)-O(4)$^{\#7}$	137.4(3)	O(4)-Ba(3)-O(1)$^{\#5}$	95.30(15)
O(3)$^{\#4}$-Ba(1)-O(4)$^{\#7}$	93.1(3)	O(4)$^{\#7}$-Ba(3)-O(1)$^{\#5}$	73.6(3)
O(3)-Ba(1)-O(4)	80.5(3)	O(4)$^{\#6}$-Ba(3)-O(1)	95.30(15)
O(3)$^{\#3}$-Ba(1)-O(4)	93.1(3)	O(4)-Ba(3)-O(1)	128.9(3)
O(3)$^{\#4}$-Ba(1)-O(4)	137.4(3)	O(4)$^{\#7}$-Ba(3)-O(1)	73.6(3)
Cl(1)-Ba(1)-O(4)$^{\#7}$	139.2(3)	O(1)$^{\#11}$-B(1)-O(3)$^{\#12}$	120.9(7)
Cl(1)-Ba(1)-O(4)	139.2(3)	O(1)-B(1)-O(3)$^{\#12}$	120.9(7)
O(1)$^{\#5}$-Ba(2)-O(1)	78.5(3)	O(4)-Si(1)-O(4)$^{\#6}$	106.9(7)
O(1)$^{\#5}$-Ba(2)-O(4)$^{\#7}$	79.7(3)	O(4)-Si(1)-O(4)$^{\#7}$	106.9(7)
O(1)-Ba(2)-O(4)$^{\#7}$	79.7(3)	O(4)$^{\#6}$-Si(1)-O(4)$^{\#7}$	106.9(7)
O(1)$^{\#5}$-Ba(2)-O(2)$^{\#1}$	122.0(4)	O(4)-Si(1)-O(2)$^{\#1}$3	111.9(6)
O(1)-Ba(2)-O(2)$^{\#1}$	122.0(4)	O(4)$^{\#6}$-Si(1)-O(2)$^{\#13}$	111.9(6)
O(1)$^{\#5}$-Ba(2)-O(1)$^{\#8}$	153.55(16)	O(4)$^{\#7}$-Si(1)-O(2)$^{\#13}$	111.9(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z+1/2 #2 -x+1,-x+y,z+1/2 #3 y,-x+y,z-1/2 #4 x-y,x,z-1/2 #5 -y+1,-x+1,z #6 -y+1,x-y,z #7 -x+y+1,-x+1,z #8 y,x,z+1/2 #9 -x+1,-y+1,z-1/2 #10 x,x-y,z #11 -x+y+1,y,z #12 -x+y+1,-x+1,z-1 #13 x,y,z+1

Table S2(b) Selected bond lengths (Å) and angles (deg.) for $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$.

$Ba(1)-O(1)^{\#4}$	2.924(10)	$O(1)^{\#8}-Ba(1)-O(1)^{\#9}$	70.3(4)
$Ba(1)-O(1)^{\#5}$	2.924(10)	$O(1)^{\#11}-Ba(2)-O(1)^{\#12}$	138.2(3)
$Ba(1)-O(1)^{\#6}$	2.924(10)	$O(2)^{\#10}-Ba(2)-O(1)^{\#9}$	144.6(3)
$Ba(1)-O(1)^{\#7}$	2.924(11)	$O(1)^{\#11}-Ba(2)-O(1)^{\#9}$	85.5(2)
$Ba(1)-O(3)^{\#2}$	2.80(2)	$O(1)^{\#12}-Ba(2)-O(1)^{\#9}$	130.5(3)
$Ba(1)-O(3)$	2.80(2)	$O(2)^{\#10}-Ba(2)-O(1)^{\#7}$	144.6(3)
$Ba(1)-O(1)^{\#8}$	2.924(10)	$O(1)^{\#11}-Ba(2)-O(1)^{\#7}$	130.5(3)
$Ba(1)-O(1)^{\#9}$	2.924(10)	$O(1)^{\#12}-Ba(2)-O(1)^{\#7}$	85.5(2)
$Ba(1)-O(3)^{\#3}$	2.80(2)	$O(2)^{\#10}-Ba(2)-O(2)^{\#13}$	108.8(3)
$Ba(1)-O(4)^{\#1}$	2.71(3)	$O(1)^{\#12}-Ba(2)-O(2)^{\#13}$	158.4(3)
$Ba(2)-O(1)^{\#11}$	2.959(11)	$O(1)^{\#7}-Ba(2)-O(2)^{\#13}$	103.7(3)
$Ba(2)-O(1)^{\#12}$	2.959(11)	$O(2)^{\#10}-Ba(2)-O(2)^{\#5}$	108.8(3)
$Ba(2)-O(1)^{\#9}$	3.059(9)	$O(1)^{\#11}-Ba(2)-O(2)^{\#5}$	158.4(3)
$Ba(2)-O(1)^{\#7}$	3.059(9)	$O(1)^{\#9}-Ba(2)-O(2)^{\#5}$	103.7(3)
$Ba(2)-O(2)^{\#5}$	3.110(11)	$O(2)^{\#13}-Ba(2)-O(2)^{\#5}$	120.4(5)
$Ba(2)-O(2)^{\#10}$	2.800(15)	$O(2)^{\#10}-Ba(2)-O(3)^{\#3}$	80.7(5)
$Ba(2)-O(2)^{\#13}$	3.110(11)	$O(1)^{\#12}-Ba(2)-O(3)^{\#3}$	107.6(4)
$Ba(2)-O(3)^{\#3}$	3.217(3)	$O(1)^{\#7}-Ba(2)-O(3)^{\#3}$	84.2(4)
$Ba(2)-O(3)$	3.217(3)	$O(2)^{\#13}-Ba(2)-O(3)^{\#3}$	92.9(4)
$Ba(2)-Br(1)^{\#14}$	3.272(2)	$O(2)^{\#5}-Ba(2)-O(3)^{\#3}$	137.5(4)
$Ba(3)-O(1)$	2.648(9)	$O(2)^{\#10}-Ba(2)-O(3)$	80.7(5)
$Ba(3)-O(1)^{\#16}$	2.648(9)	$O(1)^{\#11}-Ba(2)-O(3)$	107.6(4)
$Ba(3)-O(1)^{\#4}$	2.786(9)	$O(1)^{\#9}-Ba(2)-O(3)$	84.2(4)
$Ba(3)-O(1)^{\#6}$	2.786(9)	$O(2)^{\#13}-Ba(2)-O(3)$	137.5(4)
$Ba(3)-O(3)^{\#15}$	2.64(2)	$O(2)^{\#5}-Ba(2)-O(3)$	92.9(4)
$Ba(3)-O(3)^{\#17}$	2.66(2)	$O(1)^{\#11}-Ba(2)-Br(1)^{\#14}$	82.17(18)
$Ba(3)-O(2)^{\#3}$	3.136(11)	$O(1)^{\#12}-Ba(2)-Br(1)^{\#14}$	82.17(18)
$Ba(3)-O(2)$	3.136(11)	$O(1)^{\#9}-Ba(2)-Br(1)^{\#14}$	136.5(2)
$Ba(3)-O(4)^{\#1}$	2.7556(14)	$O(1)^{\#7}-Ba(2)-Br(1)^{\#14}$	136.5(2)
$Si(1)-O(3)$	1.59(2)	$O(2)^{\#13}-Ba(2)-Br(1)^{\#14}$	77.7(3)
$Si(1)-O(3)^{\#2}$	1.59(2)	$O(2)^{\#5}-Ba(2)-Br(1)^{\#14}$	77.7(3)
$Si(1)-O(3)^{\#3}$	1.59(2)	$O(3)^{\#3}-Ba(2)-Br(1)^{\#14}$	139.3(4)
$Si(1)-O(4)$	1.62(3)	$O(3)-Ba(2)-Br(1)^{\#14}$	139.3(4)
$B(1)-O(2)$	1.35(2)	$O(3)^{\#15}-Ba(3)-O(1)$	76.7(4)
$B(1)-O(1)^{\#6}$	1.394(13)	$O(3)^{\#15}-Ba(3)-O(1)^{\#16}$	76.7(4)
$B(1)-O(1)^{\#8}$	1.394(13)	$O(1)-Ba(3)-O(1)^{\#16}$	79.0(4)
$O(4)^{\#1}-Ba(1)-O(3)^{\#2}$	148.3(4)	$O(3)^{\#15}-Ba(3)-O(3)^{\#17}$	149.8(6)
$O(4)^{\#1}-Ba(1)-O(3)$	148.3(4)	$O(1)-Ba(3)-O(3)^{\#17}$	80.0(4)
$O(4)^{\#1}-Ba(1)-O(3)^{\#3}$	148.3(4)	$O(1)^{\#16}-Ba(3)-O(3)^{\#17}$	80.0(4)
$O(4)^{\#1}-Ba(1)-O(1)^{\#4}$	81.13(18)	$O(1)-Ba(3)-O(4)^{\#1}$	121.2(4)
$O(3)^{\#2}-Ba(1)-O(1)^{\#4}$	73.1(4)	$O(1)^{\#16}-Ba(3)-O(4)^{\#1}$	121.2(4)
$O(3)-Ba(1)-O(1)^{\#4}$	94.60(19)	$O(3)^{\#17}-Ba(3)-O(4)^{\#1}$	150.9(7)

O(3)$^{\#3}$-Ba(1)-O(1)$^{\#4}$	127.1(4)	O(3)$^{\#15}$-Ba(3)-O(1)$^{\#4}$	127.8(3)
O(4)$^{\#1}$-Ba(1)-O(1)$^{\#5}$	81.13(18)	O(1)-Ba(3)-O(1)$^{\#4}$	97.5(3)
O(3)$^{\#2}$-Ba(1)-O(1)$^{\#5}$	94.60(19)	O(1)$^{\#16}$-Ba(3)-O(1)$^{\#4}$	154.1(2)
O(3)-Ba(1)-O(1)$^{\#5}$	73.1(4)	O(3)$^{\#17}$-Ba(3)-O(1)$^{\#4}$	74.1(4)
O(3)$^{\#3}$-Ba(1)-O(1)$^{\#5}$	127.1(4)	O(4)$^{\#1}$-Ba(3)-O(1)$^{\#4}$	82.8(5)
O(4)$^{\#1}$-Ba(1)-O(1)$^{\#6}$	81.13(18)	O(3)$^{\#15}$-Ba(3)-O(1)$^{\#6}$	127.8(3)
O(3)$^{\#2}$-Ba(1)-O(1)$^{\#6}$	73.1(4)	O(1)-Ba(3)-O(1)$^{\#6}$	154.1(2)
O(3)-Ba(1)-O(1)$^{\#6}$	127.1(4)	O(1)$^{\#16}$-Ba(3)-O(1)$^{\#6}$	97.5(3)
O(3)$^{\#3}$-Ba(1)-O(1)$^{\#6}$	94.60(19)	O(3)$^{\#17}$-Ba(3)-O(1)$^{\#6}$	74.1(4)
O(1)$^{\#4}$-Ba(1)-O(1)$^{\#6}$	70.3(4)	O(4)$^{\#1}$-Ba(3)-O(1)$^{\#6}$	82.8(5)
O(1)$^{\#5}$-Ba(1)-O(1)$^{\#6}$	117.67(10)	O(1)$^{\#4}$-Ba(3)-O(1)$^{\#6}$	74.4(4)
O(4)$^{\#1}$-Ba(1)-O(1)$^{\#7}$	81.13(18)	O(3)$^{\#15}$-Ba(3)-O(2)$^{\#3}$	84.7(3)
O(3)$^{\#2}$-Ba(1)-O(1)$^{\#7}$	127.1(4)	O(1)$^{\#16}$-Ba(3)-O(2)$^{\#3}$	145.3(3)
O(3)-Ba(1)-O(1)$^{\#7}$	73.1(4)	O(3)$^{\#17}$-Ba(3)-O(2)$^{\#3}$	104.3(3)
O(3)$^{\#3}$-Ba(1)-O(1)$^{\#7}$	94.60(19)	O(4)$^{\#1}$-Ba(3)-O(2)$^{\#3}$	70.5(2)
O(1)$^{\#4}$-Ba(1)-O(1)$^{\#7}$	117.67(9)	O(1)$^{\#4}$-Ba(3)-O(2)$^{\#3}$	47.1(3)
O(1)$^{\#5}$-Ba(1)-O(1)$^{\#7}$	70.3(4)	O(1)$^{\#6}$-Ba(3)-O(2)$^{\#3}$	116.9(3)
O(1)$^{\#6}$-Ba(1)-O(1)$^{\#7}$	159.0(4)	O(3)$^{\#15}$-Ba(3)-O(2)	84.7(3)
O(4)$^{\#1}$-Ba(1)-O(1)$^{\#8}$	81.13(18)	O(1)-Ba(3)-O(2)	145.3(3)
O(3)$^{\#2}$-Ba(1)-O(1)$^{\#8}$	94.60(19)	O(3)$^{\#17}$-Ba(3)-O(2)	104.3(3)
O(3)-Ba(1)-O(1)$^{\#8}$	127.1(4)	O(4)$^{\#1}$-Ba(3)-O(2)	70.5(2)
O(3)$^{\#3}$-Ba(1)-O(1)$^{\#8}$	73.1(4)	O(1)$^{\#4}$-Ba(3)-O(2)	116.9(3)
O(1)$^{\#4}$-Ba(1)-O(1)$^{\#8}$	117.67(10)	O(2)$^{\#3}$-Ba(3)-O(2)	139.4(4)
O(1)$^{\#5}$-Ba(1)-O(1)$^{\#8}$	159.0(4)	O(3)-Si(1)-O(3)$^{\#2}$	106.3(9)
O(1)$^{\#7}$-Ba(1)-O(1)$^{\#8}$	117.67(10)	O(3)-Si(1)-O(3)$^{\#3}$	106.3(9)
O(4)$^{\#1}$-Ba(1)-O(1)$^{\#9}$	81.13(18)	O(3)$^{\#2}$-Si(1)-O(3)$^{\#3}$	106.3(9)
O(3)$^{\#2}$-Ba(1)-O(1)$^{\#9}$	127.1(4)	O(3)-Si(1)-O(4)	112.5(8)
O(3)-Ba(1)-O(1)$^{\#9}$	94.60(19)	O(3)$^{\#2}$-Si(1)-O(4)	112.5(8)
O(3)$^{\#3}$-Ba(1)-O(1)$^{\#9}$	73.1(4)	O(3)$^{\#3}$-Si(1)-O(4)	112.5(8)
O(1)$^{\#4}$-Ba(1)-O(1)$^{\#9}$	159.0(4)	O(2)-B(1)-O(1)$^{\#6}$	121.1(8)
O(1)$^{\#5}$-Ba(1)-O(1)$^{\#9}$	117.67(10)	O(2)-B(1)-O(1)$^{\#8}$	121.1(8)
O(1)$^{\#6}$-Ba(1)-O(1)$^{\#9}$	117.67(9)	O(1)$^{\#6}$-B(1)-O(1)$^{\#8}$	117.5(17)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z+1 #2 -y+1,x-y+1,z #3 -x+y,-x+1,z #4 -x,-x+y,z-1/2 #5 x-y+1,x+1,z-1/2 #6 -x,-y+1,z-1/2 #7 y,x+1,z-1/2 #8 x-y+1,-y+1,z-1/2 #9 y,-x+y,z-1/2 #10 -y+1,x-y+1,z-1 #11 -x+y,y,z-1 #12 -x+y,-x+1,z-1 #13 -x+1,-y+1,z-1/2 #14 -x+2,-y+2,z-1/2 #15 -y+1,x-y+1,z+1 #16 x,x-y+1,z #17 y-1,-x+y,z+1/2

Table S3 The direction and magnitude (in Debye) of the dipole moments of the XBa_6 octahedra and $_{\infty}{}^{1}[Ba_3X]$ chains in the unit cell for $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3X$ and $Ba_5(BO_3)_3X$ (X = Cl, Br).

Species	$x(a)$	$y(b)$	$z(c)$	Magnitude
		$Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$		
$ClBa_6$	0	0	– 5.82	5.82
$_{\infty}{}^{1}[Ba_3Cl]$	0	0	– 11.64	11.64
		$Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$		
$BrBa_6$	0	0	4.64	4.64
$_{\infty}{}^{1}[Ba_3Br]$	0	0	9.28	9.28
		$Ba_5(BO_3)_3Cl$		
$ClBa_6$	0	– 33.35	0	33.35
$_{\infty}{}^{1}[Ba_3Cl]$	0	0	0	0
		$Ba_5(BO_3)_3Br$		
$BrBa_6$	0	– 24.35	0	24.35
$_{\infty}{}^{1}[Ba_3Br]$	0	0	0	0

Figure S1 The crystal photograph of $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$ (a) and $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$ (b).

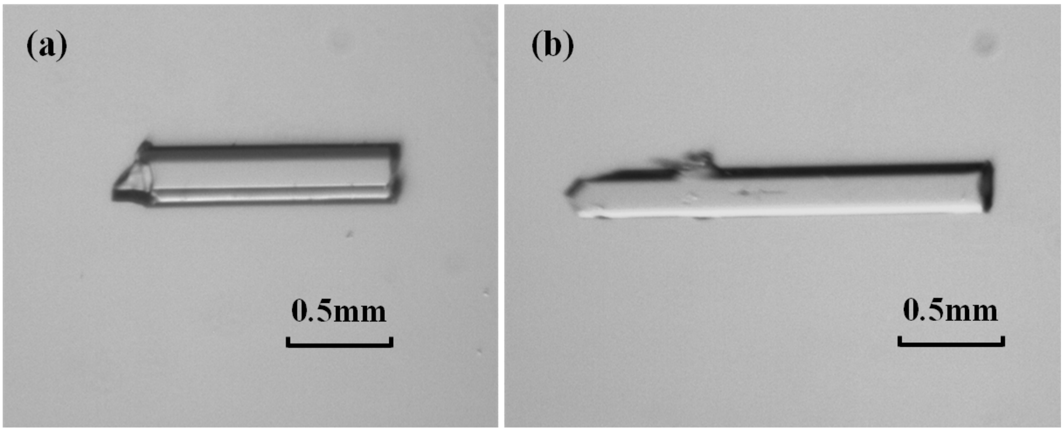


Fig. S2 Schematic drawing of the distorted direction of the octahedral XBa_6 SBU in the $_\infty{}^1[Ba_3X]$ chains for (a) $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$, (b) $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$, (c) $Ba_5(BO_3)_3Cl$, (d) $Ba_5(BO_3)_3Br$. Yellow (Cl), bright green (Br), dark blue (Ba).

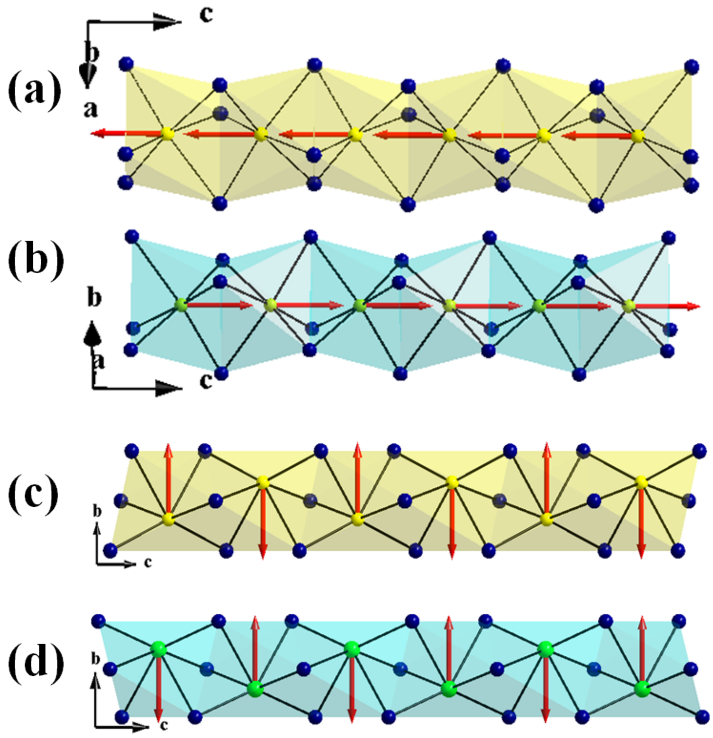


Fig. S3 IR spectra of $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$ (a) and $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$ (b).

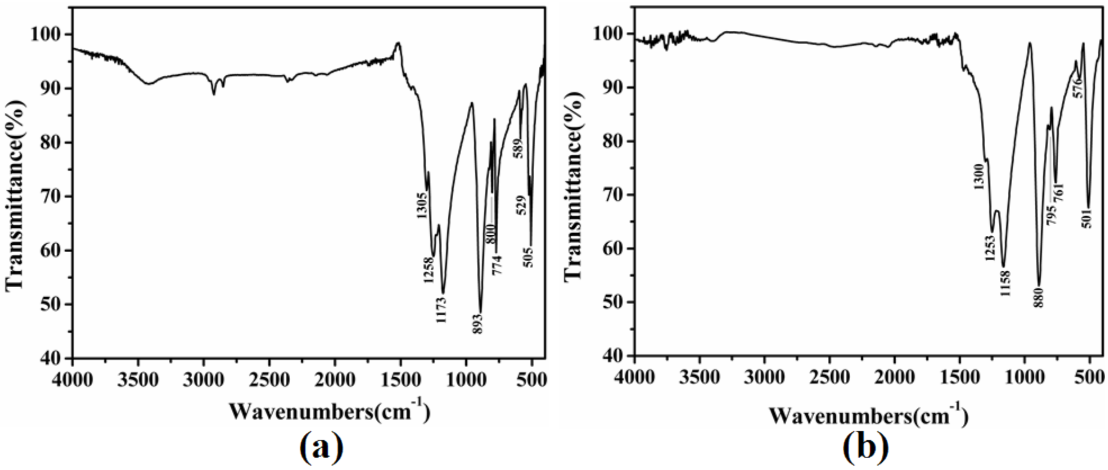


Fig. S4 TG-DSC curves of $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$ (a) and $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$ (b).

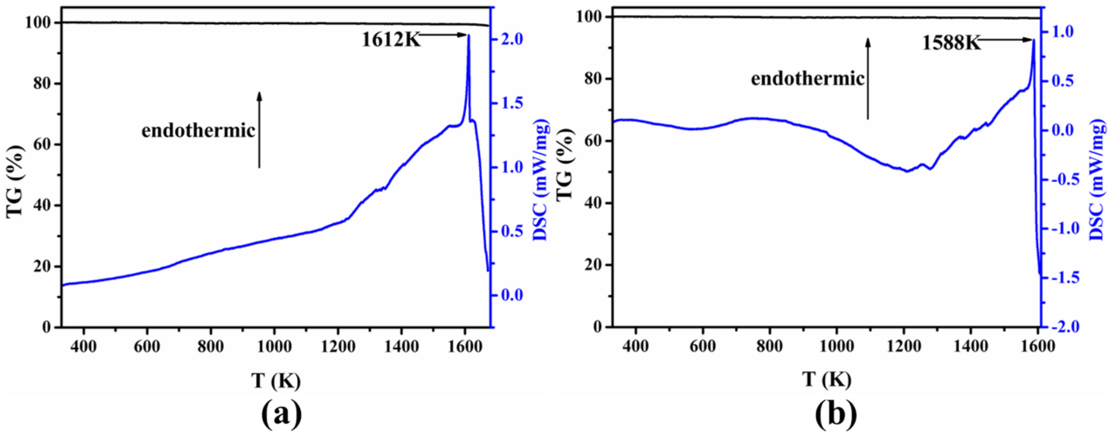


Fig. S5 Piezoelectric measurement data for $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$ (a) and $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$ (b).

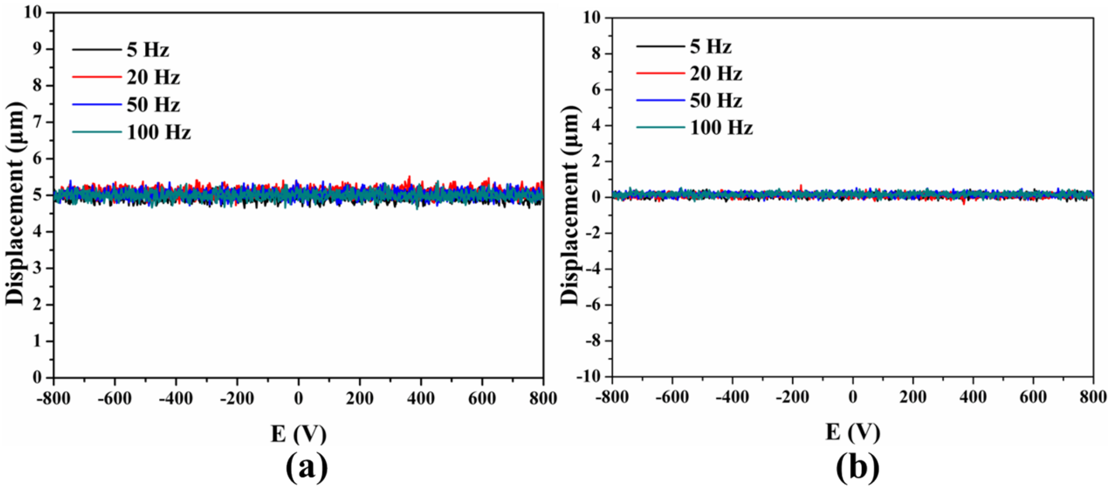


Fig. S6 Polarization versus electric field plots at 8 kV/cm for $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$ (a) and ~6 kV/cm for $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$ (b) at different frequencies.

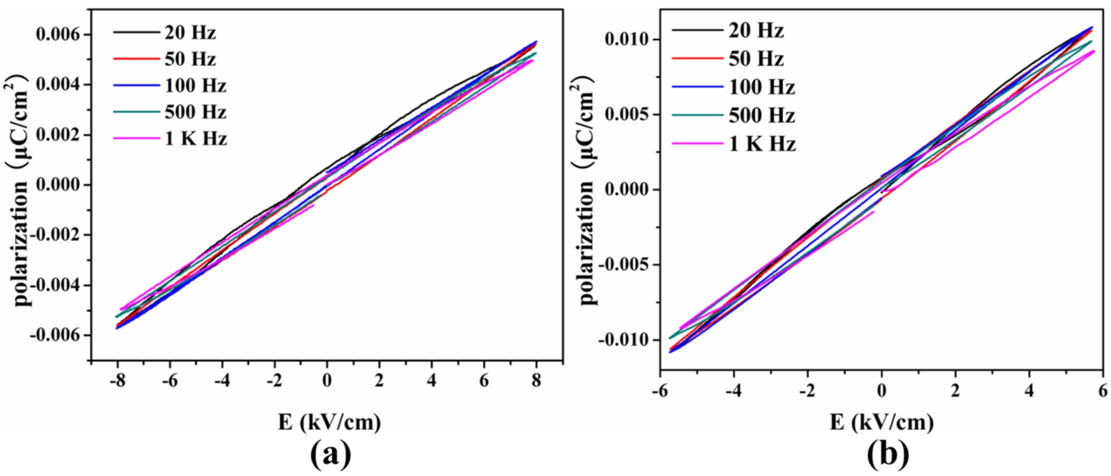
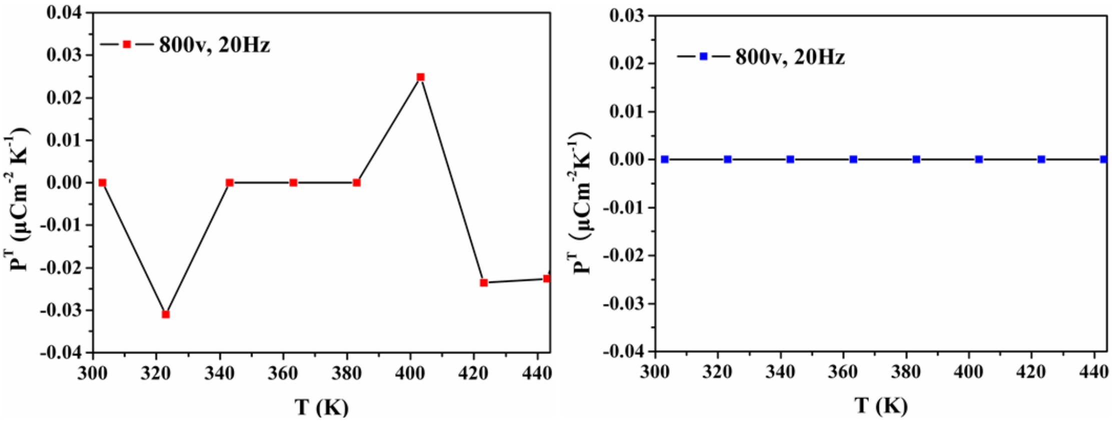


Fig. S7 Pyroelectric measurement data for $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$ (a) and $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$ (b).



(a) (b)

The experimental section of piezoelectric and polarization measurements

Piezoelectric Measurements. Converse piezoelectric measurements were performed using a Radiant Technologies RT66A piezoelectric test system with a TREK (model 609B) high-voltage amplifier, Precision Materials Analyzer, Precision High Voltage Interface. The $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$ powder was pressed into 12-mm-diameter and 1.0-mm-thick pellet and the $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$ powder was pressed into 12.6-mm-diameter and 1.4-mm-thick pellet and then both pellets sintered for 8 h at 1273 K. Conducting silver paste was applied on both sides of the pellet surfaces for electrode. A maximum voltage of 1000 V was applied to the pellets at room temperature. The piezoelectric data from the converse method have been deposited in ESI as Fig. S5. From Fig. S5, we do not observe any piezoelectric response, suggesting that the piezoelectric response is not detectable under used experimental conditions.

Polarization Measurements. The pellets of $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3X$ used in the piezoelectric measurements were also used in the polarization measurements. The polarization was measured on a Radiant Technologies RT66A Ferroelectric Test System with a TREK high voltage amplifier between 303 and 443 K in 20 K increments in a Delta 9023 environmental test chamber. The temperature was allowed to stabilize before the polarization was measured. The unclamped pyroelectric coefficient, defined as dP/dT (change in the polarization with respect to the change in temperature), was determined by measuring the polarization as a function of temperature. A detailed description of the methodology has been published elsewhere.[1] To determine their ferroelectric behaviors, polarization measurements were done at room temperature under a static electric field of 8 kV/cm for $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Cl$, and ~ 6 kV/cm for $Ba_4(BO_3)_3(SiO_4)\cdot Ba_3Br$, at frequencies ranging from 20 to 1000 Hz. The test curves are all shown in Fig. S6 and Fig. S7 in the ESI. Although ferroelectric “loops” were observed in the ferroelectric measurements, the materials are not ferroelectric. The loops are attributable to dielectric loss and not ferroelectric hysteresis. In other words, the polarization cannot be switched in the present of an external electric field. The measured pyroelectric coefficient (p) is about 0.03 $\mu C/m^2K$ at 323 K. The coefficient (p) is so small, and we cannot prove that it is attributed to the pure pyroelectric coefficients and may be the result of space charge. Hence the pyroelectric property for each material is negligible.

Reference:

[1] K. M. Ok, E. O. Chi and P. S. Halasyamani, *Chem. Soc. Rev.*, 2006, **35**, 710.