BaTi(BO$_3$)$_2$: An Excellent Birefringent Material with Highly Coplanar Isolated [BO$_3$] Groups

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Experimental and Computational Methods

Synthesis

BaTi(BO$_3$)$_2$: Single crystals were synthesized through the high-temperature flux method by mixing B$_2$O$_3$, BaCl$_2$·2H$_2$O, NaBF$_4$, TiO$_2$ with the molar ratio (1:1:2:1) in a platinum crucible. The mixture was heated to 700 ℃ for 12 h after fully ground, held at this temperature for 10 h to melt completely, and cooled down to 600 ℃ with 1 ℃/h. After that, it was cooled to room temperature at a rate of 2 ℃/h, and the colorless crystals were acquired for the measurement of X-ray diffraction. In addition, it is worth mentioning that the raw materials were synthesized by lower temperature owing to NaBF$_4$ in this reaction.

The pure powder of BaTi(BO$_3$)$_2$ was acquired with the same stoichiometric ratio by the high-temperature flux method. The mixture was ground thoroughly in an agate mortar, preheated at 250 °C for several hours, and the mixture was sintered at 700 °C. During the sintering process, the samples were ground several times and thoroughly mixed. Last but not least, the sample was washed with deionized water to get rid of NaBF$_4$ in the reaction.

BaSn^{IV}(BO$_3$)$_2$: The single crystals were also synthesized by the high-temperature flux method by mixing B$_2$O$_3$, BaCO$_3$, SnO$_2$ with the molar ratio (2:1:1) in a platinum crucible. The mixture was heated to 850 ℃ for 12 h after fully ground, held at this temperature for 10 h to melt completely, and cooled down to 750 ℃ at a rate of 1 ℃/h. After that, it was cooled to room temperature at a rate of 2 ℃/h, and the colorless crystals were acquired for the measurement of X-ray diffraction.

The pure powder of BaSn^{IV}(BO$_3$)$_2$ was acquired with the same stoichiometric ratio by the high-temperature flux method. The mixture was ground thoroughly in an agate mortar and sintered at 900 °C. During the sintering process, the samples were ground several times and

thoroughly mixed.

Structure Determination

Single-crystal XRD data were collected on a Bruker SMART APEX II CCD detector equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and integrated with the SAINT[1]. The crystal structure was identified with programs from the SHELXTL-97[2]. Final least-squares refinement on F_o^2 with data having $F_o^2 \geq 2\sigma$ (F_o^2) includes anisotropic displacement parameters for non-hydrogen atoms. The structure was inspected for missing symmetry elements with PLATON[3]. Crystal data and structure refinement information of $BaM^{IV}(BO_3)_2$ (M^{IV} = Ti, Sn) are summarized in Table S1. Final atomic coordinates and equivalent isotropic displacement parameters, selected bond lengths, and angles are listed in Table S2 and Table S3, respectively.

Powder XRD tests of the two compounds were performed on a Bruker D2 Phaser X-ray diffractometer. The 2θ range is 10-70 ° with a scan step width of 0.02 ° and a fixed counting time of 0.1 s/step. The experimental and calculated powder XRD patterns of $BaM^{IV}(BO_3)_2$ (M^{IV} = Ti, Sn) are presented in Figure S2.

Birefringence Measurement

The birefringence of $BaTi(BO_3)_2$ was measured by using the cross-polarizing microscope (ZEISS Axio Scope. A1) with a Berek compensator. The wavelength of the light source was 546 nm. The thickness of the block-shaped crystal is 40.5 μm (Figure S9), and the retardation is about 6.86 μm, the refractive index difference of the crystal at 546 nm was calculated by the equation of R= Δn × d, where R, Δn, and d were retardation, refractive index difference, and thickness, respectively. Hence, the birefringence of $BaTi(BO_3)_2$ should be equal to or larger than 0.169 at 546 nm.

Infrared Spectrum Measurement

The IR spectrum of $BaM^{IV}(BO_3)_2$ (M^{IV} = Ti, Sn) was measured on a Shimadzu IR Affinity-1 spectrometer with the range of 400-4000 cm^{-1} and the resolution of 2 cm^{-1}. The sample was mixed with dried KBr.

UV−Vis−NIR Diffuse Reflectance Measurement

The UV−Vis−NIR diffuse reflectance spectra of $BaM^{IV}(BO_3)_2$ (M^{IV} = Ti, Sn) were measured using a Shimadzu Solid Spec-3700 DUV spectrophotometer with the measurement range extending from 200 to 1400 nm at room temperature. The reflectance spectra were converted to absorbance via the Kubelka-Munk function[4].

Theoretical Calculation Methods

Density functional theory based on electronic structure calculations was carried out with total energy mode of CASETEP package from the Materials Studio 5.5[5]. The exchange and correlation effects were implemented via the Perdew-Burke-Ernzerhof (PBE) functional[6] with the generalized gradient approximation (GGA)[7]. The relations between the ionic cores and the valence electrons were depicted by norm-conserving pseudopotentials (NCP)[8]. The valence electrons of $BaTi(BO_3)_2$ were calculated as $Ba-6s^2$, $Ti-3d^24s^2$, $B-2s^22p^1$ and $O-2s^22p^4$. The number of plane waves included in the basis sets was determined by the cut-off energy of 750 eV for the title compound. The numerical integration of the Brillouin zone was performed using the Monkhorst-Pack 24 k-point grids of 3 × 3 × 3. The other parameters and convergent criteria were the same as the default values of the CASTEP program. In addition, the theoretical calculation of $BaSn^{IV}(BO_3)_2$ is unable to be carried out, because the O atoms are disordered in the crystal structure.

Table S1. Crystal data and structure refinement for $BaM^{IV}(BO_3)_2$ (M^{IV} = Ti, Sn)

	$BaTi(BO_3)_2$	$BaSn^{IV}(BO_3)_2$
Empirical formula	$BaTi(BO_3)_2$	$BaSn^{IV}(BO_3)_2$
Formula weight	302.86	373.65
Crystal system	Trigonal	
Space group	Rm	
Unit cell dimensions(Å)	a = 5.0256(10)	a = 5.054(2)
	c = 16.397(6)	c = 17.564(14)
Volume (Å^3), Z	358.65(17), 3	388.6(5), 3
Density (Mg/m^3)	4.207	4.791
Absorption coefficient (mm^{-1})	9.802	12.329
F(000)	408	492
Theta range for data collection (°)	3.73 to 29.62	3.48 to 27.26
R(int)	0.0239	0.0150
Completeness (%)	97.3	99.1
Goodness-of-fit on F^2	1.174	1.274
Final R indices [I>2sigma(I)] [a]	R_1 = 0.0143, wR_2 = 0.0355	R_1 = 0.0091, wR_2 = 0.0230
R indices (all data) [a]	R_1 = 0.0143, wR_2 = 0.0355	R_1 = 0.0098, wR_2 = 0.0234
Largest diff. peak and hole (e.Å^{-3})	0.568 and -0.626	0.329 and -0.303

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma w\, F_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. The final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $BaM^{IV}(BO_3)_2$ (M^{IV} = Ti, Sn), U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, and the Bond Valence Sum (BVS) for each atom in the asymmetric unit.

Atom	x	y	z	U(eq)	BVS
		BaTi(BO$_3$)$_2$			
Ba(1)	6667	3333	3333	11(1)	1.89
Ti(1)	10000	10000	5000	7(1)	4.37
B(1)	3333	6667	4330(3)	8(1)	3.14
O(1)	6441(6)	8220(3)	4296(1)	32(1)	2.09
		BaSn^{IV}(BO$_3$)$_2$			
Ba(1)	3333	6667	6667	8(1)	2.06
Sn(1)	0	0	5000	5(1)	4.09
B(1)	6667	3333	5652(3)	6(1)	2.92
O(1)	3651(7)	2613(6)	5691(2)	10(1)	2.00

Table S3. Bond lengths [Å] and angles [deg] for $BaM^{IV}(BO_3)_2$ (M^{IV} = Ti, Sn)

BaTi(BO₃)₂			
Ba(1)-O(1)	2.9687(13)	O(1)#3-Ba(1)-O(1)#9	94.38(5)
Ba(1)-O(1)#1	2.9687(13)	O(1)#4-Ba(1)-O(1)#9	46.47(10)
Ba(1)-O(1)#2	2.9687(13)	O(1)#5-Ba(1)-O(1)#9	180.00(7)
Ba(1)-O(1)#3	2.9687(13)	O(1)#6-Ba(1)-O(1)#9	94.38(5)
Ba(1)-O(1)#4	2.9687(13)	O(1)#7-Ba(1)-O(1)#9	64.35(8)
Ba(1)-O(1)#5	2.9687(13)	O(1)#8-Ba(1)-O(1)#9	133.53(10)
Ba(1)-O(1)#6	2.9687(13)	O(1)#1-Ba(1)-O(1)#10	180.00(10)
Ba(1)-O(1)#7	2.9687(13)	O(1)#2-Ba(1)-O(1)#10	133.53(10)
Ba(1)-O(1)#8	2.9687(13)	O(1)#3-Ba(1)-O(1)#10	115.65(8)
Ba(1)-O(1)#9	2.9687(13)	O(1)#4-Ba(1)-O(1)#10	94.38(5)
Ba(1)-O(1)#10	2.9687(13)	O(1)#5-Ba(1)-O(1)#10	126.27(10)
Ba(1)-O(1)#11	2.9687(13)	O(1)#6-Ba(1)-O(1)#10	46.47(10)
Ti(1)-O(1)	1.932(2)	O(1)#7-Ba(1)-O(1)#10	85.62(5)
Ti(1)-O(1)#12	1.932(2)	O(1)#8-Ba(1)-O(1)#10	85.62(5)
Ti(1)-O(1)#13	1.932(2)	O(1)#9-Ba(1)-O(1)#10	53.73(10)
Ti(1)-O(1)#14	1.932(2)	O(1)#1-Ba(1)-O(1)#11	115.65(8)
Ti(1)-O(1)#15	1.932(2)	O(1)#2-Ba(1)-O(1)#11	94.38(5)
Ti(1)-O(1)#6	1.932(2)	O(1)#3-Ba(1)-O(1)#11	180.00(7)
B(1)-O(1)	1.354(3)	O(1)#4-Ba(1)-O(1)#11	126.27(10)
B(1)-O(1)#3	1.354(3)	O(1)#5-Ba(1)-O(1)#11	94.38(5)
B(1)-O(1)#16	1.354(3)	O(1)#6-Ba(1)-O(1)#11	85.62(5)
O(1)#1-Ba(1)-O(1)#2	46.47(10)	O(1)#7-Ba(1)-O(1)#11	46.47(10)
O(1)#1-Ba(1)-O(1)#3	64.35(8)	O(1)#8-Ba(1)-O(1)#11	53.73(10)
O(1)#2-Ba(1)-O(1)#3	85.62(5)	O(1)#9-Ba(1)-O(1)#11	85.62(5)
O(1)#1-Ba(1)-O(1)#4	85.62(5)	O(1)#10-Ba(1)-O(1)#11	64.35(8)
O(1)#2-Ba(1)-O(1)#4	64.35(8)	O(1)#1-Ba(1)-O(1)	85.62(5)
O(1)#3-Ba(1)-O(1)#4	53.73(10)	O(1)#2-Ba(1)-O(1)	126.27(10)
O(1)#1-Ba(1)-O(1)#5	53.73(10)	O(1)#3-Ba(1)-O(1)	46.47(10)
O(1)#2-Ba(1)-O(1)#5	94.38(5)	O(1)#4-Ba(1)-O(1)	94.38(5)
O(1)#3-Ba(1)-O(1)#5	85.62(5)	O(1)#5-Ba(1)-O(1)	64.35(8)
O(1)#4-Ba(1)-O(1)#5	133.53(10)	O(1)#6-Ba(1)-O(1)	53.73(10)
O(1)#1-Ba(1)-O(1)#6	133.53(10)	O(1)#7-Ba(1)-O(1)	179.999(1)
O(1)#2-Ba(1)-O(1)#6	180.00(7)	O(1)#8-Ba(1)-O(1)	85.62(5)

O(1)$^{\#3}$-Ba(1)-O(1)$^{\#6}$	94.38(5)	O(1)$^{\#4}$-Ba(1)-O(1)$^{\#8}$	180.00(7)
O(1)$^{\#4}$-Ba(1)-O(1)$^{\#6}$	115.65(8)	O(1)$^{\#5}$-Ba(1)-O(1)$^{\#8}$	46.47(10)
O(1)$^{\#5}$-Ba(1)-O(1)$^{\#6}$	85.62(5)	O(1)$^{\#6}$-Ba(1)-O(1)$^{\#8}$	64.35(8)
O(1)$^{\#1}$-Ba(1)-O(1)$^{\#7}$	94.38(5)	O(1)$^{\#7}$-Ba(1)-O(1)$^{\#8}$	94.38(5)
O(1)$^{\#2}$-Ba(1)-O(1)$^{\#7}$	53.73(10)	O(1)$^{\#1}$-Ba(1)-O(1)$^{\#9}$	126.27(10)
O(1)$^{\#3}$-Ba(1)-O(1)$^{\#7}$	133.53(10)	O(1)$^{\#2}$-Ba(1)-O(1)$^{\#9}$	85.62(5)
O(1)$^{\#4}$-Ba(1)-O(1)$^{\#7}$	85.62(5)	O(1)$^{\#9}$-Ba(1)-O(1)	115.65(8)
O(1)$^{\#5}$-Ba(1)-O(1)$^{\#7}$	115.65(8)	O(1)$^{\#10}$-Ba(1)-O(1)	94.38(5)
O(1)$^{\#6}$-Ba(1)-O(1)$^{\#7}$	126.27(10)	O(1)$^{\#11}$-Ba(1)-O(1)	133.53(10)
O(1)$^{\#1}$-Ba(1)-O(1)$^{\#8}$	94.38(5)	O(1)$^{\#16}$-B(1)-O(1)$^{\#3}$	119.83(4)
O(1)$^{\#2}$-Ba(1)-O(1)$^{\#8}$	115.65(8)	O(1)$^{\#16}$-B(1)-O(1)	119.83(4)
O(1)$^{\#3}$-Ba(1)-O(1)$^{\#8}$	126.27(10)	O(1)$^{\#3}$-B(1)-O(1)	119.83(4)

Symmetry transformations used to generate equivalent atoms:

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

[#6] -y+2,x-y+1,z   [#7] -x+4/3,-y+2/3,-z+2/3   [#8] y+1/3,-x+y+2/3,-z+2/3   [#9] x,y-1,z   [#10] -x+y+1,-x+1,z

[#11] x-y+4/3,x-1/3,-z+2/3   [#12] x-y+1,x,-z+1   [#13] -x+2,-y+2,-z+1   [#14] y,-x+y+1,-z+1   [#15] -x+y+1,-x+2,z

[#16] -y+1,x-y+1,z

	$BaSn^{IV}(BO_3)_2$		
Ba(1)-O(1)	2.737(3)	O(1)#6-Ba(1)-O(1)	84.6(7)
Ba(1)-O(1)#1	2.737(3)	O(1)#6-Ba(1)-O(1)#7	140.1(10)
Ba(1)-O(1)#2	2.737(3)	O(1)#8-Ba(1)-O(1)#5	128.6(11)
Ba(1)-O(1)#3	2.737(3)	O(1)#9-Ba(1)-O(1)	128.6(11)
Ba(1)-O(1)#4	2.737(3)	O(1)#9-Ba(1)-O(1)#1	51.4(11)
Ba(1)-O(1)#5	2.737(3)	O(1)#6-Ba(1)-O(1)#2	128.6(11)
Ba(1)-O(1)#6	2.737(3)	O(1)#6-Ba(1)-O(1)#3	95.4(7)
Ba(1)-O(1)#7	2.737(3)	O(1)#1-Ba(1)-O(1)#5	140.1(10)
Ba(1)-O(1)#8	2.737(3)	O(1)#2-Ba(1)-O(1)#9	84.6(7)
Ba(1)-O(1)#9	2.737(3)	O(1)#4-Ba(1)-O(1)#5	84.6(7)
Ba(1)-O(1)#10	2.737(3)	O(1)#2-Ba(1)-O(1)	140.1(10)
Ba(1)-O(1)#11	2.737(3)	O(1)#10-Ba(1)-O(1)	84.6(7)
Sn(1)-O(1)	2.046(4)	O(1)#1-Ba(1)-O(1)#8	84.6(7)
Sn(1)-O(1)#4	2.046(4)	O(1)#11-Ba(1)-O(1)#4	84.6(7)
Sn(1)-O(1)#12	2.046(4)	O(1)#1-Ba(1)-O(1)#6	95.4(7)
Sn(1)-O(1)#13	2.046(4)	O(1)#8-Ba(1)-O(1)#6	180.0(0)
Sn(1)-O(1)#14	2.046(4)	O(1)#2-Ba(1)-O(1)#8	51.4(11)
Sn(1)-O(1)#15	2.046(4)	O(1)#11-Ba(1)-O(1)#6	39.9(10)
Sn(1)-O(1)#16	2.046(4)	O(1)#4-Ba(1)-O(1)#6	101.7(9)
Sn(1)-O(1)#17	2.046(4)	O(1)#9-Ba(1)-O(1)#5	95.4(7)
Sn(1)-O(1)#18	2.046(4)	O(1)#9-Ba(1)-O(1)#8	101.7(9)
Sn(1)-O(1)#19	2.046(4)	O(1)#10-Ba(1)-O(1)#5	101.7(9)
Sn(1)-O(1)#20	2.046(4)	O(1)#11-Ba(1)-O(1)#5	84.6(7)
Sn(1)-O(1)#21	2.046(4)	O(1)#1-Ba(1)-O(1)	180.0(0)
B(1)-O(1)#4	1.380(4)	O(1)#1-Ba(1)-O(1)#3	84.6(7)
B(1)-O(1)#20	1.380(4)	O(1)#3-Ba(1)-O(1)	95.4(7)
B(1)-O(1)#22	1.380(4)	O(1)#7-Ba(1)-O(1)	78.3(9)
B(1)-O(1)#23	1.380(4)	O(1)#4-Ba(1)-O(1)	51.4(11)
B(1)-O(1)#24	1.380(4)	O(1)#2-Ba(1)-O(1)#3	101.7(9)
B(1)-O(1)#6	1.380(4)	O(1)#2-Ba(1)-O(1)#10	78.3(9)
O(1)#1-Ba(1)-O(1)#2	39.9(10)	O(1)#10-Ba(1)-O(1)#4	39.9(10)
O(1)#3-Ba(1)-O(1)#4	140.1(10)	O(1)#9-Ba(1)-O(1)#10	140.1(10)
O(1)#4-Ba(1)-O(1)#5	78.3(9)	O(1)#9-Ba(1)-O(1)#3	39.9(10)
O(1)#8-Ba(1)-O(1)#10	95.4(7)	O(1)#10-Ba(1)-O(1)#11	51.4(11)

O(1)#9-Ba(1)-O(1)#6	78.3(9)	O(1)#7-Ba(1)-O(1)#8	39.9(10)
O(1)#3-Ba(1)-O(1)#10	180.0(0)	O(1)#1-Ba(1)-O(1)#4	128.6(11)
O(1)#3-Ba(1)-O(1)#8	84.6(7)	O(1)#8-Ba(1)-O(1)	95.4(7)
O(1)#7-Ba(1)-O(1)#10	128.6(11)	O(1)#2-Ba(1)-O(1)#4	95.4(7)
O(1)#6-Ba(1)-O(1)#10	84.6(7)	O(1)#3-Ba(1)-O(1)#7	51.4(11)
O(1)#1-Ba(1)-O(1)#11	78.3(9)	O(1)#9-Ba(1)-O(1)#4	180.0(0)
O(1)#7-Ba(1)-O(1)#1	101.7(9)	O(1)#11-Ba(1)-O(1)	101.7(9)
O(1)#2-Ba(1)-O(1)#11	95.4(7)	O(1)#8-Ba(1)-O(1)#4	78.3(9)
O(1)#2-Ba(1)-O(1)#5	180.0(0)	O(1)#1-Ba(1)-O(1)#10	95.4(7)
O(1)#9-Ba(1)-O(1)#11	95.4(7)	O(1)#4-Ba(1)-O(1)#7	95.4(7)
O(1)#2-Ba(1)-O(1)#7	84.6(7)	O(1)#5-Ba(1)-O(1)	39.9(10)
O(1)#8-Ba(1)-O(1)#11	140.1(10)	O(1)#25-B (1)-O(1)#24	119.5(5)
O(1)#7-Ba(1)-O(1)#5	95.4(7)	O(1)#18-B (1)-O(1)#10	119.5(5)
O(1)#3-Ba(1)-O(1)#11	128.6(11)	O(1)#4-B (1)-O(1)#24	119.5(5)
O(1)#7-Ba(1)-O(1)#9	84.6(7)	O(1)#4-B (1)-O(1)#25	119.5(5)
O(1)#7-Ba(1)-O(1)#11	180.0(0)	O(1)#10-B (1)-O(1)#23	119.5(5)
O(1)#6-Ba(1)-O(1)#5	51.4(11)	O(1)#18-B (1)-O(1)#23	119.5(5)

Symmetry transformations used to generate equivalent atoms:

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

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

#12 -x,-x+y,1-z   #13 y,-x+y,1-z   #14 -y+x,-y,1-z   #15 y,x,1-z   #16 -y+x,x,1-z   #17 -x,-y,1-z; 18-y,-x,z

#19 y-x,-x,z   #20 -y,x-y,z   #21 x,x-y,z   #22 -1+x,+y,z   #23 -1+x,x-y,z   #24 -y,1-x,z   #25 -1+x,x-y,z

Table S4. Atom-cutting analysis and calculated birefringence of $BaTi(BO_3)_2$.

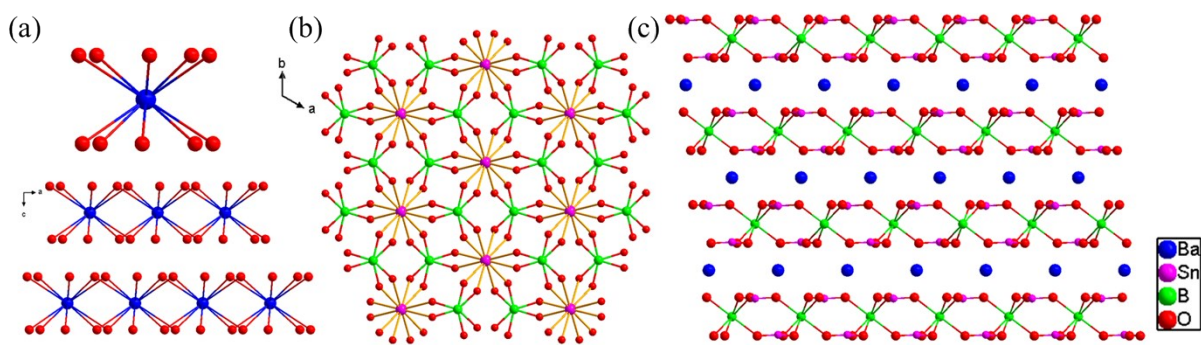| Compound	Δn (@546nm)	$[BaO_{12}]$ and $[TiO_6]$ polyhedra	B-O groups
$BaTi(BO_3)_2$	0.185	0.0304	0.1546

Figure S1 (a) The coordination of the Ba atoms; (b) The arrangement of $[SnO_6]$ and $[BO_3]$groups; (c)The whole crystal structure of $BaSn^{IV}(BO_3)_2$.

The coordination of $[BaO_{12}]$ polyhedra, isolated $[SnO_6]$, and isolated $[BO_3]$ groups in the structure of $BaSn^{IV}(BO_3)_2$ is similar to that of $BaTi(BO_3)_2$. Unfortunately, the O atoms are disordered in $BaSn^{IV}(BO_3)_2$.
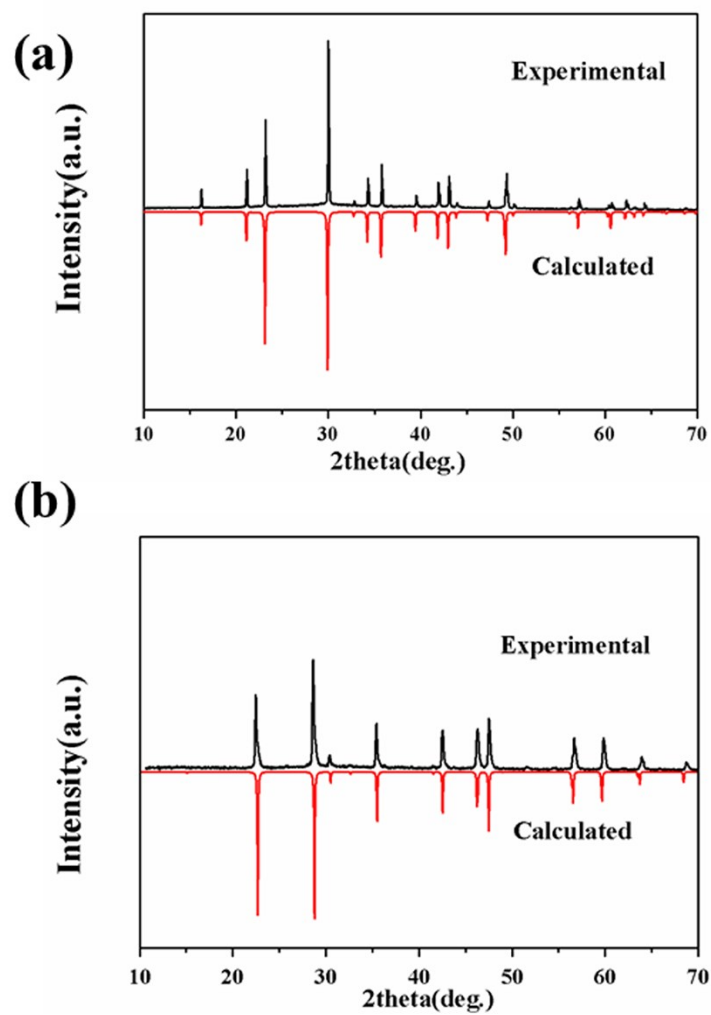
Figure S2. The experimental and calculated XRD patterns of (a) $BaTi(BO_3)_2$; (b) $BaSn^{IV}(BO_3)_2$.
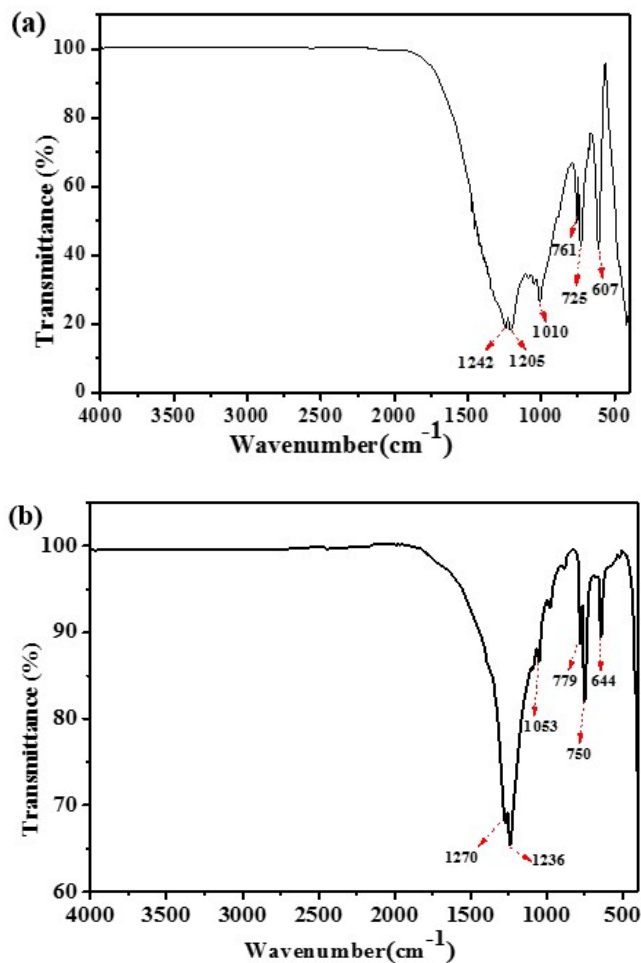
Figure S3. The infrared spectrum of (a) BaTi(BO$_3$)$_2$; (b) BaSn^{IV}(BO$_3$)$_2$.

The infrared spectrum of BaTi(BO$_3$)$_2$ and BaSn^{IV}(BO$_3$)$_2$ are shown in Figure S3. The bending vibrations for the trigonal planar [BO$_3$] groups can be found ranging from 600 to 800 cm^{-1}. The peaks in the range of 950-1500 cm^{-1} may be the [BO$_3$] groups of symmetric and antisymmetric stretching modes, respectively[9].
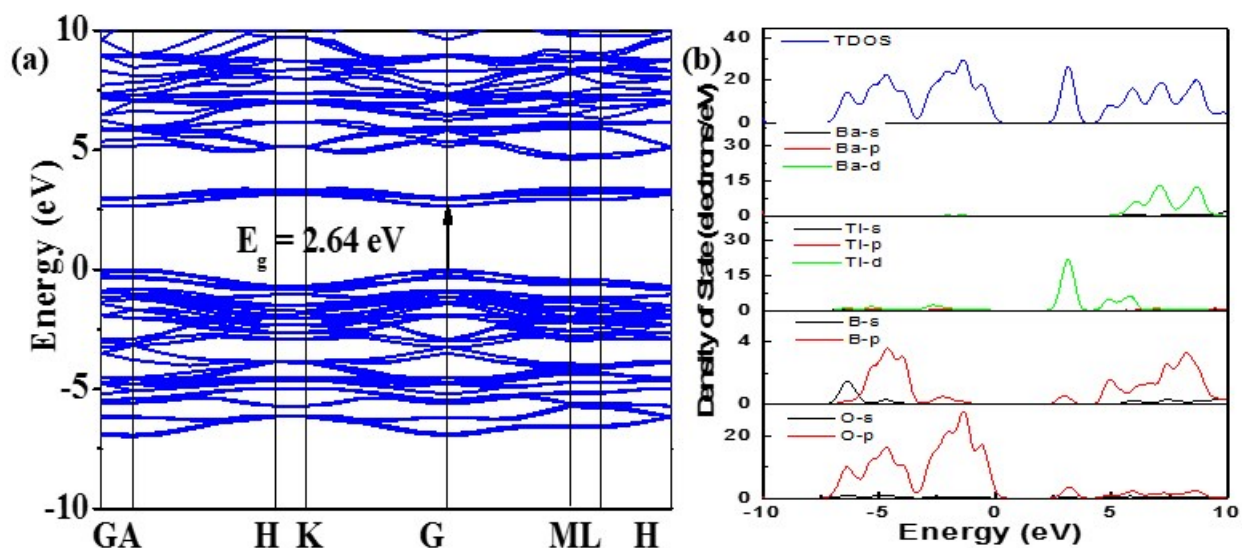
Figure S4 (a) Electronic band structure; (b) Partial and Total density of states for BaTi(BO$_3$)$_2$.

To further understand the relationship between structure and properties, the first-principles calculation was performed using the CASTEP program[5]. As is shown in Figure S4 (a), the theoretical band gap of BaTi(BO$_3$)$_2$ is 2.64 eV, which agrees with the experimental one. The partial density of states (PDOS) was drawn in Figure S4(b), and we can note that the valence band (VB) is mainly composed of B *sp* states and O *p* states. The conduction band (CB) mainly consists of O *p* states, B *p* states, Ti *d* states and Ba *d* states, which manifests that the [BO$_3$] and [TiO$_6$] groups determine the electronic structure and optical properties.
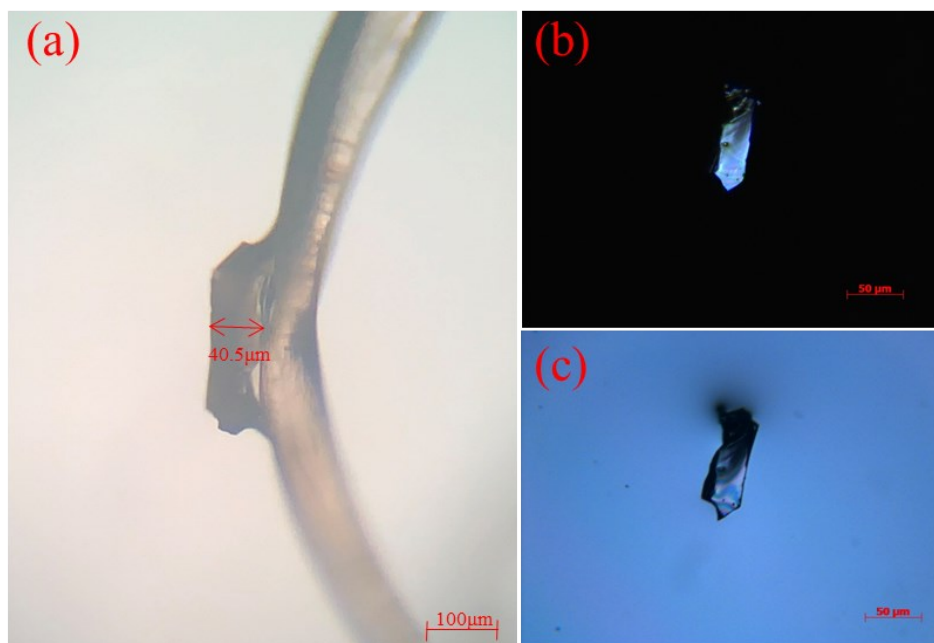
Figure S5 Birefringence measurements on the BaTi(BO$_3$)$_2$ crystal. (a) The thickness of BaTi(BO$_3$)$_2$ crystal; (b) and (c) BaTi(BO$_3$)$_2$ single crystal under the polarizing microscope lighted before and after.

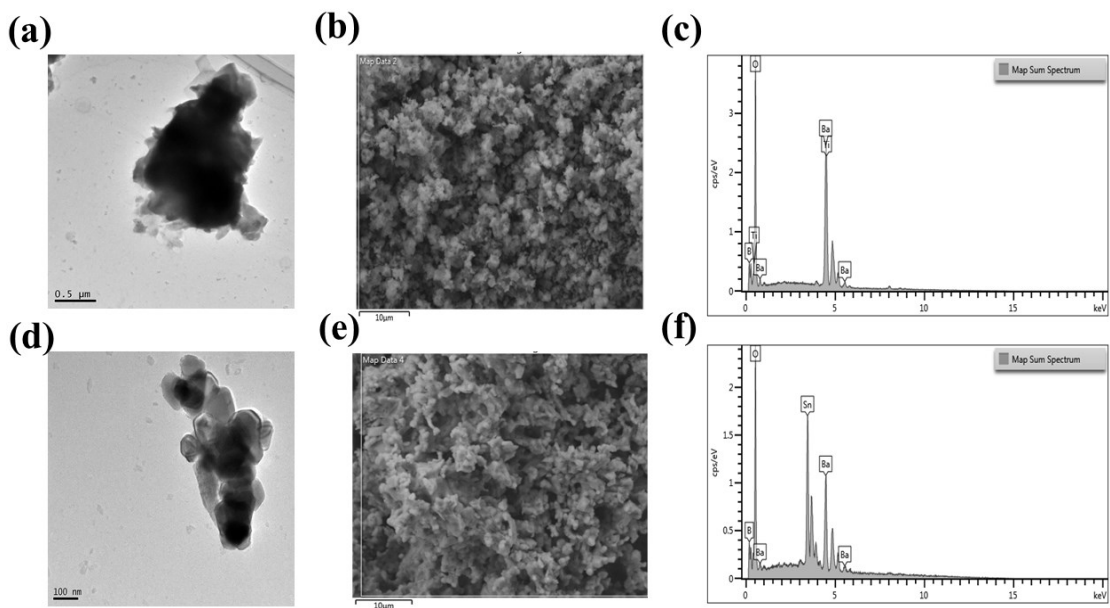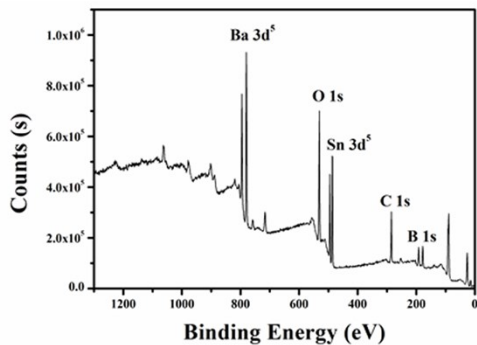**Figure S6** (a) The TEM of BaTi(BO$_3$)$_2$; (b) The SEM of BaTi(BO$_3$)$_2$; (c) The EDS of BaTi(BO$_3$)$_2$; (d) The TEM of BaSn^{IV}(BO$_3$)$_2$; (e) The SEM of BaSn^{IV}(BO$_3$)$_2$; (f) The EDS of BaSn^{IV}(BO$_3$)$_2$.
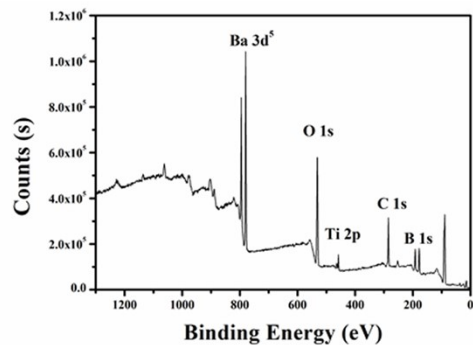
Figure S7 (a) The XPS spectrum of BaSn^{IV}(BO$_3$)$_2$ (b) The XPS spectrum of BaTi(BO$_3$)$_2$. Owing to using BaCO$_3$ as the raw material in preparation of pure phase, the XPS spectrum shows the peak of the C element.

Reference

[1] V. SAINT, *Inc., Madison, WI,* 2008.

[2] G. M. Sheldrick, *Acta. Crystallogr. A,* 2008, **64**, 112.

[3] A. L. Spek, *J. Appl. Crystallogr.,* 2003, **36**, 7.

[4] J. Tauc, *Mater. Res. Bull.,* 1970, **5**, 721.

[5] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson and M. C. Payne, *Z. Kristallogr.-Cryst. Mater.,* 2005, **220**, 567.

[6] A. M. Rappe, K. M. Rabe, E. Kaxiras and J. D. Joannopoulos, *Phys. Rev. B.,* 1990, **41**, 1227.

[7] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Let.,* 1998, **80**, 891.

[8] J. S. Lin, A. Qteish, M. C. Payne and V. Heine, *Phys. Rev. B.,* 1993, **47**, 4174.

[9] V. Falkowski, A. Zeugner, L. Bayarjargal, A. Saxer, M. Ruck and H. Huppertz, *Eur. J. Inorg. Chem.,* 2019, **34**, 3854.