

Electronic Supplementary Information

CsB₃O₄(OH)₂: A new deep-ultraviolet birefringent crystal with [B₃O₄(OH)₂] anionic group

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Table of Contents

Experimental Section	S2
Results and Discussion.....	S5
References.....	S19

Experimental Section.

Reagents.

Cesium fluoride (CsF, 99 %), Boron oxide (B_2O_3 , 98 %), and ethanol (99 %) were obtained from Aladdin Chemical Industry Co., Ltd. All materials were used as received.

Syntheses.

The synthesis of the title compound requires the following two steps: First, the Polycrystalline samples of CsB_4O_6F were synthesized by conventional solid state method using stoichiometric ratio of CsF (7.956 g, 0.05 mol) and B_2O_3 (6.183 g, 0.1 mol).¹ The mixture was dwelled at 360 °C for 48h. The purity of the products was checked by PXRD analysis. Second, CsB_4O_6F samples were mixed with a small amount of deionized water (0.10 mL) and ethanol (0.30 mL) in a 23 mL Teflon-lined stainless-steel autoclave. The autoclave was tightly sealed and quickly heated to 210 °C, held at this temperature for 96 h, and then slowly cooled to 180 °C at 0.5°C/h, after which they were cooled to 100 °C at a rate of 1 °C /h, subsequently cooled to room temperature by switching off the furnace. The pH values before and after the hydrothermal reaction were 8.0 and 7.0, respectively. After washing with deionized water, colorless crystals of $CsB_3O_4(OH)_2$ were collected and dried in air.

Structure Determination.

The crystal data of $CsB_3O_4(OH)_2$ was collected by a Bruker D8 VENTURE diffractometer using Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. The data integration and absorption corrections were carried out using the Bruker SAINT program.² The single-crystal data were analyzed with the Olex2 program.³ The crystal structures were solved with the direct method and refined with the SHELXL least-squares refinement package.⁴ The structure was checked for possible higher symmetry using the ADDSYM algorithm from the program PLATON.⁵ Crystal data and structure refinements are listed in Table S1. The atomic coordinates and equivalent isotropic displacement parameters selected bond distances and angles, and hydrogen bonds are given in Tables S2-S4.

Powder X-ray Diffraction (PXRD).

PXRD data were collected at room temperature with a DX-27 mini X-ray diffractometer equipped with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature.

The PXRD pattern was scanned over the 2θ angles range of $5-70^\circ$, at a scanning step width of 0.02° and a fixed counting time of 2 s.

Infrared spectrum.

The Infrared spectrum was carried out on a Shimadzu IR Affinity Fourier transform infrared spectrometer in the range of $400 - 4000 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . Pellets for measurement were prepared by pressing a thoroughly ground mixture of 6mg sample and 600 mg dried KBr at room temperature.

Elemental analysis.

Elemental analysis including Energy dispersive X-ray spectroscopy (EDX) and corresponding elemental mappings were carried on using a Hitachi TM 4000 Plus field emission scanning electron microscope.

Thermal Analysis.

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were measured on a simultaneous NETZSCH STA 449 F3 thermal analyzer instrument in a flowing N_2 atmosphere. The sample was placed in the Pt crucible, and heated from 40 to 800°C at a rate of $10 \text{ }^\circ\text{C min}^{-1}$.

UV–Vis–NIR Diffuse Reflectance Spectroscopy.

Ultraviolet–visible–near infrared diffuse-reflectance spectroscopy data in the wavelength range of $190-1100 \text{ nm}$ was recorded at room temperature using a crystal of $\text{CsB}_3\text{O}_4(\text{OH})_2$ on a Metash UV-8000 spectrophotometer.

Birefringence (Δn).

The birefringence value of CBOH has further been measured with a (NIKON Eclipse Ci-POL) polarizing microscope under the light source of 546 nm . The thickness of the selected crystal was measured by single crystal X-ray diffractometer. According to the equation ΔR (optical path difference) = $(|N_e - N_o|) \times d = \Delta n$ (birefringence) $\times d$ (crystal thickness), the experimental birefringence value of $\text{CsB}_3\text{O}_4(\text{OH})_2$ can be obtained.

Computational Methods.

The first principles calculations for $\text{CsB}_3\text{O}_4(\text{OH})_2$ were investigated using the plane wave Density Functional Theory (DFT) software⁶ package CASTEP.^{7, 8} After the DFT geometry optimization, the H atoms positions are refined. The norm-conserving pseudopotentials (NCPs) and Perdew-Burke-Emzerhoff (PBE) functional within the

generalized gradient approximation (GGA) were adopted⁹. The NCPs are as follows: Cs: $5s^2 5p^6 6s^1$, B: $2s^2 2p^1$, O: $2s^2 2p^4$, H: $1s^1$. The cutoff energy of plane waves was set to 750 eV. Brillouin zone integrations were performed by using the Monkhorst-Pack scheme with a k -point grid of $2 \times 2 \times 1$ and a k -point spacing of 0.07 \AA^{-1} . The existence of discontinuity of exchange-correlation energy makes GGA typically underestimates the band gap, so the HSE06 hybrid function was chosen to provide more accurate bandgap values in this study.¹⁰ Based on the scissor-corrected (1.46 eV) electron structure, the linear optical properties were obtained by the Kramers–Kronig transform. The complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ is used for calculation. On the basis of the obtained electronic structures, the imaginary part of the dielectric function $\epsilon_2(\omega)$ can be calculated from the electronic transition between the occupied and unoccupied states caused by the interaction with photons.

Results and Discussion

Table S1. Crystal data and structure refinement for CsB₃O₄(OH)₂.

formula	CsB ₃ O ₄ (OH) ₂
Formula weight	263.36
Temperature [K]	273(2)
Crystal system	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>c</i> (14)
<i>a</i> [Å]	7.5289(10)
<i>b</i> [Å]	6.4534(7)
<i>c</i> [Å]	12.4902(19)
α [°]	90
β [°]	98.716(6)
γ [°]	90
Volume [Å ³]	599.85(14)
<i>Z</i>	4
ρ_{calc} [g·cm ⁻³]	2.916
μ [mm ⁻¹]	6.132
<i>F</i> (000)	480
Radiation	MoK α (λ =0.71073 Å)
2 θ range [°]	5.47 to 67.68 (0.64 Å)
Index ranges	-10 ≤ <i>h</i> ≤ 11 -10 ≤ <i>k</i> ≤ 9 -19 ≤ <i>l</i> ≤ 19
Reflections collected	14646
Independent reflections	2162 <i>R</i> _{int} = 0.0512 <i>R</i> _{sigma} = 0.0380
Completeness to θ =25.242°	99.9 %
Data / Restraints / Parameters	2162/2/98
Goodness-of-fit on <i>F</i> ²	1.069
Final <i>R</i> indexes [<i>I</i> ≥2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0380 <i>wR</i> ₂ = 0.0778
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0658 <i>wR</i> ₂ = 0.0867
Largest peak/hole [eÅ ⁻³]	1.32/-0.77
Extinction coefficient	0.0044(6)

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

Table S2. Atomic coordinates and U_{eq} [\AA^2] for $\text{CsB}_3\text{O}_4(\text{OH})_2$.

Atom	x	y	z	U_{eq}
Cs1	0.00790(3)	1.26698(4)	0.13280(2)	0.03342(12)
B1	0.3411(5)	0.8036(6)	0.1524(3)	0.0231(7)
B2	0.3883(6)	0.5120(6)	0.2896(3)	0.0250(8)
B3	0.3731(6)	0.2320(6)	0.4137(3)	0.0253(8)
O1	0.1766(3)	0.8714(4)	0.0901(2)	0.0225(5)
H1	0.217(5)	0.979(4)	0.095(4)	0.027
O2	0.2890(3)	0.6565(4)	0.2292(2)	0.0294(6)
O3	0.5672(3)	0.4843(4)	0.2945(2)	0.0296(6)
O4	0.2880(3)	0.3842(4)	0.3482(2)	0.0301(6)
O5	0.5534(3)	0.2049(4)	0.4232(2)	0.0269(5)
O6	0.2695(4)	0.1099(5)	0.4686(3)	0.0365(7)
H2	0.334(6)	0.016(6)	0.505(4)	0.044

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor

Table S3. Selected bond lengths (Å) and angles (deg.) for CsB₃O₄(OH)₂.

Cs1–O1	2.936(2)	B1–O1	1.427(4)
Cs1–O1 ^{#1}	3.051(2)	B1–O2	1.446(5)
Cs1–O2 ^{#2}	3.105(3)	B1–O3 ^{#6}	1.462(5)
Cs1–O6 ^{#3}	3.153(3)	B1–O5 ^{#6}	1.468(5)
Cs1–O6 ^{#4}	3.172(3)	B2–O3	1.351(5)
Cs1–O4 ^{#5}	3.247(3)	B2–O2	1.352(5)
Cs1–O4 ^{#2}	3.359(3)	B2–O4	1.398(5)
Cs1–O2 ^{#5}	3.388(3)	B3–O5	1.356(5)
Cs1–O3 ^{#6}	3.675(3)	B3–O6	1.364(5)
		B3–O4	1.373(5)
O1–B1–O2	105.2(3)	O3–B2–O2	125.5(3)
O1–B1–O3	108.3(3)	O3–B2–O4	120.8(3)
O2–B1–O3	112.3(3)	O2–B2–O4	113.7(3)
O1–B1–O5	107.0(3)	O5–B3–O6	121.5(3)
O2–B1–O5	111.7(3)	O5–B3–O4	121.0(3)
O3–B1–O5	111.9(3)	O6–B3–O4	117.5(3)

Symmetry transformations used to generate equivalent atoms:

#1: -X, 2-Y, -Z; #2: -X, 0.5+Y, 0.5-Z; #3: +X, 1.5-Y, -0.5+Z;
#4: -X, 1.5+Y, 0.5-Z; #5: +X, 1+Y, +Z; #6: 1-X, 0.5+Y, 0.5-Z;

Table S4. Hydrogen bonds for CsB₃O₄(OH)₂.

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
O6–H2···O5 ^{#1}	0.866(19)	1.82(2)	2.681(4)	173(5)

Symmetry transformations used to generate equivalent atoms:

#1: 1-X, -Y, 1-Z;

Table S5. Bond valence analysis of CsB₃O₄(OH)₂.

Atom	O1	O2	O3	O4	O5	O6	Σ_{cation}
Cs1	0.309	0.166	0.024	0.134	–	0.193	0.826
B1	0.860	0.817	0.782	–	0.769	–	3.228
B2	–	1.053	1.056	0.93	–	–	3.039
B3	–	–	–	0.995	1.041	1.019	3.055
H1	0.866	–	–	–	–	–	–
H2	–	–	–	–	–	0.866	–
Σ_{anion}	2.035	2.036	1.862	2.059	1.81	2.078	–

Table S6. alkali- and/or alkaline-earth metal cations-containing hydroxyl borates.

Compounds	Space groups	FBB (&FBB descriptor)	Anionic framework	Birefringence (@1064 nm)	Bandgap(eV)	Refs
Na ₃ B ₃ O ₄ (OH) ₄	<i>Cc</i>	[B ₃ O ₄ (OH) ₄] 3:Δ+2T	[B ₃ O ₄ (OH) ₄] chain	-	-	11
KB ₃ O ₄ (OH) ₂	<i>P4/ncc</i>	[B ₁₂ O ₁₆ (OH) ₈] 12:4[3:2Δ+T]	[B ₁₂ O ₁₆ (OH) ₈] layer	-	-	12
Na ₃ B ₃ O ₅ (OH) ₂	<i>Pnma</i>	[B ₃ O ₅ (OH) ₂] 3:Δ+T	[B ₃ O ₅ (OH) ₂] layer	-	-	13
K ₃ B ₃ O ₄ (OH) ₄ ·2H ₂ O	<i>Cmc2₁</i>	[B ₃ O ₄ (OH) ₄] 3:Δ+2T	[B ₃ O ₄ (OH) ₄] layer	-	>6.1 eV (Exp.)	14
Rb ₃ [B ₃ O ₄ (OH) ₄] ₃ ·2H ₂ O	<i>Pna2₁</i>	[B ₃ O ₄ (OH) ₄] 3:Δ+2T	[B ₃ O ₄ (OH) ₄] layer	-	-	15
SrB ₃ O ₄ (OH) ₃	<i>P2₁/c</i>	[B ₃ O ₄ (OH) ₃] 3:Δ+2T	[B ₃ O ₄ (OH) ₃] chain	-	6.15 eV (Exp.) 5.76 eV (Cal.)	16
Tl[B ₃ O ₄ (OH) ₂] ₂ ·0.5H ₂ O	<i>Pnma</i>	[B ₃ O ₄ (OH) ₂] 3:2 Δ+T	[B ₃ O ₄ (OH) ₂] chain	-	-	17
K ₂ [B ₄ O ₅ (OH) ₄] ₂ ·H ₂ O	<i>P1</i>	[B ₄ O ₅ (OH) ₄] 4:2Δ+2T	[B ₄ O ₅ (OH) ₄] chain	0.051	5.24 eV (Cal.)	18
K ₂ [B ₄ O ₅ (OH) ₄]	<i>Pbcn</i>	[B ₄ O ₅ (OH) ₄] 4:2Δ+2T	[B ₄ O ₅ (OH) ₄] layer	0.058	5.16 eV (Cal.)	18
Rb ₂ [B ₄ O ₅ (OH) ₄] ₂ ·3.6H ₂ O	<i>Pbcn</i>	[B ₄ O ₅ (OH) ₄] 4:2Δ+2T	[B ₄ O ₅ (OH) ₄] unit	-	-	19
Cs ₂ [B ₄ O ₅ (OH) ₄] ₂ ·3H ₂ O	<i>P2₁/c</i>	[B ₄ O ₅ (OH) ₄] 4:2Δ+2T	[B ₄ O ₅ (OH) ₄] unit	-	-	20
Ba ₂ [B ₄ O ₇ (OH) ₂]	<i>P3₁2₁</i>	[B ₅ O ₁₃] 5:1Δ+4T	[B ₅ O ₁₃] chain	-	5.12 eV (Cal.)	21
Rb ₄ [B ₄ O ₅ (OH) ₄] ₂ ·3H ₂ O	<i>Pbcn</i>	[B ₄ O ₅ (OH) ₄] 4:2Δ+2T	[B ₄ O ₅ (OH) ₄] chain	-	-	22
Mg(H ₂ O) ₆ B ₄ O ₅ (OH) ₄ (H ₂ O) ₃	<i>P2₁/c</i>	[B ₄ O ₅ (OH) ₄] 4:2Δ+2T	[B ₄ O ₅ (OH) ₄] layer	-	-	23
Na ₂ B ₄ O ₆ (OH) ₂	<i>Pbca</i>	[B ₄ O ₆ (OH) ₂] 4:2Δ+ 2T	[B ₄ O ₆ (OH) ₂] chain	-	-	24
Na[B ₅ O ₇ (OH) ₂] ₂ ·H ₂ O	<i>Pca2₁</i>	[B ₅ O ₁₀] 5:4Δ+1T	[B ₅ O ₁₀] chain	-	5.61 eV (Cal.)	21
K[B ₅ O ₇ (OH) ₂] ₂ ·H ₂ O	<i>P2₁/c</i>	[B ₅ O ₇ (OH) ₂] 5:4Δ+1T	[B ₅ O ₇ (OH) ₂] layer	-	-	25
Rb[B ₅ O ₇ (OH) ₂] ₂ ·0.5H ₂ O	<i>P1</i>	[B ₅ O ₇ (OH) ₂] 5:4Δ+1T	[B ₅ O ₇ (OH) ₂] layer	-	-	26
Na[B ₅ O ₆ (OH) ₄]	<i>P2₁/c</i>	[B ₅ O ₆ (OH) ₄] 5:4Δ+1T	[B ₅ O ₆ (OH) ₄] unit	-	-	27
K[B ₅ O ₆ (OH) ₄] ₂ ·2H ₂ O	<i>Aba2</i>	[B ₅ O ₆ (OH) ₄] 5:4Δ+1T	[B ₅ O ₆ (OH) ₄] unit	-	-	28
Cs[B ₅ O ₆ (OH) ₄]	<i>P2₁/c</i>	[B ₅ O ₆ (OH) ₄] 5:4Δ+1T	[B ₅ O ₆ (OH) ₄] unit	-	-	29
Cs[B ₅ O ₇ (OH) ₂] ₂ ·0.5H ₂ O	<i>P1</i>	[B ₁₀ O ₁₄ (OH) ₄] 5:4Δ+1T	[B ₁₀ O ₁₄ (OH) ₄] layer	-	-	30
LiK[B ₅ O ₈ (OH)] ₂ ·1.5H ₂ O	<i>C222₁</i>	[B ₅ O ₁₀ (OH)] 5:3Δ+2T	[B ₅ O ₁₀ (OH)] layer	-	5.82 eV (Exp.)	31
Na ₃ B ₅ O ₈ (OH) ₂ ·H ₂ O	<i>Pbca</i>	[B ₅ O ₈ (OH) ₂] 6:2Δ+4T	[B ₅ O ₈ (OH) ₂] layer	-	-	32
K ₃ B ₅ O ₈ (OH) ₂	<i>Fdd2</i>	[B ₅ O ₈ (OH) ₂] 5:4Δ+1T	[B ₅ O ₈ (OH) ₂] layer	-	5.72 eV (Exp.) 4.72 eV (Cal.)	33
MgB ₆ O ₉ (OH) ₂ ·(H ₂ O) ₄	<i>Pna2₁</i>	[B ₆ O ₁₁ (OH) ₂] 6:2[(3:2Δ+T)]	[B ₆ O ₁₁ (OH) ₂] layer	-	>6.2 eV (Exp.) 4.9 eV (Cal.)	34
Sr ₂ [B ₆ O ₉ (OH) ₄]	<i>P2₁</i>	[B ₆ O ₉ (OH) ₄] 6:2[(3:2Δ+T)]	[B ₆ O ₉ (OH) ₄] layer	-	-	35
Ba ₂ [B ₆ O ₉ (OH) ₄]	<i>P2₁</i>	[B ₆ O ₉ (OH) ₄] 3: Δ+2T	[B ₆ O ₉ (OH) ₄] layer	-	>6.53 eV (Exp.)	36
NaSr ₃ (OH)(B ₉ O ₁₆)[B(OH) ₄]	<i>P3₁c</i>	[B ₉ O ₁₉] 9: 3Δ+6T	[B ₉ O ₁₉] cluster	-	6.98 eV (Cal.)	37
Na ₂ [B ₈ O ₁₁ (OH) ₄] ₂ ·B(OH) ₃ ·H ₂ O	<i>P2₁/n</i>	[B ₈ O ₁₁ (OH) ₄] [5:(4Δ+T)+3:(2Δ+T)]	[B ₈ O ₁₁ (OH) ₄] chain	-	-	38
CsB ₇ O ₁₀ (OH) ₂	<i>C2/c</i>	[B ₇ O ₁₀ (OH) ₂] 7: [2Δ+ (5:4Δ+T)]	[B ₇ O ₁₀ (OH) ₂] layer	0.08	6.6 eV (Exp.) 6.0 eV (Cal.)	39
CsB ₃ O ₄ (OH) ₂	<i>P2₁/c</i>	[B ₃ O ₄ (OH) ₄] 3:Δ+2T	[B ₃ O ₄ (OH) ₄] chain	0.09	6.3eV (Exp.) 5.56 eV (Cal.)	This work

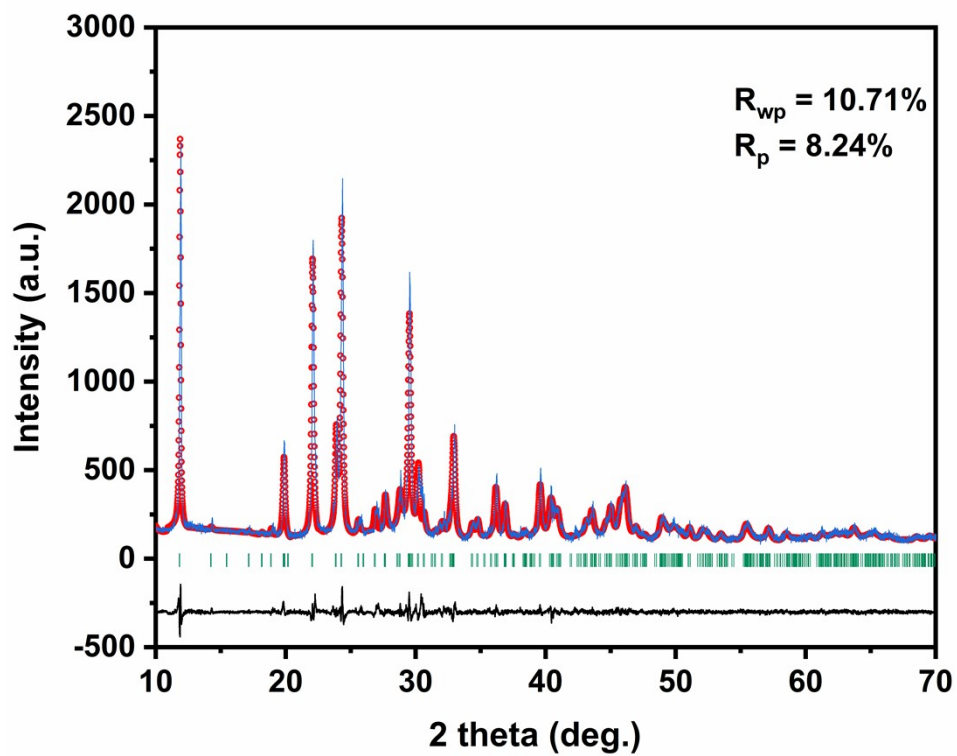


Figure S1. Rietveld refinement of the powder XRD profile.

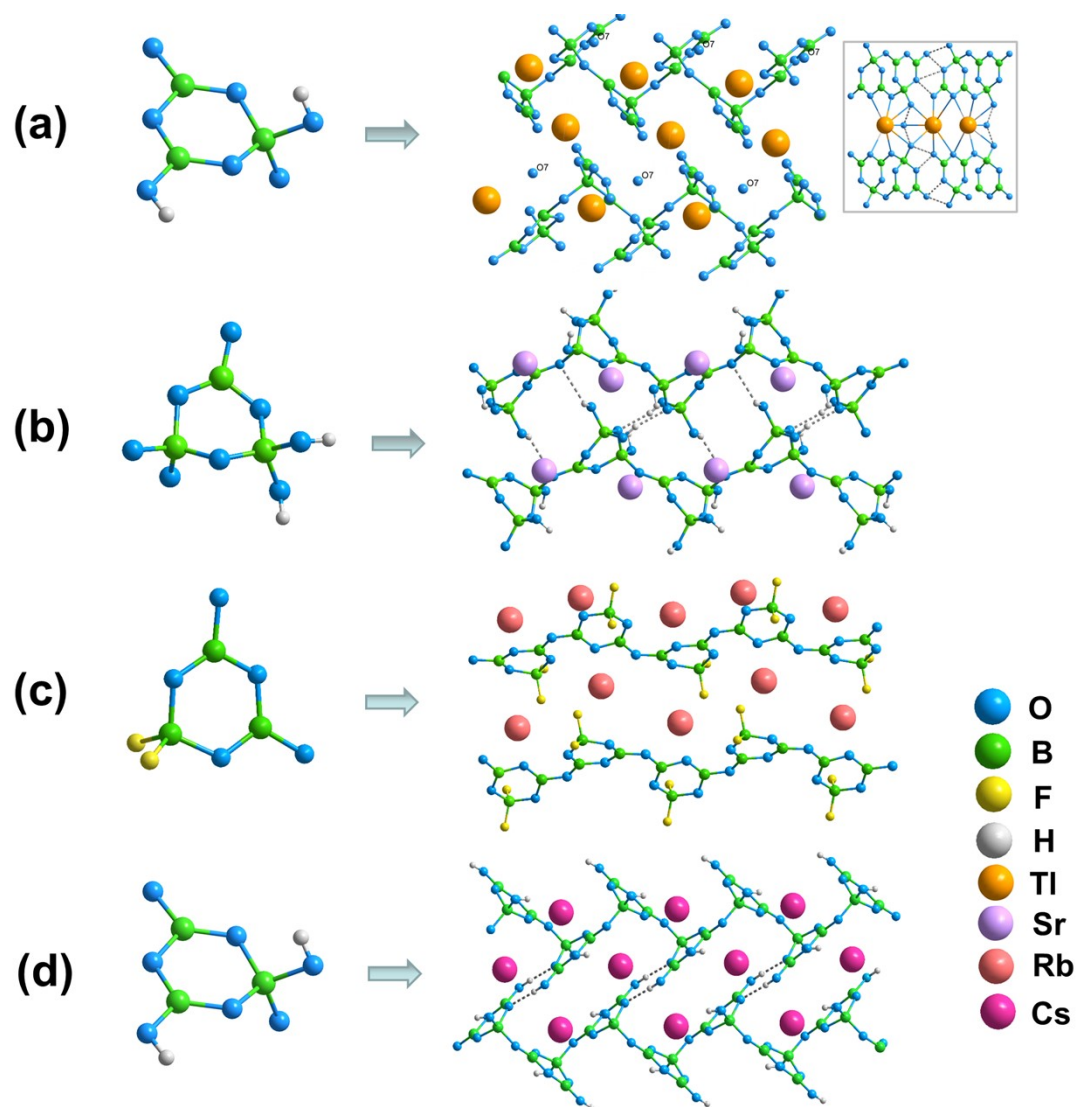


Figure S2. (a) $[B_3O_4(OH)_2]$ FBB and $[B_3O_4(OH)_2]$ chains of $TlB_3O_4(OH)_2 \cdot 0.5H_2O$. (b) $[B_3O_4(OH)_3]$ FBB and $[B_3O_4(OH)_3]$ chains of $SrB_3O_4(OH)_3 \cdot H_2O$. (c) $[B_3O_5F_2]$ FBB and $[B_3O_4F_2]$ chains of $RbB_3O_4F_2$. (d) $[B_3O_4(OH)_2]$ FBB and $[B_3O_4(OH)_2]$ chains of $CsB_3O_4(OH)_2$.

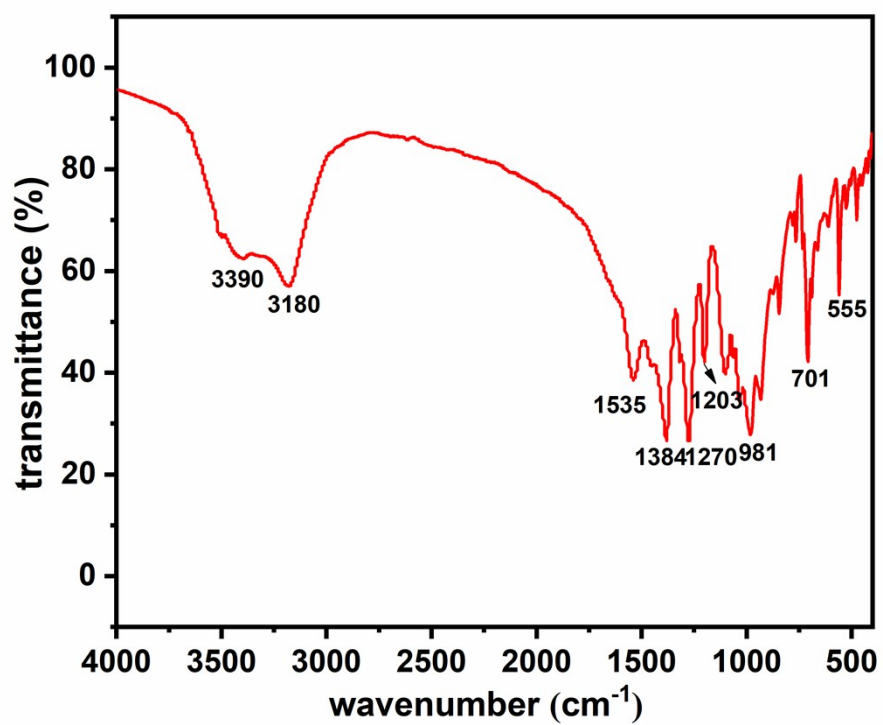


Figure S3. The IR spectrum of CsB₃O₄(OH)₂.

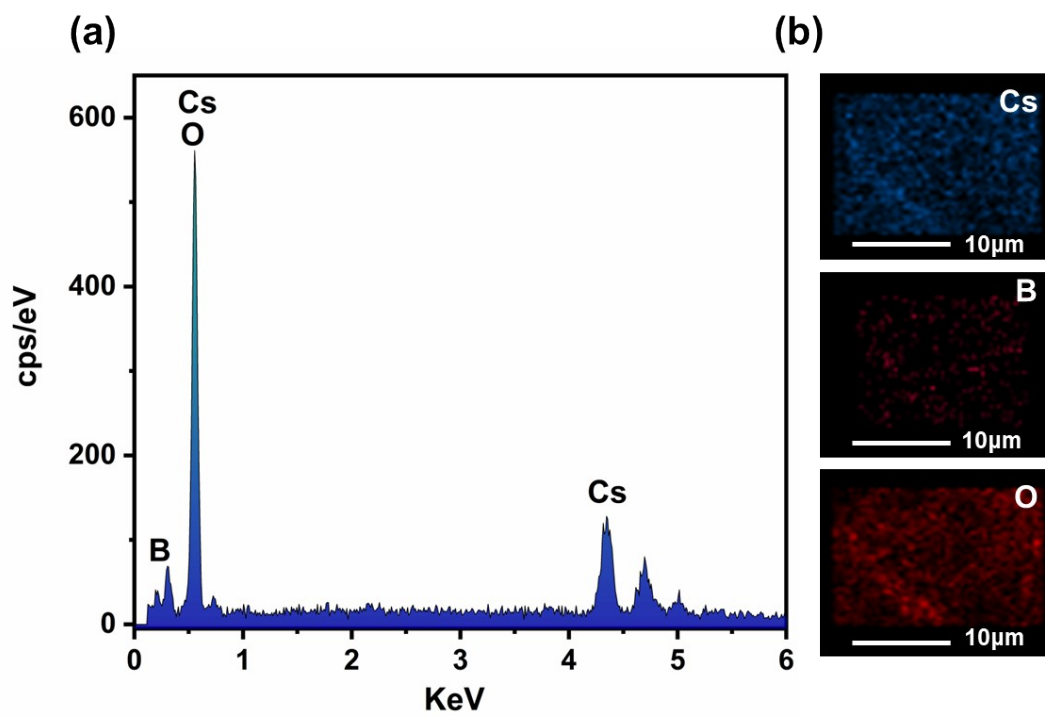


Figure S4. (a) EDX and (b) corresponding elemental mappings (Cs, B, and O elements) of $\text{CsB}_3\text{O}_4(\text{OH}_2)$.

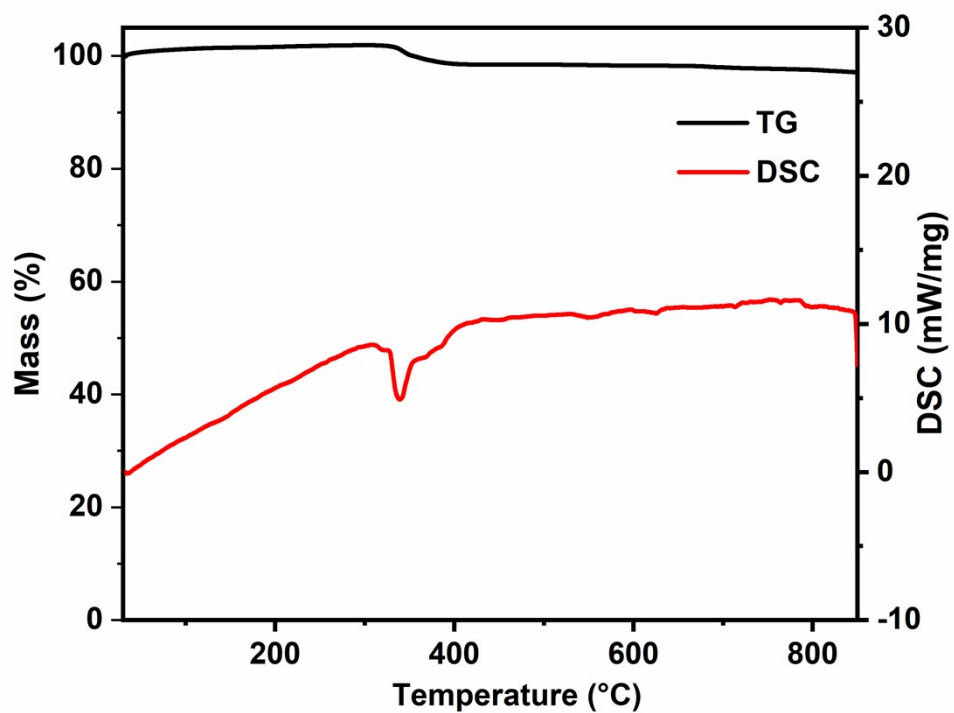


Figure S5. The TG and DSC curves of $\text{CsB}_3\text{O}_4(\text{OH})_2$.

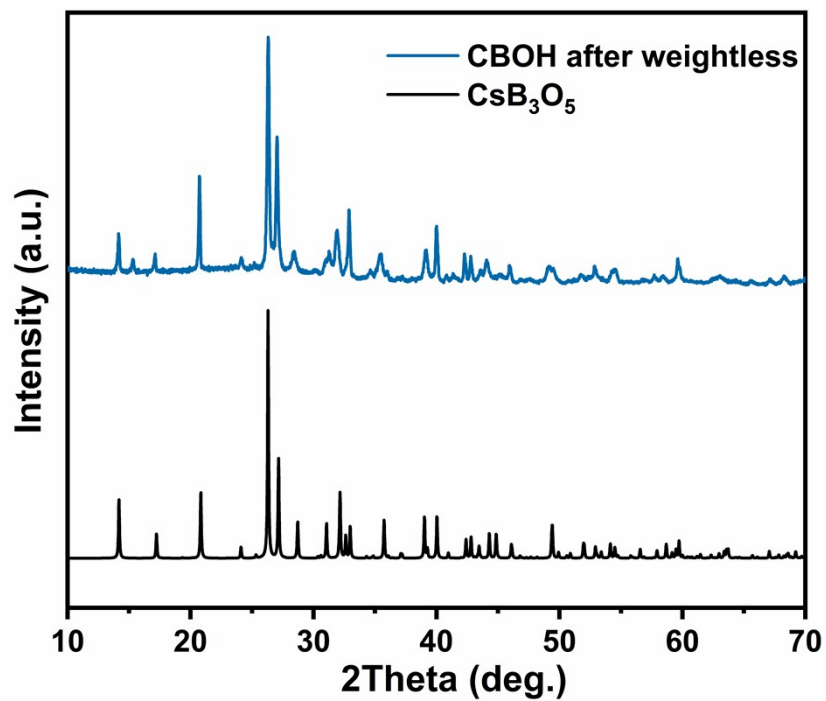


Figure S6. The XRD pattern after weightless of CsB₃O₄(OH)₂.

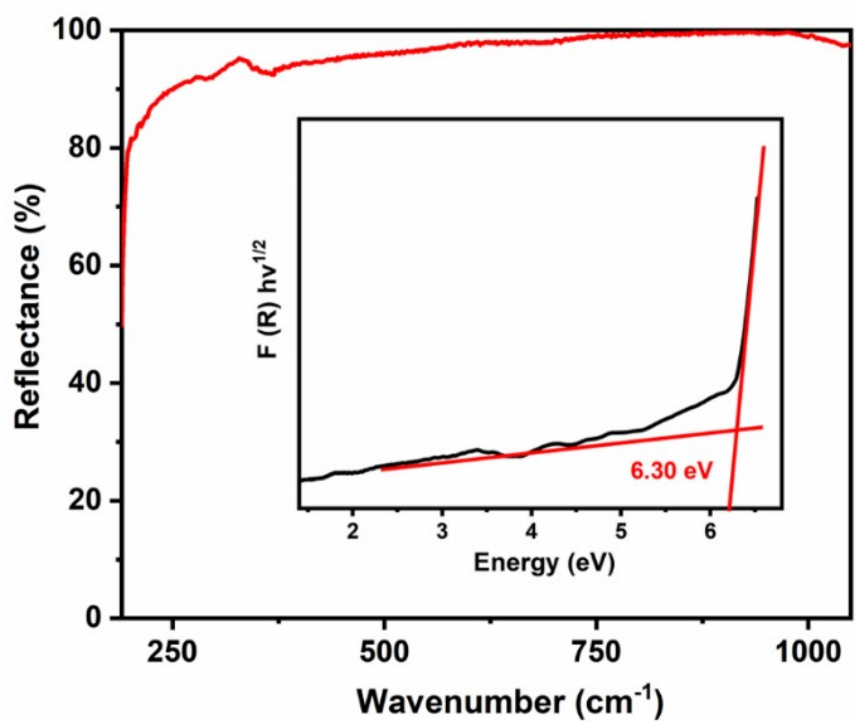


Figure S7. UV-vis-NIR diffuse reflectance spectrum of CsB₃O₄(OH)₂.

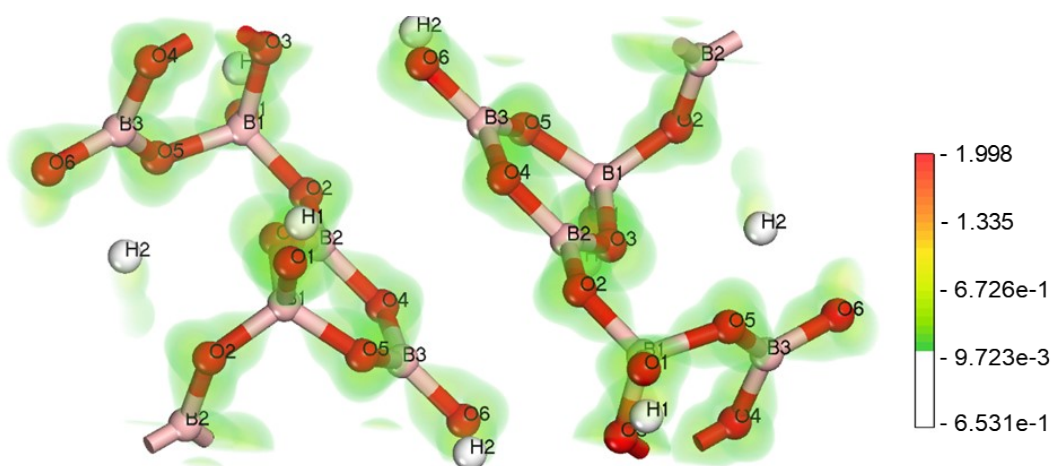


Figure S8. The electron density difference of $\text{CsB}_3\text{O}_4(\text{OH})_2$.

References.

1. X. F. Wang, Y. Wang, B. B. Zhang, F. F. Zhang, Z. H. Yang and S. L. Pan, *Angew. Chem. Int. Ed.*, 2017, **56**, 14119-14123.
2. *SAINT ver. 7.60A, Inc.:Madison, WI*, 2008.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
4. G. Sheldrick, *Acta. Cryst.*, 2015, **C71**, 3-8.
5. A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7-13.
6. D. R. Hamann, *Phys. Rev. B*, 1989, **40**, 2980-2987.
7. M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *J. Phys.-Condens. Mat.*, 2002, **14**, 2717-2744.
8. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson and M. C. Payne, *Z. Kristallogr.*, 2005, **220**, 567-570.
9. W. Jia, J. Fu, Z. Cao, L. Wang, X. Chi, W. Gao and L.-W. Wang, *J. Comput. Phys.*, 2013, **251**, 102-115.
10. D. R. Hamann, *Phys. Rev. B*, 2013, **88**, 1-10.
11. J. Andrieux, C. Goutaudier, L. Laversenne, E. Jeanneau and P. Miele, *Inorg. Chem.*, 2010, **49**, 4830-4835.
12. G. M. Wang, Y. Q. Sun, S. T. Zheng and G. Y. Yang, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1586-1590.
13. N. A. Sennova, R. S. Bubnova, S. K. Filatov, P. Paufler, D. C. Meyer, A. A. Levin and I. G. Polyakova, *Cryst. Res. Technol.*, 2005, **40**, 563-572.
14. Q. Liu, X. Y. Zhang, Z. H. Yang, F. F. Zhang, L. L. Liu, J. Han, Z. Li and S. L. Pan, *Inorg. Chem.*, 2016, **55**, 8744-8749.
15. I. Zviedre and A. Ievins, *Chem. Mater.*, 1974, **4**, 395-400.
16. H. J. Zhou, L. X. Chang, Y. H. Zhang, L. Wang and M. Kurmoo, *Inorg. Chem. Commun.*, 2018, **92**, 35-39.
17. M. T. Par, B. Claudette and M. Denis, *Acta. Cryst.*, 1983, **C39**, 685-689.
18. T. T. Shi, F. F. Zhang, A. Tudi, Z. H. Yang and S. L. Pan, *New J. Chem.*, 2019, **43**, 11660-11665.
19. M. Touboul, N. Penin and G. Nowogrocki, *J. Solid State Chem.*, 2000, **149**, 197-202.
20. M. Touboul, N. Penin and G. Nowogrocki, *J. Solid State Chem.*, 1999, **143**, 260-265.
21. C. Wu, L. H. Li, J. L. Song, G. Yang, M. G. Humphrey and C. Zhang, *Inorg. Chem.*, 2017, **56**, 1340-1348.
22. Y. Zhao, S. L. Pan, F. Li, Y. J. Wang, X. Y. Fan, X. Y. Dong, D. Z. Jia, J. X. Guo and Z. X. Zhou, *Solid State Sci.*, 2011, **13**, 82-87.
23. Y. Wang, J. Han, F. J. Guo, S. C. Cheng, Z. H. Yang and S. L. Pan, *Dalton Trans.*, 2019, **48**, 17408-17413.
24. M. Silvio and S. Cesare, *Acta. Cryst.*, 1978, **B34**, 1080-1084.
25. I. V. Pekov, N. V. Zubkova, O. V. Korotchenkova, I. I. Chaikovskiy, V. O. Yapaskurt, N. V. Chukanov, D. I. Belakovskiy, I. S. Lykova, S. N. Britvin and D. Y. Pushcharovsky, *Mineral. Mag.*, 2019, **84**, 335-342.
26. E. L. Belokoneva, T. A. Borisova and O. V. Dimitrova, *Crystallogr. Rep.*, 2003, **48**, 583-590.
27. Silvio.M. and Cesare.S., *Acta. Cryst.*, 1978, **B34**, 45-49.
28. J. P. Ashmore and H. E. Petch, *Can. J. Phys.*, 1969, **48**, 1901-1907.

29. H. Behm, *Acta. Cryst.*, 1984, **C40**, 1114-1116.
30. L. V. Shvanskaya and A. V. Sapegina, *Crystallogr. Rep.*, 2019, **64**, 260-265.
31. X.-Y. Li and G.-Y. Yang, *Inorg. Chem. Commun.*, 2019, **102**, 262-266.
32. M. Silvio and S. Cesare *Acta. Cryst.*, 1977, **B33**, 3730-3733.
33. F. Ding, M. L. Nisbet, W. Zhang, P. S. Halasyamani, L. Chai and K. R. Poeppelmeier, *Inorg. Chem.*, 2018, **57**, 11801-11808.
34. H. Wu, Q. Wei, H. He, B. Yang, Q. Zhang and G. Yang, *Inorg. Chem. Commun.*, 2014, **46**, 69-72.
35. Q. Meng, G. Wang, J. Xue, B. Yang, H. He and G. Yang, *J. Clust. Sci.*, 2014, **25**, 1319-1329.
36. L. Wang, S. L. Pan, L. X. Chang, J. Y. Hu and H. W. Yu, *Inorg. Chem.*, 2012, **51**, 1852-1858.
37. C. Wu, X. X. Jiang, L. Lin, W. Y. Dan, Z. S. Lin, Z. P. Huang, M. G. Humphrey and C. Zhang, *Angew. Chem. Int. Ed.*, 2021, **60**, 27151-27157.
38. D. Neiner, Y. V. Sevryugina, L. S. Harrower and D. M. Schubert, *Inorg. Chem.*, 2017, **56**, 7175-7181.
39. Z. H. Miao, Y. Yang, Z. L. Wei, Z. H. Yang and S. L. Pan, *Dalton Trans.*, 2020, **49**, 1292-1299.