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Supporting Information for

$AB_{11}O_{16}(OH)_2$ (A = K and Cs): Interpenetrating 2D Layer with Large Birefringence

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Experimental Section

Synthesis.

KCl (Shanghai Aladdin Reagent Co., Ltd., 99.5%), CsCl (Tianjin Baishi Chemical Reagent Co., Ltd, 99.5%), B_2O_3 (Shanghai Aladdin Reagent Co., Ltd., 99.0%) and H_3BO_3 (Shanghai Aladdin Reagent Co., Ltd., 99.5%) were of analytical grade and obtained from commercial sources without further purification.

Crystals of $KB_{11}O_{16}(OH)_2$ (KBOH) and $CsB_{11}O_{16}(OH)_2$ (CBOH) were grown in closed system by high-temperature solution method. A mixture of B_2O_3 (0.278 g, 4 mmol), HBO_3 (0.062 g, 1 mmol) and KCl (0.075 g, 1 mmol) was placed in a fused-silica tube (Φ10 mm x 100 mm) which was washed by using deionized water. Then it was flame-sealed under a high vacuum of 10^{-3} Pa. Subsequently, the tube was moved into a muffle furnace and heated to 400 °C at a rate of 20 °C/h, held at this temperature for 36 h, and then cooled to 300 °C with a rate of 1.0 °C/h, finally cooled to room temperature with a rate of 10 °C/h. $CsB_{11}O_{16}(OH)_2$ (CBOH) was obtained through the similar process and the maximum temperature was 370 °C. The mixture was weighed as follows: CsCl (0.168 g, 1 mmol), HBO_3 (0.092 g, 1.5 mmol) and B_2O_3 (0.278 g, 4 mmol).

The polycrystalline sample of KBOH was obtained from a reaction of KCl (0.746 g, 10 mmol), B_2O_3 (0.618 g, 10 mmol) and H_3BO_3 (3.481 g, 50 mmol). The above materials were fully ground in an agate mortar, then transfered to a tidy quartz tube which was flame-sealed under 10^{-3} Pa. The mixture was heated to 220 °C with a rate of 10 °C/h, held at this temperature for 72 h, then slowly dropped to room temperature. The synthesis of the polycrystalline was followed by this chemical reaction:

$$KCl + H_3BO_3 + 5B_2O_3 \rightarrow KB_{11}O_{16}(OH)_2 + HCl \quad (1)$$

Meanwhile, we also tried to synthesize the polycrystalline sample of CBOH using the same method in the different temperatures; however, these attempts were failed.

Powder X-ray Diffraction.

The pure phase was examined by the powder X-ray diffraction (XRD) carried on a Bruker D2 PHASER diffractometer with Cu Kα radiation (λ = 1.54056 Å) operating at room temperature. The pattern was taken in the 2θ range from 5° to 70° with a scan step width of 0.02° and a fixed counting time of 1s per step.

Single Crystal X-ray Diffraction.

The APEX II CCD X-ray diffractometer with monochromatic Mo Kα radiation (λ = 0.71073 Å) was utilized to record the X-ray diffraction data for colorless $KB_{11}O_{16}(OH)_2$ and $CsB_{11}O_{16}(OH)_2$ single crystal at 296(2) K. The direct methods and SHELXTL system were used to solve and refine the crystal structure, respectively.[1] Use full matrix least-squares techniques to determine all atom positions, and the final least-squares refinement is on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. The structure was checked for missed symmetry elements using PLATON.[2] The information of crystal data and structural refinements is summarized in Tables S1. Similarly, Tables S2 and S3 listed the atomic coordinates, site occupancy factors (SOF), equivalent isotropic displacement parameters, and selected bond lengths and angles, respectively.

Infrared Measurement.

The coordination of B atoms was determined by measuring infrared (IR) spectroscopy measured on a Shimadzu IRAffinity-1 Fourier transform IR spectrometer. The sample was mixed thoroughly with dried KBr (~ 6 mg of the sample and 600 mg of KBr), and the IR spectrum was collected in the range from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}.

UV-Vis-NIR Diffuse Reflectance Measurement.

A Shimadzu SolidSpec-3700DUV spectrophotometer was used to collect the UV-Vis-NIR diffuse reflectance data of the reported samples, and the measurement range extended from 190 to 2600 nm at room temperature.[3]

Thermal Analysis.

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of KBOH were performed on a simultaneous NETZSCH STA 449C instrument at a temperature range of 40-800 °C with a rate of 5 °C·min^{-1} in an atmosphere of flowing N_2. When the sample is heated to 110 °C, the TG curve shows the weight loss (hydroxyl begins to decompose), and the absorption peak on the DSC curve at 335 °C corresponds to the melting of the decomposed sample of KBOH (Figure S7).

Birefringence.

The birefringence was measured by polarizing microscope (ZEISS Axio Scope. A1) with Berek compensator, the wavelength of the light source was 546 nm. In order to improve the precision of birefringence, thin and transparent lamellar crystals were screened under a microscope for measurement before scanning.

The formula for calculating the birefringence can be given by the following equation:

$$R = V_0\,(t_g\text{-}t_p) = d\,(V_0/V_g\text{-}V_0/V_p) = d\,(N_g\text{-}N_p) = d^*\Delta n \quad (2)$$

Here, R represents the optical path difference, V_0 represents in the speed of light in air, V_g and V_p represent the propagation speed of light through the crystal, t_g and t_p mean the time required to pass through the wafer in slow and fast light, Δn means the birefringence, N_g and N_p denote the refractive index of light in a crystal, and d denotes the thickness of the crystal.

Theoretical Calculation.

The density functional theory method was utilized for calculating the band structure, the total/partial density of states (T/PDOS) for KBOH and CBOH, which were performed by the plane wave pseudopotential implemented in the CASTEP code.[4] The cutoff energy of plane waves was set to 830 eV. The region integration of Brillouin was carried out using the Monkhorst-Pack18 scheme, with the grid of k-point being 2×2×1 and the spacing of k-point being 0.07 Å^{-1}.[5] The Perdew-Burke-Ernzerhof (PBE) method in generalized gradient approximation (GGA) was chosen to describe the exchange-correlation potential,[6] and the norm conserving pseudopotential (NCP) was used for the following valence electrons, K: $4s^1$, Cs: $6s^1$, B: $2s^22p^1$, O: $2s^22p^4$, H: $1s^1$. Other calculation parameters were set as the default values in the CASTEP.

Table S1. Crystal data and structure refinement for $KB_{11}O_{16}(OH)_2$ and $CsB_{11}O_{16}(OH)_2$.

Empirical formula	$KB_{11}O_{16}(OH)_2$	$CsB_{11}O_{16}(OH)_2$
Temperature	296(2) K	
Crystal system, space group	Monoclinic, *C*2/*c*	
Unit cell dimensions (Å)	*a* =14.163(17)	*a* =14.183(7)
	b =10.101(12) β =106.827(15)	*b* =10.192(5) β =106.022(6)
	c =10.664(12)	*c* =11.348(5)
Volume (Å)	1460(3)	1576.7(13)
Z, Calculated density (g/cm^3)	4, 2.038	4, 2.300
Absorption coefficient(mm^{-1})	0.468	2.446
F(000)	880	1040
Theta range for data collection(°)	2.510 - 25.000	2.495 - 24.997
Limiting indices	$-16 \le h \le 16$, $-11 \le k \le 12$, $-12 \le l \le 11$	$-16 \le h \le 15$, $-10 \le k \le 12$, $-13 \le l \le 13$
Reflections collected / unique	3675 / 1284 [R_{int} =0.0542]	3800 / 1391 [R_{int} =0.1037]
Completeness to theta	99.70%	99.90%
Data / restraints / parameters	1284 / 1 / 141	1391 / 1 / 142
Goodness-of-fit on F_o^2	1.045	0.932
Final *R* indices [$F_o^2 > 2(F_c^2)$][a]	R_1 =0.0443, wR_2 =0.0913	R_1 =0.0488, wR_2 =0.0762
R indices (all data)[a]	R_1 =0.0652, wR_2 =0.1014	R_1 =0.0663, wR_2 =0.0811
Largest diff. peak and hole (e·Å^{-3})	0.277 and - 0.387	1.449 and - 1.445

[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 S2a. Atomic coordinates (x 10^4), equivalent isotropic displacement parameters ($Å^2$ x 10^3) and bond valence sum (BVS) calculations for $KB_{11}O_{16}(OH)_2$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	*U*(eq)	BVS
K(1)	5000	2002(1)	2500	34(1)	1.10
B(1)	2241(3)	1252(3)	1758(4)	17(1)	3.05
B(2)	4718(3)	2537(4)	5380(4)	19(1)	3.06
B(3)	3557(3)	4302(4)	4259(4)	21(1)	3.07
B(4)	4049(3)	863(3)	-1004(4)	17(1)	3.08
B(5)	5000	-1453(5)	2500	15(1)	3.09
B(6)	2785(3)	189(4)	98(4)	20(1)	3.05
O(1)	2861(2)	1211(2)	981(2)	21(1)	2.05
O(2)	4321(2)	3445(2)	4410(2)	24(1)	2.15
O(3)	4425(1)	2313(2)	6435(2)	19(1)	1.89
O(4)	1531(2)	292(2)	1645(2)	25(1)	1.99
O(5)	4497(2)	1856(2)	-140(2)	22(1)	2.12
O(6)	3356(2)	76(2)	-707(2)	23(1)	2.08
O(7)	5677(1)	-599(2)	2070(2)	18(1)	2.04
O(8)	2311(2)	2291(2)	2574(2)	25(1)	1.52
O(9)	2923(2)	4233(2)	5001(2)	25(1)	2.02
H(1)	1908(3)	2239(3)	3039(4)	62(15)	0.74

Table S2b. Atomic coordinates (x 10^4), equivalent isotropic displacement parameters (Å^2 x 10^3) and bond valence sum (BVS) calculations for $CsB_{11}O_{16}(OH)_2$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	*U*(eq)	BVS
Cs(1)	5000	2279(1)	2500	31(1)	1.191
B(1)	2258(6)	1181(8)	1619(7)	24(2)	3.002
B(2)	4734(5)	2594(8)	5518(6)	23(2)	3.069
B(3)	3575(6)	4339(8)	4446(7)	26(2)	3.053
B(4)	4052(5)	934(8)	-1062(7)	23(2)	3.092
B(5)	5000	-1487(11)	2500	22(3)	2.988
B(6)	2787(5)	241(9)	0(7)	29(2)	3.017
O(1)	2887(3)	1184(4)	874(4)	25(1)	2.087
O(2)	4341(3)	3502(5)	4617(4)	29(1)	2.205
O(3)	4424(3)	2359(4)	6493(3)	24(1)	1.855
O(4)	1543(3)	252(5)	1476(4)	29(1)	2.003
O(5)	4484(3)	1911(4)	-286(3)	28(1)	2.144
O(6)	3363(3)	124(5)	-777(4)	32(1)	1.987
O(7)	5672(3)	-651(4)	2069(4)	24(1)	1.996
O(8)	2371(3)	2152(5)	2470(4)	32(1)	1.514
O(9)	2936(3)	4296(5)	5151(4)	36(1)	1.984
H(1)	2130(6)	2030(10)	3080(5)	120(4)	0.733

Table S3a. Selected bond lengths (Å) and angles (°) for $KB_{11}O_{16}(OH)_2$.

K(1)-O(1)	3.098(4)	B(3)#3-O(4)	1.370(4)
K(1)-O(1)#1	3.098(4)	B(3)-O(4)#5	1.370(4)
K(1)-O(2)#1	2.887(3)	B(3)-O(9)	1.360(4)
K(1)-O(2)	2.887(3)	B(4)#4-O(7)	1.330(4)
K(1)-O(5)	2.701(4)	B(4)-O(5)	1.385(4)
K(1)-O(5)#1	2.701(4)	B(4)-O(7)#4	1.330(4)
K(1)-O(7)#1	2.878(4)	B(4)-O(6)	1.369(4)
K(1)-O(7)	2.878(4)	B(5)#2-O(3)	1.474(4)
B(1)-O(1)	1.371(4)	B(5)-O(3)#6	1.474(4)
B(1)-O(4)	1.377(4)	B(5)-O(3)#2	1.474(4)
B(1)-O(8)	1.349(4)	B(5)-O(7)#1	1.459(4)
B(2)-O(2)	1.375(4)	B(5)-O(7)	1.459(4)
B(2)-O(3)	1.327(4)	B(6)-O(1)	1.380(4)
B(2)#1-O(5)	1.392(4)	B(6)-O(6)	1.345(4)
B(2)-O(5)#1	1.392(4)	B(6)#5-O(9)	1.373(4)
B(3)-O(2)	1.358(4)	B(6)-O(9)#3	1.373(4)
O(1)-H(1)	0.858(4)	O(7)-K(1)-O(1)#1	61.81(6)
O(5)-K(1)-O(5)#1	173.75(10)	O(2)#1-K(1)-O(1)#1	91.38(9)
O(5)-K(1)-O(7)#1	96.72(7)	O(2)-K(1)-O(1)#1	103.67(9)
O(5)#1-K(1)-O(7)#1	77.50(7)	O(1)-K(1)-O(1)#1	150.12(9)
O(5)-K(1)-O(7)	77.50(6)	O(8)-B(1)-O(1)	118.2(3)
O(5)#1-K(1)-O(7)	96.72(7)	O(8)-B(1)-O(4)	121.3(3)
O(7)#1-K(1)-O(7)	48.27(10)	O(1)-B(1)-O(4)	120.4(3)
O(5)-K(1)-O(2)#1	48.18(8)	O(3)-B(2)-O(2)	126.2(3)
O(5)#1-K(1)-O(2)#1	136.20(8)	O(3)-B(2)-O(5)#1	122.3(3)
O(7)#1-K(1)-O(2)#1	140.16(7)	O(2)-B(2)-O(5)#1	111.5(3)
O(7)-K(1)-O(2)#1	98.86(9)	O(2)-B(3)-O(9)	122.4(3)
O(5)-K(1)-O(2)	136.20(8)	O(2)-B(3)-O(4)#5	117.1(3)
O(5)#1-K(1)-O(2)	48.18(8)	O(9)-B(3)-O(4)#5	120.4(3)
O(7)#1-K(1)-O(2)	98.86(9)	O(7)#4-B(4)-O(6)	119.2(3)
O(7)-K(1)-O(2)	140.16(7)	O(7)#4-B(4)-O(5)	121.5(3)
O(2)#1-K(1)-O(2)	119.33(12)	O(6)-B(4)-O(5)	119.1(3)
O(5)-K(1)-O(1)	61.19(6)	O(7)-B(5)-O(7)#1	107.5(4)

O(5)#1-K(1)-O(1)	116.99(7)	O(7)-B(5)-O(3)#6	111.90(13)
O(7)#1-K(1)-O(1)	61.81(6)	O(7)#1-B(5)-O(3)#6	108.91(13)
O(7)-K(1)-O(1)	90.10(8)	O(7)-B(5)-O(3)#2	108.91(13)
O(2)#1-K(1)-O(1)	103.67(9)	O(7)#1-B(5)-O(3)#2	111.90(13)
O(2)-K(1)-O(1)	91.38(9)	O(3)#6-B(5)-O(3)#2	107.7(4)
O(5)-K(1)-O(1)#1	116.99(6)	O(6)-B(6)-O(9)#3	116.9(3)
O(5)#1-K(1)-O(1)#1	61.18(6)	O(6)-B(6)-O(1)	123.8(3)
O(7)#1-K(1)-O(1)#1	90.10(8)	O(9)#3-B(6)-O(1)	119.4(3)

Symmetry transformations used to generate equivalent atoms:

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

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

Table S3b. Selected bond lengths (Å) and angles (°) for $CsB_{11}O_{16}(OH)_2$.

Cs(1)-O(1)	3.253(4)	B(2)-O(3)	1.320(8)
Cs(1)-O(1)#1	3.253(4)	B(2)#1-O(5)	1.395(8)
Cs(1)-O(2)	3.072(4)	B(3)-O(2)	1.353(8)
Cs(1)-O(2)#1	3.072(4)	B(3)#3-O(4)	1.376(8)
Cs(1)-O(5)	3.065(4)	B(3)-O(9)	1.366(9)
Cs(1)-O(5)#1	3.065(4)	B(4)-O(5)	1.359(8)
Cs(1)-O(7)	3.213(5)	B(4)-O(6)	1.384(8)
Cs(1)-O(7)#1	3.213(5)	B(4)#4-O(7)	1.337(8)
Cs(1)-O(8)	3.722(5)	B(5)#2-O(3)	1.499(7)
Cs(1)-O(8)#1	3.722(5)	B(5)-O(7)	1.460(7)
B(1)-O(1)	1.388(8)	B(6)-O(1)	1.360(9)
B(1)-O(4)	1.364(9)	B(6)-O(6)	1.363(8)
B(1)-O(8)	1.361(9)	B(6)#5-O(9)	1.382(9)
B(2)-O(2)	1.378(8)	O(1)-H(1)	0.861(4)
O(5)-Cs(1)-O(5)#1	165.95(17)	O(7)#1-Cs(1)-O(8)	68.31(11)
O(5)-Cs(1)-O(2)	144.96(11)	O(1)-Cs(1)-O(8)	38.65(10)
O(5)#1-Cs(1)-O(2)	43.99(11)	O(1)#1-Cs(1)-O(8)	139.20(11)
O(5)-Cs(1)-O(2)#1	43.99(11)	O(5)-Cs(1)-O(8)#1	87.62(10)
O(5)#1-Cs(1)-O(2)#1	144.96(11)	O(5)#1-Cs(1)-O(8)#1	91.89(10)
O(2)-Cs(1)-O(2)#1	132.13(17)	O(2)-Cs(1)-O(8)#1	121.82(11)
O(5)-Cs(1)-O(7)	74.08(11)	O(2)#1-Cs(1)-O(8)#1	60.07(10)
O(5)#1-Cs(1)-O(7)	92.69(11)	O(7)-Cs(1)-O(8)#1	68.31(11)
O(2)-Cs(1)-O(7)	131.54(11)	O(7)#1-Cs(1)-O(8)#1	107.74(11)
O(2)#1-Cs(1)-O(7)	95.22(11)	O(1)-Cs(1)-O(8)#1	139.20(11)
O(5)-Cs(1)-O(7)#1	92.69(11)	O(1)#1-Cs(1)-O(8)#1	38.65(10)
O(5)#1-Cs(1)-O(7)#1	74.08(11)	O(8)-Cs(1)-O(8)#1	176.00(17)
O(2)-Cs(1)-O(7)#1	95.22(11)	O(8)-B(1)-O(4)	121.8(6)
O(2)#1-Cs(1)-O(7)#1	131.54(11)	O(8)-B(1)-O(1)	117.5(6)
O(7)-Cs(1)-O(7)#1	43.29(14)	O(4)-B(1)-O(1)	120.7(6)
O(5)-Cs(1)-O(1)	56.80(10)	O(3)-B(2)-O(2)	125.8(6)
O(5)#1-Cs(1)-O(1)	117.62(11)	O(3)-B(2)-O(5)#1	122.2(6)
O(2)-Cs(1)-O(1)	98.71(11)	O(2)-B(2)-O(5)#1	112.0(5)
O(2)#1-Cs(1)-O(1)	97.29(11)	O(2)-B(3)-O(9)	122.2(6)
O(7)-Cs(1)-O(1)	81.97(11)	O(2)-B(3)-O(4)#5	117.4(6)
O(7)#1-Cs(1)-O(1)	60.13(11)	O(9)-B(3)-O(4)#5	120.4(6)

O(5)-Cs(1)-O(1)#1	117.62(11)	O(7)#4-B(4)-O(5)	121.7(6)
O(5)#1-Cs(1)-O(1)#1	56.80(10)	O(7)#4-B(4)-O(6)	117.6(6)
O(2)-Cs(1)-O(1)#1	97.29(11)	O(5)-B(4)-O(6)	120.4(6)
O(2)#1-Cs(1)-O(1)#1	98.71(11)	O(7)#1-B(5)-O(7)	108.5(8)
O(7)-Cs(1)-O(1)#1	60.13(11)	O(7)#1-B(5)-O(3)#6	109.4(2)
O(7)#1-Cs(1)-O(1)#1	81.97(11)	O(7)-B(5)-O(3)#6	111.1(2)
O(1)-Cs(1)-O(1)#1	139.87(16)	O(7)#1-B(5)-O(3)#2	111.1(2)
O(5)-Cs(1)-O(8)	91.89(10)	O(7)-B(5)-O(3)#2	109.4(2)
O(5)#1-Cs(1)-O(8)	87.62(10)	O(3)#6-B(5)-O(3)#2	107.3(7)
O(2)-Cs(1)-O(8)	60.07(10)	O(1)-B(6)-O(6)	124.9(7)
O(2)#1-Cs(1)-O(8)	121.82(11)	O(1)-B(6)-O(9)#3	120.5(6)
O(7)-Cs(1)-O(8)	107.74(11)	O(6)-B(6)-O(9)#3	114.6(7)

Symmetry transformations used to generate equivalent atoms:

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

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

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

Table 4. The hydroxyl potassium borates.

No.	Compounds	Space group	B-O anionic framework	Cutoff edge	Reference
1	$KB_{11}O_{16}(OH)_2$*	*C*2/*c*	$^{2}{}_{\infty}[B_{11}O_{18}(OH)_2]$ layer	195 nm	/
2	$K_2(B_5O_8(OH))(H_2O)_2$	*Pna*2$_1$	$^{2}{}_{\infty}[B_5O_{10}(OH)]$ layer	/	7
3	$K_2(B_{10}O_{14}(OH)_4)$ (H_2O)	$P\bar{1}$	$^{1}{}_{\infty}[B_5O_8(OH)_2]$ chain	/	8
4	$KB_5O_7(OH)_2(H_2O)$	*P*2$_1$/*c*	$^{1}{}_{\infty}[B_5O_7(OH)_2]$ chain	/	9
5	$K_2(B_6O_9(OH)_2)$	*P*2$_1$/*c*	$^{1}{}_{\infty}[B_6O_9(OH)_2]$ chain	/	10
6	$KB_5O_7(OH)_2$	*P*2$_1$/*c*	$^{1}{}_{\infty}[B_5O_7(OH)_2]$ chain	/	11
7	$K_4B_{10}O_{15}(OH)_4$	*C*2/*c*	$^{1}{}_{\infty}[B_5O_{10}(OH)_2]$ chain	/	9
8	$K_3B_5O_8(OH)_2$	*Fdd*2	Isolated $[B_5O_8(OH)_2]$	200 nm	12
9	$K(B_5O_6(OH)_4)(H_2O)_2$	*Aba*2	Isolated $[B_5O_6(OH)_4]$	/	13
10	$KB_3O_4(OH)_2$	*P*4/*ncc*	isolated $[B_{12}O_{16}(OH)_8]$	/	14
11	$K_2(B_4O_5(OH)_4)(H_2O)_2$	*P*2$_1$2$_1$2$_1$	Isolated $[B_4O_5(OH)_4]$	/	15
12	$K_2(B_3O_3(OH)_5)$	*Ama*2	Isolated $[B_3O_3(OH)_5]$	200 nm	16
13	$K_3B_3O_4(OH)_4(H_2O)_2$	*Cmc*2$_1$	Isolated $[B_3O_4(OH)_4]$	190 nm	17
14	$K(B_5O_8)(H_2O)_4$	*Aba*2	Isolated $[B_5O_8(OH)_2]$	/	18
15	$K_2(B_{12}(OH)_{12})$	*P*2$_1$/*c*	Isolated [BOH]	/	19
16	$KB_3O_5(H_2O)_3$	*C*2/*c*	Isolated $[B_3O_3(OH)_4]$	/	20
17	$K_2B_4O_5(OH)_4$	*Pbcn*	isolated $[B_4O_5(OH)_4]$	/	21

* represents the work

Note: the above compounds are all derived from the Inorganic Crystal Structure Database (ICSD), and all hydroxyl potassium borates except for disordered repetition and other irrational structure are summarized.

Table S5. The hydroxyl cesium borates.

No.	Compounds	Space group	B-O anionic framework	Cutoff edge	Reference
1	$CsB_{11}O_{16}(OH)_2$*	$C2/c$	$^{2}_{\infty}[B_{11}O_{18}(OH)_2]$ layer	/	/
2	$Cs_{0.4}(H_3O)_{0.6}B_3O_5$	$C2/c$	$^{2}_{\infty}[B_3O_7(H_3O)]$ layer	/	[22]
3	$CsB_7O_{10}(OH)_2$	$C2/c$	$^{2}_{\infty}[B_7O_{10}(OH)_2]$ layer	188 nm	[23]
4	$Cs_2(B_4O_5(OH)_4)(H_2O)_3$	$P2_1/c$	Isolated $[B_4O_5(OH)_4]$	/	[24]
5	$Cs_2(B_{12}(OH)_{12})$ $(H_2O)_2$	$P2_1/c$	Isolated $[B_{12}(OH)_{12}]$	/	[25]
6	$Cs(B_5O_6(OH)_4)(H_2O)_2$	$C2/c$	Isolated $[B_5O_6(OH)_4]$	/	[26]
7	$Cs(B_5O_6(OH)_4)(H_2O)_2$	$P2_1/c$	Isolated $[B_5O_6(OH)_4]$	/	[27]

* represents the work

Note: the above compounds are all derived from ICSD, and all hydroxyl cesium borates except for disordered repetition and other irrational structure are summarized.

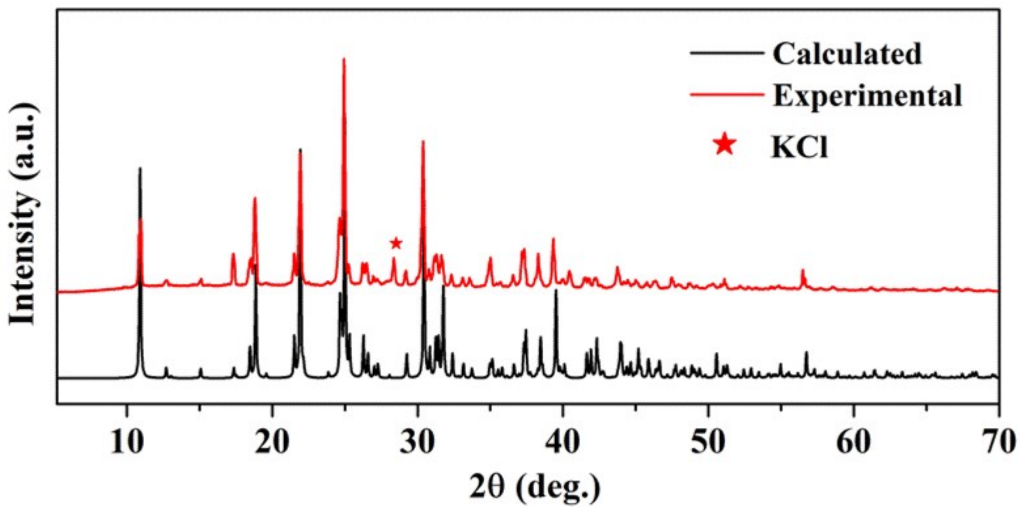

Figure S1. Experimental and calculated XRD patterns of $KB_{11}O_{16}(OH)_2$.

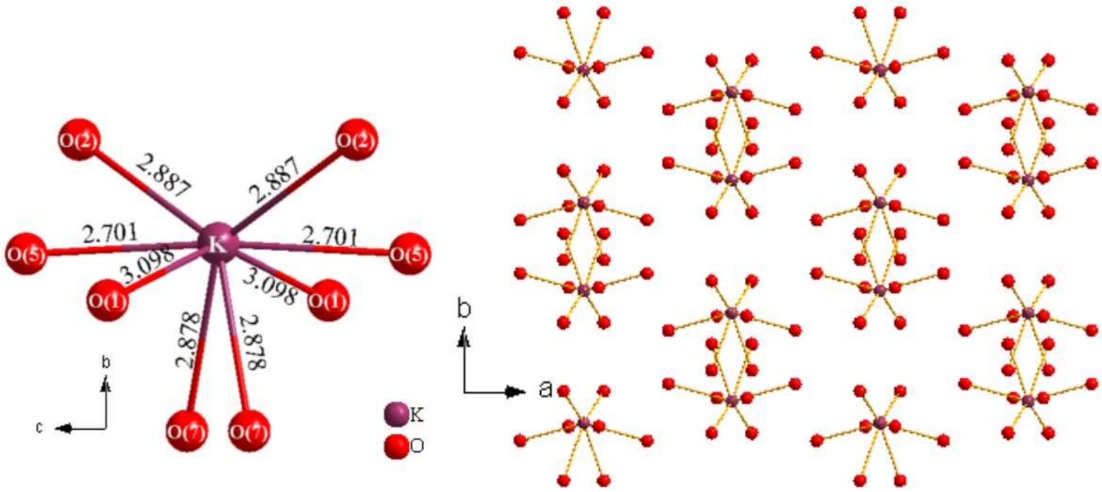

Figure S2. The coordination environments of the K cations.

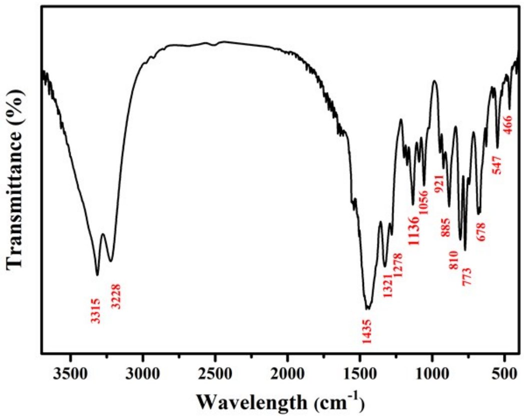

Figure S3. The IR spectrum of $KB_{11}O_{16}(OH)_2$.

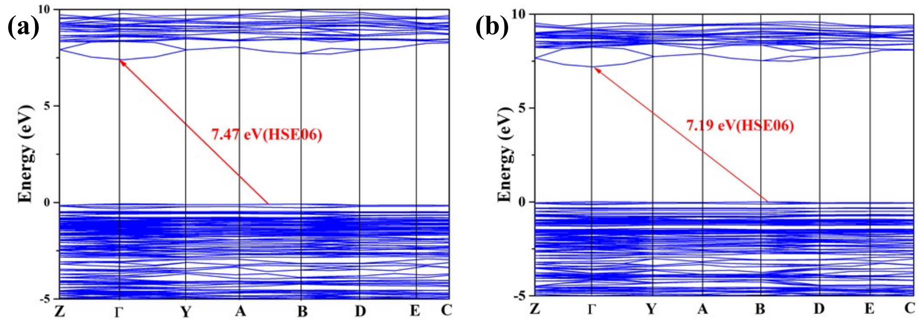

Figure S4. Calculated electronic band structures based on HSE06 for (a) KBOH, and (b) CBOH.

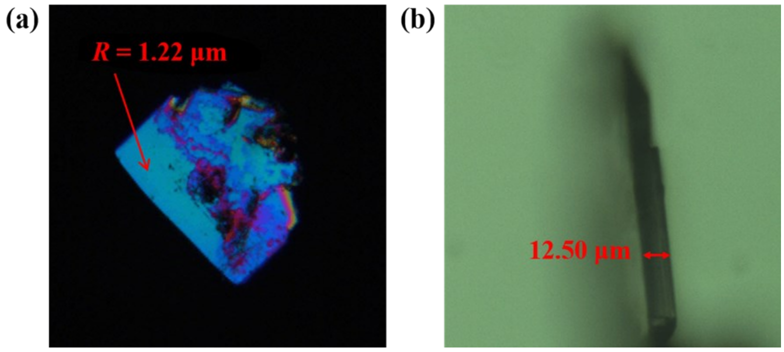

Figure S5. A $KB_{11}O_{16}(OH)_2$ single crystal under the polarizing microscope (a); The thickness of $KB_{11}O_{16}(OH)_2$ crystal (b).

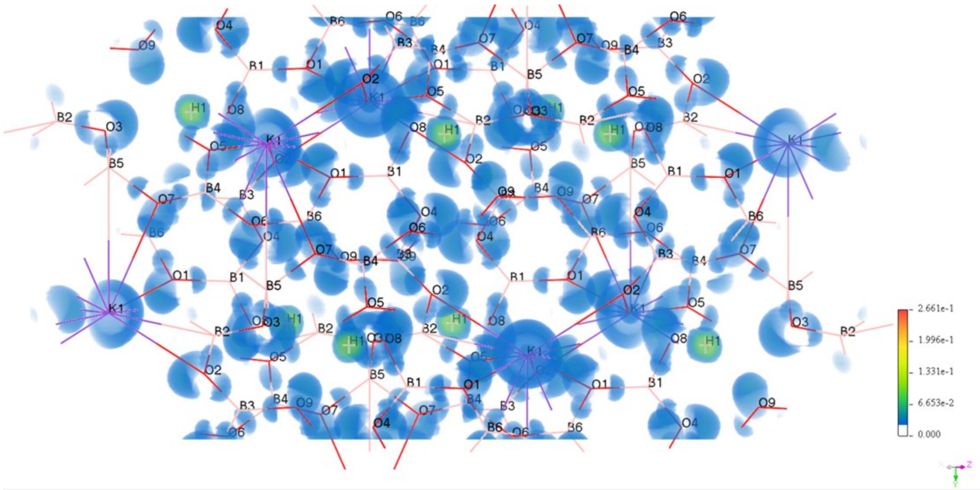

Figure S6. The Electron localization function (ELF) of $KB_{11}O_{16}(OH)_2$.

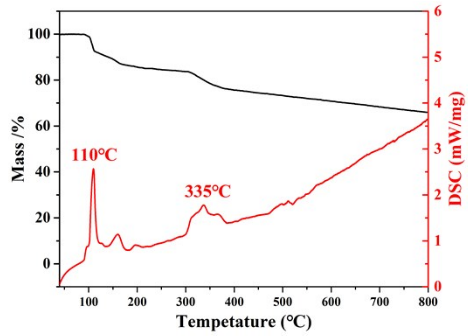

Figure S7. The TG/DSC curves for KBOH.

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