Supporting information

$RbB_7O_{10}(OH)_2$ and $NaB_{11}O_{16(}OH)_2$: Alkali Metal Hydroxyborates with Two-dimensional Layered Structure and Large Birefringence

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CONTENTS

1. Experimental section

Synthesis

The reagents used, $RbNO_3$, $NaNO_3$, RbF, NH_4Cl, and B_2O_3, were purchased from Aladdin with a purity of more than 99 % and were used directly without further purification. $RbB_7O_{10}(OH)_2$ single crystals were synthesized by using the high temperature solution method in a closed system. The ingredients $RbNO_3$, NH_4Cl, and B_2O_3 were mixed in a molar ratio of 1:1:3, and then transferred to a platinum crucible, and the platinum crucible was sealed in an alloy liner, and put into a programmable high-temperature furnace, which was heated up to 300 °C in 10 h, kept at this temperature for 7 days, and then cooled down to room temperature at a rate of 1 °C·h^{-1}. Finally, the single crystals of $RbB_7O_{10}(OH)_2$ were obtained. Polycrystalline samples of $RbB_7O_{10}(OH)_2$ can be obtained by high temperature solid phase reaction. A mixture of RbF B_2O_3 and HBO_2 with a molar ratio of 1:2:3 was mixed homogeneously in an agate mortar, and then it was transferred to a quartz glass tube (Φ10 mm × 150 mm), and the tube was flame-sealed under ~ 10^{-3} Pa to create a vacuum environment. Subsequently, the tube was placed in a programmable temperature furnace, where the temperature was raised to 300 ℃ in 5 h, and held at this temperature for 12 h, after the power was turned off, the powder polycrystalline of $RbB_7O_{10}(OH)_2$ can be obtained. The yield is 73.3%.

The single crystals of $NaB_{11}O_{16}(OH)_2$ were synthesized by the high temperature solution method. A mixture of $NaNO_3$, NH_4Cl, and B_2O_3 was weighed in a molar ratio of 1:1:3.5, put into a quartz glass tube, pumped into a vacuum environment, and then put into a programmable temperature furnace to be heated to 300 ℃, held for 7 days, and then cooled down to room temperature at a rate of 1 ℃·h^{-1} to obtain the $NaB_{11}O_{16}(OH)_2$ single crystal. In the synthesis of polycrystalline powder samples, we have attempted various raw material ratios and experimental methods. The sodium sources selected include NaF, NaCl, $NaNO_3$, $NaBO_2$, $Na_2B_4O_7$, $Na_2B_4O_7·10H_2O$, etc., and the boron sources include B_2O_3, HBO_2, H_3BO_3. We accurately weighed the raw materials according to the stoichiometric ratios, and successively tried methods such as the high-temperature solid-phase method and the hydrothermal method, and carried out the firing process under different temperature conditions. After comparing and analyzing the obtained products through XRD patterns, it was found that the products obtained included B_2O_3, $Na_2B_4O_7·10H_2O$, etc., but there were more unknown impurity phases in terms of composition.

2. Characterizations and Measurements

Structure Determination

Single-crystal XRD data of the two compounds were collected on Bruker D8 Venture diffractometer assembled with monochromatic Mo-Kα (λ = 0.71073 Å) as the radiation source. By using the Bruker SAINT program, data integration was performed.[1] The crystal structure of the two compounds were settled down by the direct method and refined through SHELXTL system with the Olex2 software.[2, 3] The atomic coordinates for all atoms were determined through full matrix least-squares optimization. PLATON[4] were utilized to verify the space group, and no higher symmetry was observed. For detailed crystallographic data, refer to Table S1, while additional relevant data can be found in Tables S3−S5.

Powder X-ray Diffraction (PXRD)

PXRD data of the $RbB_7O_{10}(OH)_2$ was measured using a Bruker D2 PHASER diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). The scanning step width was 0.02 ° in the 2θ range from 5 to 70 °, and the fixed time of each step was 1 second.

Infrared Spectroscopy

The infrared (IR) spectrum was recorded by Shimadzu IR Affinity^{-1} Fourier transform infrared spectrometer in the range of 500-3500 cm^{-1} at room temperature.

UV-Vis-NIR Diffuse Reflectance Spectrum

UV-Vis-NIR diffuse reflectance data were collected with a Shimadzu SolidSpec 3700 DUV spectrophotometer at room temperature in the wavelength range of 200 to 1600 nm.

Thermal Analysis

A NETZSCH STA 449 F3 simultaneous analyzer instrument was applied to measure the thermal gravimetric analysis (TGA)-differential scanning calorimetry (DSC) curves. The powder samples of $RbB_7O_{10}(OH)_2$ were placed in Pt crucibles to heat, respectively, with the temperature ranging from 40 to 500 °C at a heating rate of 5 °C·min^{-1} under a N_2 atmosphere.

3. Computation Details

Theoretical Calculations

The electronic band structures, total/partial density of states (DOS/PDOS) and birefringence values of two compounds were calculated using density functional theory (DFT) calculations performed with the CASTEP program.[5, 6] The exchange-correlation potential was calculated using the generalized gradient approximation (GGA) with

Perdew - Bruker - Ernzerhof (PBE) functional. Using the norm - conserving pseudopotential (NCP), the following orbital electrons were treated as valence electrons: Na: $2s^2\ 2p^6\ 3s^1$, Rb: $4s^2\ 4p^6\ 5s^1$, B: $2s2\ 2p^1$, O:$2s^2\ 2p^4$, and H: $1s^1$. The cutoff energy was set as 750 eV, and the numerical integration of the Brillouin zone was performed via utilizing Monkhorst - Pack kpoint meshes 0.04 for $RbB_7O_{10}(OH)_2$, 2 × 5 × 3 for $NaB_{11}O_{16}(OH)_2$. The linear optical properties of the title compounds were evaluated based on the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The response electron distribution anisotropy (REDA)[7] method was conducted to further investigate the cause of birefringence. Under REDA approximation, the birefringence can be estimated by the anisotropic valence bond of anionic groups as:

$$\Delta n = \frac{R\sum_{g}\left[N_c Z_a \Delta\rho^b\right]g}{2n_1 E_0}$$

Here, $\mathcal{R}$ is the correction coefficient, N_c is the coordination number of the nearest neighbor cations to the central anion, Z_a is the formal chemical valence of the anion, $\Delta\rho^b$ is the difference between the maximum and minimum bonding electron density of covalent bond in an anionic group on the optical principal axes of a crystal, E_o is the optical band gap, n_1 is the minimum refractive index and usually has little change in a system. The REDA index was expressed as:

$$\zeta = \sum_g [N_c Z_a \Delta\rho^b]_g / (n_1 E_o)$$

4. Tables and Figures

Table S1. Crystallographic data for $RbB_7O_{10}(OH)_2$ and $NaB_{11}O_{16}(OH)_2$.

Empirical formula	$RbB_7O_{10}(OH)_2$	$Na\ B_{11}O_{16}(OH)_2$
Formula weight	355.16	431.92
Temperature (K)	298.0	298.0
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
a (Å)	9.0996(16)	14.1609(17)
b (Å)	9.4753(18)	10.1654(13)
c (Å)	11.653(2)	10.2568(13)
α (°)	90	90
β (°)	98.936(7)	107.199(5)
γ (°)	90	90
Volume (Å^3)	992.5(3)	1410.5(3)
Z	4	4
ρ_{calcd} (g·cm^{-3})	2.377	2.034
μ (mm^{-1})	5.053	0.220
F (000)	680.0	848.0
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Theta range for data collection (°)	6.248 to 54.99	5.012 to 55.056
Index ranges	$-11 \le h \le 11, -12 \le k \le 11, -15 \le l \le 15$	$-18 \le h \le 18, -13 \le k \le 13, 13 \le l \le 13$
Reflections collected	5287	9349
Data / restraints / parameters	1150 / 1 / 96	1581 / 0 / 139
Goodness-of-fit on F^2	1.066	1.091
Final R indexes [$F_o^2 > 2\sigma(F_o^2)$][a]	R_1 = 0.0497, wR_2 = 0.0962	R_1 = 0.0486, wR_2 = 0.1184
Final R indexes [all data][a]	R_1 = 0.0810, wR_2 = 0.1072	R_1 = 0.0626, wR_2 = 0.1286
Largest diff. peak / hole (e·Å^{-3})	0.55 / – 0.55	0.37 / – 0.39

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

Table S2. Atomic coordinates ($\times 10^4$) and equivalent Isotropic displacement parameters ($Å^2 \times 10^3$) for $RbB_7O_{10}(OH)_2$ and $NaB_{11}O_{16}(OH)_2$. U_{eq} is defined as 1/3 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[a]
$RbB_7O_{10}(OH)_2$					
Rb1	0	1815.0(8)	2500	34.1(3)	0.99
B1	4207(6)	6554(5)	5464(5)	20.3(11)	3.09
B2	2239(6)	4865(6)	4595(5)	21.0(11)	3.07
B3	1096(6)	3288(6)	5920(5)	22.4(11)	3.06
B4	5000	7154(8)	7500	24.9(18)	3.09
O1	1102(4)	3072(4)	7055(3)	24.5(7)	1.91
O2	3315(4)	5879(4)	4562(3)	26.8(8)	1.89
O3	4223(4)	6260(3)	6584(3)	23.1(8)	2.09
O4	5105(4)	7578(4)	5097(3)	28.9(8)	2.15
O5	2120(4)	4189(4)	5596(3)	28.3(9)	2.21
O6	1323(4)	4559(4)	3594(3)	36.6(10)	/
$NaB_{11}O_{16}(OH)_2$					
Na1	5000	3328.6(18)	2500	64.9(7)	0.74
B1	5000	3584(3)	7500	18.7(7)	3.08
B2	5943.6(18)	4197(2)	5940(3)	19.5(5)	3.06
B3	9693.5(18)	7550(2)	5250(3)	21.6(5)	3.05
B4	7235.7(19)	4860(2)	4858(3)	21.0(5)	3.04
B5	8554(2)	5756(3)	4140(3)	24.8(6)	3.05
B6	7814.1(19)	3736(2)	3207(3)	22.5(5)	3.06
O1	9431.4(11)	7725.2(15)	6380.6(16)	21.8(4)	1.87
O2	5680.1(11)	4433.9(14)	7065.1(15)	21.2(4)	2.15
O3	6654.9(12)	4979.9(15)	5682.4(17)	24.4(4)	2.07
O4	7923.9(12)	5829.1(16)	4932.6(17)	25.4(4)	1.99
O5	5452.6(12)	3272.7(16)	4981.4(17)	25.2(4)	2.25
O6	7184.2(12)	3802.3(15)	3996.8(17)	24.2(4)	1.97
O7	8491.9(13)	4727.9(17)	3268.8(18)	30.1(4)	2.00
O8	9277.4(13)	6661.9(17)	4230.4(18)	29.7(4)	2.14
O9	7784.1(13)	2660.3(16)	2438.4(17)	27.5(4)	/

[a]BVS are calculated by using the bond-valence model ($S_i = \exp[(R_o - R_i) / b]$, where R_o (in angstroms) is an empirical constant with values 2.263, 1.803 for Rb-O, Na-O bonds and 1.371 for B-O bonds and, R_i is the length of bond *i* (in angstroms), and b = 0.37 Å).

Table S3. Selected bond lengths for $RbB_7O_{10}(OH)_2$ and $NaB_{11}O_{16}(OH)_2$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
$RbB_7O_{10}(OH)_2$					
Rb1	O1[1]	3.506(3)	B1	O2	1.381(6)
Rb1	O1[2]	3.506(3)	B1	O3	1.332(6)
Rb1	O2[3]	3.171(3)	B1	O4	1.379(6)
Rb1	O2[4]	3.171(3)	B2	O2	1.377(6)
Rb1	O3[1]	3.146(3)	B2	O5	1.350(6)
Rb1	O3[2]	3.146(3)	B2	O6	1.355(6)
Rb1	O4[4]	3.099(4)	B3	O1	1.337(7)
Rb1	O4[3]	3.099(4)	B3[6]	O4	1.384(6)
Rb1	O5[1]	3.300(3)	B3	O5	1.360(6)
Rb1	O5[2]	3.300(3)	B4[4]	O1	1.480(6)
Rb1	O6	3.060(4)	B4	O3	1.457(6)
Rb1	O6[5]	3.060(4)			

[1]-1/2+X, 1/2-Y, -1/2+Z; [2]1/2-X, 1/2-Y, 1-Z; [3]1/2-X, -1/2+Y, 1/2-Z; [4]-1/2+X, -1/2+Y, +Z; [5]-X, +Y, 1/2-Z; [6]1/2+X, 1/2+Y, +Z

$NaB_{11}O_{16}(OH)_2$					
Na1	O2[1]	2.560(2)	B3[4]	O5	1.395(3)
Na1	O2[2]	2.560(2)	B3	O8	1.375(3)
Na1	O5[3]	2.4346(17)	B4	O3	1.348(3)
Na1	O5	2.4346(17)	B4	O4	1.372(3)
Na1	O8[4]	2.853(2)	B4	O6	1.380(3)
Na1	O8[5]	2.853(2)	B5	O4	1.375(3)
B1[6]	O1	1.477(2)	B5	O7	1.361(3)
B1	O2	1.459(2)	B5	O8	1.360(3)
B2	O2	1.335(3)	B6	O6	1.372(3)
B2	O3	1.369(3)	B6	O7	1.381(3)
B2	O5	1.389(3)	B6	O9	1.342(3)
B3	O1	1.330(3)			

[1]+X, 1-Y, -1/2+Z; [2]1-X, 1-Y, 1-Z; [3]1-X, +Y, 1/2-Z; [4]-1/2+X, -1/2+Y, +Z; [5]3/2-X, -1/2+Y, 1/2-Z; [6]1/2+X, 1/2+Y, +Z

Table S4. Selected bond angles for $RbB_7O_{10}(OH)_2$ and $NaB_{11}O_{16}(OH)_2$.

Band	Angle/°	Band	Angle/°
$RbB_7O_{10}(OH)_2$			
$O1^1$-Rb1-$O1^2$	176.51(11)	$O5^2$-Rb1-$O1^1$	141.98(8)
$O2^3$-Rb1-$O1^2$	61.55(8)	$O5^1$-Rb1-$O1^2$	141.98(8)
$O2^4$-Rb1-$O1^2$	119.57(8)	$O5^1$-Rb1-$O1^1$	39.63(8)
$O2^4$-Rb1-$O1^1$	61.55(8)	$O5^2$-Rb1-$O5^1$	146.47(12)
$O2^3$-Rb1-$O1^1$	119.57(8)	O6-Rb1-$O1^1$	65.73(10)
$O2^4$-Rb1-$O2^3$	147.53(13)	O6-Rb1-$O1^2$	111.06(10)
$O2^4$-Rb1-$O5^2$	80.60(9)	$O6^5$-Rb1-$O1^1$	111.06(10)
$O2^3$-Rb1-$O5^1$	80.60(9)	$O6^5$-Rb1-$O1^2$	65.73(10)
$O2^3$-Rb1-$O5^2$	90.12(9)	$O6^5$-Rb1-$O1^4$	97.30(10)
$O2^4$-Rb1-$O5^1$	90.12(9)	O6-Rb1-$O2^3$	97.30(10)
$O3^2$-Rb1-$O1^1$	104.32(8)	O6-Rb1-$O2^4$	110.39(10)
$O3^1$-Rb1-$O1^2$	104.32(8)	$O6^5$-Rb1-$O2^3$	110.38(10)
$O3^2$-Rb1-$O1^2$	79.00(8)	$O6^5$-Rb1-$O3^2$	126.36(10)
$O3^1$-Rb1-$O1^1$	79.00(8)	O6-Rb1-$O3^1$	126.36(10)
$O3^2$-Rb1-$O2^3$	83.60(9)	O6-Rb1-$O3^2$	169.07(10)
$O3^2$-Rb1-$O2^4$	66.01(9)	$O6^5$-Rb1-$O3^1$	169.07(10)
$O3^1$-Rb1-$O2^4$	83.60(9)	O6-Rb1-$O4^4$	99.16(10)
$O3^1$-Rb1-$O2^3$	66.01(9)	$O6^5$-Rb1-$O4^4$	56.23(9)
$O3^2$-Rb1-$O3^1$	44.26(12)	$O6^5$-Rb1-$O4^3$	99.16(10)
$O3^1$-Rb1-$O5^2$	94.25(9)	O6-Rb1-$O4^3$	56.22(9)
$O3^1$-Rb1-$O5^1$	52.53(9)	$O6^5$-Rb1-$O5^2$	75.22(10)
$O3^2$-Rb1-$O5^2$	52.53(9)	$O6^5$-Rb1-$O5^1$	138.19(10)
$O3^2$-Rb1-$O5^1$	94.25(9)	O6-Rb1-$O5^2$	138.19(10)
$O4^4$-Rb1-$O1^1$	90.83(9)	O6-Rb1-$O5^1$	75.22(10)
$O4^4$-Rb1-$O1^2$	88.36(9)	$O6^5$-Rb1-O^6	63.59(15)
$O4^3$-Rb1-$O1^1$	88.36(9)	O3-B1-O2	124.3(4)
$O4^3$-Rb1-$O1^2$	90.83(9)	O3-B1-O4	122.3(4)
$O4^3$-Rb1-$O2^4$	149.34(9)	O4-B1-O2	113.4(4)
$O4^4$-Rb1-$O2^3$	149.34(9)	O5-B2-O2	120.5(4)
$O4^4$-Rb1-$O2^4$	43.14(8)	O5-B2-O6	121.4(5)
$O4^3$-Rb1-$O2^3$	43.14(8)	O6-B2-O2	118.1(4)
$O4^4$-Rb1-$O3^2$	85.04(9)	O1-B3-$O4^3$	120.9(5)
$O4^4$-Rb1-$O3^1$	121.25(9)	O1-B3-O5	118.2(4)
$O4^3$-Rb1-O31	85.04(9)	O5-B3-$O4^3$	120.9(5)
$O4^3$-Rb1-$O3^2$	121.25(9)	$O1^6$-B4-$O1^7$	108.0(6)
$O4^3$-Rb1-$O4^4$	153.01(14)	$O3^8$-B4-$O1^7$	111.28(18)
$O4^3$-Rb1-$O5^2$	128.67(9)	O3-B4-$O1^6$	111.28(18)

O4[4]-Rb1-O5[1]	128.67(9)	O3-B4-O1[7]	108.69(19)
O4[4]-Rb1-O5[2]	60.64(10)	O3[8]-B4-O1[6]	108.69(19)
O4[3]-Rb1-O5[1]	60.64(10)	O3[8]-B4-O3	108.9(6)
O5[2]-Rb1-O1[2]	39.63(8)		

[1]1/2-X, 1/2-Y, 1-Z; [2]-1/2+X, 1/2-Y, -1/2+Z; [3]-1/2+X, -1/2+Y, +Z; [4]1/2-X, -1/2+Y, 1/2-Z; [5]-X, +Y,1/2-Z; [6]1/2+X, 1/2+Y, +Z; [7]1/2-X, 1/2+Y, 3/2-Z; [8]1-X, +Y, 3/2-Z

$NaB_{11}O_{16}(OH)_2$			
O2[1]-Na1-O2[2]	54.64(8)	O2-B1-O1[4]	111.71(8)
O2[2]-Na1-O8[3]	149.15(6)	O2[8]-B1-O1[7]	111.71(8)
O2[1]-Na1-O8[4]	149.15(6)	O2[8]-B1-O2	107.3(2)
O2[1]-Na1-O8[3]	101.34(5)	O2-B2-O3	118.12(19)
O2[2]-Na1-O8[4]	101.34(5)	O2-B2-O5	121.6(2)
O5[5]-Na1-O2[2]	101.92(7)	O3-B2-O5	120.0(2)
O5-Na1-O2[1]	101.92(7)	O1-B3-O5[6]	122.1(2)
O5[5]-Na1-O2[1]	80.50(6)	O1-B3-O8	125.7(2)
O5-Na1-O2[2]	80.50(6)	O8-B3-O5[6]	112.2(2)
O5[5]-Na1-O[5]	177.33(12)	O3-B4-O4	117.1(2)
O5-Na1-O8[3]	127.19(7)	O3-B4-O6	123.0(2)
O5[5]-Na1-O8[4]	127.19(7)	O4-B4-O6	119.8(2)
O5-Na1-O8[4]	50.79(5)	O7-B5-O4	120.1(2)
O5[5]-Na1-O8[3]	50.79(5)	O8-B5-O4	122.0(2)
O8[3]-Na1-O8[4]	107.15(9)	O8-B5-O7	117.8(2)
O1[4]-B1-O1[7]	107.6(2)	O6-B6-O7	120.1(2)
O2[8]-B1-O1[4]	109.29(8)	O9-B6-O6	118.3(2)
O2-B1-O1[7]	109.29(8)	O9-B6-O7	121.5(2)

[1]+X, 1-Y, -1/2+Z; [2]1-X, 1-Y, 1-Z; [3]3/2-X, -1/2+Y, 1/2-Z; [4]-1/2+X, -1/2+Y, +Z; [5]1-X, +Y, 1/2-Z; [6]1/2+X, 1/2+Y, +Z; [7]3/2-X, -1/2+Y, 3/2-Z; [8]1-X, +Y, 3/2-Z

Table S5. Hydrogen bonds for $RbB_7O_{10}(OH)_2$ and $NaB_{11}O_{16}(OH)_2$.

D-H···A	**$d_{(D-H)}$ (Å)**	**$d_{(H\cdots A)}$ (Å)**	**$d_{(D\cdots A)}$ (Å)**	**D-H···A (°)**
$RbB_7O_{10}(OH)_2$				
O6-H1···O1[1]	0.949(10)	2.02(5)	2.860(5)	147(8)

[1]+X, 1-Y, -1/2+Z

$NaB_{11}O_{16}(OH)_2$				
O9-H1···O1[1]	0.84	2.11	2.876(2)	152.1

[1]+X, 1-Y, -1/2+Z

Table S6. Comparison of the structures of alkali metal and alkaline earth metal heptaborate (FBB contains seven boron atoms).

Compounds	Space group	Birefringence (@ 1064nm)	Band gap /eV	λ cut-off / nm	FBB	Ref.
$RbB_7O_{10}(OH)_2$	***C*2/*c***	**0.074**	**7.40**	**＜200**	**$B_7O_{12}(OH)_2$**	**This work**
$CsB_7O_{10}(OH)_2$	*C*2/*c*	0.082	7.5		$B_7O_{12}(OH)_2$	[8]
$Li_2CsB_7O_{10}(OH)_4$	*C*222	0.061	6.35	＜190	$B_7O_{12}(OH)_4$	[9]
$Ba_3[Ge_2B_7O_{16}(OH)_2](OH)(H_2O)$	*Cc*		5.53	<350	$B_7O_{16}(OH)_2$	[10]
$NaBa_3[Ge_2B_7O_{16}(OH)_2]F_2$	*C*2/*c*	0.021	4.97	<200	$B_7O_{16}(OH)_2$	[11]
$NaBa_3[Si_2B_7O_{16}(OH)_2]F_2$	*C*2/*c*	0.016	5.59	<200	$B_7O_{16}(OH)_2$	[11]
$Rb_2B_7O_9(OH)_5$	$P2_1/n$				$B_7O_9(OH)_5$	[12]
$Cs_2B_7O_9(OH)_5$	$P2_1/n$				$B_7O_9(OH)_5$	[13]
$K(C_2H_{10}N_2)B_7O_9(OH)_5$	$P\bar{1}$				$B_7O_9(OH)_5$	[14]
$Na(C_2H_{10}N_2)B_7O_{10}(OH)_4$	$P\bar{1}$				$B_7O_{10}(OH)_4$	[15]

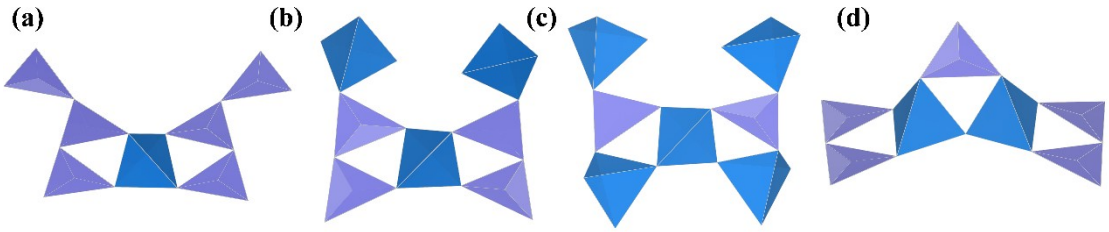

Figure S1. Different B-O frameworks containing seven B atoms. (H has been omitted for a clearer observation).

Table S7. Structural comparison of borate compounds containing eleven B atoms.

Compounds	Space group	Birefringence	Band gap /eV	λ cut-off / nm	FBB	Ref.
$NaB_{11}O_{16}(OH)_2$	***C*2/*c***	**0.105 @ 1064nm**	**7.41**		**$B_{11}O_{18}(OH)_2$**	**This work**
$NH_4B_{11}O_{16}(OH)_2$	*C*2/*c*	(0.26-0.11) @ (180-1500) nm	6.90	＜180	$B_{11}O_{18}(OH)_2$	[16]
$KB_{11}O_{16}(OH)_2$	*C*2/*c*	0.104 @ 546nm	7.47	＜195	$B_{11}O_{18}(OH)_2$	[17]
$RbB_{11}O_{16}(OH)_2$	*C*2/*c*	0.09 @ 1064nm	7.24		$B_{11}O_{18}(OH)_2$	[18]
$CsB_{11}O_{16}(OH)_2$	*C*2/*c*	0.1 @ 546nm	7.19		$B_{11}O_{18}(OH)_2$	[17]
$Li_3B_{11}O_{18}$	$P2_1/c$				$B_{11}O_{22}$	[19]
$Li_6Rb_5B_{11}O_{22}$	*C*2			190	$B_{11}O_{22}$	[20]
$Ba_4B_{11}O_{20}F$	$Cmc2_1$	0.0146 @ 1064nm		190	$B_{11}O_{24}$	[21]
$Ba_3Pb(H_2O)[B_{11}O_{19}(OH)_3]$	$P2_1/n$				$B_{11}O_{23}(OH)_3$	[22]
$Ba_3B_{11}O_{18}(OH)_3(H_2O)$	$P\bar{1}$	0.026 @ 1064nm	5.53		$B_{11}O_{22}(OH)_3$	[23]

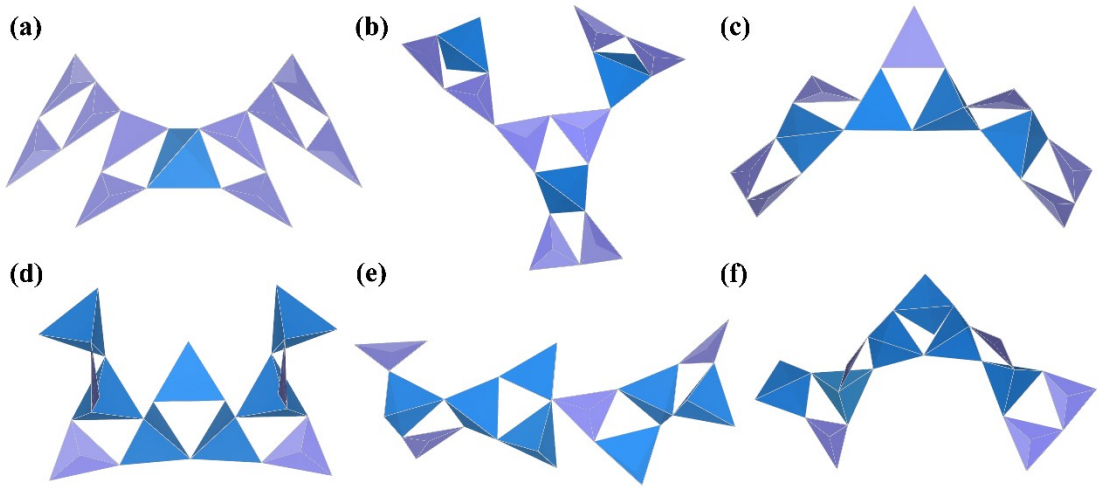

Figure S2. Different B-O frameworks containing eleven B atoms. (H has been omitted for a clearer observation).

Table S8. Bonding electron density difference ($\Delta\rho$) of anionic groups calculated by adopting the REDA method for $RbB_7O_{10}(OH)_2$ and $NaB_{11}O_{16}(OH)_2$.

	Units	$\Delta\rho$	$\Delta\omega$
$RbB_7O_{10}(OH)_2$	BO_3	0.007015568	50.86%
	$BO_2(OH)$	0.006199406	44.94%
	BO_4	0.000131376	0.95%
	RbO_{12}	0.000446984	3.24%
$NaB_{11}O_{16}(OH)_2$	BO_4	0.000034925	0.24%
	BO_3	0.011161918	76.71%
	$BO_2(OH)$	0.003224609	22.16%
	NaO_6	0.000129341	0.89%

Table S9. Spatial density of [BO_3], [$BO_2(OH)$], [BO_4] have been calculated for $RbB_7O_{10}(OH)_2$ and $NaB_{11}O_{16}(OH)_2$.

	Units	Spatial density ($Å^{-3}$)
$RbB_7O_{10}(OH)_2$	BO_3	1.6×10^{-2}
	$BO_2(OH)$	0.8×10^{-2}
	BO_4	0.4×10^{-2}
$NaB_{11}O_{16}(OH)_2$	BO_3	2.3×10^{-2}
	$BO_2(OH)$	0.6×10^{-2}
	BO_4	0.3×10^{-2}

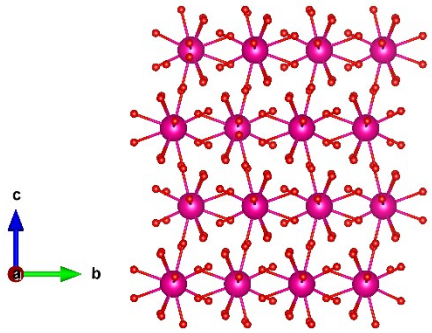

Figure S3. The isolated [RbO_{12}] polyhedra in $RbB_7O_{10}(OH)_2$.

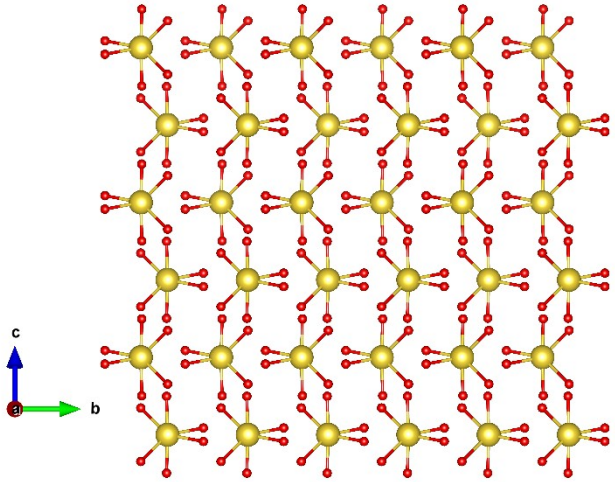

Figure S4. The isolated [NaO_6] polyhedra in $NaB_{11}O_{16}(OH)_2$.

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