Supporting Information

Design of Borate-Squarate Hybrid Crystals with Large Birefringence by Synergistic Assembly of Planar π-Conjugated Groups

Haowen Li,[ac] Xiao Wang,[bc] Hui Chai*[a] and Fangfang Zhang*[ac]

[a] State Key Laboratory of Chemistry and Utilization of Carbon Based Energy Resources, College of Chemistry, Xinjiang University, Urumqi 830017, China.

[b] College of Materials Science and Engineering, Xinjiang University, Urumqi 830017, China.

[c] Research Center for Crystal Materials; CAS Key Laboratory of Functional Materials and Devices for Special Environmental Conditions; Xinjiang Key Laboratory of Functional Crystal Materials; Xinjiang Technical Institute of Physics and Chemistry, CAS, 40-1 South Beijing Road, Urumqi 830011, China.

* Corresponding authors: hchchh@sina.com; ffzhang@ms.xjb.ac.cn

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Table S1. Crystallographic data and structure refinement parameters for $Rb_2(C_4O_4)[B(OH)_3]_2{\cdot}2H_2O$, $Cs_2(C_4O_4)[B(OH)_3]_2{\cdot}2H_2O$, and $Rb(C_4O_4)_{0.5}{\cdot}B(OH)_3$.

Empirical formula	$Rb_2(C_4O_4)[B(OH)_3]_2{\cdot}2H_2O$	$Cs_2(C_4O_4)[B(OH)_3]_2{\cdot}2H_2O$	$Rb(C_4O_4)_{0.5}{\cdot}B(OH)_3$
CCDC number	**2535144**	**2535145**	**2535146**
Formula weight	442.68	537.56	203.32
Temperature/K	298		
Crystal system	orthorhombic		monoclinic
Space group	$Pca2_1$		$C2/m$
a/Å	16.2257(10)	16.4512(6）	11.591(2)
b/Å	6.7803(4)	7.0876(2)	7.3534(12)
c/Å	12.2028(9)	12.3802(4)	8.4758(16)
β/°	90	90	123.365(6)
Volume/Å³	1342.49(15)	1443.53(8)	603.36(19)
Z	4		
ρ_{calc}/g·cm^{-3}	2.190	2.473	2.238
μ/mm^{-1}	7.346	5.103	8.150
F(000)	856	1000.0	388
Radiation	MoKα (λ = 0.71073)		
2θ range for data collection/°	6.008 to 54.986	5.748 to 54.976	5.756 to 55.036
Index ranges	$-20 \le h \le 21$, $-8 \le k \le 8$, $-15 \le l \le 15$	$-21 \le h \le 20$, $-8 \le k \le 9$, $-15 \le l \le 16$	$-14 \le h \le 14$, $-9 \le k \le 9$, $-11 \le l \le 10$
Independent reflections	3056 [R_{int} = 0.0783, R_{sigma} = 0.0582]	3303 [R_{int} = 0.0538, R_{sigma} = 0.0291]	751 [R_{int} = 0.0682, R_{sigma} = 0.0362]
Completeness to theta	99.9%	99.9%	100%
Data/restraints/parameters	3056/1/193	3303/1/199	751/1/64
Goodness-of-fit on F²	0.910	1.012	1.038
Final R indexes [$I \ge 2\sigma(I)$]^a	R_1 = 0.0264, wR_2 = 0.0468	R_1 = 0.0170, wR_2 = 0.0350	R_1 = 0.0270, wR_2 = 0.0508
Final R indexes [all data]^a	R_1 = 0.0396, wR_2 = 0.0497	R_1 = 0.0212, wR_2 = 0.0359	R_1 = 0.0442, wR_2 = 0.0558
Largest diff. peak/hole / e Å^{-3}	0.32/-0.33	1.10/-0.36	0.38/-0.41
Flack parameter	0.016(9)	0.009(12)	/

$^{a}R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Rb_2(C_4O_4)[B(OH)_3]_2·2H_2O$, $Cs_2(C_4O_4)[B(OH)_3]_2·2H_2O$, and $Rb(C_4O_4)_{0.5}·B(OH)_3$. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	*X*	*y*	*z*	*U*(eq)
$Rb_2(C_4O_4)[B(OH)_3]_2·2H_2O$				
Rb1	0.73167(2)	0.94247(7)	0.47950(6)	0.03265(12)
Rb2	0.79499(3)	0.58764(7)	0.73077(6)	0.04044(14)
B1	0.5922(3)	0.2550(9)	0.6691(5)	0.0247(13)
B2	0.9206(4)	0.7562(10)	0.4266(5)	0.0283(14)
C1	0.5250(3)	0.7535(7)	0.4710(5)	0.0256(10)
C2	0.5497(3)	0.7518(9)	0.5864(4)	0.0264(13)
C3	0.4630(3)	0.7379(8)	0.6192(4)	0.0251(11)
C4	0.4391(3)	0.7421(7)	0.5049(4)	0.0254(12)
O1	0.7101(2)	1.0106(5)	0.2305(5)	0.0456(9)
O2	0.7339(2)	0.5124(5)	0.4705(8)	0.0504(13)
O3	0.6179(2)	0.2549(6)	0.5607(3)	0.0325(9)
O4	0.6537(2)	0.2684(5)	0.7437(3)	0.0325(8)
O5	0.5107(2)	0.2427(8)	0.6899(3)	0.0378(10)
O6	0.8616(2)	0.7662(8)	0.3480(4)	0.0391(10)
O7	1.0031(2)	0.7401(7)	0.4057(3)	0.0391(10)
O8	0.8940(2)	0.7627(7)	0.5318(3)	0.0354(10)
O9	0.5627(2)	0.7629(8)	0.3818(3)	0.0356(10)
O10	0.6168(2)	0.7605(7)	0.6364(3)	0.0376(10)
O11	0.4253(2)	0.7285(5)	0.7093(3)	0.0311(9)
O12	0.3705(2)	0.7404(6)	0.4558(3)	0.0362(10)
$Cs_2(C_4O_4)[B(OH)_3]_2·2H_2O$				
Cs1	0.77057(2)	0.46685(4)	0.52410(3)	0.03442(8)
Cs2	0.20420(2)	0.89374(4)	0.27163(3)	0.03790(8)
B1	0.9101(3)	0.7774(8)	0.3272(4)	0.0301(11)
B2	0.5732(4)	0.2696(9)	0.5760(5)	0.0330(12)
C1	0.5616(3)	0.7700(6)	0.4938(3)	0.0279(10)
C2	0.5382(3)	0.7643(7)	0.3809(4)	0.0279(9)
C3	0.4527(3)	0.7439(7)	0.4122(4)	0.0296(10)
C4	0.4765(2)	0.7499(6)	0.5270(5)	0.0297(8)
O1	0.7138(2)	0.5464(5)	0.2776(5)	0.0464(8)
O2	0.76466(16)	0.0228(4)	0.5251(6)	0.0383(7)
O3	0.6004(2)	0.2823(7)	0.4717(3)	0.0440(10)
O4	0.4933(2)	0.2389(6)	0.5944(3)	0.0441(9)
O5	0.6309(2)	0.2890(7)	0.6529(3)	0.0484(10)
O6	0.99057(19)	0.7581(7)	0.3071(3)	0.0420(9)
O7	0.88458(18)	0.7887(6)	0.4340(3)	0.0366(8)

O8	0.85033(18)	0.7902(5)	0.2530(3)	0.0383(8)
O9	0.62844(18)	0.7849(5)	0.5433(3)	0.0386(8)
O10	0.57499(18)	0.7733(5)	0.2921(3)	0.0355(8)
O11	0.3875(2)	0.7266(7)	0.3626(3)	0.0453(10)
O12	0.4407(2)	0.7389(6)	0.6146(3)	0.0409(10)
$Rb(C_4O_4)_{0.5}\cdot B(OH)_3$				
Rb1	0.500000	0.75829(5)	0.500000	0.0390(2)
B1	0.1642(5)	0.500000	0.2638(6)	0.0313(11)
C1	0.6000(4)	0.500000	0.1172(5)	0.0269(9)
C2	0.4634(4)	0.500000	0.0862(5)	0.0279(9)
O1	0.0442(3)	0.500000	0.2560(4)	0.0370(8)
O2	0.1650(3)	0.500000	0.1039(4)	0.0445(9)
O3	0.2877(3)	0.500000	0.4344(4)	0.0390(8)
O4	0.4202(3)	0.500000	0.1932(4)	0.0384(8)
O5	0.7220(3)	0.500000	0.2609(4)	0.0410(8)

Table S3. Selected bond lengths (Å) and angles (°) for $Rb_2(C_4O_4)[B(OH)_3]_2 \cdot 2H_2O$.

$Rb_2(C_4O_4)[B(OH)_3]_2 \cdot 2H_2O$			
B(1)-O(3)	1.386(7)	Rb(2)#1-O(1)	2.869(3)
B(1)-O(4)	1.354(7)	Rb(1)-O(2)	2.919(4)
B(1)-O(5)	1.349(6)	Rb(2)-O(2)	3.367(9)
B(2)-O(6)	1.357(7)	Rb(2)#1-O(2)	3.006(9)
B(2)-O(7)	1.367(7)	Rb(1)#2-O(3)	2.980(4)
B(2)-O(8)	1.356(7)	Rb(2)-O(4)	3.156(3)
C(1)-C(2)	1.464(7)	Rb(1)-O(6)	2.907(4)
C(1)-C(4)	1.456(6)	Rb(2)#1-O(6)	3.157(4)
C(1)-O(9)	1.250(6)	Rb(1)-O(8)	2.972(4)
C(2)-C(3)	1.465(7)	Rb(2)-O(8)	3.144(4)
C(2)-O(10)	1.250(7)	Rb(1)-O(9)	3.228(4)
C(3)-C(4)	1.449(7)	Rb(2)#1-O(9)	3.185(4)
C(3)-O(11)	1.260(6)	Rb(1)-O(10)	2.944(4)
C(4)-O(12)	1.264(6)	Rb(2)-O(10)	3.326(4)
Rb(1)-O(1)	3.093(6)	Rb(2)#3-O(11)	3.023(3)
Rb(1)#1-O(1)	3.239(6)	Rb(1)#4-O(12)	3.127(4)
O(4)-B(1)-O(3)	114.9(4)	O(12)#6-Rb(1)-O(9)	146.82(11)
O(5)-B(1)-O(3)	118.3(4)	O(1)#5-Rb(2)-O(2)	98.16(15)
O(5)-B(1)-O(4)	126.8(5)	O(1)#5-Rb(2)-O(2)#5	99.58(16)
O(6)-B(2)-O(7)	124.3(5)	O(1)#5-Rb(2)-O(4)	131.64(10)
O(8)-B(2)-O(6)	116.3(5)	O(1)#5-Rb(2)-O(6)#5	66.04(12)
O(8)-B(2)-O(7)	119.4(5)	O(1)#5-Rb(2)-O(8)	68.69(14)
O(2)-Rb(1)-O(1)	96.5(2)	O(1)#5-Rb(2)-O(9)#5	69.43(14)
O(2)-Rb(1)-O(1)#5	100.06(19)	O(1)#5-Rb(2)-O(10)	67.81(12)
O(2)-Rb(1)-O(3)#7	136.93(14)	O(1)#5-Rb(2)-O(11)#8	136.81(10)
O(2)-Rb(1)-O(8)	65.63(12)	O(2)#5-Rb(2)-O(2)	147.83(8)
O(2)-Rb(1)-O(9)	67.65(13)	O(2)#5-Rb(2)-O(4)	73.85(11)
O(2)-Rb(1)-O(10)	67.26(17)	O(2)#5-Rb(2)-O(6)#5	59.93(11)
O(2)-Rb(1)-O(12)#6	132.43(11)	O(2)#5-Rb(2)-O(8)	153.54(11)
O(3)#7-Rb(1)-O(1)#5	76.38(10)	O(2)#5-Rb(2)-O(9)#5	67.25(11)
O(3)#7-Rb(1)-O(1)	98.66(10)	O(2)#5-Rb(2)-O(10)	105.14(10)
O(3)#7-Rb(1)-O(9)	82.22(11)	O(2)#5-Rb(2)-O(11)#8	94.18(10)
O(3)#7-Rb(1)-O(12)#6	89.32(10)	O(4)-Rb(2)-O(2)	74.29(11)
O(6)-Rb(1)-O(1)#5	111.68(11)	O(4)-Rb(2)-O(6)#5	69.88(11)
O(6)-Rb(1)-O(1)	66.49(12)	O(4)-Rb(2)-O(9)#5	138.90(11)
O(6)-Rb(1)-O(2)	63.86(16)	O(4)-Rb(2)-O(10)	68.13(10)
O(6)-Rb(1)-O(3)#7	157.73(13)	O(6)#5-Rb(2)-O(2)	104.39(10)
O(6)-Rb(1)-O(8)	46.13(11)	O(6)#5-Rb(2)-O(9)#5	100.27(11)
O(6)-Rb(1)-O(9)	104.90(12)	O(6)#5-Rb(2)-O(10)	47.31(10)
O(6)-Rb(1)-O(10)	130.26(11)	O(8)-Rb(2)-O(2)	58.61(11)

O(6)-Rb(1)-O(12)#6	73.10(12)	O(8)-Rb(2)-O(4)	131.95(11)
O(8)-Rb(1)-O(1)#5	66.23(10)	O(8)-Rb(2)-O(6)#5	128.05(12)
O(8)-Rb(1)-O(1)	111.86(10)	O(8)-Rb(2)-O(9)#5	86.31(10)
O(8)-Rb(1)-O(3)#7	140.30(12)	O(8)-Rb(2)-O(10)	92.52(10)
O(8)-Rb(1)-O(9)	132.65(13)	O(9)#5-Rb(2)-O(2)	144.71(11)
O(8)-Rb(1)-O(12)#6	70.33(11)	O(9)#5-Rb(2)-O(10)	134.37(12)
O(9)-Rb(1)-O(1)#5	130.60(10)	O(10)-Rb(2)-O(2)	58.04(10)
O(10)-Rb(1)-O(1)#5	68.24(11)	O(11)#8-Rb(2)-O(2)	90.96(9)
O(10)-Rb(1)-O(1)	129.05(10)	O(11)#8-Rb(2)-O(4)	91.49(9)
O(10)-Rb(1)-O(3)#7	71.89(13)	O(11)#8-Rb(2)-O(6)#5	150.96(11)
O(10)-Rb(1)-O(8)	104.46(11)	O(11)#8-Rb(2)-O(8)	80.99(11)
O(10)-Rb(1)-O(9)	62.89(10)	O(11)#8-Rb(2)-O(9)#5	78.90(11)
O(10)-Rb(1)-O(12)#6	143.55(12)	O(11)#8-Rb(2)-O(10)	145.92(10)
O(12)#6-Rb(1)-O(1)#5	77.24(9)		

Symmetry transformations used to generate equivalent atoms:

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

Table S4. Selected bond lengths (Å) and angles (°) for $Cs_2(C_4O_4)[B(OH)_3]_2·2H_2O$.

$Cs_2(C_4O_4)[B(OH)_3]_2·2H_2O$			
B(1)-O(6)	1.355(6)	Cs(1)-O(2)	3.150(3)
B(1)-O(7)	1.390(6)	Cs(1)-O(3)	3.157(4)
B(1)-O(8)	1.347(6)	Cs(1)-O(5)	3.068(4)
B(2)-O(3)	1.369(7)	Cs(1)-O(7)	3.157(4)
B(2)-O(4)	1.352(7)	Cs(1)-O(9)	3.257(3)
B(2)-O(5)	1.350(7)	Cs(1)-O(11)#4	3.095(4)
C(1)-C(2)	1.450(6)	Cs(1)-O(12)#4	3.348(4)
C(1)-C(4)	1.465(6)	Cs(2)-O(1)#2	3.119(4)
C(1)-O(9)	1.263(5)	Cs(2)-O(2)#2	3.346(8)
C(2)-C(3)	1.467(6)	Cs(2)-O(2)#5	3.150(8)
C(2)-O(10)	1.255(6)	Cs(2)-O(3)#2	3.257(4)
C(3)-C(4)	1.476(7)	Cs(2)-O(5)#5	3.346(4)
C(3)-O(11)	1.241(6)	Cs(2)-O(8)#7	3.295(3)
C(4)-O(12)	1.237(7)	Cs(2)-O(10)#7	3.186(3)
Cs(1)-O(1)	3.240(6)	Cs(2)-O(11)	3.430(4)
Cs(1)-O(1)#3	3.198(6)	Cs(2)-O(12)#8	3.266(4)
O(6)-B(1)-O(7)	118.4(4)	O(1)#2-Cs(2)-O(3)#2	68.03(13)
O(8)-B(1)-O(6)	126.5(5)	O(1)#2-Cs(2)-O(5)#6	65.34(11)
O(8)-B(1)-O(7)	115.0(4)	O(1)#2-Cs(2)-O(6)#7	77.54(10)
O(4)-B(2)-O(3)	115.3(5)	O(1)#2-Cs(2)-O(8)#5	130.06(9)
O(5)-B(2)-O(4)	125.5(5)	O(1)#2-Cs(2)-O(10)#5	140.48(9)
O(1)#4-Cs(1)-O(1)	156.38(11)	O(1)#2-Cs(2)-O(11)	66.58(11)
O(1)-Cs(1)-O(9)	75.01(10)	O(1)#2-Cs(2)-O(12)#8	73.48(12)
O(1)#4-Cs(1)-O(9)	82.18(9)	O(2)#6-Cs(2)-O(2)#2	145.82(6)
O(1)#4-Cs(1)-O(12)#3	71.43(9)	O(2)#6-Cs(2)-O(3)#2	153.37(9)
O(1)-Cs(1)-O(12)#3	129.17(9)	O(2)#6-Cs(2)-O(5)#6	61.01(9)
O(2)-Cs(1)-O(1)	99.73(16)	O(2)#2-Cs(2)-O(5)#6	103.86(8)
O(2)-Cs(1)-O(1)#4	100.06(16)	O(2)#6-Cs(2)-O(6)#7	108.72(7)
O(2)-Cs(1)-O(3)	63.86(10)	O(2)#2-Cs(2)-O(6)#7	102.63(8)
O(2)-Cs(1)-O(7)	137.92(10)	O(2)#6-Cs(2)-O(8)#5	71.69(9)
O(2)-Cs(1)-O(9)	132.02(8)	O(2)#6-Cs(2)-O(10)#5	92.67(8)
O(2)-Cs(1)-O(12)#3	65.74(10)	O(2)#2-Cs(2)-O(11)	59.45(8)
O(3)-Cs(1)-O(1)	67.87(10)	O(2)#6-Cs(2)-O(11)	103.88(8)
O(3)-Cs(1)-O(1)#4	110.21(9)	O(2)#6-Cs(2)-O(12)#8	66.74(9)
O(3)-Cs(1)-O(9)	70.43(10)	O(3)#2-Cs(2)-O(2)#2	60.66(9)
O(3)-Cs(1)-O(12)#3	129.00(11)	O(3)#2-Cs(2)-O(5)#6	127.64(11)
O(5)-Cs(1)-O(1)	110.20(10)	O(3)#2-Cs(2)-O(6)#7	46.10(8)
O(5)-Cs(1)-O(1)#4	67.82(10)	O(3)#2-Cs(2)-O(8)#5	134.13(9)
O(5)-Cs(1)-O(2)	64.16(13)	O(3)#2-Cs(2)-O(11)	94.52(9)
O(5)-Cs(1)-O(3)	43.31(11)	O(3)#2-Cs(2)-O(12)#8	86.65(9)

O(5)-Cs(1)-O(7)	157.74(11)	O(5)#6-Cs(2)-O(6)#7	136.68(10)
O(5)-Cs(1)-O(9)	73.06(11)	O(5)#6-Cs(2)-O(11)	45.39(9)
O(5)-Cs(1)-O(11)#3	128.27(12)	O(8)#5-Cs(2)-O(2)#2	74.23(8)
O(5)-Cs(1)-O(12)#3	105.85(11)	O(8)#5-Cs(2)-O(5)#6	68.95(10)
O(7)-Cs(1)-O(1)	73.31(9)	O(8)#5-Cs(2)-O(6)#7	152.30(10)
O(7)-Cs(1)-O(1)#4	99.87(9)	O(8)#5-Cs(2)-O(11)	67.43(10)
O(7)-Cs(1)-O(3)	138.91(10)	O(10)#5-Cs(2)-O(2)#2	89.57(8)
O(7)-Cs(1)-O(9)	87.26(9)	O(10)#5-Cs(2)-O(3)#2	82.73(10)
O(7)-Cs(1)-O(12)#3	86.35(10)	O(10)#5-Cs(2)-O(5)#6	149.61(10)
O(9)-Cs(1)-O(12)#3	151.30(9)	O(10)#5-Cs(2)-O(6)#7	62.97(9)
O(11)#3-Cs(1)-O(1)#4	131.48(9)	O(10)#5-Cs(2)-O(8)#5	89.36(9)
O(11)#3-Cs(1)-O(1)	69.36(10)	O(10)#5-Cs(2)-O(11)	144.71(10)
O(11)#3-Cs(1)-O(2)	65.11(14)	O(10)#5-Cs(2)-O(12)#8	79.02(9)
O(11)#3-Cs(1)-O(3)	103.58(10)	O(11)-Cs(2)-O(6)#7	135.41(10)
O(11)#3-Cs(1)-O(7)	73.90(11)	O(12)#8-Cs(2)-O(2)#2	146.62(9)
O(11)#3-Cs(1)-O(9)	143.12(10)	O(12)#8-Cs(2)-O(5)#6	101.54(9)
O(11)#3-Cs(1)-O(12)#3	60.26(9)	O(12)#8-Cs(2)-O(6)#7	44.31(8)
O(1)#2-Cs(2)-O(2)#6	101.68(13)	O(12)#8-Cs(2)-O(8)#5	136.02(9)
O(1)#2-Cs(2)-O(2)#2	98.00(11)	O(12)#8-Cs(2)-O(11)	136.13(11)

Symmetry transformations used to generate equivalent atoms:

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

Table S5. Selected bond lengths (Å) and angles (°) for $Rb(C_4O_4)_{0.5}\cdot B(OH)_3$.

$Rb(C_4O_4)_{0.5}\cdot B(OH)_3$			
B(1)-O(1)	1.356(5)	Rb(1)#4-O(1)	2.977(2)
B(1)-O(2)	1.361(5)	Rb(1)-O(3)	2.910(2)
B(1)-O(3)	1.365(5)	Rb(1)#1-O(3)	2.910(2)
C(1)-C(2)#2	1.455(5)	Rb(1)-O(4)	2.9289(19)
C(1)-C(2)	1.455(5)	Rb(1)#1-O(4)	2.9289(19)
C(1)-O(5)	1.261(4)	Rb(1)#5-O(5)	3.235(2)
C(2)-O(4)	1.255(4)	Rb(1)#6-O(5)	3.235(2)
Rb(1)#3-O(1)	2.977(2)		
O(1)-B(1)-O(2)	121.4(4)	O(3)-Rb(1)-O(4)	65.55(7)
O(1)-B(1)-O(3)	120.1(4)	O(3)#1-Rb(1)-O(5)#8	157.61(8)
O(2)-B(1)-O(3)	118.6(4)	O(3)-Rb(1)-O(5)#5	157.61(7)
O(1)#3-Rb(1)-O(1)#7	106.70(6)	O(3)-Rb(1)-O(5)#8	78.02(5)
O(1)#7-Rb(1)-O(5)#8	74.32(7)	O(3)#1-Rb(1)-O(5)#5	78.02(5)
O(1)#3-Rb(1)-O(5)#5	74.32(7)	O(4)#1-Rb(1)-O(1)#7	155.89(8)
O(1)#7-Rb(1)-O(5)#5	67.32(7)	O(4)-Rb(1)-O(1)#3	155.89(8)
O(1)#3-Rb(1)-O(5)#8	67.32(7)	O(4)-Rb(1)-O(1)#7	82.04(5)
O(3)#1-Rb(1)-O(1)#3	135.03(8)	O(4)#1-Rb(1)-O(1)#3	82.04(5)
O(3)-Rb(1)-O(1)#7	135.03(8)	O(4)#1-Rb(1)-O(4)	99.15(7)
O(3)#1-Rb(1)-O(1)#7	94.11(6)	O(4)-Rb(1)-O(5)#8	94.63(6)
O(3)-Rb(1)-O(1)#3	94.11(7)	O(4)#1-Rb(1)-O(5)#8	129.18(7)
O(3)#1-Rb(1)-O(3)	98.52(7)	O(4)-Rb(1)-O(5)#5	129.18(7)
O(3)-Rb(1)-O(4)#1	64.37(7)	O(4)#1-Rb(1)-O(5)#5	94.63(6)
O(3)#1-Rb(1)-O(4)#1	65.55(7)	O(5)#5-Rb(1)-O(5)#8	113.35(5)
O(3)#1-Rb(1)-O(4)	64.37(7)		

Symmetry transformations used to generate equivalent atoms:

#1 1-X, 1-Y, 1-Z; #2 1-X, 1-Y, -Z; #3 1/2-X, 1.5-Y, 1-Z; #4 -1/2+X, -0.5+Y, +Z; #5 3/2-X, 3/2-Y, 1-Z; #6 1/2+X, -1/2+Y, +Z; #7 1/2+X, 1/2+Y, +Z; #8 -1/2+X, 1/2+Y, +Z;

Table S6. Studies on reported borate-squarates.

Compound	**Space Group**	**Birefringence**	**Interlayer Distance (Å)**	**Dihedral Angle (°)**	**Anion Groups**	**Refs.**
$Na_2C_4O_4(H_3BO_3)(H_2O)\cdot H_3BO_3$	$Cmc2_1$	0.26@1064 nm	3.481	0	$[B(OH)_3]$, $[C_4O_4]$	[1]
$Li_2C_4O_4(H_3BO_3)(H_2O)\cdot H_3BO_3$	$Cmc2_1$	0.267@1064 nm	3.301	0	$[B(OH)_3]$, $[C_4O_4]$	[2]
$K(C_4O_4)_{0.5}\cdot B(OH)_3$	$P\bar{1}$	0.346@1064 nm	3.310	0	$[B(OH)_3]$, $[C_4O_4]$	[3]
$Rb_2(C_4O_4)[B(OH)_3]_2\cdot 2H_2O$	$Pca2_1$	0.281@546 nm	3.384	5.79	$[B(OH)_3]$, $[C_4O_4]$	This work
$Cs_2(C_4O_4)[B(OH)_3]_2\cdot 2H_2O$	$Pca2_1$	0.262@546 nm	3.525	11.91	$[B(OH)_3]$, $[C_4O_4]$	This work
$Rb(C_4O_4)_{0.5}\cdot B(OH)_3$	$C2/m$	0.328@546 nm	3.677	0	$[B(OH)_3]$, $[C_4O_4]$	This work

Table S7. The assignments of the infrared absorption peaks for $Rb_2(C_4O_4)[B(OH)_3]_2\cdot 2H_2O$, $Cs_2(C_4O_4)[B(OH)_3]_2\cdot 2H_2O$, and $Rb(C_4O_4)_{0.5}\cdot B(OH)_3$.

Assignments	Absorption bands for $Rb_2(C_4O_4)[B(OH)_3]_2\cdot 2H_2O$ (cm^{-1})	Absorption bands for $Cs_2(C_4O_4)[B(OH)_3]_2\cdot 2H_2O$ (cm^{-1})	Absorption bands for $Rb(C_4O_4)_{0.5}\cdot B(OH)_3$ (cm^{-1})
asymmetric stretching of H-O	3435/3277/2975	3454/3323/2980	3154/2965
the bending of group H-O-H	1650	1645	/
vibrations of C-C and C-O	1459	1461	1474/1423
deformation vibration of C-C	1223/1152/1096	1212/1136/1098	1239/1173/1079
symmetric stretching of B-O	876	870/798	847
out-of-plane bending of the $[BO_3]^{3-}$ triangles	753/662/540	727/662/543	702/674/550/526

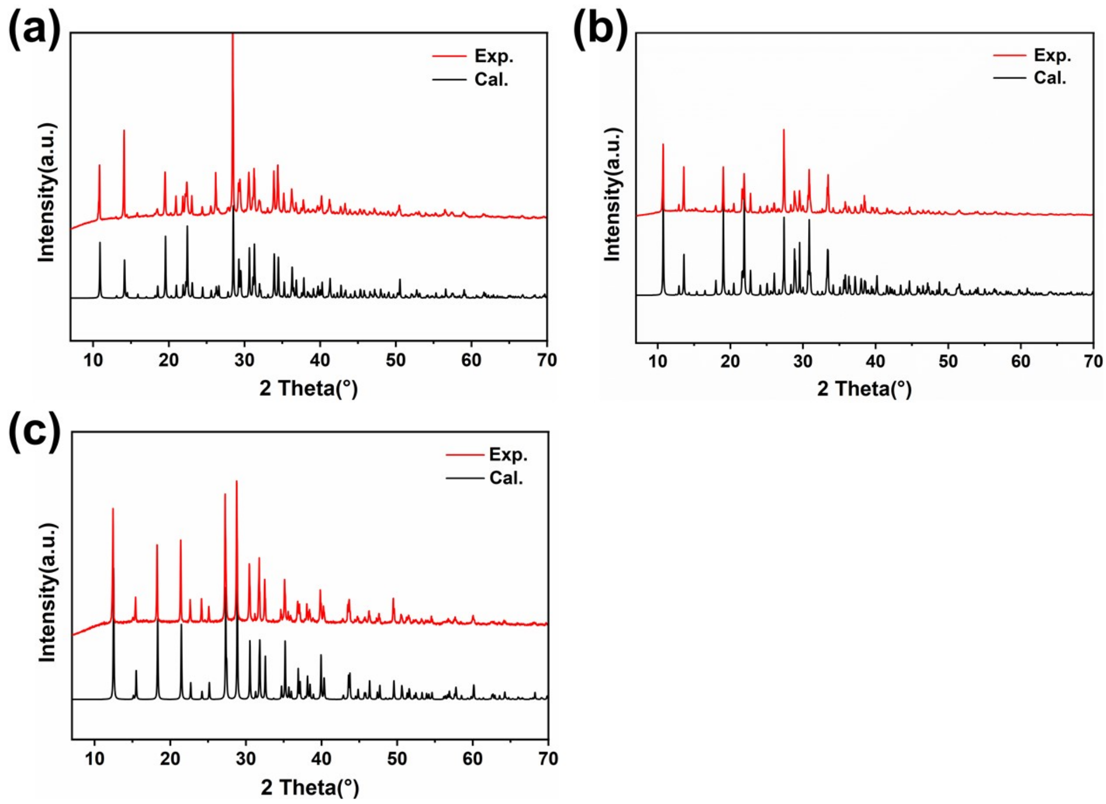

Figure S1. Powder XRD patterns of $Rb_2(C_4O_4)[B(OH)_3]_2 \cdot 2H_2O$ (a), $Cs_2(C_4O_4)[B(OH)_3]_2 \cdot 2H_2O$ (b), and $Rb(C_4O_4)_{0.5} \cdot B(OH)_3$ (c).

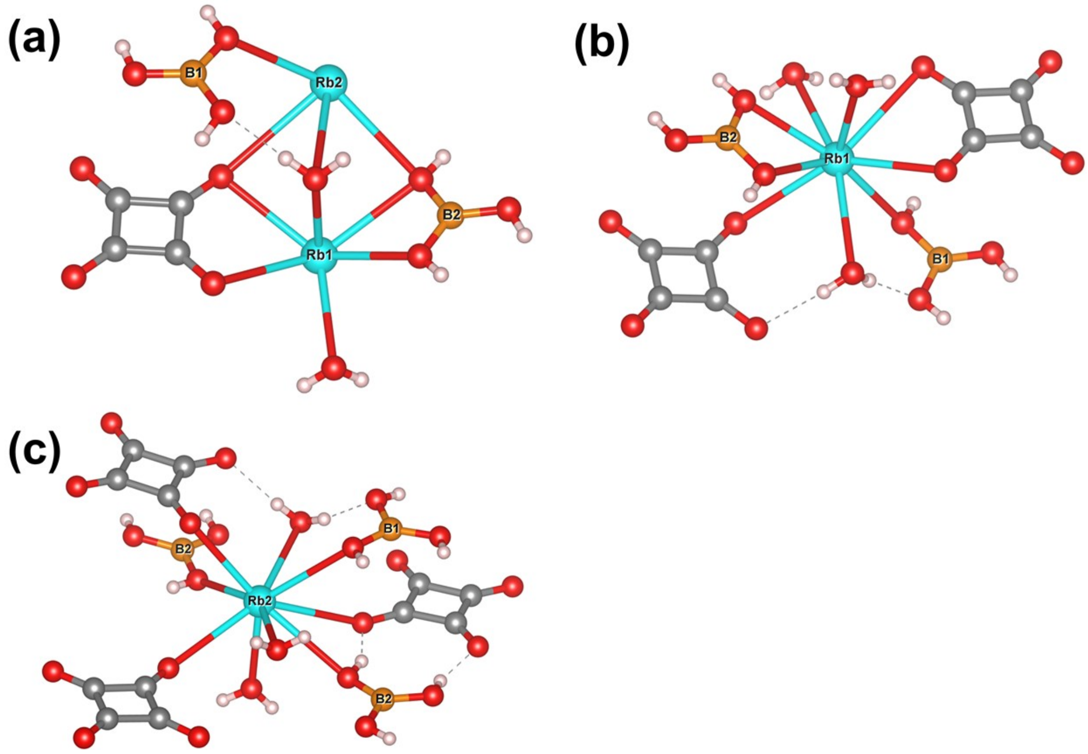

Figure S2. (a) View of asymmetric unit of $Rb_2(C_4O_4)[B(OH)_3]_2 \cdot 2H_2O$; The coordination of Rb1 (b) and Rb2 (c) atoms in $Rb_2(C_4O_4)[B(OH)_3]_2 \cdot 2H_2O$.

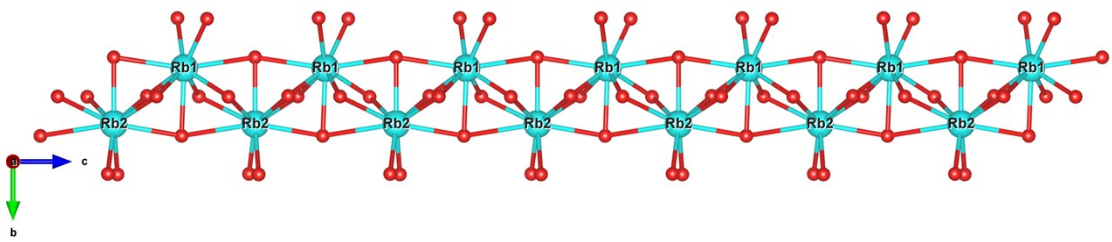

Figure S3. The one-dimensional $[Rb\text{-}O]_\infty$ polyhedral chains in $Rb_2(C_4O_4)[B(OH)_3]_2 \cdot 2H_2O$.

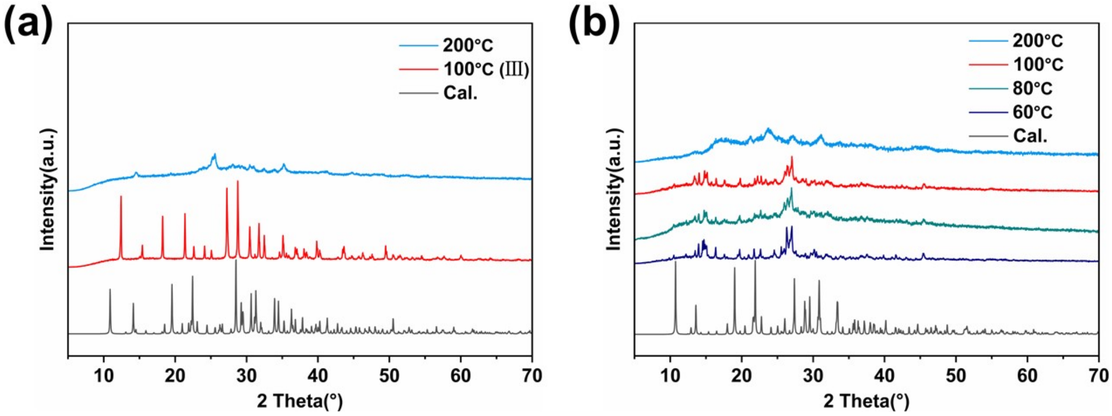

Figure S4. Powder XRD patterns of calcined polycrystalline samples of $Rb_2(C_4O_4)[B(OH)_3]_2·2H_2O$ (a) and $Cs_2(C_4O_4)[B(OH)_3]_2·2H_2O$ (b). Note: The theoretical XRD pattern of $Rb(C_4O_4)_{0.5}·B(OH)_3$ matches the XRD pattern of $Rb_2(C_4O_4)[B(OH)_3]_2·2H_2O$ after calcination at 100°C.

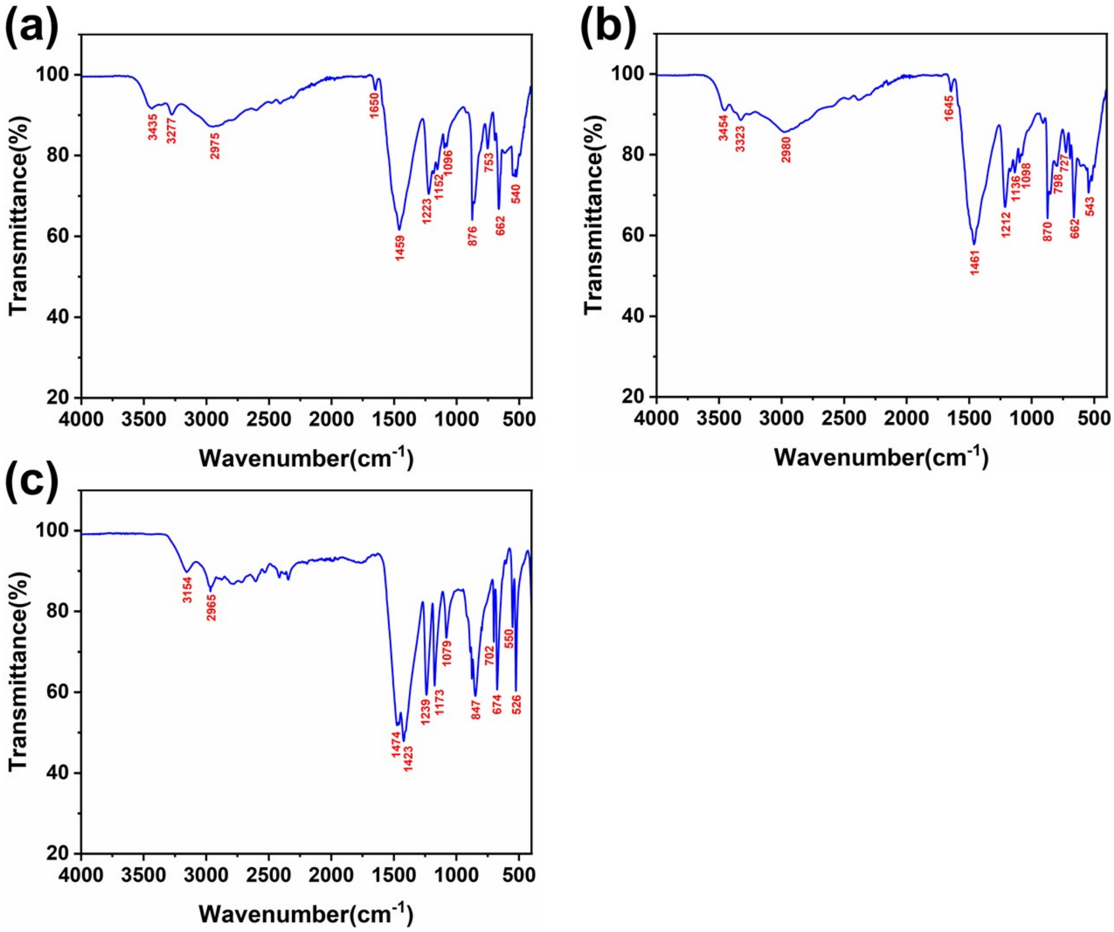

Figure S5. FT-IR spectra of $Rb_2(C_4O_4)[B(OH)_3]_2·2H_2O$ (a), $Cs_2(C_4O_4)[B(OH)_3]_2·2H_2O$ (b), and $Rb(C_4O_4)_{0.5}·B(OH)_3$ (c).

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