# Supporting Information

# Structural modification of hydroxyborates by adjusting the number of shared oxygen atoms and hydroxyl groups for further performance enhancement

Xiaoqin Ma[a], Xinjun Zhao*[a], Qianzhen Zhang[b,c], Xifa Long[b,c], Yun Yang*[b,c]

*[a]Xinjiang Laboratory of Phase Transitions and Microstructures in Condensed Matter Physics, College of Physical Science and Technology, Yili Normal University, Yining, Xinjiang, 835000, China.*

*[b]Research Center for Crystal Materials, State Key Laboratory of Functional Materials and Devices for Special Environmental Conditions; Xinjiang Key Laboratory of Functional Crystal Materials; Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, Urumqi 830011, China.*

*[c]Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China*

**Corresponding authors: Xinjun Zhao; Yun Yang*
*E-mails: zhaoxinjunzxj@163.com; yangyun@ms.xjb.ac.cn*

**Table S1.** Crystal data and structure refinements for $K_2B_5O_8(OH)$, $CsB_5O_6(OH)_4$ and $CsB_5O_7(OH)_2$.

| Empirical formula | $K_2B_5O_8(OH)$ | $CsB_5O_6(OH)_4$ | $CsB_5O_7(OH)_2$ |
|---|---|---|---|
| **Formula weight** | 277.26 | 350.99 | 332.98 |
| **Temperature** | 301K | 301K | 301K |
| **Crystal system, Space group** | Orthorhombic, $Pca2_1$ | Monoclinic, $P2_1/c$ | Monoclinic, $P2_1/c$ |
| ***a* (Å)** | 8.5523(8) | 10.1898(19) | 9.0270(13) |
| ***b* (Å)** | 7.3326(7) | 7.6098(17) | 7.7023(13) |
| ***c* (Å)** | 12.9739(10) | 13.3055(3) | 12.0291(18) |
| ***β* (°)** | 90 | 114.787(6) | 110.149(4) |
| **Volume (Å$^3$)** | 813.60(13) | 936.7(3) | 785.2(2) |
| **Z** | 4 | 4 | 4 |
| **Calculated density (Mg·m$^{-3}$)** | 2.264 | 2.489 | 2.817 |
| **Absorption coefficient (mm$^{-1}$)** | 1.193 | 3.989 | 4.741 |
| ***F* (000)** | 544 | 656 | 616 |
| **Crystal size (mm$^3$)** | 0.12 × 0.09 × 0.08 | 0.14 × 0.09 × 0.04 | 0.15 x 0.09 x 0.07 |
| **Theta range for data collection (°)** | 2.778 to 27.506 | 2.201 to 27.601 | 2.458 to 27.476 |
| **Limiting indices** | -11 ≤ h ≤ 10, -9 ≤ k ≤ 9, -16 ≤ l ≤ 16 | -13 ≤ h ≤ 11, -9 ≤ k ≤ 9, -16 ≤ l ≤ 16 | -11 ≤ h ≤ 11, -10 ≤ k ≤ 9, -15 ≤ l ≤ 15 |
| **Reflections collected / unique** | 6084/1868 [$R_{int}$=0.0549] | 10264/2164 [$R_{int}$=0.0971] | 4964/1762 [$R_{int}$ = 0.0517] |
| **Data / restraints / parameters** | 1868/1/145 | 2164/4/161 | 1762/1/144 |
| **Goodness-of-fit on $F^2$** | 1.055 | 1.050 | 1.075 |
| **Final *R* indices [$I > 2\sigma(I)$][a]** | $R_1$ =0.0334, $wR_2$ = 0.0693 | $R_1$=0.0460, $wR_2$= 0.0847 | $R_1$ = 0.0490, $wR_2$ = 0.0965 |
| ***R* indices (all data)[a]** | $R_1$= 0.0389, $wR_2$ = 0.0735 | $R_1$=0.0835, $wR_2$ = 0.1013 | $R_1$ = 0.0688, $wR_2$ = 0.1076 |
| **Largest diff. peak and hole (e·Å$^{-3}$)** | 0.350 and -0.420 | 0.849 and -1.206 | 1.040 and -1.730 |
| **Flack parameter** | 0.05(4) | | |

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

**Table S2.** Bond valence sums (BVSs) of fluorine atoms and oxygen atoms in three compounds.

| Compounds | Atoms | BVS | Atoms | BVS |
|---|---|---|---|---|
| $K_2B_5O_8(OH)$ | F (9) | 0.79 | O (9) | 2.11 |
| $CsB_5O_6(OH)_4$ | F (1) | 0.80 | O (1) | 1.95 |
| | F (4) | 0.78 | O (4) | 1.97 |
| | F (6) | 0.78 | O (6) | 2.08 |
| | F (9) | 0.81 | O (9) | 2.12 |
| $CsB_5O_7(OH)_2$ | F (1) | 0.79 | O (1) | 1.87 |
| | F (9) | 0.79 | O (9) | 1.89 |

**Table S3.** Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and BVS for $K_2B_5O_8(OH)$. $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom | x | y | z | *U*(eq) | BVS |
|---|---|---|---|---|---|
| **K(1)** | 6453(1) | 10668(2) | 3866(1) | 29(1) | 1.07 |
| **K(2)** | 8114(1) | 3684(1) | 6188(1) | 27(1) | 1.05 |
| **B(1)** | 5754(6) | 10003(7) | 6318(4) | 13(1) | 3.03 |
| **B(2)** | 6397(5) | 7508(6) | 7543(4) | 13(1) | 3.01 |
| **B(3)** | 8167(5) | 8350(6) | 6077(4) | 12(1) | 3.12 |
| **B(4)** | 8075(5) | 6644(7) | 4351(4) | 13(1) | 3.04 |
| **B(5)** | 9003(6) | 4389(7) | 3205(4) | 16(1) | 3.04 |
| **O(1)** | 4816(3) | 11305(4) | 5893(2) | 13(1) | 1.95 |
| **O(2)** | 7254(3) | 10023(4) | 5937(2) | 15(1) | 2.09 |
| **O(3)** | 5287(4) | 8773(4) | 7044(2) | 14(1) | 2.08 |
| **O(4)** | 7935(3) | 7607(4) | 7107(2) | 15(1) | 1.76 |
| **O(5)** | 7631(4) | 6957(4) | 5332(2) | 16(1) | 2.04 |
| **O(6)** | 8504(3) | 7953(4) | 3668(2) | 14(1) | 2.18 |
| **O(7)** | 8113(4) | 4809(4) | 4064(2) | 20(1) | 2.07 |
| **O(8)** | 9297(4) | 5631(4) | 2463(2) | 17(1) | 2.02 |
| **O(9)** | 9503(4) | 2624(5) | 3154(3) | 26(1) | 2.11 |

BVS are calculated by using the bond-valence model ($S_i = \exp [(R_o - R_i / b]$, where $R_o$ is an empirical constant with values 2.132 for K-O bonds and 1.371 for B-O bonds, $R_i$ is the length of bond *i* (in angstroms), and b = 0.37 Å.

**Table S4.** Hydrogen bonds for $K_2B_5O_8(OH)$.

| D−H···A | *d*(D−H)/Å | *d*(H−A)/Å | *d*(D−A)/Å | D−H−A/Å |
|---|---|---|---|---|
| O(9)-H(9)...O(1)#1 | 0.99 | 2.21 | 3.143(4) | 158 |
| O(9)-H(9)...O(3)#1 | 0.99 | 2.71 | 3.175(5) | 109 |
| O(9)-H(9)...O(4)#2 | 0.99 | 2.26 | 2.584(5) | 98 |

#1 3/2-X, -1+Y, -1/2+Z; #2 2-X, 1-Y, -1/2+Z

**Table S5.** Selected bond lengths (Å) and bond angles (°) for $K_2B_5O_8(OH)$.

| | | | |
|---|---|---|---|
| **B(1)-O(1)** | **1.363(5)** | **B(5)-O(7)** | **1.384(6)** |
| **B(1)-O(2)** | 1.376(6) | B(5)-O(8) | 1.349(6) |
| **B(1)-O(3)** | 1.363(6) | B(5)-O(9) | 1.365(6) |
| **B(2)-O(3)** | 1.477(6) | K(1)-O(1) | 3.015(3) |
| **B(2)-O(4)** | 1.434(5) | K(1)-O(2) | 2.812(3) |
| **B(2)-O(6)#4** | 1.498(6) | K(1)-O(3)#7 | 2.824(3) |
| **B(2)-O(8)#4** | 1.503(5) | K(1)-O(4)#6 | 3.244(3) |
| **B(3)-O(1)#5** | 1.453(5) | K(1)-O(6)#8 | 2.730(3) |
| **B(3)-O(2)** | 1.465(5) | K(1)-O(6) | 2.665(3) |
| **B(3)-O(4)** | 1.457(6) | K(1)-O(7)#1 | 3.362(3) |
| **B(3)-O(5)** | 1.480(5) | K(1)-O(9)#1 | 3.117(4) |
| **B(4)-O(5)** | 1.347(6) | K(1)-O(9)#2 | 3.076(4) |
| **B(4)-O(6)** | 1.357(6) | K(2)-O(1)#9 | 3.339(3) |
| **B(4)-O(7)** | 1.397(6) | K(2)-O(2)#9 | 2.802(3) |
| **K(2)-O(3)#10** | 2.817(3) | K(2)-O(7) | 2.876(3) |
| **K(2)-O(4)** | 3.117(3) | K(2)-O(8)#4 | 3.005(3) |
| **K(2)-O(5)** | 2.676(3) | K(2)-O(8)#11 | 2.809(3) |

| | | | |
|---|---|---|---|
| **O(1)-B(1)-O(2)** | 113.3(4) | O(1)-K(1)-O(9)#1 | 125.16(10) |
| **O(3)-B(1)-O(1)** | 124.8(4) | O(2)-K(1)-O(1) | 46.08(8) |
| **O(3)-B(1)-O(2)** | 121.9(4) | O(2)-K(1)-O(3)#7 | 162.30(10) |
| **O(3)-B(2)-O(6)#4** | 109.1(3) | O(2)-K(1)-O(4)#6 | 121.10(8) |
| **O(3)-B(2)-O(8)#4** | 106.9(3) | O(2)-K(1)-O(7)#1 | 88.64(9) |
| **O(4)-B(2)-O(3)** | 112.6(4) | O(2)-K(1)-O(9)#1 | 99.01(10) |
| **O(4)-B(2)-O(6)#4** | 108.8(4) | O(2)-K(1)-O(9)#2 | 106.70(10) |
| **O(4)-B(2)-O(8)#4** | 112.4(3) | O(3)#7-K(1)-O(1) | 117.58(8) |
| **O(6)#4-B(2)-O(8)#4** | 106.8(3) | O(3)#7-K(1)-O(4)#6 | 66.19(8) |
| **O(1)#5-B(3)-O(2)** | 110.5(3) | O(3)#7-K(1)-O(7)#1 | 98.92(9) |
| **O(1)#5-B(3)-O(4)** | 110.4(4) | O(3)#7-K(1)-O(9)#1 | 97.23(10) |
| **O(1)#5-B(3)-O(5)** | 108.3(3) | O(3)#7-K(1)-O(9)#2 | 64.95(10) |
| **O(2)-B(3)-O(5)** | 109.4(4) | O(4)#6-K(1)-O(7)#1 | 127.63(8) |
| **O(4)-B(3)-O(2)** | 110.8(3) | O(6)#8-K(1)-O(1) | 66.15(8) |
| **O(4)-B(3)-O(5)** | 107.4(3) | O(6)-K(1)-O(1) | 120.36(9) |
| **O(5)-B(4)-O(6)** | 124.9(4) | O(6)#8-K(1)-O(2) | 112.18(9) |

| | | | |
|---|---|---|---|
| **O(5)-B(4)-O(7)** | 115.0(4) | O(6)-K(1)-O(2) | 78.83(9) |
| **O(6)-B(4)-O(7)** | 120.0(4) | O(6)#8-K(1)-O(3)#7 | 51.70(8) |
| **O(8)-B(5)-O(7)** | 121.8(4) | O(6)-K(1)-O(3)#7 | 111.99(9) |
| **O(8)-B(5)-O(9)** | 123.2(4) | O(6)#8-K(1)-O(4)#6 | 109.82(9) |
| **O(9)-B(5)-O(7)** | 115.0(4) | O(6)-K(1)-O(4)#6 | 46.30(8) |
| **O(1)-K(1)-O(4)#6** | 142.72(9) | O(6)-K(1)-O(6)#8 | 151.12(9) |
| **O(1)-K(1)-O(7)#1** | 89.41(8) | O(6)-K(1)-O(7)#1 | 113.83(10) |
| **O(1)-K(1)-O(9)#2** | 97.57(9) | O(6)#8-K(1)-O(7)#1 | 93.59(9) |
| **O(6)-K(1)-O(9)#2** | 75.04(10) | O(2)#9-K(2)-O(8)#4 | 109.81(9) |
| **O(6)#8-K(1)-O(9)#1** | 125.09(10) | O(2)#9-K(2)-O(8)#11 | 116.52(9) |
| **O(6)-K(1)-O(9)#1** | 76.37(9) | O(3)#10-K(2)-O(1)#9 | 105.57(8) |
| **O(6)#8-K(1)-O(9)#2** | 76.19(10) | O(3)#10-K(2)-O(4) | 118.14(9) |
| **O(9)#1-K(1)-O(4)#6** | 88.55(9) | O(3)#10-K(2)-O(7) | 124.17(10) |
| **O(9)#2-K(1)-O(4)#6** | 48.17(8) | O(3)#10-K(2)-O(8)#4 | 122.65(9) |
| **O(9)#2-K(1)-O(7)#1** | 163.86(10) | O(4)-K(2)-O(1)#9 | 118.97(8) |
| **O(9)#1-K(1)-O(7)#1** | 41.72(8) | O(5)-K(2)-O(1)#9 | 106.89(9) |
| **O(9)#2-K(1)-O(9)#1** | 136.53(12) | O(5)-K(2)-O(2)#9 | 140.37(10) |
| **O(2)#9-K(2)-O(1)#9** | 42.64(8) | O(5)-K(2)-O(3)#10 | 147.05(10) |
| **O(2)#9-K(2)-O(3)#10** | 66.81(9) | O(5)-K(2)-O(4) | 47.46(8) |
| **O(2)#9-K(2)-O(4)** | 156.25(9) | O(5)-K(2)-O(7) | 49.11(9) |
| **O(2)#9-K(2)-O(7)** | 99.39(10) | O(5)-K(2)-O(8)#11 | 101.88(10) |
| **O(5)-K(2)-O(8)#4** | 72.33(9) | O(8)#11-K(2)-O(3)#10 | 50.37(9) |
| **O(7)-K(2)-O(1)#9** | 92.27(9) | O(8)#11-K(2)-O(4) | 69.41(9) |
| **O(7)-K(2)-O(4)** | 95.86(9) | O(8)#4-K(2)-O(4) | 46.94(8) |
| **O(7)-K(2)-O(8)#4** | 113.01(9) | O(8)#11-K(2)-O(7) | 120.89(10) |
| **O(8)#11-K(2)-O(1)#9** | 145.77(9) | O(8)#11-K(2)-O(8)#4 | 97.57(9) |
| **O(8)#4-K(2)-O(1)#9** | 74.42(8) | | |

Symmetry transformations used to generate equivalent atoms:

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

#5 x+1/2,-y+2, z; #6 -x+3/2, y, z-1/2; #7 -x+1, -y+2, z-1/2; #8 x-1/2, -y+2, z;

#9 x, y-1, z; #10 x+1/2, -y+1, z; #11 -x+2, -y+1, z+1/2; #12 -x+2, -y+1, z-1/2

**Table S6.** Atomic coordinates ($\times 10^4$ ), equivalent isotropic displacement parameters ($Å^2 \times 10^3$ ) and BVS for $CsB_5O_6(OH)_4$. $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atoms | x/a | y/b | z/c | *U*(eq) | BVS |
|---|---|---|---|---|---|
| **Cs(1)** | 8197(1) | 8384(1) | 6897(1) | 34(1) | 0.99 |
| **B(1)** | -170(8) | 5749(11) | 2830(7) | 25(2) | 3.07 |
| **B(2)** | -602(8) | 8092(11) | 3884(6) | 20(2) | 3.06 |
| **B(3)** | 1833(8) | 6935(10) | 4357(7) | 20(2) | 3.09 |
| **B(4)** | 4380(7) | 7424(11) | 5032(7) | 21(2) | 3.08 |
| **B(5)** | 3417(8) | 5589(10) | 6067(7) | 21(2) | 3.05 |
| **O(1)** | -1568(5) | 9078(7) | 4117(4) | 27(1) | 1.95 |
| **O(2)** | -1119(4) | 6796(6) | 3100(4) | 20(1) | 1.93 |
| **O(3)** | 806(4) | 8315(7) | 4388(4) | 24(1) | 1.83 |
| **O(4)** | -673(5) | 4561(7) | 1988(4) | 29(1) | 1.97 |
| **O(5)** | 2128(5) | 5847(7) | 5330(4) | 29(1) | 1.92 |
| **O(6)** | 3711(5) | 4552(7) | 6983(4) | 27(1) | 2.08 |
| **O(7)** | 3092(4) | 7793(6) | 4300(4) | 24(1) | 2.03 |
| **O(8)** | 4596(4) | 6383(7) | 5953(4) | 27(1) | 1.96 |
| **O(9)** | 5564(5) | 8019(7) | 4898(4) | 32(1) | 2.12 |
| **O(10)** | 1214(4) | 5884(6) | 3353(4) | 24(1) | 2.07 |

BVS are calculated by using the bond-valence model ($S_i$ = exp [($R_o$ - $R_i$ / b], where $R_o$ is an empirical constant with values 2.417 for Cs-O bonds and 1.371 for B-O bonds, $R_i$ is the length of bond *i* (in angstroms), and b = 0.37 Å.

**Table S7.** Selected bond lengths (Å) and bond angles (°) for $CsB_5O_6(OH)_4$.

| | | | |
|---|---|---|---|
| **Cs(1)-O(3)#1** | **3.362(5)** | **B(2)-O(3)** | **1.358(8)** |
| **Cs(1)-O(7)#2** | 3.273(5) | B(2)-O(1) | 1.354(9) |
| **Cs(1)-O(7)#1** | 3.337(5) | B(3)-O(5) | 1.445(9) |
| **Cs(1)-O(1)#3** | 3.723(5) | B(3)O-(10) | 1.463(9) |
| **Cs(1)-O(10)#2** | 3.264(5) | B(3)-O(7) | 1.464(9) |
| **Cs(1)-O(10)#4** | 3.339(5) | B(3)-O(3) | 1.492(9) |
| **Cs(1)-O(8)** | 3.753(4) | B(4)-O(8) | 1.382(9) |
| **Cs(1)-O(8)#5** | 3.679(5) | B(4)-O(7) | 1.346(8) |
| **Cs(1)-O(6)#5** | 3.092(5) | B(4)-O(9) | 1.356(9) |
| **Cs(1)-O(4)#4** | 3.297(5) | B(5)-O(5) | 1.334(8) |
| **Cs(1)-O(9)** | 3.002(5) | B(5)-O(8) | 1.398(9) |
| **B(1)-O(2)** | 1.389(9) | B(5)-O(6) | 1.364(9) |
| **B(1)-O(10)** | 1.333(9) | B(1)-O(4) | 1.367(10) |
| **B(2)-O(2)** | 1.378(9) | | |

| | | | |
|---|---|---|---|
| **O(4)#4-Cs(1)-O(8)#5** | 85.69(11) | O(9)-Cs(1)-O(3)#1 | 88.77(12) |
| **O(3)#1-Cs(1)-O(1)#3** | 44.16(11) | O(9)-Cs(1)-O(7)#1 | 66.31(13) |
| **O(3)#1-Cs(1)-O(8)** | 125.12(10) | O(7)#2-Cs(1)-O(1)#3 | 172.10(11) |
| **O(3)#1-Cs(1)-O(8)#5** | 72.49(11) | O(7)#2-Cs(1)-O(10)#4 | 83.87(12) |
| **O(7)#2-Cs(1)-O(3)#1** | 142.34(12) | O(7)#1-Cs(1)-O(10)#4 | 149.06(12) |
| **O(7)#1-Cs(1)-O(3)#1** | 42.07(11) | O(7)#2-Cs(1)-O(8) | 80.68(11) |
| **O(7)#2-Cs(1)-O(7)#1** | 122.57(12) | O(7)#1-Cs(1)-O(8) | 91.46(11) |
| **O(7)#1-Cs(1)-O(1)#3** | 65.09(12) | O(7)#2-Cs(1)-O(8)#5 | 70.75(11) |
| **O(1)#3-Cs(1)-O(8)** | 97.80(10) | O(7)#1-Cs(1)-O(8)#5 | 80.99(11) |
| **O(10)#2-Cs(1)-O(3)#1** | 121.04(12) | O(7)#2-Cs(1)-O(4)#4 | 71.19(12) |
| **O(10)#4-Cs(1)-O(3)#1** | 125.65(12) | O(9)-Cs(1)-O(1)#3 | 61.79(12) |
| **O(10)#2-Cs(1)-O(7)#1** | 84.06(12) | O(9)-Cs(1)-O(10)#2 | 88.01(13) |
| **O(10)#2-Cs(1)-O(7)#2** | 42.45(11) | O(9)-Cs(1)-O(10)#4 | 87.87(13) |
| **O(10)#4-Cs(1)-O(1)#3** | 88.23(12) | O(9)-Cs(1)-O(8)#5 | 145.69(13) |
| **O(10)#2-Cs(1)-O(1)#3** | 143.00(11) | O(9)-Cs(1)-O(8) | 38.03(12) |
| **O(10)#2-Cs(1)-O(10)#4** | 113.03(13) | O(9)-Cs(1)-O(6)#5 | 151.49(14) |
| **O(10)#2-Cs(1)-O(8)#5** | 78.20(11) | O(9)-Cs(1)-O(4)#4 | 128.55(14) |
| **O(10)#4-Cs(1)-O(8)** | 76.25(11) | O(10)-B(1)-O(2) | 122.3(7) |
| **O(10)#2-Cs(1)-O(8)** | 61.44(11) | O(10)-B(1)-O(4) | 118.8(7) |

| | | | |
|---|---|---|---|
| **O(10)#4-Cs(1)-O(8)#5** | 126.42(11) | O(4)-B(1)-O(2) | 118.9(6) |
| **O(10)#2-Cs(1)-O(4)#4** | 113.46(12) | O(3)-B(2)-O(2) | 120.2(6) |
| **O(8)#5-Cs(1)-O(1)#3** | 114.16(11) | O(1)-B(2)-O(2) | 116.3(6) |
| **O(8)#5-Cs(1)-O(8)** | 139.53(6) | O(1)-B(2)-O(3) | 123.5(6) |
| **O(6)#5-Cs(1)-O(3)#1** | 65.17(12) | O(7)-B(3)-O(3) | 108.8(6) |
| **O(6)#5-Cs(1)-O(7)#1** | 97.68(12) | O(10)-B(3)-O(3) | 108.9(5) |
| **O(6)#5-Cs(1)-O(7)#2** | 90.38(12) | O(10)-B(3)-O(7) | 107.9(6) |
| **O(6)#5-Cs(1)-O(1)#3** | 90.36(12) | O(5)-B(3)-O(3) | 108.1(6) |
| **O(6)#5-Cs(1)-O(10)#2** | 114.69(13) | O(5)-B(3)-O(7) | 112.6(5) |
| **O(6)#5-Cs(1)-O(10)#4** | 97.86(12) | O(5)-B(3)-O(10) | 110.4(6) |
| **O(6)#5-Cs(1)-O(8)#5** | 38.87(11) | O(7)-B(4)-O(8) | 122.7(6) |
| **O(6)#5-Cs(1)-O(8)** | 169.71(12) | O(7)-B(4)-O(9) | 122.0(7) |
| **O(6)#5-Cs(1)-O(4)#4** | 59.84(13) | O(9)-B(4)-O(8) | 115.3(6) |
| **O(4)#4-Cs(1)-O(3)#1** | 113.92(12) | O(5)-B(5)-O(8) | 121.7(7) |
| **O(4)#4-Cs(1)-O(7)#1** | 155.34(12) | O(5)-B(5)-O(6) | 124.1(6) |
| **O(4)#4-Cs(1)-O(1)#3** | 102.49(12) | O(6)-B(5)-O(8) | 114.3(6) |
| **O(9)-Cs(1)-O(7)#2** | 118.05(13) | O(4)#4-Cs(1)-O(8) | 111.91(12) |
| **O(4)#4-Cs(1)-O(10)#4** | 41.01(11) | | |

Symmetry transformations used to generate equivalent atoms:

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

#5 -x+3/2, y+1/2, -z+3/2; #6 x-1/2, -y+3/2, z-1/2; #7 x-1, y, z;

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

**Table S8.** Hydrogen bonds for $CsB_5O_6(OH)_4$.

| D−H···A | *d*(D−H)/Å | *d*(H−A)/Å | *d*(D−A)/Å | D−H−A/Å |
|---|---|---|---|---|
| O(1)-H(1)...O(3)#9 | 0.94 | 1.76 | 2.684(7) | 166 |
| O(9)-H(9)...O(4)#10 | 0.95 | 1.87 | 2.743(7) | 153 |
| O(4)-H(4)...O(1)#11 | 0.95 | 1.75 | 2.686(6) | 172 |
| O(6)-H(6)...O(2)#12 | 0.94 | 1.87 | 2.799(6) | 170 |

#9 -x, -y+2, -z+1; #10 -x+1/2, y+1/2, -z+1/2; #11 -x-1/2, y-1/2, -z+1/2;

#12 -x, -y+1, -z+1

**Table S9.** Atomic coordinates ($\times 10^4$ ), equivalent isotropic displacement parameters ($Å^2 \times 10^3$ ) and BVS for $CsB_5O_7(OH)_2$. $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atoms | x/a | y/b | z/c | *U*(eq) | BVS |
|---|---|---|---|---|---|
| **Cs(1)** | 835(1) | 1435(1) | 7732(1) | 36(1) | 1.03 |
| **B(1)** | 6383(10) | 8951(11) | 4820(7) | 22(2) | 3.02 |
| **B(2)** | 4204(10) | 7000(11) | 4206(7) | 21(2) | 3.09 |
| **B(3)** | 1941(10) | 4963(11) | 4037(7) | 20(2) | 3.06 |
| **B(4)** | 158(10) | 2924(12) | 4332(8) | 23(2) | 3.06 |
| **B(5)** | 17(10) | 3544(12) | 2313(7) | 23(2) | 3.04 |
| **O(1)** | 7561(7) | 9725(8) | 5715(5) | 28(1) | 1.87 |
| **O(2)** | 6237(6) | 9292(7) | 3678(4) | 25(1) | 1.87 |
| **O(3)** | 5333(6) | 7880(7) | 5101(4) | 25(1) | 1.95 |
| **O(4)** | 4102(6) | 7155(7) | 3072(4) | 26(1) | 1.79 |
| **O(5)** | 3266(6) | 5952(6) | 4588(4) | 22(1) | 2.01 |
| **O(6)** | 1203(6) | 4934(7) | 2865(4) | 23(1) | 1.81 |
| **O(7)** | 1456(6) | 3978(7) | 4804(4) | 24(1) | 1.97 |
| **O(8)** | -622(6) | 2794(7) | 3153(5) | 26(1) | 1.87 |
| **O(9)** | -335(8) | 2092(8) | 5141(5) | 31(1) | 1.89 |

BVS are calculated by using the bond-valence model ($S_i$ = exp [($R_o$ - $R_i$ / b], where $R_o$ is an empirical constant with values 2.417 for Cs-O bonds and 1.371 for B-O bonds, $R_i$ is the length of bond i (in angstroms), and b = 0.37 Å.

**Table S10.** Hydrogen bonds for $CsB_5O_7(OH)_2$.

| D−H···A | *d*(D−H)/Å | *d*(H−A)/Å | *d*(D−A)/Å | D−H−A/Å |
|---|---|---|---|---|
| O(9)-H(9)...O(1)#1 | 0.73 | 2.41 | 2.883 | 125 |
| O(1)-H(1)...O(6)#16 | 0.80 | 2.50 | 3.232 | 152 |

#1 x-1, y-1, z; #16 x+1/2, -y+3/2, z+1/2

**Table S11.** Selected bond lengths (Å) and bond angles (°) for $CsB_5O_7(OH)_2$.

| | | | |
|---|---|---|---|
| **Cs(1)-O(1)#1** | **3.378(5)** | **B(2)-O(3)** | **1.379(10)** |
| **Cs(1)-O(2)#2** | 3.641(5) | B(1)-O(3) | 1.383(10) |
| **Cs(1)-O(2)#3** | 3.460(5) | B(2)-O(4) | 1.340(9) |
| **Cs(1)-O(3)#4** | 3.322(5) | B(5)#9-O(4) | 1.498(9) |
| **Cs(1)-O(4)#5** | 3.271(6) | B(2)-O(5) | 1.359(10) |
| **Cs(1)-O(5)#4** | 3.064(5) | B(3)-O(5) | 1.380(10) |
| **Cs(1)-O(6)#6** | 3.288(5) | B(5)-O(6) | 1.498(10) |
| **Cs(1)-O(7)#4** | 3.654(5) | B(3)-O(6) | 1.337(9) |
| **Cs(1)-O(8)#7** | 3.118(5) | B(3)-O(7) | 1.377(9) |
| **Cs(1)-O(8)#8** | 3.412(5) | B(4)-O(7) | 1.377(10) |
| **Cs(1)-O(9)** | 2.970(6) | B(5)-O(8) | 1.445(10) |
| **B(1)-O(1)** | 1.363(10) | B(4)-O(8) | 1.352(10) |
| **B(5)#9-O(2)** | 1.451(10) | B(4)-O(9) | 1.361(10) |
| **B(1)-O(2)** | 1.360(9) | | |

| | | | |
|---|---|---|---|
| **O(1)#1-Cs(1)-O(2)#3** | 125.01(13) | O(5)#4-Cs(1)-O(8)#8 | 100.27(13) |
| **O(1)#1-Cs(1)-O(2)#2** | 101.62(13) | O(6)#6-Cs(1)-O(1)#1 | 83.66(13) |
| **O(1)#1-Cs(1)-O(7)#4** | 123.78(13) | O(6)#6-Cs(1)-O(2)#3 | 41.43(12) |
| **O(1)#1-Cs(1)-O(8)#8** | 57.48(14) | O(6)#6-Cs(1)-O(2)#2 | 118.06(12) |
| **O(2)#3-Cs(1)-O(2)#2** | 106.77(12) | O(6)#6-Cs(1)-O(3)#4 | 65.26(12) |
| **O(2)#3-Cs(1)-O(7)#4** | 105.11(12) | O(6)#6-Cs(1)-O(7)#4 | 141.75(11) |
| **O(2)#2-Cs(1)-O(7)#4** | 84.70(11) | O(6)#6-Cs(1)-O(8)#8 | 140.98(13) |
| **O(3)#4-Cs(1)-O(1)#1** | 104.98(14) | O(8)#7-Cs(1)-O(1)#1 | 141.77(14) |
| **O(3)#4-Cs(1)-O(2)#2** | 153.40(12) | O(8)#7-Cs(1)-O(2)#3 | 77.28(13) |
| **O(3)#4-Cs(1)-O(2)#3** | 56.57(13) | O(8)#8-Cs(1)-O(2)#2 | 71.33(12) |
| **O(3)#4-Cs(1)-O(7)#4** | 80.89(11) | O(8)#8-Cs(1)-O(2)#3 | 177.37(12) |
| **O(3)#4-Cs(1)-O(8)#8** | 124.45(13) | O(8)#7-Cs(1)-O(2)#2 | 40.23(13) |
| **O(4)#5-Cs(1)-O(1)#1** | 54.73(13) | O(8)#7-Cs(1)-O(3)#4 | 113.18(13) |
| **O(4)#5-Cs(1)-O(2)#3** | 139.77(12) | O(8)#7-Cs(1)-O(4)#5 | 130.43(14) |
| **O(4)#5-Cs(1)-O(2)#2** | 112.53(12) | O(8)#7-Cs(1)-O(6)#6 | 109.81(13) |
| **O(4)#5-Cs(1)-O(3)#4** | 83.71(13) | O(8)#8-Cs(1)-O(7)#4 | 73.06(12) |
| **O(4)#5-Cs(1)-O(6)#6** | 119.39(13) | O(8)#7-Cs(1)-O(7)#4 | 66.70(13) |
| **O(4)#5-Cs(1)-O(7)#4** | 71.10(13) | O(8)#7-Cs(1)-O(8)#8 | 100.19(12) |
| **O(4)#5-Cs(1)-O(8)#8** | 41.75(12) | O(9)-Cs(1)-O(1)#1 | 53.56(16) |

| | | | |
|---|---|---|---|
| **O(5)#4-Cs(1)-O(1)#1** | 123.86(14) | O(9)-Cs(1)-O(2)#3 | 98.17(15) |
| **O(5)#4-Cs(1)-O(2)#2** | 119.97(12) | O(9)-Cs(1)-O(2)#2 | 65.81(14) |
| **O(5)#4-Cs(1)-O(2)#3** | 79.03(12) | O(9)-Cs(1)-O(3)#4 | 132.23(15) |
| **O(5)#4-Cs(1)-O(3)#4** | 41.91(13) | O(9)-Cs(1)-O(4)#5 | 105.25(15) |
| **O(5)#4-Cs(1)-O(4)#5** | 74.36(13) | O(9)-Cs(1)-O(5)#4 | 174.04(15) |
| **O(5)#4-Cs(1)-O(6)#6** | 104.98(12) | O(9)-Cs(1)-O(6)#6 | 69.87(15) |
| **O(5)#4-Cs(1)-O(7)#4** | 39.02(12) | O(9)-Cs(1)-O(7)#4 | 146.75(14) |
| **O(5)#4-Cs(1)-O(8)#7** | 88.12(14) | O(9)-Cs(1)-O(8)#8 | 82.76(15) |
| **O(9)-Cs(1)-O(8)#7** | 96.43(15) | O(6)-B(3)-O(5) | 123.4(7) |
| **O(4)-B(2)-O(3)** | 121.6(7) | O(6)-B(3)-O(7) | 122.7(7) |
| **O(4)-B(2)-O(5)** | 124.4(7) | O(7)-B(3)-O(5) | 113.9(6) |
| **O(5)-B(2)-O(3)** | 114.0(6) | O(8)-B(4)-O(7) | 122.6(7) |
| **O(2)#15-B(5)-O(4)#15** | 112.2(6) | O(8)-B(4)-O(9) | 122.3(7) |
| **O(2)#15-B(5)-O(6)** | 108.4(7) | O(9)-B(4)-O(7) | 115.0(7) |
| **O(4)#15-B(5)-O(6)** | 105.9(6) | O(1)-B(1)-O(3) | 118.8(7) |
| **O(8)-B(5)-O(2)#15** | 110.3(6) | O(2)-B(1)-O(1) | 119.4(7) |
| **O(8)-B(5)-O(4)#15** | 108.2(6) | O(2)-B(1)-O(3) | 121.8(7) |
| **O(8)-B(5)-O(6)** | 111.8(6) | | |

Symmetry transformations used to generate equivalent atoms:

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

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

#6 -x, -y+1, -z+1; #7 x+1/2, -y+1/2, z+1/2; #8 -x,-y, -z+1;

#9 -x+1/2, y+1/2, -z+1/2; #10 x+1, y+1, z; #11 x+1/2, -y+3/2, z-1/2;

#12 -x+1/2, y+1/2, -z+3/2; #13 x+1/2, -y+1/2, z-1/2; #14 x-1/2, -y+1/2, z-1/2;

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

**Table S12.** The structural comparison of alkali and alkaline-earth metal hydroxyborates containing five boron atoms.

| NO. | Compounds | Space group (No.) | FBB | Number of shared O atoms | Dimension | Ref. |
|---|---|---|---|---|---|---|
| **1** | $Li_3(B_5O_8(OH)_2)$ | $P4_12_12$(92) | $B_5O_{10}(OH)_2$ | 2 | 2 | [1] |
| **2** | $Li_3(B_5O_8(OH)_2)$ | *Pnc*2(30) | $B_5O_{10}(OH)_2$ | 2 | 2 | [2] |
| **3** | $Li((OH)_2B_5O_7)$ | $P2_1/c$(14) | $B_5O_7(OH)_2$ | 1 | 1 | [3] |
| **4** | $Li(B_5O_6(OH)_4)(H_2O)_3$ | *C*2/*c*(15) | $B_5O_6(OH)_4$ | 0 | 0 | [4] |
| **5** | $Li_3(B_5O_8(OH)_2)$ | $P4_32_12$(96) | $B_5O_{10}(OH)_2$ | 3 | 3 | [5] |
| **6** | $(Na(H_2O))_2(B_5O_8(OH))$ | $Pna2_1$(33) | $B_5O_{10}(OH)$ | 2 | 2 | [6] |
| **7** | $Na(B_5O_6(OH)_4)$ | $P2_1/c$(14) | $B_5O_6(OH)_4$ | 0 | 0 | [7] |
| **8** | $Na(B_5O_6(OH)_4)(H_2O)_3$ | *C*2/*c*(15) | $B_5O_6(OH)_4$ | 0 | 0 | [8] |
| **9** | $Na(B_5O_7(OH)_2(H_2O)$ | $Pca2_1$(29) | $B_5O_8(OH)_2$ | 1 | 1 | [9] |
| **10** | $Na(B_5O_8(OH)_2(H2O)_3$ | *C*2/*c*(15) | $B_5O_8(OH)_2$ | 0 | 0 | [10] |
| **11** | $Na_2B_5O_8(OH)(H_2O)_2$ | $Pna2_1$(33) | $B_5O_{10}(OH)$ | 2 | 2 | [11] |
| **12** | $Na_3(B_5O_8(OH)_2)(H_2O)$ | *Pbca*(61) | $B_5O_{10}(OH)_2$ | 2 | 2 | [12] |
| **13** | $Na_4(B_5O_7(OH)_3)_2(H_2O)_4$ | $P\bar{1}$(2) | $B_{10}O_{14}(OH)_6$ | 0 | 0 | [13] |
| **14** | $K(B_5O_6(OH)_4)(H_2O)_2$ | *Aba*2(41) | $B_5O_6(OH)_4$ | 0 | 0 | [14] |
| **15** | $K(B_5O_7(OH)_2)$ | $P2_1/c$(14) | $B_5O_8(OH)_2$ | 1 | 1 | [15] |
| **16** | $K(B_5O_7(OH)_2)(H_2O)$ | $P2_1/c$(14) | $B_5O_8(OH)_2$ | 1 | 1 | [16] |
| **17** | $K(B_5O_7(OH)_2)(H_2O)$ | $P2_1/c$(14) | $B_5O_8(OH)_2$ | 1 | 1 | [17] |
| **18** | $K_2(B_5O_8(OH))(H_2O)_2$ | $Pna2_1$(33) | $B_5O_{10}(OH)$ | 2 | 2 | [18] |
| **19** | $K_3B_5O_8(OH)_2$ | *Fdd*2(43) | $B_5O_8(OH)_2$ | 0 | 0 | [19] |
| **20** | $RbB_5O_6(OH)_4(H_2O)_2$ | *Aba*2(41) | $B_5O_6(OH)_4$ | 0 | 0 | [20] |
| **21** | $RbB_5O_7(OH)_2)(H_2O)_{0.5}$ | $P\bar{1}$(2) | $B_5O_8(OH)_2$ | 1 | 1 | [21] |
| **22** | $Cs(B_5O_6(OH)_4)(H_2O)_2$ | $P2_1/c$(14) | $B_5O_6(OH)_4$ | 0 | 0 | [22] |
| **23** | $Cs(B_5O_6(OH)_4)(H_2O)_2$ | *C*2/*c*(15) | $B_5O_6(OH)_4$ | 0 | 0 | [23] |
| **24** | $Ca(B_5O_8(OH))(B(OH)_3)(H_2O)_3$ | $P2_1/c$(14) | $B_5O_{10}(OH)$ | 2 | 2 | [24] |
| **25** | $Ca(B_5O_8(OH))(H_2O)$ | $P2_1/c$(14) | $B_5O_{10}(OH)$ | 2 | 2 | [25] |
| **26** | $Ca_2(B_5O_7)(OH)_5(H20)$ | $P2_1/c$(14) | $B_5O_8(OH)_5$ | 1 | 1 | [26] |
| **27** | $Ca_2(B_5O_8(OH))_2(B(OH)_3)(H_2O)$ | *P*1(1) | $B_{10}O_{20}(OH)_2$ | 2 | 2 | [27] |
| **28** | $Ca_2(B_5O_8(OH))_2(B(OH)_3)(H_2O)$ | $P2_1$(4) | $B_{10}O_{20}(OH)_2$ | 2 | 2 | [28] |
| **29** | $Ca_2(B_5O_9)(OH)(H_2O)$ | $C_C$(9) | $B_5O_{11}(OH)$ | 2 | 2 | [29] |
| **30** | $B_5Sr_2O_9(OH)$ | $P2_1/c$(14) | $B_5O_{11}(OH)$ | 2 | 2 | [30] |
| **31** | $Sr(B_5O_8(OH))(H_2O)$ | $P\bar{1}$(2) | $B_5O_{10}(OH)$ | 2 | 2 | [31] |
| **32** | $Sr_2(B_5O_8(OH))_2(B(OH)_3)(H_2O)$ | $C_C$(9) | $B_5O_{10}(OH)$ | 2 | 2 | [32] |
| **33** | $Sr_2(B_5O_8(OH))_2B(OH)_3(H_2O)$ | $P2_1$(4) | $B_{10}O_{20}(OH)_2$ | 2 | 2 | [33] |
| **34** | $Ba(B_5O_8(OH))(H_2O)$ | $P\bar{1}$(2) | $B_5O_{10}(OH)$ | 2 | 2 | [34] |

| | | | | | | |
|---|---|---|---|---|---|---|
| **35** | $Ba_2(B_5O_8(OH))_2(B(OH)_3)(H_2O)$ | $P2_1(4)$ | $B_{10}O_{20}(OH)_2$ | 2 | 2 | [35] |
| **36** | $Ba_2(B_5O_8(OH)_2)(OH)$ | $P2_1/c(14)$ | $B_5O_{10}(OH)_2$ | 2 | 2 | [36] |
| **37** | $Ba_2B_5O_9(OH)$ | $P2_1/c(14)$ | $B_5O_{11}(OH)$ | 2 | 2 | [30] |
| **38** | $K_2B_5O_8(OH)$ | $Pca2_1(29)$ | $B_5O_{10}(OH)$ | 2 | 2 | This work |
| **39** | $CsB_5O_6(OH)_4$ | $P2_1/c(14)$ | $B_5O_6(OH)_4$ | 0 | 0 | This work |
| **40** | $CsB_5O_7(OH)_2$ | $P2_1/c(14)$ | $B_5O_8(OH)_2$ | 1 | 1 | This work |

**Table S13.** The calculated bonding electron density differences ($\Delta\rho$) of different units in $K_2B_5O_8(OH)$, $CsB_5O_6(OH)_4$, and $CsB_5O_7(OH)_2$. Using the response electron distribution anisotropy (REDA) method.

| | **units** | $\Delta\rho$ | $\Delta\omega$ |
|---|---|---|---|
| **$K_2B_5O_8(OH)$** | $BO_3$ | 0.008943 | 58.8 % |
| | $BO_4$ | 0.001253 | 8.2 % |
| | $BO_2(OH)$ | 0.004197 | 27.6 % |
| | $KO_9$ | 0.000638 | 4.2 % |
| | $KO_8$ | 0.000171 | 1.1 % |
| **$CsB_5O_6(OH)_4$** | $BO_2(OH)$ | 0.016789 | 93.4 % |
| | $BO_4$ | 0.000443 | 2.5 % |
| | $CsO_{11}$ | 0.000747 | 4.2 % |
| **$CsB_5O_7(OH)_2$** | $BO_3$ | 0.010603 | 47.5 % |
| | $BO_2(OH)$ | 0.010541 | 47.2 % |
| | $BO_4$ | 0.000318 | 1.4 % |
| | $CsO_9$ | 0.000866 | 3.9 % |

**Table S14.** The number of hydroxyl groups in the unit cell, the density of hydroxyl groups, and the layer spacing between adjacent layers of $K_2B_5O_8(OH)$, $CsB_5O_6(OH)_4$, and $CsB_5O_7(OH)_2$.

| **Compounds** | **The number of hydroxyl groups in the unit cell** | **The density of hydroxyl groups (n/V) ($Å^{-3}$)** | **The spacing between adjacent layers (Å)** |
|---|---|---|---|
| $K_2B_5O_8(OH)$ | 4 | 4.92 | 7.33 |
| $CsB_5O_6(OH)_4$ | 16 | 17.08 | 7.61 |
| $CsB_5O_7(OH)_2$ | 8 | 10.19 | 7.70 |

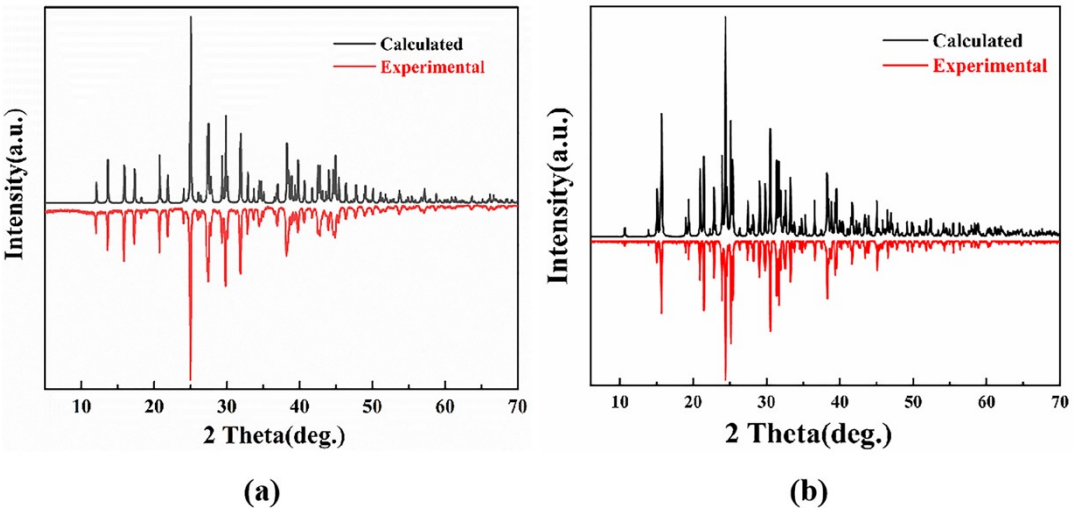


**Figure S1.** Experimental and calculated X-ray powder diffraction patterns of (a) $K_2B_5O_8(OH)$ and (b) $CsB_5O_7(OH)_2$.

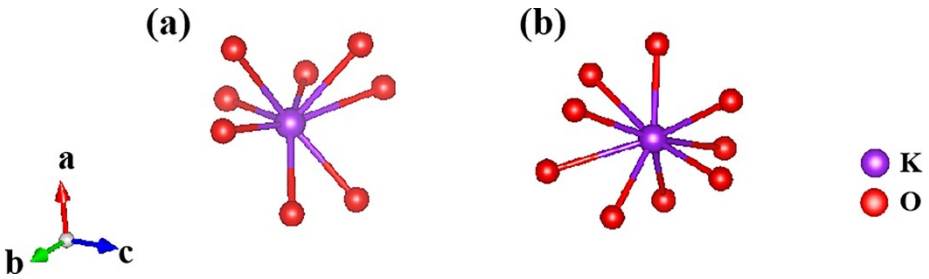


**Figure S2.** Coordination form of K in $K_2B_5O_8(OH)$: (a) [$KO_8$], (b) [$KO_9$].

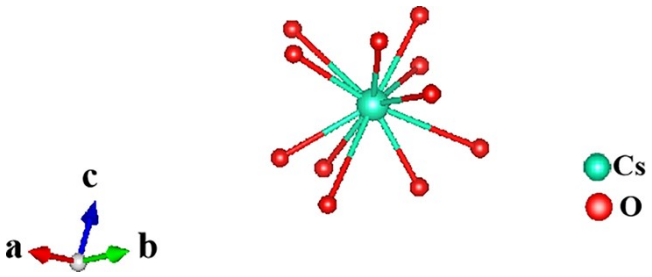


**Figure S3.** Coordination form of Cs in $CsB_5O_6(OH)_4$: [$CsO_{11}$].

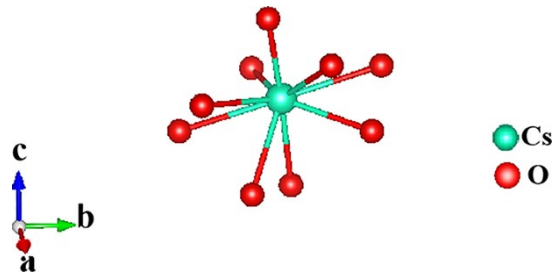


**Figure S4.** Coordination form of Cs in $CsB_5O_7(OH)_2$: $[CsO_9]$.

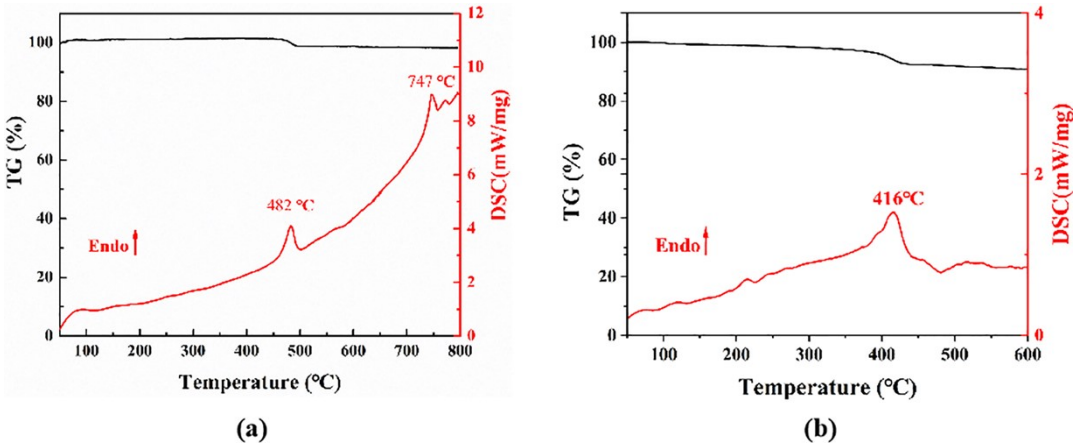


**Figure S5.** TG−DSC curves of (a) $K_2B_5O_8(OH)$ and (b) $CsB_5O_7(OH)_2$.

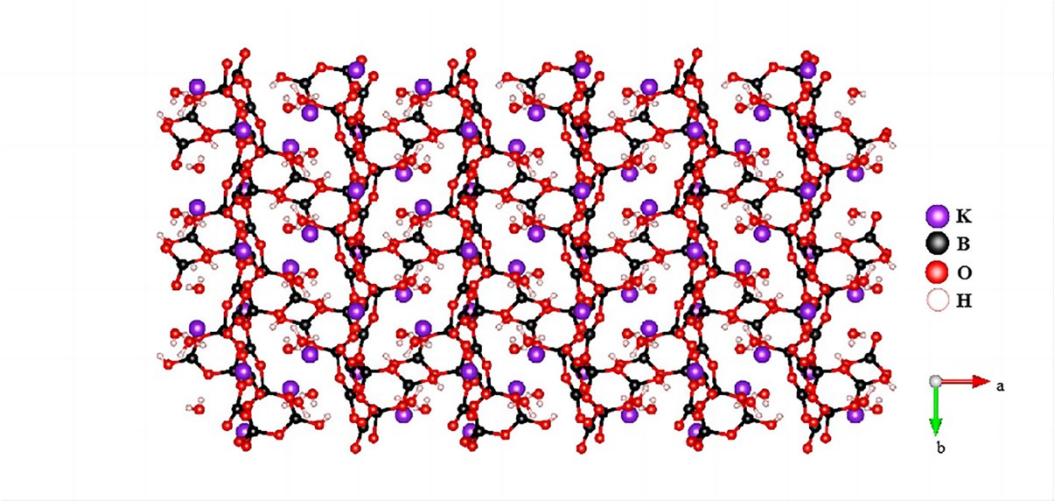


**Figure S6.** Crystal structure of $K_2B_5O_8(OH)\cdot 2H_2O$.

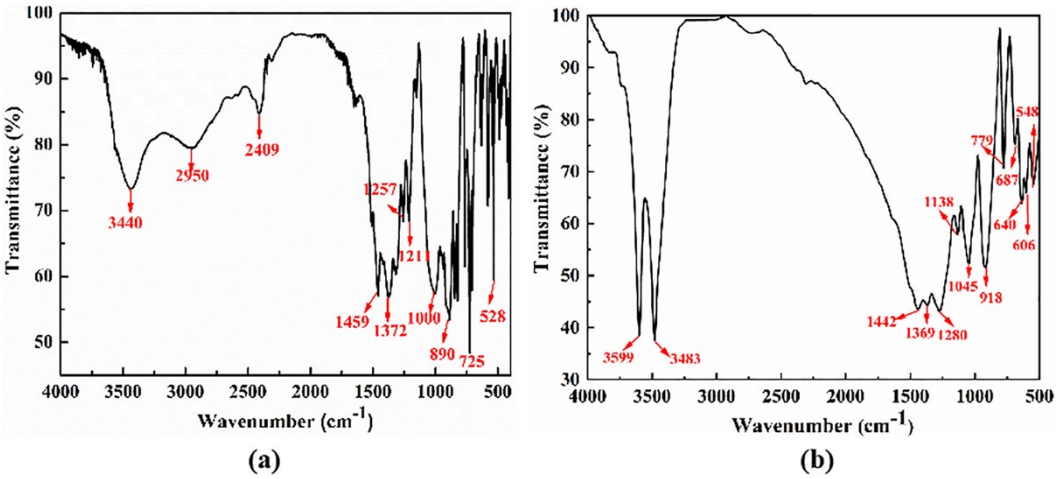


**Figure S7.** IR spectra of (a) $K_2B_5O_8(OH)$ and (b) $CsB_5O_7(OH)_2$.

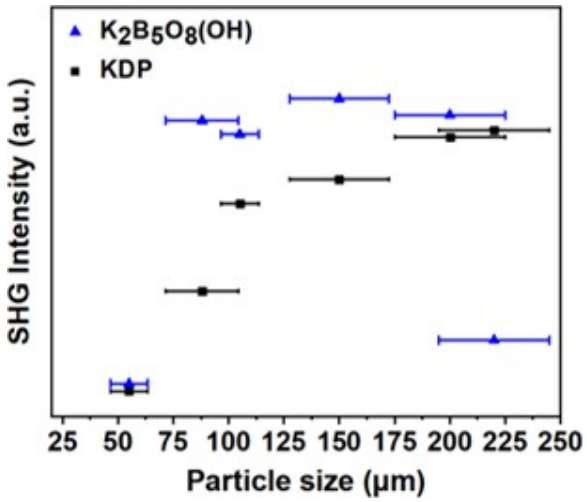


**Figure S8.** Phase-matching SHG signals for $K_2B_5O_8(OH)$ and standard KDP with 1064 nm laser radiation.

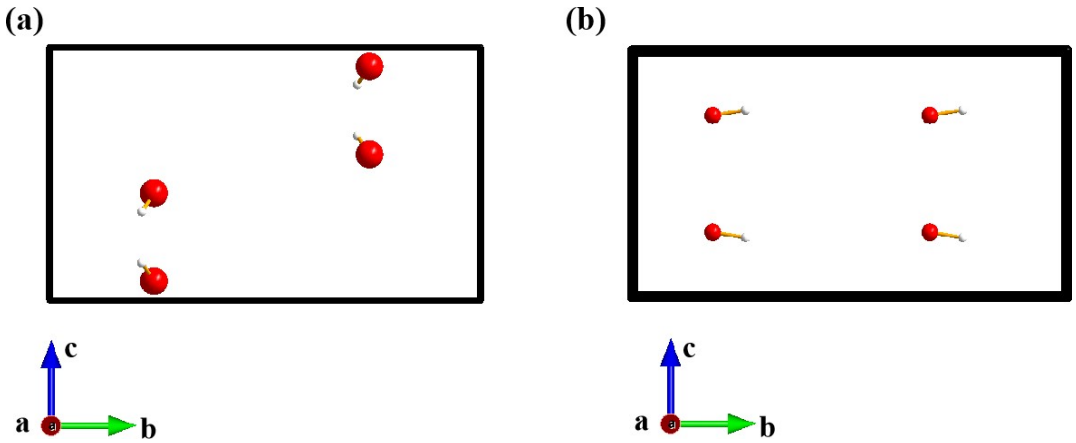


**Figure S9.** The arrangement of hydroxyl groups within the unit cell: (a) $Na_2B_5O_8(OH)\cdot 2H_2O$ and (b) $K_2B_5O_8(OH)$.

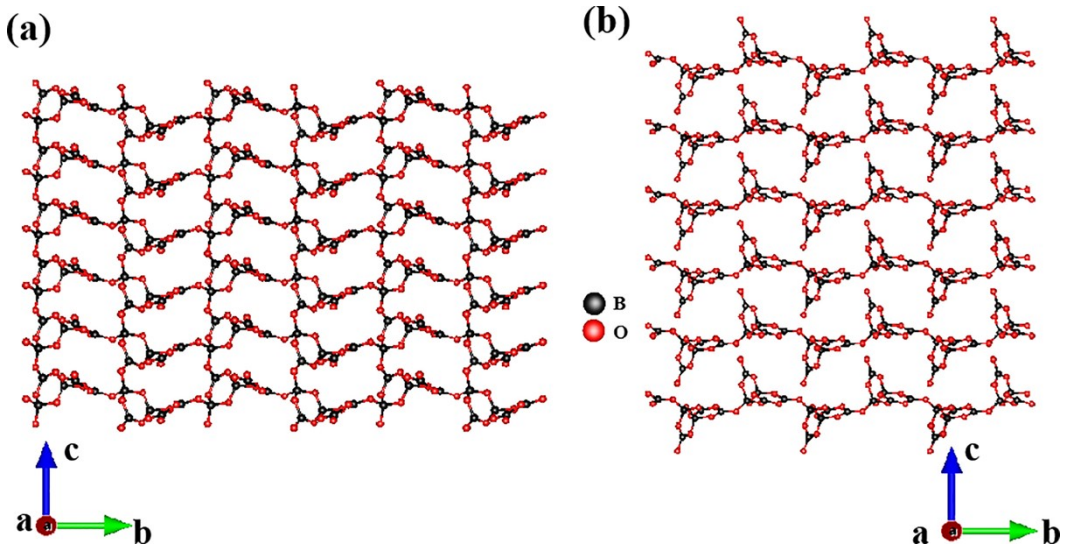


**Figure S10.** Arrangement of boron-oxygen groups in two-dimensional layered structures: (a) $K_2B_5O_8(OH)$ and (b) $Na_2B_5O_8(OH)\cdot 2H_2O$.

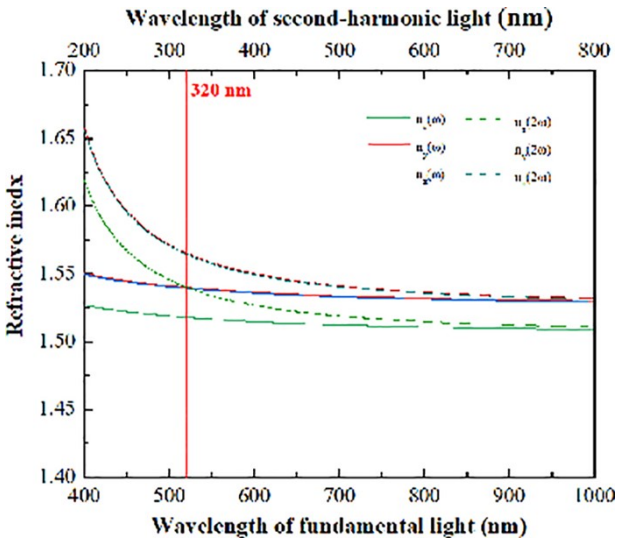


**Figure S11.** Predicted shortest SHG phase-matching wavelength for $K_2B_5O_8(OH)$.

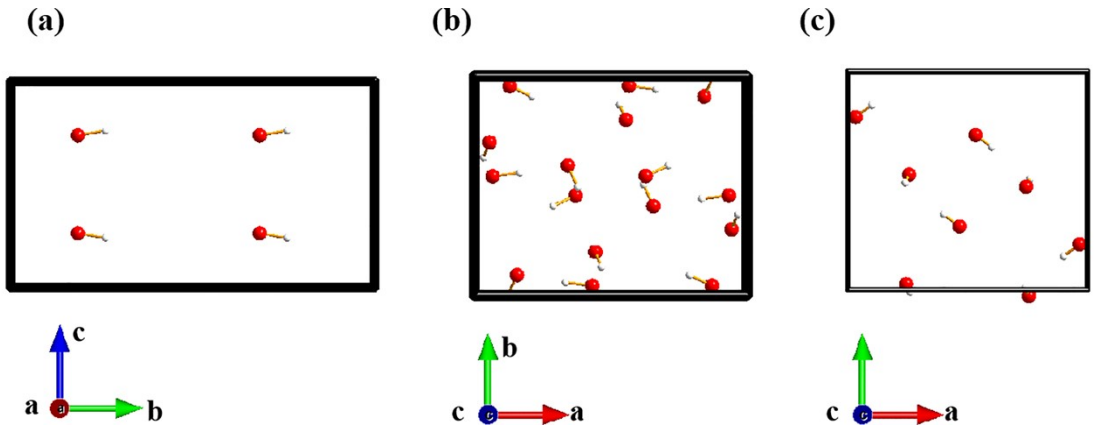


**Figure S12.** The number of hydroxyl groups in the unit cell of (a)$K_2B_5O_8(OH)$, (b)$CsB_5O_6(OH)_4$, and (c) $CsB_5O_7(OH)_2$.

# References


1. A. A. Sheviren, L. A.Muradyan, V. I. Simonov, Yu. K. Egorov Tismenko, M. A. Simonov and N. V. Belov, The Deformation Electronic Density in Lithium Borate $Li_3B_5O_8(OH)_2$, *Dokl. Akad. Nauk SSSR*, 1981, **257**, 111-114.
2. E. V. Sokolova, N. A. Yamnova and N. V. Belov, Crystal Structure of Orthorhombic Li-Borate $Li_3(B_5O_8(OH)_2)$, *Kristallogr.,* 1980, **25**,716-721.
3. A. Cárdenas, J. Solans, K. Byrappa and K. V. K. Shekar, Structure of Lithium Catena-Poly[3,4-Dihydroxopentaborate-1:5-μ-oxo], *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1993, **49**, 645-647.
4. M. Touboul, E. Bétourné and L. Seguin, Crystal Structure of $LiB_5O_8{\cdot}5H_2O$, *Mater. Sci. Forum*, 1996, **228-231**, 741-746.
5. P. Li and Z. H. Liu, Hydrothermal Synthesis, Characterization, and Thermodynamic Properties of a New Lithium Borate, $Li_3B_5O_8(OH)_2$, *J. Chem. Eng. Data*, 2010, **55**, 2682-2686.
6. E. Corazza, S. Menchetti and C. Sabelli, The Crystal Structure of Nasinite, $Na_2[B_5O_8(OH)]{\cdot}2H_2O$, *Acta Crystallogr., Sect. B*, 1975, **31**, 2405-2410.
7. S. Menchetti and C. Sabelli, The Crystal Structure of $NaB_5O_6(OH)_4$, *Acta Crystallogr., Sect. B*, 1978, **34**, 45-49.
8. U. Timper, G. Heller and M. Shakibaie-Moghadam, Sborgit und β-Sborgit — Eine Zweite Synthetische Modifikation von $Na[B_5O_6(OH)_4] \cdot 3\ H_2O$ / Sborgit and β-Sborgit – a Second Synthetic Modification of $Na[B_5O_6(OH)_4] \cdot 3\ H_2O$, *Z. Naturforsch., B*, 1990, **45**, 1155-1166.
9. C. Wu, L. H. Li, J. L. Song, G. Yang, M. G. Humphrey and C. Zhang, Facile Syntheses of $Ba_2[B_4O_7(OH)_2]$ and $Na[B_5O_7(OH)_2](H_2O)$ Borate Salts Exhibiting Nonlinear Optical Activity in the Ultraviolet, *Inorg. Chem.*, 2017, **56**, 1340-1348.
10. Y. J. Wang, A. Q. Jia, X. S. Chen, H. T. Shi and Q. F. Zhang, Syntheses and Crystal Structures of Two New Sodium Borates $[Na_2(H_2O)_3][B_5O_8(OH)_2]$ and $Na[enH_2][B_7O_{10}(OH)_4]$, *Z. Naturforsch., B*, 2016, **71**, 15-21.
11. Y. J. Wang, S. L. Pan, X. L. Tian, Z. X. Zhou, G. Liu, J. Wang and D. Z. Jia, Synthesis, Structure, and Properties of the Noncentrosymmetric Hydrated Borate $Na_2B_5O_8(OH){\cdot}2H_2O$, *Inorg. Chem.*, 2009, **48**, 7800-7804.
12. S. Menchetti and C. Sabelli, The Crystal Structure of Synthetic Sodium Pentaborate Monohydrate, *Acta Crystallogr., Sect. B*, 1977, **33**, 3730-3733.
13. E. Cannillo, A. Dal Negro and L. Ungaretti, The Crystal Structure of Ezcurrite, *Am. Mineral.*, 1973, **58**, 110-115.
14. J. P. Ashmore and H. E. Petch, Hydrogen Positions in Potassium Pentaborate Tetrahydrate as Determined by Neutron Diffraction, *Can. J. Phys*, 1970, **48**, 1091-1097.
15. Q. Wu, Potassium Pentaborate, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, 2011, **67**, i67-i67.
16. H. X. Zhang, J. Zhang, S. T. Zheng and G. Y. Yang, Two New Potassium Borates, $K_4B_{10}O_{15}(OH)_4$ with Stepped Chain and $KB_5O_7(OH)_2{\cdot}H_2O$ with Double Helical Chain, *Cryst. Growth Des.*, 2004, **5**, 157-161.
17. 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. Yarzhemskiite.

Pushcharovsky, $K[B_5O_7(OH)_2]\cdot H_2O$, a New Mineral from the Chelkar Salt Dome, *Western Kazakhstan. Mineral. Mag.,* 2020, **84**, 335-342.

18. Y. T. Shi, M. Luo, C. S. Lin, G. Peng and N. Ye, Two Deep Ultraviolet Hydrated Borate Crystals: Centrosymmetric $LiRbB_5O_8(OH)\cdot H_2O$ and Non-Centrosymmetric $K_2B_5O_8(OH)\cdot 2H_2O$, *Cryst. Growth Des.*, 2019, **19**, 3052-3059.
19. F. H. Ding, M. L. Nisbet, W. G. Zhang, P. S. Halasyamani, L. Y. Chai and K. R. Poeppelmeier, Why Some Noncentrosymmetric Borates Do Not Make Good Nonlinear Optical Materials: A Case Study with $K_3B_5O_8(OH)_2$, *Inorg. Chem.*, 2018, **57**, 11801-11808.
20. H. Behm, Rubidium Pentaborate Tetrahydrate, $Rb[B_5O_6(OH)_4]\cdot 2H_2O$, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, **40**, 217-220.
21. E. L. Belokoneva, T. A. Borisova and O. V. Dimitrova, New Rubidium Pentaborate $Rb(B_5O_7(OH)_2)\cdot 0.5(H_2O)$ with a 5:(4Δ+1T) Anionic Block and its Relation to Larderellite $(NH_4)(B_5O_7(OH)_2)\cdot(H_2O)$ on the Basis of the OD Theory, *Kristallogr.,* 2003, **48**, 634-641.
22. H. Behm, Structure Determination on a Twinned Crystal of Cesium Pentaborate Tetrahydrate, $Cs(B_5O_6(OH)_4)(H_2O)_2$, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1984, **40**, 1114-1116.
23. N. Penin, L. Seguin, B. Gérand, M. Touboul and G. Nowogrocki, Crystal Structure of a New form of $Cs[B_5O_6(OH)_4]\cdot 2H_2O$ and Thermal Behavior of $M[B_5O_6(OH)_4]\cdot 2H_2O$ (M=Cs, Rb, Tl), *J. Alloys Compd.*, 2002, **334**, 97-109.
24. J. A. Konnert, J. R. Clark and C. L. G. Christ, $CaB_5O_8(OH)B(OH)_3(H_2O)_3$: Crystal Structure and Comparison with Related Borates, *Am. Mineral.,* 1972, **57,** 381-396.
25. N. A. Yamnova, Y. K. E. Tismenko, N. V. Zubkova, O. V. Dimitrova, A. P. Kantor, Danian and Y. Ming X. Crystal Structure of New Synthetic Calcium Pentaborate $Ca(B_5O_8(OH))H_2O$ and its Relation to Pentaborates with Similar Boron-Oxygen Radicals, *Kristallogr.*, 2003, **48**, 608-613.
26. K. S. Wallwork, Pring A., M. R. Taylor and B. A. Hunter, The Structure of Priceite, a Basic Hydrated Calcium Borate, by ab Initio Powder-diffraction Methods, *Can. Mineral*, 2002, **40**, 1199-1206.
27. Q. M. Qiu, X. Y. Li, C. A. Chen, K. N. Sun and G. Y. Yang, Polar Polymorphism: β-$Ca_2[B_5O_8(OH)]_2[B(OH)_3]\cdot H_2O$. Synthesis, Structure and Nonlinear Optical Property, *Solid State Chem*, 2021, **299**, 122193.
28. Q. Wei, L. Sun, J. Zhang and G. Y. Yang, Two Deep-ultraviolet Nonlinear Optical Alkaline-Earth Metal Borates Based on Different Types of Oxoboron Clusters, *Dalton Trans.*, 2017, **46**, 7911-7916.
29. Q. Wei, J. W. Cheng, C. He and G. Y. Yang, An Acentric Calcium Borate $Ca_2[B_5O_9](OH)H_2O$: Synthesis, Structure, and Nonliner Optical Property, *Inorg. Chem.*, 2014, **53**, 11757-11763.
30. C. McMillen, C. Heyward, H. Giesber and J. Kolis, Crystal Structures of the Novel Hydrated Borates $Ba_2B_5O_9(OH)$, $Sr_2B_5O_9(OH)$ and $Li_2Sr_8B_{22}O_{41}(OH)_2$, *Solid State Chem.*, 2011, **184**, 2966-2971.
31. G. Huang, R. Pan, H. He, B. F. Yang and G. Y. Yang, Two New Borates Made of $[B_5O_6(OH)_4]^-$ and $[B_5O_{10}(OH)]^{6-}$ Clusters, Accompanying a Novel in Situ Organic Reaction, *Cluster Sci.*, 2015, **26**, 2023-2032.
32. J. R. Clark and C. L. Christ, Veatchite: Crystal Structure and Correlations with Pveatchite, *Am. Mineral.*, 1971, **56**, 1934-1954.

33. I. M. Rumanova and O. Gandymov, The Crystal Structure of the Natural Strontium Borate, P-Veatchite, $Sr_2(B_5O_8(OH)_2)B(OH)_3H_2O$, *Kristallogr.,* 1971, **16**, 99-106.
34. D. Y. Pushcharovskii, S. Merlino, O. Ferro, S. A. Vinogradova and O. V. Dimitrova, The Crystal Structures of Two New Ba Borates: Pentaborate Hydrate, $Ba(B_5O_8(OH))\cdot(H_2O)$, and Decaborate, $LiBa_2(B_{10}O_{16}(OH)_3)$. *J. Alloys Compd.*, 2000, **306**, 163-169.
35. H. Q. Wu and Y. Y. Li, A New Acentric Borate of $Ba_2[B_5O_8(OH)]_2[B(OH)_3]\cdot H_2O$. Synthesis, Structure and Nonlinear Optical Property, *Inorg. Chem. Commun.*, 2020, **121**, 108220.
36. E. L. Belokoneva, O. V. Dimitrova and S. Y. Stefanovich, Structures and Properties of Layered Barium Borates $Ba_{0.975}[B_6O_9(OH)(O_{0.975}Br_{0.025})\cdot B_2O(OH)_3]$, $Ba_2[B_5O_8(OH)_2](OH)$, $Na_2Ba_2[B_{20}O_{34}(OH)_4]$, and $Ba_5[B_{20}O_{33}(OH)_4]H_2O$, *Crystallogr. Rep.*, 2012, **57**, 64-72.