Supporting Information

Synthesis, characterization and theoretical studies of the nonlinear optical crystal \( \text{Sr}_2\text{B}_5\text{O}_9(\text{OH})\cdot\text{H}_2\text{O} \)

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Single crystal X-ray diffraction measurement

Single crystal X-ray diffraction data were collected at RT on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å). The data were integrated using the SAINT program, and numerical absorption corrections were performed using the SADABS program. The structure was solved by direct method and refined with a full-matrix least-squares technique using programs from the SHELXL crystallographic software package. Anisotropic thermal parameters were applied to all nonhydrogen atoms. Hydrogen atoms were placed in geometrically idealized positions. The structure was verified using the Addsym subroutine of PLATON and no higher symmetries were found.
Table S1. Crystal data and structural refinement for Sr$_2$B$_5$O$_9$(OH)-H$_2$O at 297K

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Sr$_2$B$_5$O$_9$(OH)-H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>Sr$_2$B$_5$O$_9$(OH)-H$_2$O</td>
</tr>
<tr>
<td>fw /g·mol$^{-1}$</td>
<td>408.31</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>C2 (No. 5)</td>
</tr>
<tr>
<td>$a$ / Å</td>
<td>10.2342(15)</td>
</tr>
<tr>
<td>$b$ / Å</td>
<td>8.0240(13)</td>
</tr>
<tr>
<td>$c$ / Å</td>
<td>6.3898(9)</td>
</tr>
<tr>
<td>$\beta$ / deg</td>
<td>127.882(7)</td>
</tr>
<tr>
<td>$V$ / Å$^3$</td>
<td>414.15(11)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>$\rho_{\text{calc}}$ / g·cm$^{-3}$</td>
<td>3.274</td>
</tr>
<tr>
<td>$\mu$ / mm$^{-1}$</td>
<td>12.938</td>
</tr>
<tr>
<td>$F$(000)</td>
<td>384</td>
</tr>
<tr>
<td>crystal size / mm$^3$</td>
<td>0.146 $\times$ 0.110 $\times$ 0.085</td>
</tr>
<tr>
<td>$\theta$ max / deg</td>
<td>27.45</td>
</tr>
<tr>
<td>reflections collected / unique</td>
<td>2374 / 867</td>
</tr>
<tr>
<td>$R$ (int)</td>
<td>0.0246</td>
</tr>
<tr>
<td>completeness</td>
<td>100 %</td>
</tr>
<tr>
<td>GOF on $R^2$</td>
<td>0.940</td>
</tr>
<tr>
<td>$R_1$, w$R_2$ (I$&gt;2\sigma$(I))$^a$</td>
<td>0.0174, 0.0392</td>
</tr>
<tr>
<td>$R_1$, w$R_2$ (all data)</td>
<td>0.0183, 0.0395</td>
</tr>
<tr>
<td>flack parameter</td>
<td>0.006(9)</td>
</tr>
</tbody>
</table>

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

53
Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for Sr$_2$B$_5$O$_9$(OH)·H$_2$O. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Wyckoff positions</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>$U_{eq}$</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr1</td>
<td>4c</td>
<td>7046(1)</td>
<td>5352(1)</td>
<td>9147(1)</td>
<td>10(1)</td>
<td>2.1</td>
</tr>
<tr>
<td>B1</td>
<td>4c</td>
<td>9257(5)</td>
<td>2504(6)</td>
<td>7442(7)</td>
<td>9(1)</td>
<td>3.0</td>
</tr>
<tr>
<td>B2</td>
<td>2b</td>
<td>5000</td>
<td>9164(7)</td>
<td>5000</td>
<td>8(1)</td>
<td>3.0</td>
</tr>
<tr>
<td>B3</td>
<td>4c</td>
<td>7666(5)</td>
<td>5038(6)</td>
<td>5073(8)</td>
<td>10(1)</td>
<td>3.0</td>
</tr>
<tr>
<td>O1</td>
<td>4c</td>
<td>6466(3)</td>
<td>6092(3)</td>
<td>4532(5)</td>
<td>9(1)</td>
<td>2.1</td>
</tr>
<tr>
<td>O2</td>
<td>4c</td>
<td>7991(3)</td>
<td>3748(3)</td>
<td>6753(5)</td>
<td>9(1)</td>
<td>2.0</td>
</tr>
<tr>
<td>O3</td>
<td>2a</td>
<td>5000</td>
<td>6713(4)</td>
<td>10000</td>
<td>8(1)</td>
<td>2.0</td>
</tr>
<tr>
<td>O4</td>
<td>4c</td>
<td>5673(3)</td>
<td>2611(4)</td>
<td>8933(6)</td>
<td>18(1)</td>
<td>0.6$^a$</td>
</tr>
<tr>
<td>O5</td>
<td>4c</td>
<td>5531(3)</td>
<td>8245(3)</td>
<td>7358(5)</td>
<td>7(1)</td>
<td>2.1</td>
</tr>
<tr>
<td>O6</td>
<td>4c</td>
<td>8559(2)</td>
<td>5262(5)</td>
<td>14149(4)</td>
<td>10(1)</td>
<td>2.0</td>
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</tbody>
</table>

$^a$ bond valence sum of O4 without hydrogen coordinates.
Table S3 Selected bond lengths (Å) and bond angles (deg.) for Sr$_2$B$_5$O$_9$(OH)·H$_2$O$^a$

<table>
<thead>
<tr>
<th></th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr1–O6</td>
<td>2.555(2)</td>
<td>O3$^#7$–B1–O5$^#7$ 111.0(3)</td>
</tr>
<tr>
<td>Sr1–O4</td>
<td>2.563(3)</td>
<td>O3$^#7$–B1–O2 112.9(3)</td>
</tr>
<tr>
<td>Sr1–O2</td>
<td>2.598(3)</td>
<td>O5$^#7$–B1–O2 110.4(4)</td>
</tr>
<tr>
<td>Sr1–O4$^#1$</td>
<td>2.599(3)</td>
<td>O3$^#7$–B1–O1$^#8$ 105.2(4)</td>
</tr>
<tr>
<td>Sr1–O5</td>
<td>2.635(3)</td>
<td>O5$^#7$–B1–O1$^#8$ 105.2(3)</td>
</tr>
<tr>
<td>Sr1–O5$^#2$</td>
<td>2.684(3)</td>
<td>O2–B1–O1$^#8$ 111.7(3)</td>
</tr>
<tr>
<td>Sr1–O1</td>
<td>2.697(3)</td>
<td>O5$^#3$–B2–O5 119.0(5)</td>
</tr>
<tr>
<td>Sr1–O3</td>
<td>2.697(16)</td>
<td>O5$^#3$–B2–O6$^#1$ 109.45(14)</td>
</tr>
<tr>
<td>Sr1–O1$^#3$</td>
<td>2.900(3)</td>
<td>O5–B2–O6$^#1$ 105.40(15)</td>
</tr>
<tr>
<td>B1–O3$^#7$</td>
<td>1.453(5)</td>
<td>O5$^#3$–B2–O6$^#9$ 105.40(15)</td>
</tr>
<tr>
<td>B1–O5$^#7$</td>
<td>1.466(5)</td>
<td>O5–B2–O6$^#9$ 109.45(14)</td>
</tr>
<tr>
<td>B1–O2</td>
<td>1.471(5)</td>
<td>O6$^#1$–B2–O6$^#9$ 107.7(5)</td>
</tr>
<tr>
<td>B1–O1$^#8$</td>
<td>1.507(5)</td>
<td>O1–B3–O6$^#10$ 123.2(5)</td>
</tr>
<tr>
<td>B2–O5$^#3$</td>
<td>1.446(4)</td>
<td>O1–B3–O2 114.6(3)</td>
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<tr>
<td>B2–O5</td>
<td>1.446(4)</td>
<td>O6$^#10$–B3–O2 122.1(4)</td>
</tr>
<tr>
<td>B2–O6$^#1$</td>
<td>1.508(5)</td>
<td></td>
</tr>
<tr>
<td>B2–O6$^#9$</td>
<td>1.508(5)</td>
<td></td>
</tr>
<tr>
<td>B3–O1</td>
<td>1.350(6)</td>
<td></td>
</tr>
<tr>
<td>B3–O6$^#10$</td>
<td>1.371(4)</td>
<td></td>
</tr>
<tr>
<td>B3–O2</td>
<td>1.383(6)</td>
<td></td>
</tr>
</tbody>
</table>

Geometrically estimated hydrogen bonds

<table>
<thead>
<tr>
<th></th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O4$^#6$···H1$^#5$</td>
<td>1.2401(40)</td>
<td>O4$^#6$–H1$^#5$–O4$^#7$ 179.778(216)</td>
</tr>
<tr>
<td>O4$^#6$···O4$^#7$</td>
<td>2.4801(56)</td>
<td></td>
</tr>
<tr>
<td>O4$^#6$···H2$^#10$</td>
<td>0.8785(23)</td>
<td>O4$^#6$–H2$^#10$–O6$^#11$ 179.547(169)</td>
</tr>
<tr>
<td>O4$^#6$···O6$^#11$</td>
<td>3.0697(36)</td>
<td></td>
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</table>

Numerical refined hydrogen Bonds

<table>
<thead>
<tr>
<th></th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O4$^#6$···H1$^#5$</td>
<td>1.2219</td>
<td>O4$^#6$–H1$^#5$–O4$^#7$ 179.155</td>
</tr>
<tr>
<td>O4$^#6$···O4$^#7$</td>
<td>2.4437</td>
<td></td>
</tr>
<tr>
<td>O4$^#6$···H2$^#10$</td>
<td>0.9716</td>
<td>O4$^#6$–H2$^#10$–O6$^#11$ 150.653</td>
</tr>
<tr>
<td>O4$^#6$···O6$^#11$</td>
<td>3.1172</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Symmetry transformations used to generate equivalent atoms:

$#1$ –x+3/2, y+1/2, –z+2;  $#2$ –x+3/2, y–1/2, –z+2;  $#3$ –x+1, y, –z+1;  $#4$ x–1/2, y+1/2, z;  $#5$ x+1/2, y–1/2, z+1;  $#6$ x, y, z+1;  $#7$ x+1/2, y–1/2, z;  $#8$ –x+3/2, y–1/2, –z+1;  $#9$ x–1/2, y+1/2, z–1;  $#10$ x, y, z–1;  $#11$ –x+3/2, y+1/2, –z+1;  $#12$ –x+1, y, –z+2
Fig. S1 Photograph of the Sr₂B₅O₉(OH)·H₂O crystal.

Fig. S2. IR spectrum of Sr₂B₅O₉(OH)·H₂O.
The Mulliken analysis and electron densities

The chemical bond character can be clearly identified by Mulliken analysis and electron density calculation, which, according to the reviewer’s comment, have been carried out. Results have shown that Mulliken overlap populations of B-O and O-H bonds are 0.56 ~ 0.78 and 0.35 ~ 0.59, respectively, whereas those for Sr-O bonds are much smaller, i.e., 0.04 ~ 0.10. It indicates the covalency of the B-O and O-H bonds and iconicity of the Sr-O bonds, respectively. The chemical bond characters were further confirmed by electron densities of atoms which clearly show that the spherical electron distribution was found at strontium atoms, while the two-atom-sharing electron distribution was found in B-O bond and O-H bond (Fig. S3).

Fig. S3. Electron density of atoms in Sr₂B₅O₉(OH)·H₂O.
References


