Supporting Information

Crystal Growth and Optical Properties of a Noncentrosymmetric Haloid Borate, $\text{K}_3\text{B}_6\text{O}_{10}\text{Br}$

Figure S1. Experimental and calculated XRD patterns of the KBB.

Figure S2. The coordinations and bond lengths (Å) of Br atoms (a), K atoms (b).
Table S1. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for KBB. $U_{eq}$ 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</th>
<th>y</th>
<th>z</th>
<th>$U_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(1)</td>
<td>9b</td>
<td>0.84691(7)</td>
<td>0.15309(7)</td>
<td>0.20948(17)</td>
<td>0.0139(5)</td>
</tr>
<tr>
<td>B(1)</td>
<td>9b</td>
<td>0.7545(3)</td>
<td>0.2455(3)</td>
<td>-0.1300(7)</td>
<td>0.0049(12)</td>
</tr>
<tr>
<td>B(2)</td>
<td>9b</td>
<td>0.9656(7)</td>
<td>0.4828(3)</td>
<td>-0.0132(8)</td>
<td>0.0074(15)</td>
</tr>
<tr>
<td>O(1)</td>
<td>18c</td>
<td>0.8995(3)</td>
<td>0.3331(3)</td>
<td>-0.0483(3)</td>
<td>0.0082(7)</td>
</tr>
<tr>
<td>O(2)</td>
<td>9b</td>
<td>0.7782(2)</td>
<td>0.2218(2)</td>
<td>-0.2835(5)</td>
<td>0.0082(9)</td>
</tr>
<tr>
<td>O(3)</td>
<td>3a</td>
<td>0.6667</td>
<td>0.3333</td>
<td>-0.1232(8)</td>
<td>0.0017(14)</td>
</tr>
<tr>
<td>Br(1)</td>
<td>3a</td>
<td>0.6667</td>
<td>0.3333</td>
<td>0.32183(8)</td>
<td>0.0203(5)</td>
</tr>
</tbody>
</table>
**Table S2.** Selected bond lengths (Å) and angles (deg) for KBB.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(1)-O(1)#1</td>
<td>2.793(3)</td>
<td>B(1)-O(2) 1.422(8)</td>
</tr>
<tr>
<td>K(1)-O(1)#2</td>
<td>2.793(3)</td>
<td>B(1)-O(1) 1.470(4)</td>
</tr>
<tr>
<td>K(1)-O(1)</td>
<td>2.801(3)</td>
<td>B(1)-O(1)#3 1.470(4)</td>
</tr>
<tr>
<td>K(1)-O(1)#3</td>
<td>2.801(3)</td>
<td>B(1)-O(3) 1.539(6)</td>
</tr>
<tr>
<td>K(1)-O(2)#4</td>
<td>2.853(3)</td>
<td></td>
</tr>
<tr>
<td>K(1)-O(2)#5</td>
<td>2.853(3)</td>
<td>B(2)-O(1) 1.351(4)</td>
</tr>
<tr>
<td>K(1)-Br(1)</td>
<td>3.3111(14)</td>
<td>B(2)-O(1)#7 1.351(4)</td>
</tr>
<tr>
<td>K(1)-Br(1)#6</td>
<td>3.3207(15)</td>
<td>B(2)-O(2)#1 1.385(7)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms:

(#1) -x+y+5/3,-x+4/3,z+1/3; (#2) x-1/3,x-y-2/3,z+1/3; (#3) -y+1,-x+1,z; (#4) -y+4/3,x-y-1/3,z+2/3;
(#5) -x+y+4/3,-x+2/3,z+2/3; (#6) x+1/3,y-1/3,z-1/3; (#7) x,x-y,z.
Table S3. Bond valence analysis of the KBB.\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Atom</th>
<th>O(1)</th>
<th>O(1)#1</th>
<th>O(2)</th>
<th>O(3)</th>
<th>Br(1)</th>
<th>Br(1)#1</th>
<th>$\sum_{\text{cations}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(1)</td>
<td>0.164\textsuperscript{[x2]}</td>
<td>0.169\textsuperscript{[x2]}</td>
<td>0.143\textsuperscript{[x2]}</td>
<td>\textsuperscript{[x3]}0.179</td>
<td>\textsuperscript{[x3]}0.175</td>
<td>1.306</td>
<td></td>
</tr>
<tr>
<td>K(1)#1</td>
<td>0.169\textsuperscript{[x2]}</td>
<td>0.164\textsuperscript{[x2]}</td>
<td>0.143\textsuperscript{[x2]}</td>
<td>\textsuperscript{[x3]}0.175</td>
<td>\textsuperscript{[x3]}0.179</td>
<td>1.306</td>
<td></td>
</tr>
<tr>
<td>B(1)</td>
<td>0.766</td>
<td>0.766</td>
<td>0.848</td>
<td>\textsuperscript{[x3]}0.636</td>
<td></td>
<td>3.016</td>
<td></td>
</tr>
<tr>
<td>B(2)</td>
<td>1.063</td>
<td>1.063</td>
<td>0.951</td>
<td></td>
<td></td>
<td>3.077</td>
<td></td>
</tr>
<tr>
<td>$\sum_{\text{anions}}$</td>
<td>2.162</td>
<td>2.162</td>
<td>2.085</td>
<td>1.908</td>
<td>1.062</td>
<td>1.062</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Bond valences calculated with the program Bond Valence Calculator Version 2.00, Hormillosa, C., Healy, S., Stephen, T. McMaster University (1993).

\textsuperscript{[b]} Valence sums calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where $S_i$ = valence of bond "i", $R_0$ is a constant dependent upon the bonded elements, $R_i$ is the bond length of bond $i$ and $B$ equals 0.37. Left and right superscripts indicate the number of equivalent bonds for anions and cations, respectively.