Supporting Information:
Speciation change of uranyl in lithium borate glasses

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Crystal structures

To our knowledge, a total of 33 uranyl borate crystalline structures have been reported so far. Here, only alkali (Li, Na and K) uranyl borate and pure uranyl borate compounds are considered, including hydrated compounds. The table S1 presents the list of the crystalline structures considered for the present study. For each structure we give the number of UO$_8$, UO$_7$ and UO$_6$ sites per unitcell, the color of the compounds as reported in the literature and the fraction of BO$_3$ to the total number of unequivalent B sites in the unitcell.

Table S1: List of the crystalline structures considered for the present study and used to produce figure 1 (see main text).

<table>
<thead>
<tr>
<th>Formula</th>
<th>Number of U sites per unit cell</th>
<th>fraction BO$_3$</th>
<th>Color</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alkali uranyl borate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiUO$_2$BO$_3$</td>
<td>4</td>
<td>100%</td>
<td>Yellow</td>
<td>S1</td>
</tr>
<tr>
<td>Li[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>2</td>
<td>2/5</td>
<td>Light yellow-green</td>
<td>S2</td>
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<tr>
<td>NaUO$_2$BO$_3$</td>
<td>4</td>
<td>100%</td>
<td>Light yellow</td>
<td>S3</td>
</tr>
<tr>
<td>Na[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>2/5</td>
<td>Light yellow-green</td>
<td>S2</td>
<td></td>
</tr>
<tr>
<td>Na[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>6</td>
<td>4/10</td>
<td>Light yellow-green</td>
<td>S4</td>
</tr>
<tr>
<td>Na[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>8</td>
<td>4/10</td>
<td>Light yellow-green</td>
<td>S4</td>
</tr>
<tr>
<td>Na[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>12</td>
<td>2/5</td>
<td>Light yellow-green</td>
<td>S4</td>
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<tr>
<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>3</td>
<td>50%</td>
<td>Yellow</td>
<td>S5</td>
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<tr>
<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
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<td>3/6</td>
<td>Light yellow-green</td>
<td>S6</td>
</tr>
<tr>
<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>32</td>
<td>1/6</td>
<td>Yellow</td>
<td>S7</td>
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<tr>
<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>8</td>
<td>100%</td>
<td>Yellow</td>
<td>S7</td>
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<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>16</td>
<td>100%</td>
<td>Yellow</td>
<td>S7</td>
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<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>32</td>
<td>3/6</td>
<td>Yellow</td>
<td>S8</td>
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<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>8</td>
<td>50%</td>
<td>Light yellow-green</td>
<td>S6</td>
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<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>6</td>
<td>2/5</td>
<td>Light yellow-green</td>
<td>S6</td>
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<tr>
<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>8</td>
<td>7/13</td>
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<td>S6</td>
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<tr>
<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>4</td>
<td>2/5</td>
<td>Light yellow-green</td>
<td>S6</td>
</tr>
<tr>
<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>32</td>
<td>100%</td>
<td>Light Yellow</td>
<td>S9</td>
</tr>
<tr>
<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>4</td>
<td>3/9</td>
<td>Light yellow-green</td>
<td>S10</td>
</tr>
<tr>
<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>2</td>
<td>2/5</td>
<td>Light yellow-green</td>
<td>S10</td>
</tr>
<tr>
<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>5</td>
<td>5/13</td>
<td>Light yellow</td>
<td>S10</td>
</tr>
<tr>
<td>K$_2$[(UO$_2$)$_2$B$_5$O$_9$]·H$_2$O</td>
<td>4</td>
<td>4/8</td>
<td>Light yellow-green</td>
<td>S11</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>Number of U sites per unit cell</th>
<th>fraction BO$_3$</th>
<th>Color</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uranyl borate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UO$_2$B$_2$O$_4$</td>
<td>100%</td>
<td>Light Yellow</td>
<td>S9</td>
<td></td>
</tr>
<tr>
<td>α(UO$_2$)$_2$[B$<em>9$O$</em>{14}$(OH)$_4$]</td>
<td>4</td>
<td>3/9</td>
<td>Light yellow-green</td>
<td>S10</td>
</tr>
<tr>
<td>β(UO$_2$)$_2$[B$<em>9$O$</em>{14}$(OH)$_4$]</td>
<td>2</td>
<td>2/5</td>
<td>Light yellow-green</td>
<td>S10</td>
</tr>
<tr>
<td>(UO$<em>2$)$<em>2$[B$</em>{13}$O$</em>{20}$(OH)$_3$]$_1$·25H$_2$O</td>
<td>5</td>
<td>5/13</td>
<td>Light yellow</td>
<td>S10</td>
</tr>
<tr>
<td>UO$_2$[B$<em>4$O$</em>{11}$(OH)$_4$]</td>
<td>4</td>
<td>4/8</td>
<td>Light yellow-green</td>
<td>S11</td>
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</tbody>
</table>
Sample colors

Figure S1: Samples BUL10 and BUL30.
Determination of the scattering factor $S_0^2$

Figure S2: a) Experimental and fitted Fourier transform signals and b) EXAFS signals of uranyl(VI) nitrate crystalline reference. Only the axial and equatorial oxygen shells were fitted.

Table S2: Structural parameters obtained by fitting the EXAFS spectra of uranyl(VI) nitrate.
Transmission XANES at U L$_3$-edge

Figure S3: Transmission XANES spectra (a) and the corresponding derivative (b) of BUL10 (green) and BUL30 (red) compared to U(VI) nitrate (dotted black line).
Decomposition of BUL30 M\textsubscript{4}-edge XAS spectra

Figure S4: M\textsubscript{4}-edge XAS difference spectrum (blue) obtained by subtracting BUL10 spectrum (green) scaled by a factor of 0.4 to BUL30 spectrum (red). The scaling factor is the largest value that allows a positive difference spectrum.

Assuming BUL30 contains a mixture of UO\textsubscript{8} and UO\textsubscript{7} species, the obtained M\textsubscript{4}-edge spectrum of BUL30 $S\textsubscript{BUL30}$ should be a linear combination of both contributions $S\textsubscript{UO_{8}}$ and $S\textsubscript{UO_{7}}$ as formally described by:

$$S\textsubscript{BUL30} = c\textsubscript{UO_{7}} \cdot S\textsubscript{UO_{7}} + c\textsubscript{UO_{8}} \cdot S\textsubscript{UO_{8}}$$

(1)

where $c\textsubscript{UO_{7}}$ and $c\textsubscript{UO_{8}}$ are the fractions of UO\textsubscript{7} and UO\textsubscript{8} respectively with $c\textsubscript{UO_{7}} + c\textsubscript{UO_{8}} = 1$.

Additionally, assuming that the M\textsubscript{4}-edge spectrum of the UO\textsubscript{8} species is similar to the spectrum obtained in BUL10 $S\textsubscript{UO_{8}} = S\textsubscript{BUL10}$, we can attempt determining the spectral component of the UO\textsubscript{7} species from the spectrum of BUL30:

$$S\textsubscript{UO_{7}} = S\textsubscript{BUL30} - \frac{c\textsubscript{UO_{8}}}{1 - c\textsubscript{UO_{8}}} \cdot S\textsubscript{BUL10}.$$  \hspace{1cm} (2)

For this purpose we have subtracted the spectrum of BUL10 scaled by a coefficient to the spectrum of BUL30. The coefficient, which equals $\frac{c\textsubscript{UO_{8}}}{1-c\textsubscript{UO_{8}}}$, was determined as the highest
value that allows the obtained difference spectrum $S_{UO_7}$ to be strictly positive. This gives us the maximal fraction of UO$_8$ possible. The result is shown in Figure S4 in blue.
EXAFS fit and shell decomposition for BUL10

Figure S5: Shell by shell decomposition of the fitted FT signal of BUL10 (a) without a U-B contribution and (b) with a U-B contribution.

Table S3: Structural parameters obtained by fitting the EXAFS spectra of BUL10: effect of floating number of equatorial oxygens.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>$\sigma^2$ ($10^{-3} \text{Å}^2$)</th>
<th>$\Delta E_0$ (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>BUL10</td>
<td>$O_{ax}$</td>
<td>2 (fixed)</td>
<td>1.76±0.004</td>
<td>1.3±0.2</td>
<td>3.0±1.3</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>$O_{eq}$</td>
<td>6 (fixed)</td>
<td>2.5±0.01</td>
<td>8.2±0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_{ax,MS}$</td>
<td>2 (fixed)</td>
<td>3.61±0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BUL10</td>
<td>$O_{ax}$</td>
<td>2 (fixed)</td>
<td>1.76±0.004</td>
<td>1.3±0.2</td>
<td>3.0±1.3</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>$O_{eq}$</td>
<td>5.9</td>
<td>2.5±0.01</td>
<td>8.0±0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$O_{ax,MS}$</td>
<td>2 (fixed)</td>
<td>3.61±0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ fixed to the same as for the single scattering U-$O_{ax}$ path.

$^b$ fixed value for all paths.

MS: Multiple-scattering.
EXAFS fit and shell decomposition for BUL30

Figure S6: Shell by shell decomposition of the fitted FT signal of BUL30 (a) without a U-B contribution and (b) with a U-B contribution.
Table S4: Structural parameters obtained by fitting the EXAFS spectra of BUL30 with floating number of equatorial oxygens.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>$\sigma^2$ ($10^{-3}$Å²)</th>
<th>$\Delta E_0$ (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>BUL30</td>
<td>O$_{ax}$</td>
<td>2 (fixed)</td>
<td>1.81 ± 0.002</td>
<td>2.3 ± 0.2</td>
<td>1.0 ± 1.6</td>
<td>0.03</td>
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<tr>
<td></td>
<td>O$_{eq}$</td>
<td>5 (fixed)</td>
<td>2.28 ± 0.008</td>
<td>11.5 ± 0.9</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_{eq}$</td>
<td>1 (fixed)</td>
<td>2.53 ± 0.01</td>
<td>4.3 ± 1.8</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_{ax}$MS</td>
<td>2 (fixed)</td>
<td>3.61 ± 0.004</td>
<td>0.03</td>
<td></td>
<td></td>
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<tr>
<td>BUL30</td>
<td>O$_{ax}$</td>
<td>2 (fixed)</td>
<td>1.81 ± 0.002</td>
<td>2.3 ± 0.2</td>
<td>1.0 ± 1.6</td>
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<td>O$_{eq}$</td>
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<td>O$_{eq}$</td>
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<td>2.53 ± 0.01</td>
<td>4.3 ± 1.8</td>
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<td>O$_{ax}$MS</td>
<td>2 (fixed)</td>
<td>3.61 ± 0.004</td>
<td>0.03</td>
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</tr>
</tbody>
</table>

$^a$ fixed to the same as for the single scattering U-O$_{ax}$ path.

$^b$ fixed value for all paths.

MS: Multiple-scattering.

References


(S5) Behm, H. Hexapotassium (cyclo-octahydroxotetracosaoxohexadecaborato)dioxouranate(VI)

S-10


