Supporting information for In-situ X-Ray Raman spectroscopy of LiBH₄

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I. EXPERIMENTAL X-RAY RAMAN SPECTRA OF $\text{Li}_4\text{SiO}_4$ AND BN

FIG. S1. Li K-edge X-Ray Raman spectrum of $\text{Li}_4\text{SiO}_4$

FIG. S1 shows the Li K-edge XRS of $\text{Li}_4\text{SiO}_4$. The shape of the spectrum agrees with data from Bergmann et al., but the exact energy where peaks are is different. The data is noisy after background subtraction, which shows that the subtraction is a very delicate process in this case and actually in all cases of Li K-edges.

FIG. S2. B K-edge X-Ray Raman spectrum of h-BN

FIG. S2 shows the experimental B K-edge XRS of h-BN powder. The spectrum is similar to other XAS spectra of BN, but there are some differences with other XRS and EELS.
This difference might be ascribed to the difference in the studied samples: either single-crystal h-BN, or polycrystalline h-BN crystals or h-BN powder in this study.

II. B and Li K-edge XAS calculations: crystal structures and supercell sizes

In Table 1 the investigated materials and their crystal structures are shown together with the used supercell size and the k-points for the XANES calculations with the Quantum-Espresso package are shown.

Table 1. Crystal structures and the supercell sizes and k-point grid used in the self-consistent field (scf) calculations.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Structure information</th>
<th>Supercell size</th>
<th>K-points (scf)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiB</td>
<td>Pnma</td>
<td>2x4x2</td>
<td>4x4x4</td>
<td>J.K. Kang et al.</td>
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<tr>
<td>LiBH</td>
<td>Pnma</td>
<td>2x4x2</td>
<td>4x4x4</td>
<td>J.K. Kang et al.</td>
</tr>
<tr>
<td>LiBH₄</td>
<td>Pnma</td>
<td>2x2x2</td>
<td>3x3x3</td>
<td>J.K. Kang et al.</td>
</tr>
<tr>
<td>LiBH₄ HT</td>
<td>P6₃/mmc</td>
<td>2x2x2</td>
<td>4x4x4</td>
<td>J.-Ph. Soulié et al., data for LiBH₄ at 408K</td>
</tr>
<tr>
<td>BN</td>
<td>P 6₃/mmc</td>
<td>4x4x2</td>
<td>4x4x4</td>
<td>R.S. Pease</td>
</tr>
<tr>
<td>Li (metal)</td>
<td>Fm3m</td>
<td>2x2x2</td>
<td>4x4x4</td>
<td>www-MINCRYST(2011), card nr. 2605</td>
</tr>
<tr>
<td>B (tetra)</td>
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<td>1x1x2</td>
<td>5x5x5</td>
<td>www-MINCRYST(2011), card nr. 593</td>
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<tr>
<td>B (hexa)</td>
<td>R3(-jm)</td>
<td>2x2x1</td>
<td>4x4x4</td>
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<td>LiH</td>
<td>Fm3m</td>
<td>4x4x4 /5x5x5</td>
<td>1x1x1</td>
<td>Ref.</td>
</tr>
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<td>Li₂B₁₂H₁₂</td>
<td>Pa-3</td>
<td>1x1x1</td>
<td>4x4x4</td>
<td>J.-. Her et al.</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>P3₁21-ĉa</td>
<td>2x2x1</td>
<td>8x8x8</td>
<td>H. Effenberger et al.</td>
</tr>
</tbody>
</table>
III. B K-EDGE XAS CALCULATIONS

FIG. S3. B K-edge XAS calculations for LiBH₄ (black lines), LiBH₄-HT (red lines), BN (green lines) and B(hexamgonal) (blue lines) and B(tetragonal) (light blue lines). Solid lines represent the calculations with full core-hole and the dotted lines are the calculations without core-hole.

FIG. S3 shows the B K-edge XAS calculations for LiBH₄ (as in Fig. 2B in main text), for a high temperature phase of LiBH₄, BN, and tetragonal and hexagonal boron. It is clear that the high temperature phase is not visible in our experimental data in the main text (Fig. 3A and Fig. 3C). The only possible material that may be present in our experiment is tetragonal boron. However, the rest of the peaks is not visible in the experimental XRS.

Focusing on the BN calculations, there is agreement with our experimental spectrum FIG. S2, but the calculated peak at 197 eV is not that intense and sharp as in the XRS. However this peak is observed in other experimental spectra, so this might be due to higher crystallinity in our calculations compared to the XRS of h-BN powder.
FIG. S4. B K-edge XAS calculations for LiBH (black lines), LiB (red lines) and Li₂B₁₂H₁₂ (green lines) Solid lines represent the calculations with full core-hole and the dotted lines are the calculations without core-hole.

FIG. S4 shows the B K-edge XAS calculations for the possible intermediate compounds LiBH, LiB and Li₂B₁₂H₁₂. At first glance it might be possible that there is Li₂B₁₂H₁₂ in our experiment, since a peak close to 194 eV is visible in the solid green line calculation. However in our experimental spectra at higher temperatures shown in the main text (FIG. 3C) the second peak of the calculated Li₂B₁₂H₁₂ just at about 196 eV is not visible, which leads to the conclusion that no Li₂B₁₂H₁₂ is present in the experiments shown in the main text.
IV. Li K-EDGE XAS CALCULATIONS

FIG. S5. Li K-edge XAS calculations for LiBH₄ (black lines), LiBH₄-HT (red lines), Li(metal) (green lines) and LiH (blue lines). Solid lines represent the calculations with half core-hole and the dotted lines are the calculations without core-hole.

FIG. S5 shows the Li K-edge XAS calculations for LiBH₄, for a high temperature phase of LiBH₄, Li (metal) and LiH. Since there are clear differences between all the spectra, we can conclude that the experimental XRS of bulk LiBH₄ powder at higher temperatures in the main text (Fig. 3B) only accounts for LiBH₄.
**FIG. S6.** Li K-edge XAS calculations for LiBH (black lines), LiB (red lines), Li$_2$B$_{12}$H$_{12}$ (green lines). Solid lines represent the calculations with half core-hole and the dotted lines are the calculations without core-hole.

FIG. S6 shows the Li K-edge XAS calculations for the possible intermediate compounds LiBH, LiB and Li$_2$B$_{12}$H$_{12}$. In the experimental Li K-edge XRS at elevated temperatures shown in the main text for 25wt% LiBH$_4$/C (Fig 5D), there is a possibility that the patterns of LiBH, LiB and Li$_2$B$_{12}$H$_{12}$ are present in the experimental XRS, but then the B K-edge calculated patterns should also have been visible in the experimental XRS spectra of Fig 5C. These combined arguments lead to the conclusion that Fig. 5D shows no intermediate products, but either the intercalated Li (LiC$_6$) or LiO$_x$H$_y$ formation.

**References**


(9) [http://www.oxmat.co.uk/Crysdata/lih.htm](http://www.oxmat.co.uk/Crysdata/lih.htm).
