Supporting Information

Crystal structures and properties of solvent-free

LiYb(BH₄)₄₋ₓClₓ, Yb(BH₄)₃ and Yb(BH₄)₂₋ₓClₓ

Jørn Eirik Olsen, Christoph Frommen, Magnus H. Sørby, Bjørn C. Hauback†

Institute for Energy Technology, Physics Department, P.O. Box 40, NO-2027 Kjeller,
Norway

† Corresponding author. E-mail: bjorn.hauback@ife.no, Phone: +47 63 80 60 78, Fax: +47 63 80 63 88
**Table S1.** Comparison between experimental Raman spectra of LiYb(BH$_4$)$_{4-x}$Cl$_x$ and LiSc(BH$_4$)$_4$.

<table>
<thead>
<tr>
<th>Raman Sc$^a$ (cm$^{-1}$)</th>
<th>Raman Yb$^b$ (cm$^{-1}$)</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>216</td>
<td>199</td>
<td>17</td>
</tr>
<tr>
<td>231</td>
<td>215</td>
<td>16</td>
</tr>
<tr>
<td>474</td>
<td>455</td>
<td>19</td>
</tr>
<tr>
<td>1079</td>
<td>1085</td>
<td>-6</td>
</tr>
<tr>
<td>1112</td>
<td>1112</td>
<td>0</td>
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<td>1217</td>
<td></td>
</tr>
<tr>
<td>1247</td>
<td>1251</td>
<td>-4</td>
</tr>
<tr>
<td>1325</td>
<td>1331</td>
<td>-6</td>
</tr>
<tr>
<td></td>
<td>1368</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2140</td>
<td></td>
</tr>
<tr>
<td>2211</td>
<td>2205</td>
<td>6</td>
</tr>
<tr>
<td>2264</td>
<td>2259</td>
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</tr>
<tr>
<td>2483</td>
<td>2482</td>
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</tbody>
</table>


$^b$ From the table it seems to be some additional peaks for LiYb(BH$_4$)$_{4-x}$Cl$_x$, however visually inspection of the reported Raman spectra for LiSc(BH$_4$)$_4$ indicates weak peaks corresponding to the peaks at 1217, 2140 and 2432 cm$^{-1}$ reported here.
Table S2. Comparison between experimental Raman spectra of \text{tet-Yb(BH}_4\text{)}_{2-x}\text{Cl}_x \text{ and } \beta-\text{Ca(BH}_4\text{)}_2

<table>
<thead>
<tr>
<th>Raman Ca(^a) (\text{cm}^{-1})</th>
<th>Raman Yb (\text{cm}^{-1})</th>
<th>\Delta</th>
</tr>
</thead>
<tbody>
<tr>
<td>2355</td>
<td>2364</td>
<td>-9</td>
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<tr>
<td>2296</td>
<td>2286</td>
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<td>1309</td>
<td>1312</td>
<td>-3</td>
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<tr>
<td>1078</td>
<td>1087</td>
<td>-9</td>
</tr>
</tbody>
</table>

**Figure S1.** The Rietveld refinement for LiYb(BH$_4$)$_{3.0}$Cl$_{1.0}$ showing the experimental data as circles, the calculated diffraction pattern as a solid line, tick marks for LiBH$_4$ (top), LiCl (middle) and LiYb(BH$_4$)$_{3.0}$Cl$_{1.0}$ (bottom), respectively, and the difference plot, \( \lambda = 1.5418 \text{ Å} \).
Figure S2. The Rietveld refinement for α-Yb(BH₄)₃, showing the experimental data as circles, the calculated diffraction pattern as a solid line, tick marks for LiYb(BH₄)₃.₀Cl₁.₀ (top), LiCl (middle) and α-Yb(BH₄)₃ (bottom), respectively, and the difference plot, $\lambda = 0.503208$ Å.
**Figure S3.** The Rietveld refinement for $\beta$-Yb(BH$_4$)$_3$, showing the experimental data as circles, the calculated diffraction pattern as a solid line, tick marks for LiCl(top), LiYb(BH$_4$)$_3$.0Cl$_{1.0}$(middle) and $\beta$-Yb(BH$_4$)$_3$(bottom), respectively, and the difference plot, $\lambda = 0.503208$ Å.
**Figure S4.** In-situ SR-PXD data collected for LiYb(BH$_4$)$_{3.0}$Cl$_{1.0}$, $\lambda = 0.70947$ Å
Figure S5. The Rietveld refinement for ortho-Yb(BH$_4$)$_{1.7}$Cl$_{0.3}$, showing the experimental data as circles, the calculated diffraction pattern as a solid line, tick marks for LiCl(top) and ortho-Yb(BH$_4$)$_{1.7}$Cl$_{0.3}$(bottom), respectively, and the difference plot, $\lambda = 0.69660$ Å.

Figure S6. TPD-data collected from a LiYb(BH$_4$)$_{3,0}$Cl$_{1,0}$ sample.