

Supporting Information

Crystal structures and properties of solvent-free $\text{LiYb}(\text{BH}_4)_{4-x}\text{Cl}_x$, $\text{Yb}(\text{BH}_4)_3$ and $\text{Yb}(\text{BH}_4)_{2-x}\text{Cl}_x$

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Table S1. Comparison between experimental Raman spectra of $\text{LiYb}(\text{BH}_4)_{4-x}\text{Cl}_x$ and $\text{LiSc}(\text{BH}_4)_4$.

Raman Sc ^a (cm ⁻¹)	Raman Yb ^b (cm ⁻¹)	Δ
216	199	17
231	215	16
474	455	19
1079	1085	-6
1112	1112	0
	1217	
1247	1251	-4
1325	1331	-6
	1368	
	2140	
2211	2205	6
2264	2259	5
	2432	
2483	2482	1

^a Hagemann, H.; Longhini, M.; Kaminski, J. W.; Wesolowski, T. A.; Cerny, R.; Penin, N.; Sørby, M. H.; Hauback, B. C.; Severa, G.; Jensen, C. M. *J. Phys. Chem. A* **2008**, *112*, 7551-7555.

^bFrom the table it seems to be some additional peaks for $\text{LiYb}(\text{BH}_4)_{4-x}\text{Cl}_x$, however visually inspection of the reported Raman spectra for $\text{LiSc}(\text{BH}_4)_4$ indicates weak peaks corresponding to the peaks at 1217, 2140 and 2432 cm⁻¹ reported here.

Table S2. Comparison between experimental Raman spectra of tet-Yb(BH₄)_{2-x}Cl_x and β-Ca(BH₄)₂

Raman Ca ^a (cm ⁻¹)	Raman Yb (cm ⁻¹)	Δ
2355	2364	-9
2296	2286	-10
1309	1312	-3
1250	1255	-5
1078	1087	-9

^a Reed, D.; Book, D. *Curr. Opin. Solid State Mat. Sci.* **2011**, *15*, 62-72.

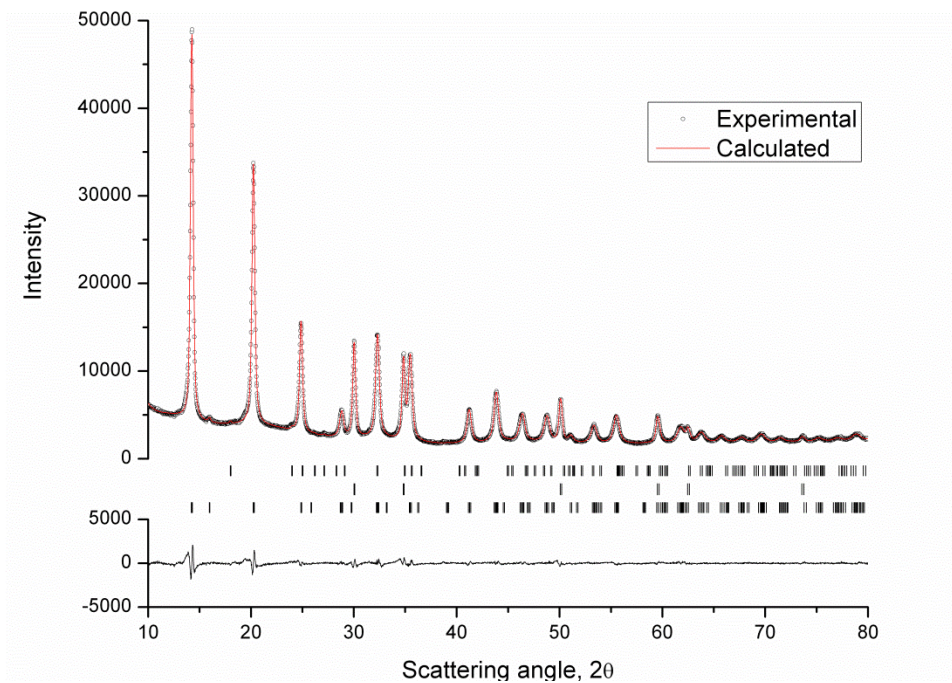


Figure S1. The Rietveld refinement for $\text{LiYb}(\text{BH}_4)_{3.0}\text{Cl}_{1.0}$. showing the experimental data as circles, the calculated diffraction pattern as a solid line, tick marks for LiBH_4 (top), LiCl (middle) and $\text{LiYb}(\text{BH}_4)_{3.0}\text{Cl}_{1.0}$ (bottom), respectively, and the difference plot, $\lambda = 1.5418 \text{ \AA}$.

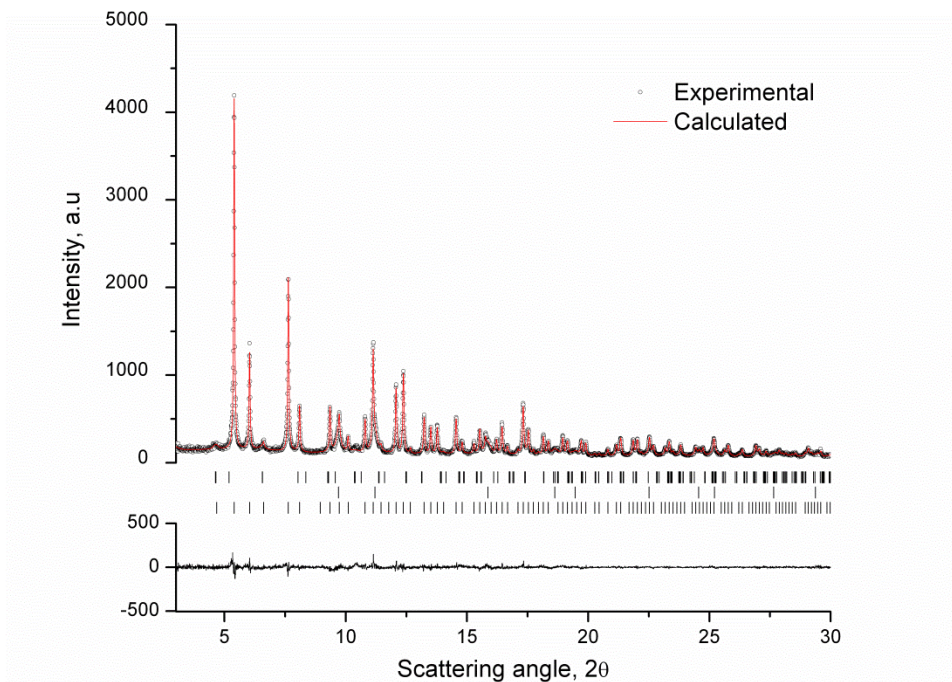


Figure S2. The Rietveld refinement for α -Yb(BH₄)₃, showing the experimental data as circles, the calculated diffraction pattern as a solid line, tick marks for LiYb(BH₄)_{3.0}Cl_{1.0} (top), LiCl (middle) and α -Yb(BH₄)₃ (bottom), respectively, and the difference plot, $\lambda = 0.503208 \text{ \AA}$.

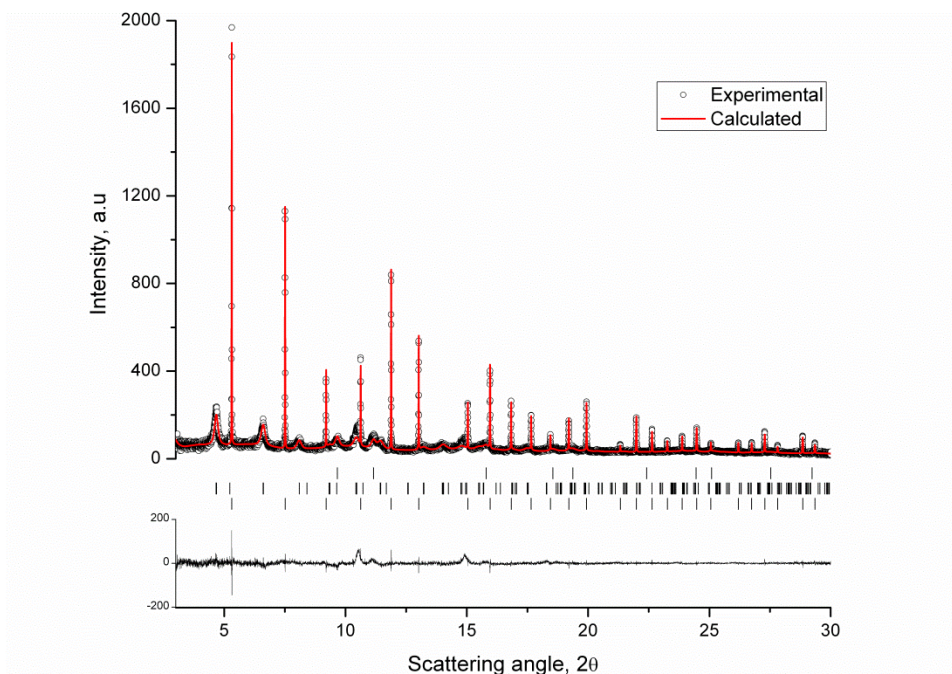


Figure S3. The Rietveld refinement for β -Yb(BH₄)₃, showing the experimental data as circles, the calculated diffraction pattern as a solid line, tick marks for LiCl(top), LiYb(BH₄)_{3.0}Cl_{1.0}(middle) and β -Yb(BH₄)₃(bottom), respectively, and the difference plot, $\lambda = 0.503208 \text{ \AA}$.

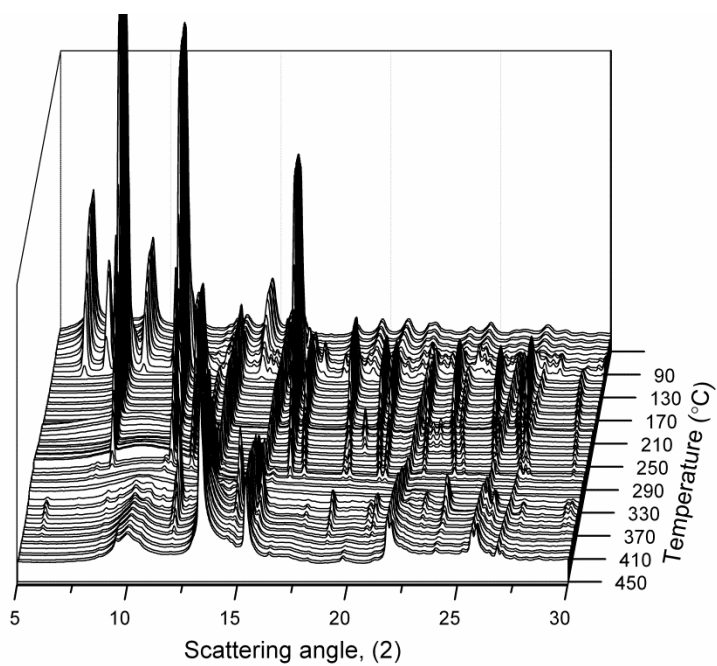


Figure S4. In-situ SR-PXD data collected for $\text{LiYb}(\text{BH}_4)_{3.0}\text{Cl}_{1.0}$, $\lambda = 0.70947 \text{ \AA}$

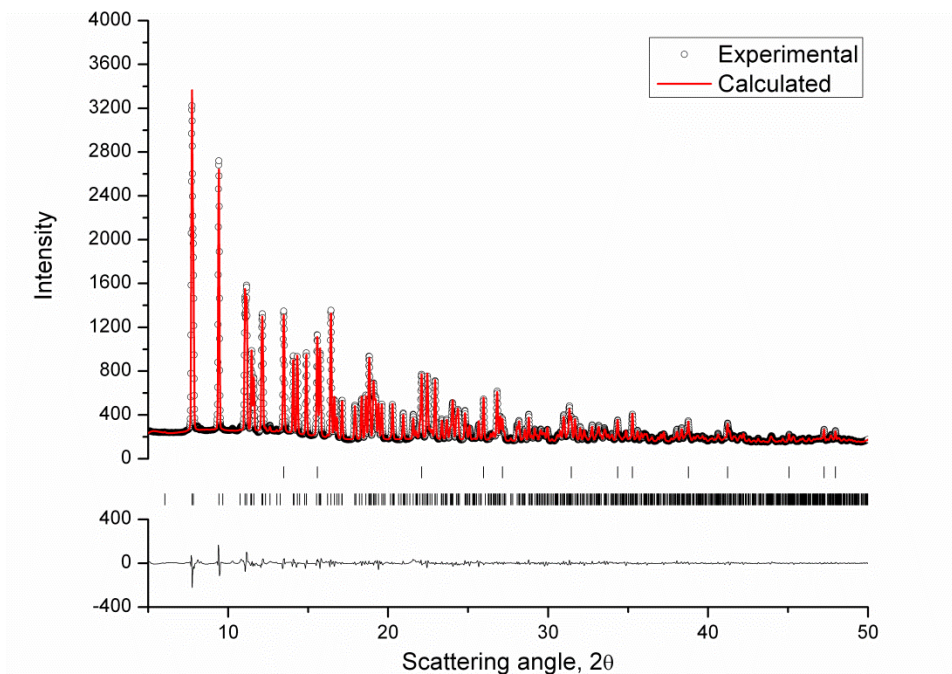


Figure S5. The Rietveld refinement for *ortho*-Yb(BH₄)_{1.7}Cl_{0.3}, showing the experimental data as circles, the calculated diffraction pattern as a solid line, tick marks for LiCl(top) and *ortho*-Yb(BH₄)_{1.7}Cl_{0.3}(bottom), respectively, and the difference plot, $\lambda = 0.69660 \text{ \AA}$.

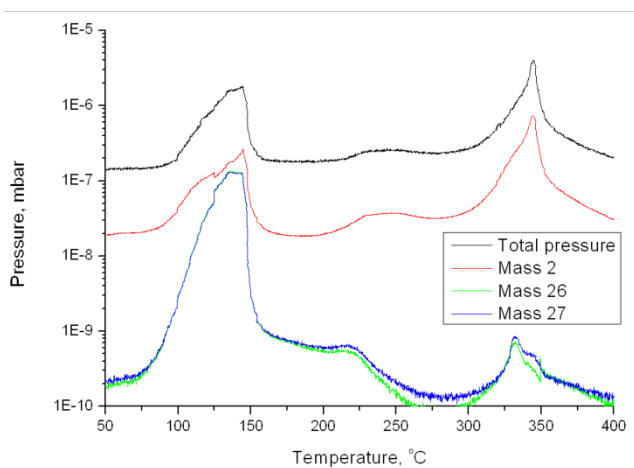


Figure S6. TPD-data collected from a LiYb(BH₄)_{3.0}Cl_{1.0} sample.