

Supplementary Information

Barium borohydride chlorides;

Synthesis, crystal structures and thermal properties

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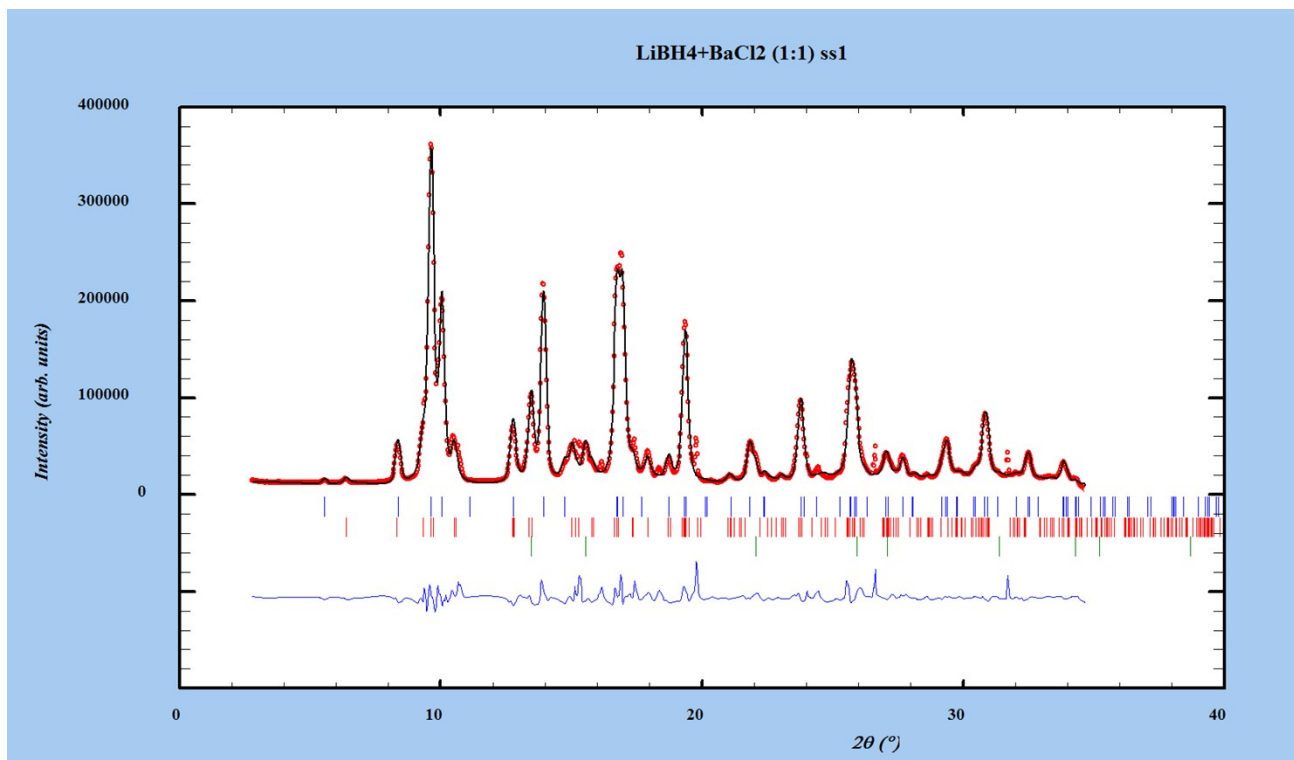


Figure S1. Powder X-ray diffraction for $\text{LiBH}_4\text{--BaCl}_2$ (1:1) measured at 295 K showing observed (circles), calculated (upper line) and difference (bottom line) plots. The position of the Bragg reflections are shown as tic marks for $h\text{-Ba}(\text{BH}_4)_{0.86}\text{Cl}_{1.14}$ (upper), $o\text{-Ba}(\text{BH}_4)_{0.16}\text{Cl}_{1.84}$ (middle), and LiCl (lower) ($\lambda = 0.70082 \text{ \AA}$).

$o\text{-Ba}(\text{BH}_4)_{0.16}\text{Cl}_{1.84}$: space group $Pnma$, $a = 8.228(6) \text{ \AA}$, $b = 4.785(3) \text{ \AA}$, $c = 9.620(6) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. $\chi^2 = 0.112 \cdot 10^6$, $R_{\text{wp}} = 10.8\%$, $R_{\text{p}} = 10.2\%$, and $R_{\text{Bragg}} = 3.00\%$.

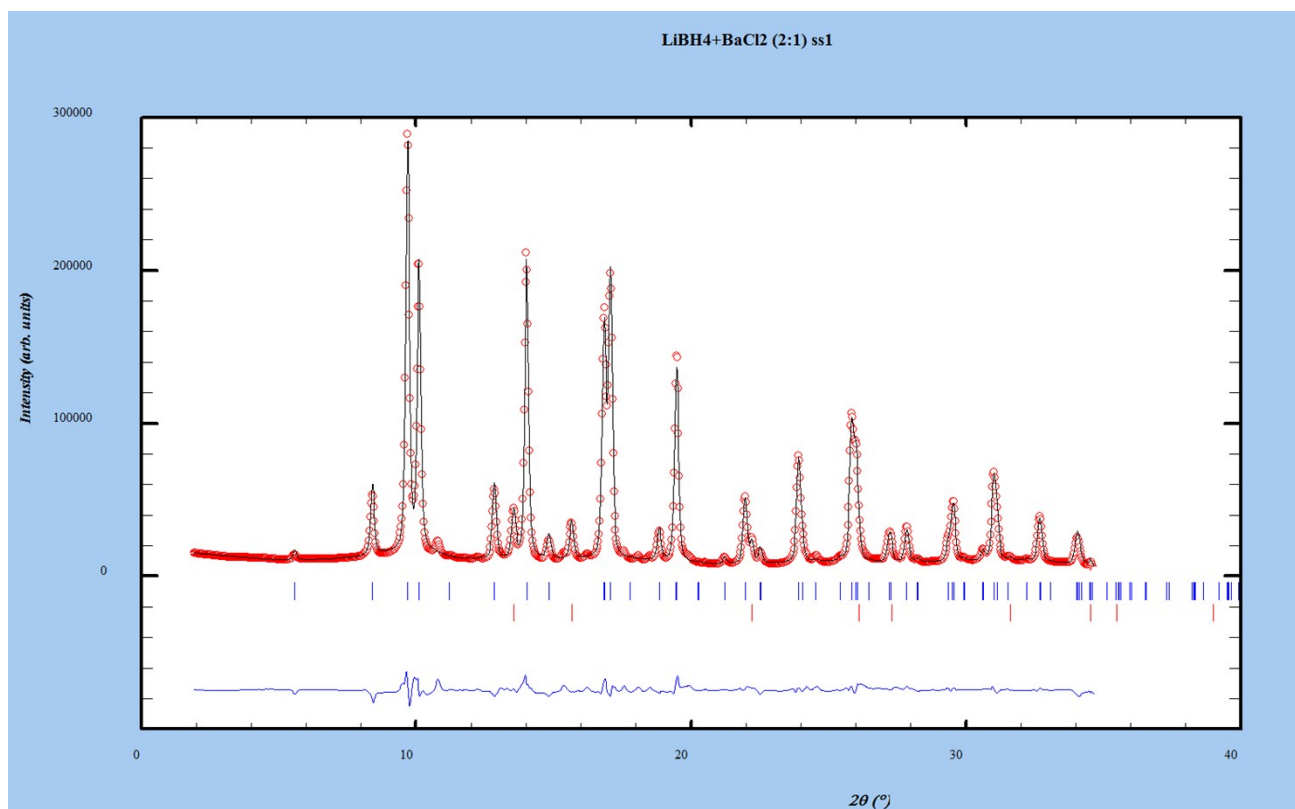


Figure S2. Powder X-ray diffraction for $\text{LiBH}_4\text{--BaCl}_2$ (2:1) measured at 295 K showing observed (circles), calculated (upper line) and difference (bottom line) plots. The position of the Bragg reflections are shown as tic marks for $h\text{-Ba}(\text{BH}_4)_{0.85}\text{Cl}_{1.15}$ (upper) and LiCl (lower). ($\lambda = 0.70082 \text{ \AA}$). $h\text{-Ba}(\text{BH}_4)_{0.85}\text{Cl}_{1.15}$: space group P-62m, $a = b = 8.2945(3) \text{ \AA}$, $c = 4.7776(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$. $\chi^2 = 0.253 \cdot 10^5$, $R_{\text{wp}} = 6.68\%$, $R_{\text{p}} = 9.95\%$, and $R_{\text{Bragg}} = 3.65\%$.

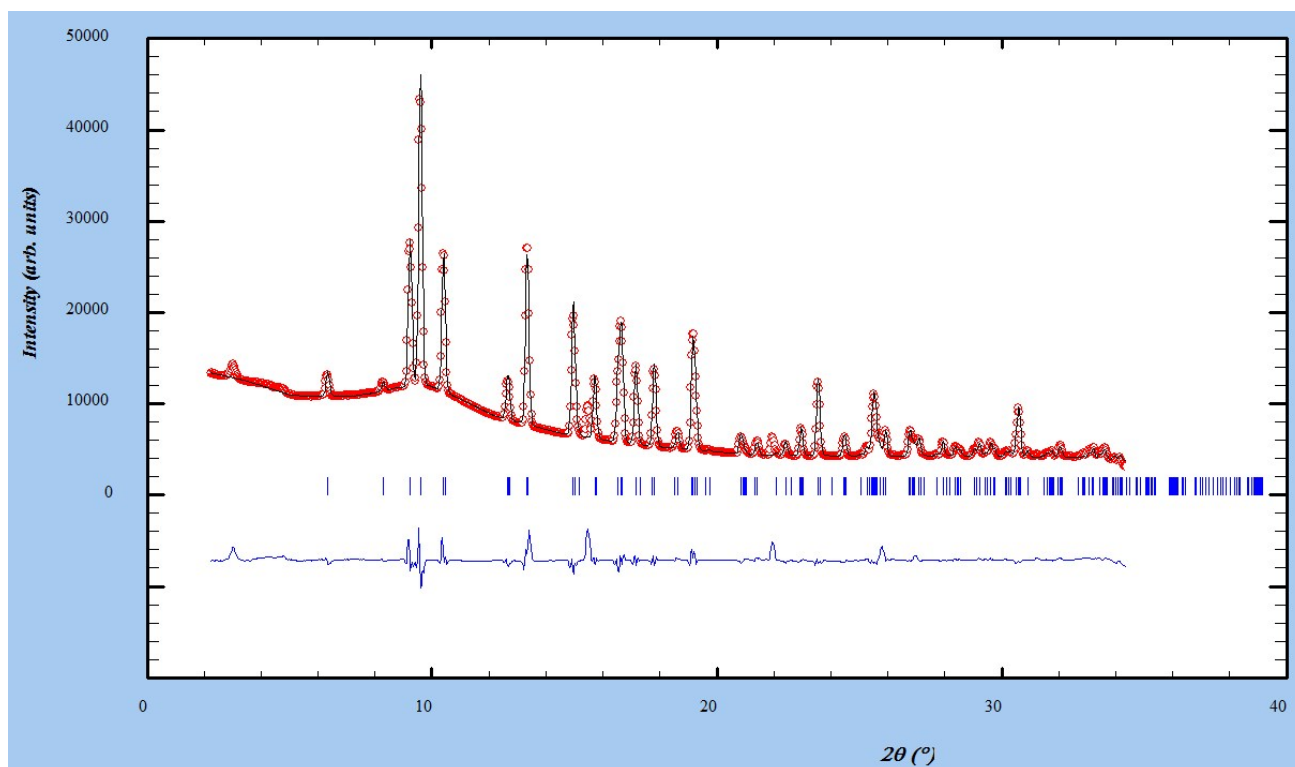


Figure S3 Powder X-ray diffraction for $\text{LiBH}_4\text{-BaCl}_2$ (2:1) measured at 473 K showing observed (circles), calculated (upper line) and difference (bottom line) plots. The position of the Bragg reflections are shown as tic marks for $o\text{-Ba}(\text{BH}_4)_{0.85}\text{Cl}_{1.15}$. ($\lambda = 0.70082 \text{ \AA}$).

$o\text{-Ba}(\text{BH}_4)_{0.85}\text{Cl}_{1.15}$: space group $Pmna$, $a = 8.3659(6) \text{ \AA}$, $b = 4.8731(3) \text{ \AA}$, $c = 9.6898(7) \text{ \AA}$, $\chi^2 = 0.351 \cdot 10^4$, $R_{\text{wp}} = 4.83\%$, $R_{\text{p}} = 14.9\%$, and $R_{\text{Bragg}} = 7.20\%$.

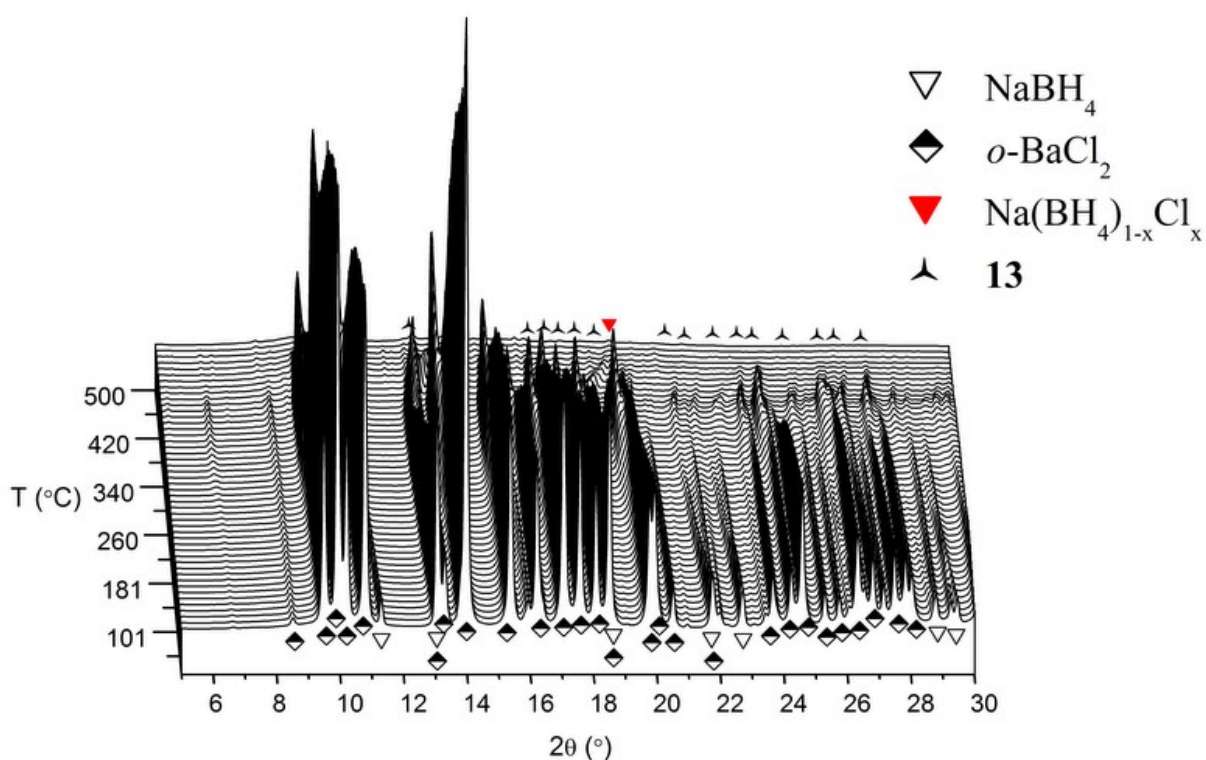


Figure S4. *In situ* SR-PXD data of a sample $\text{NaBH}_4 + \text{BaCl}_2$ 2:1 measured from *RT* to 500 °C, 5 °C/min (BM01A, ESRF, $\lambda = 0.70082 \text{ \AA}$). No reaction occurred during ball milling as reflexes from NaBH_4 and $o\text{-BaCl}_2$ are present at *RT*. As the sample is heating the reflexes are moving to lower 2θ values indicating cell expansion of NaBH_4 and $o\text{-BaCl}_2$. This expansion occurs up to 360 °C where Cl substitution into NaBH_4 begins giving a solid solution of $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$. At 320 °C reflexes from $o\text{-BaCl}_2$ disappear and reflexes from $o\text{-Ba}(\text{BH}_4)_x\text{Cl}_{2-x}$ appear.

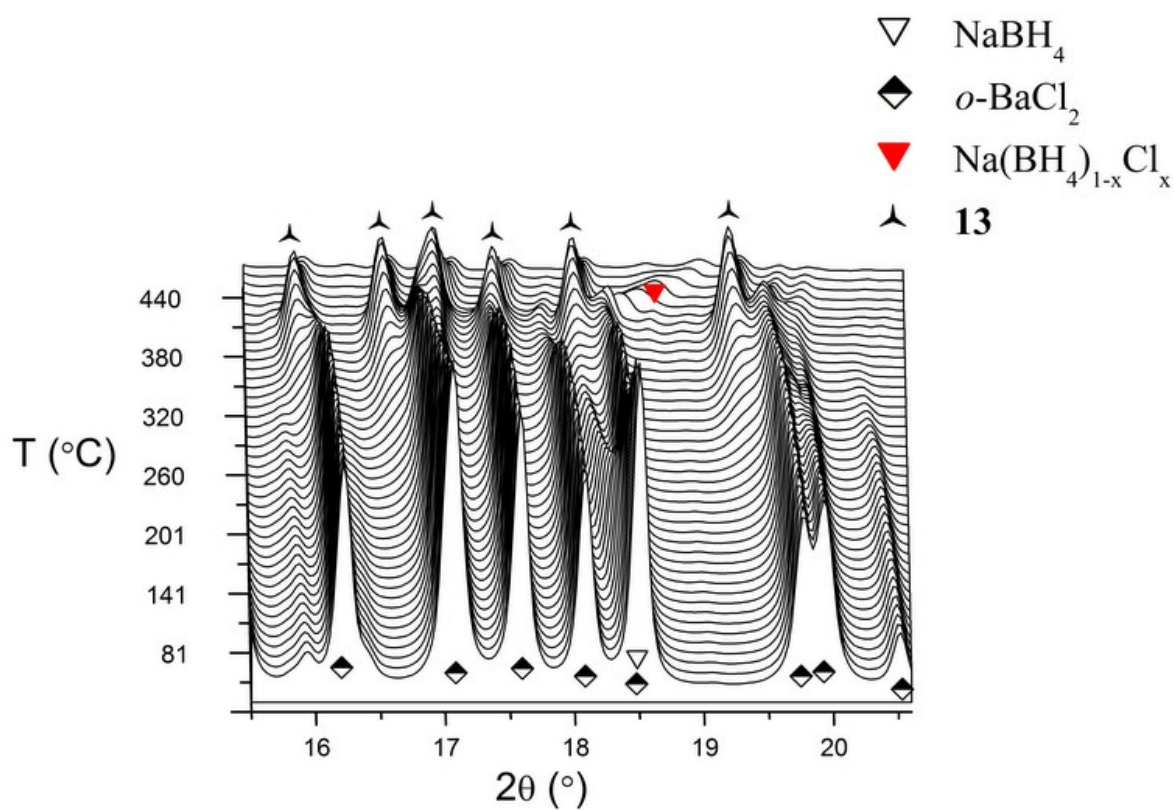


Figure S5. Zoom in of Figure S3 showing $2\theta = 15\text{--}21^\circ$. *In situ* SR-PXD data of the ball milled sample $\text{NaBH}_4\text{--BaCl}_2$ (2:1) measured from *RT* to 500 °C, 5 °C/min (BM01A, ESRF, $\lambda = 0.70082$ Å).

Table S1. Atomic coordinates of *o*-Ba(BH₄)_{0.16}Cl_{1.84} refined from the SR-PXD data measured at *RT* for LiBH₄:BaCl₂ 1:1. Space group *Pnma*, *a* = 8.228(6) Å, *b* = 4.785(3) Å, *c* = 9.620(6) Å, $\alpha = \beta = \gamma = 90^\circ$. $\chi^2 = 0.112 \cdot 10^6$, $R_{wp} = 10.8\%$, $R_p = 10.2\%$, and $R_{Bragg} = 3.00\%$.

Atom	x	y	z	occupancy
Ba1	0.2672	0.25000	0.1162	4.00
B1	0.0034	0.25000	0.8222	0.64
Cl1	0.1475	0.25000	0.4264	4.00
Cl2	0.0034	0.25000	0.8222	3.36

Table S2. Atomic coordinates of *h*-Ba(BH₄)_{0.85}Cl_{1.15} as refined from the SR-PXD data measured at *RT* for LiBH₄:BaCl₂ 2:1. Space group *P-62m*, *a* = *b* = 8.2945(3) Å, *c* = 4.7776(3) Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$. $\chi^2 = 0.253 \cdot 10^5$, $R_{wp} = 6.68\%$, $R_p = 9.95\%$, and $R_{Bragg} = 3.65\%$.

Atom	x	y	z	occupancy
Ba1	0.0000	0.0000	0.5000	1.00
Ba2	0.3333	0.6667	0.0000	2.00
B1	0.5699	0.0000	0.5000	2.55
Cl1	0.5699	0.0000	0.5000	0.45
Cl2	0.2508	0.0000	0.0000	3.00

Table S3. Atomic coordinates of *o*-Ba(BH₄)_{0.85}Cl_{1.15} as refined from the SR-PXD data measured at 200°C for LiBH₄-BaCl₂ (2:1). Space group *Pnma*, *a* = 8.3659(6) Å, *b* = 4.8731(3) Å, *c* = 9.6898(7) Å, $\chi^2 = 0.351 \cdot 10^4$, $R_{wp} = 4.83\%$, $R_p = 14.9\%$, and $R_{Bragg} = 7.20\%$.

Atom	x	y	z	occupancy
Ba1	0.2658	0.25000	0.1160	4.00
B1	0.0034	0.25000	0.8222	3.40
Cl1	0.1459	0.25000	0.4264	4.00
Cl2	0.0034	0.25000	0.8222	0.60