

Supplementary information

Fluoride substitution in LiBH₄; destabilization and decomposition

Bo Richter^a, Dorthe B. Ravnsbæk^b, Manish Sharma^c, Alexandra Spyratou^c, Hans Hagemann^c and Torben R. Jensen^{a*}

^a Center for Materials Crystallography, Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C (Denmark).

^b Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M (Denmark).

^c Department of Physical Chemistry, University of Geneva, 30, Quai Ernest-Ansermet, CH1211 Geneva 4 (Switzerland).

* Corresponding author: trj@chem.au.dk

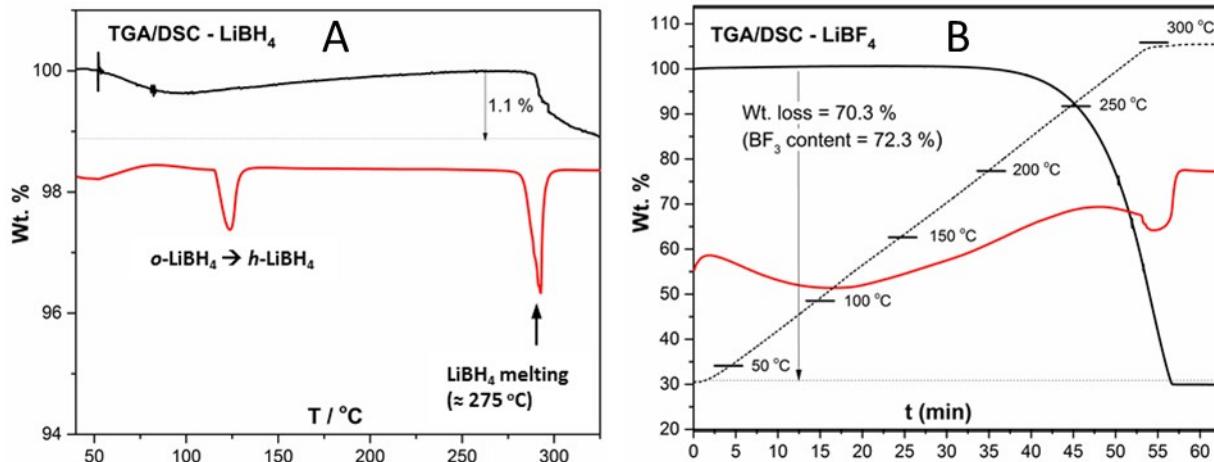


Fig. S1. Reference TGA/DSC curves for LiBH_4 and LiBF_4 . Heating rate is $5^\circ\text{C}/\text{min}$ for **A** (LiBH_4) and $5^\circ\text{C}/\text{min}$ followed by an isotherm at 300°C for **B** (LiBF_4). Endothermic peaks are pointed downwards.

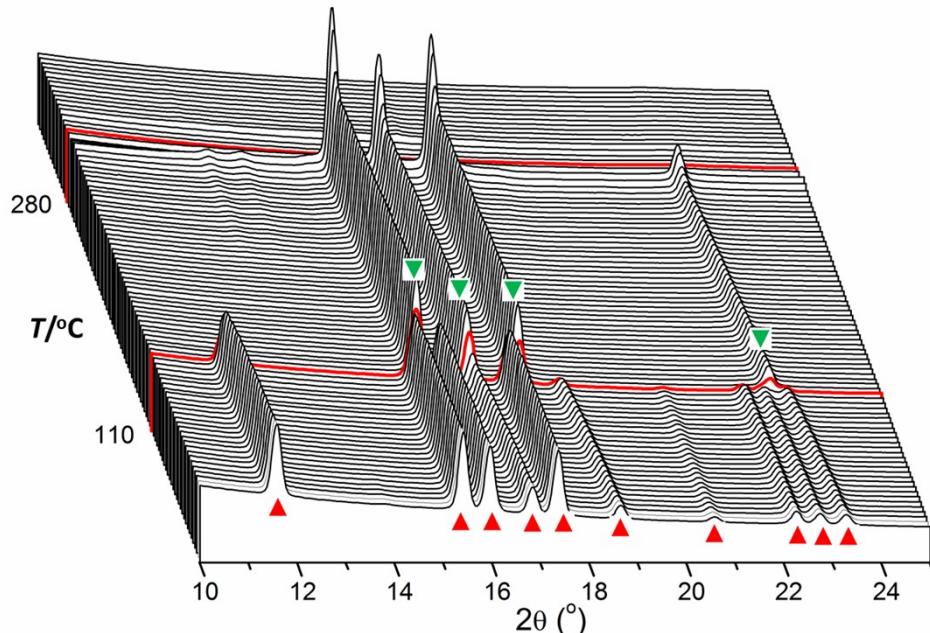


Fig. S2. *In situ* synchrotron radiation X-ray diffractogram for LiBH_4 (heating rate is $5^\circ\text{C}/\text{min}$, $\lambda = 0.93843 \text{ \AA}$). \blacktriangle ; o- LiBH_4 , \blacktriangledown ; h- LiBH_4 .

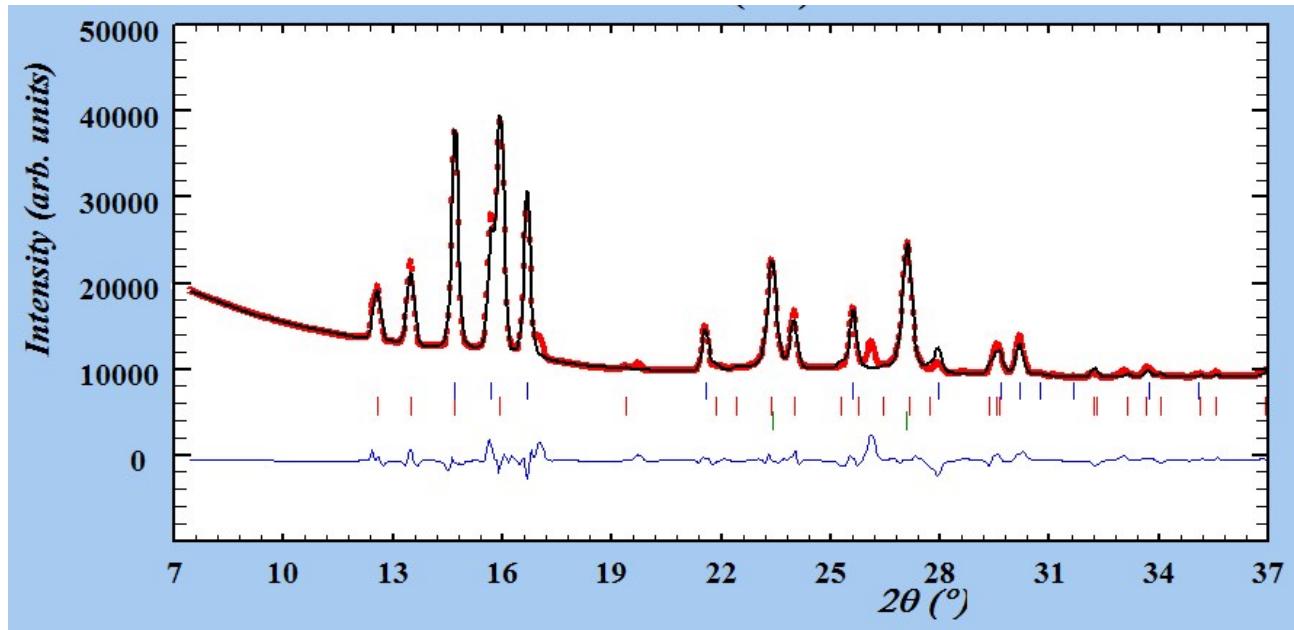


Fig. S3a. Rietveld profile of sample LiBH₄-LiBF₄ 9:1 (S9-1) at 125 °C. Blue tick marks: *h*-LiBH_{4-x}F_x ($R_{\text{Bragg}} = 8.86\%$), red tick marks: LiBF₄ ($R_{\text{Bragg}} = 6.97\%$), green tick marks: LiF ($R_{\text{Bragg}} = 2.85\%$). *R*-factors (not corrected for background): $R_p = 1.93\%$, $R_{wp} = 3.56\%$, $R_{exp} = 0.06\%$, $\chi^2 = 0.366 \cdot 10^4$.

Table S3a. Information for LiBH_{4-x}F_x at 125 °C.

Space group $P6_3mc$

Name	x	sx	y	sy	z	sz	B	sB	occ.	socc.	Mult
Li1	0.33330	(0)	0.66670	(0)	0.00000	(0)	1.000	(0)	2.000	(0)	2
B1	0.33330	(0)	0.66670	(0)	0.59607	(0)	8.600	(0)	2.000	(0)	2
H1	0.33330	(0)	0.66670	(0)	0.42206	(0)	3.500	(0)	1.701	(20)	2
F1	0.33330	(0)	0.66670	(0)	0.42206	(0)	3.500	(0)	0.299	(20)	2
H2	0.17200	(0)	0.34400	(0)	0.66707	(0)	6.400	(0)	5.745	(26)	6
F2	0.17200	(0)	0.34400	(0)	0.66707	(0)	6.400	(0)	0.255	(26)	6
Cell parameters:		a) 4.26695 (0.00040)			b) 4.26695 (0.00040)			c) 6.93312 (0.00139)			

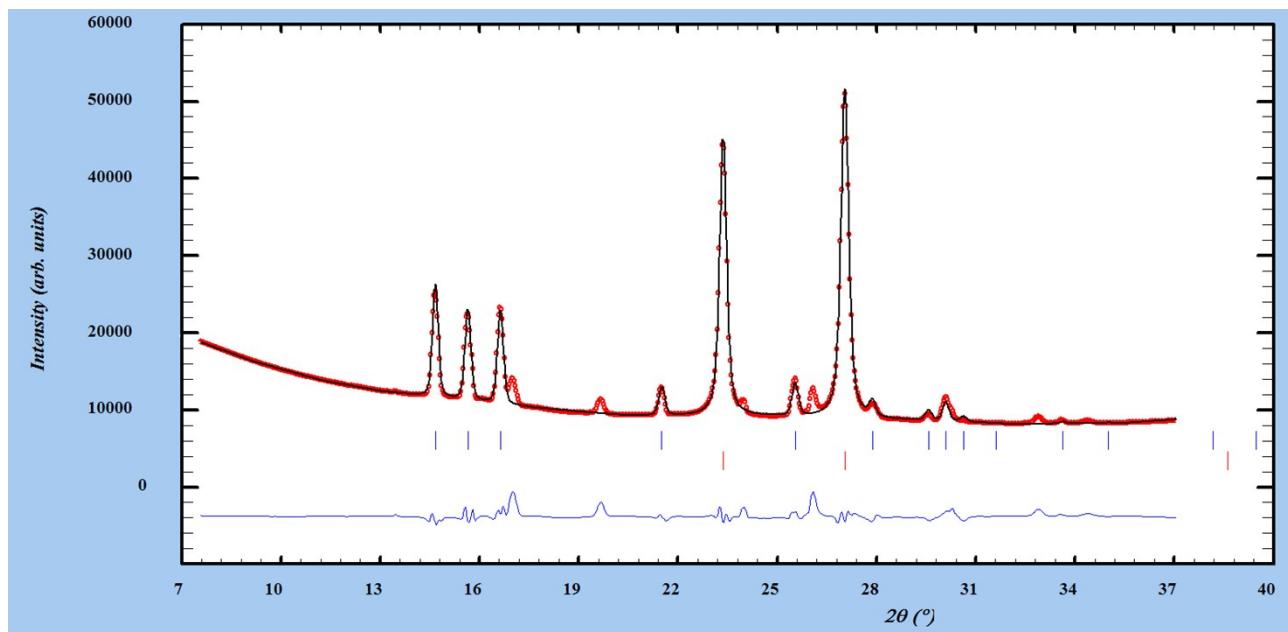


Fig. S3b. Rietveld profile of sample LiBH₄-LiBF₄ 9:1 (S9-1) at 170 °C. Blue tick marks: *h*-LiBH_{4-x}F_x (R_{Bragg} = 13.8%), red tick marks: LiF (R_{Bragg} = 1.65%). R-factors (not corrected for background): Rp = 2.12%, Rwp = 3.91%, Rexp = 0.06%, Chi2 = 0.430E+04.

Table S3b. Information for LiBH_{4-x}F_x at 170 °C.

Space group *P*6₃*mc*

Name	x	sx	y	sy	z	sz	B	sB	occ.	socc.	Mult
Li1	0.33330	(0)	0.66670	(0)	0.00000	(0)	1.000	(0)	2.000	(0)	2
B1	0.33330	(0)	0.66670	(0)	0.55302	(0)	8.600	(0)	2.000	(0)	2
H1	0.33330	(0)	0.66670	(0)	0.37002	(0)	3.500	(0)	1.763	(17)	2
F1	0.33330	(0)	0.66670	(0)	0.37002	(0)	3.500	(0)	0.237	(17)	2
H2	0.17200	(0)	0.34400	(0)	0.64602	(0)	4.600	(0)	5.586	(30)	6
F2	0.17200	(0)	0.34400	(0)	0.64602	(0)	4.600	(0)	0.414	(30)	6
Cell parameters:	a) 4.28048 (0.00055)				b) 4.28048 (0.00055)				c) 6.94776 (0.00140)		

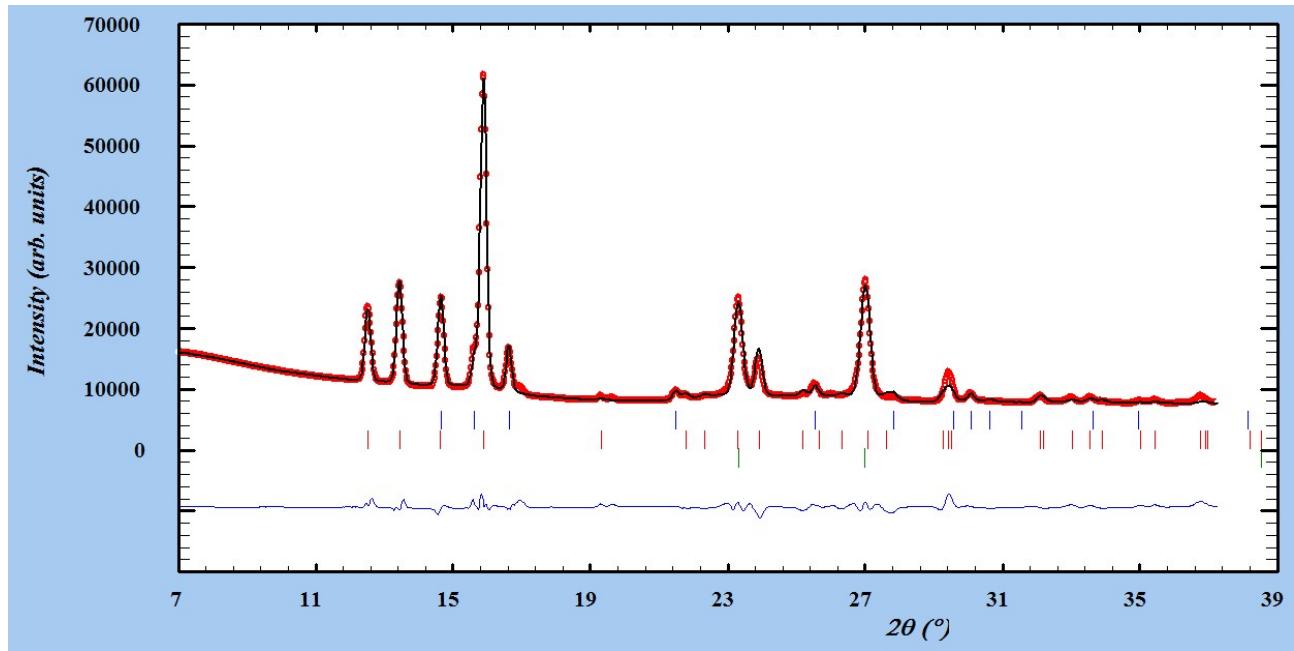


Fig. S3c. Rietveld profile of sample $\text{LiBH}_4\text{-LiBF}_4$ 3:1 (S3-1) at 125 °C. Blue tick marks: $h\text{-LiBH}_{4-x}\text{F}_x$ ($R_{\text{Bragg}} = 11.6\%$), red tick marks: LiBF_4 ($R_{\text{Bragg}} = 8.80\%$), green tick marks: LiF ($R_{\text{Bragg}} = 1.96\%$). R-factors (not corrected for background): $R_p = 2.07\%$, $R_{wp} = 3.42\%$, $R_{exp} = 0.22\%$, $\chi^2 = 0.390\text{E+04}$.

Table S3c. Information for $\text{LiBH}_{4-x}\text{F}_x$ at 125 °C.

Space group $P6_3mc$

Name	x	sx	y	sy	z	sz	B	sB	occ.	socc.	Mult
Li1	0.33330	(0)	0.66670	(0)	0.00000	(0)	1.000	(0)	2.000	(0)	2
B1	0.33330	(0)	0.66670	(0)	0.59607	(0)	8.600	(0)	2.000	(0)	2
H1	0.33330	(0)	0.66670	(0)	0.42206	(0)	3.500	(0)	1.626	(42)	2
F1	0.33330	(0)	0.66670	(0)	0.42206	(0)	3.500	(0)	0.374	(42)	2
H2	0.17200	(0)	0.34400	(0)	0.66707	(0)	6.400	(0)	5.233	(63)	6
F2	0.17200	(0)	0.34400	(0)	0.66707	(0)	6.400	(0)	0.767	(63)	6
Cell parameters:	a) 4.27942 (0.00081)			b) 4.27942 (0.00081)			c) 6.96176 (0.00239)				

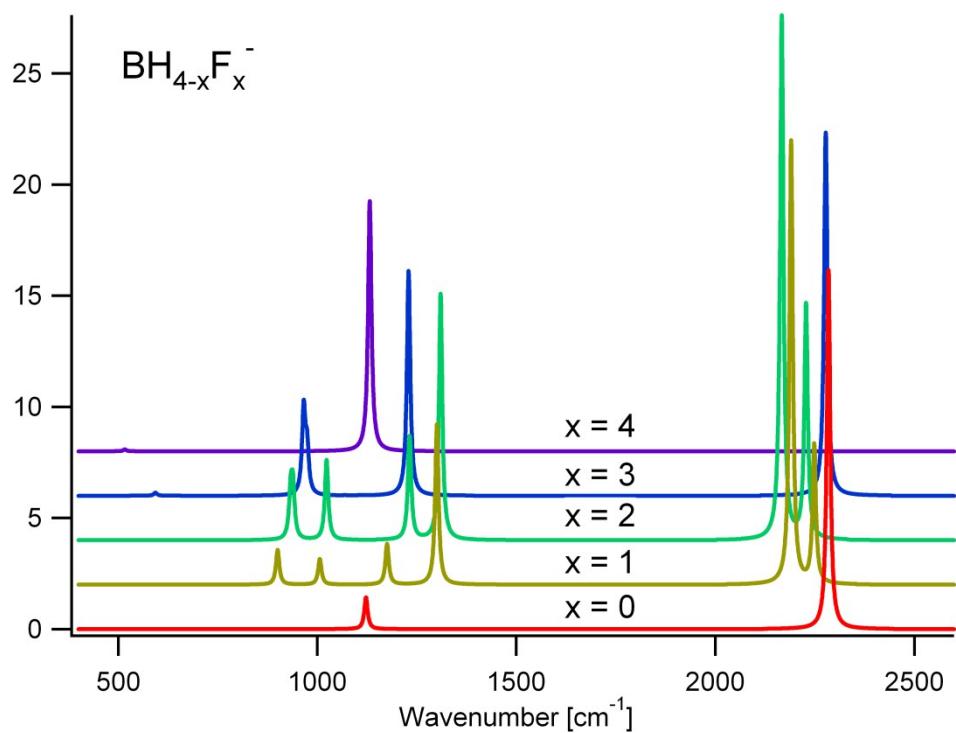


Fig. S4. DFT Calculated FTIR spectra of $\text{BH}_{(4-x)}\text{F}_{(x)}$ in the harmonic approximation (data from ref. 11d).

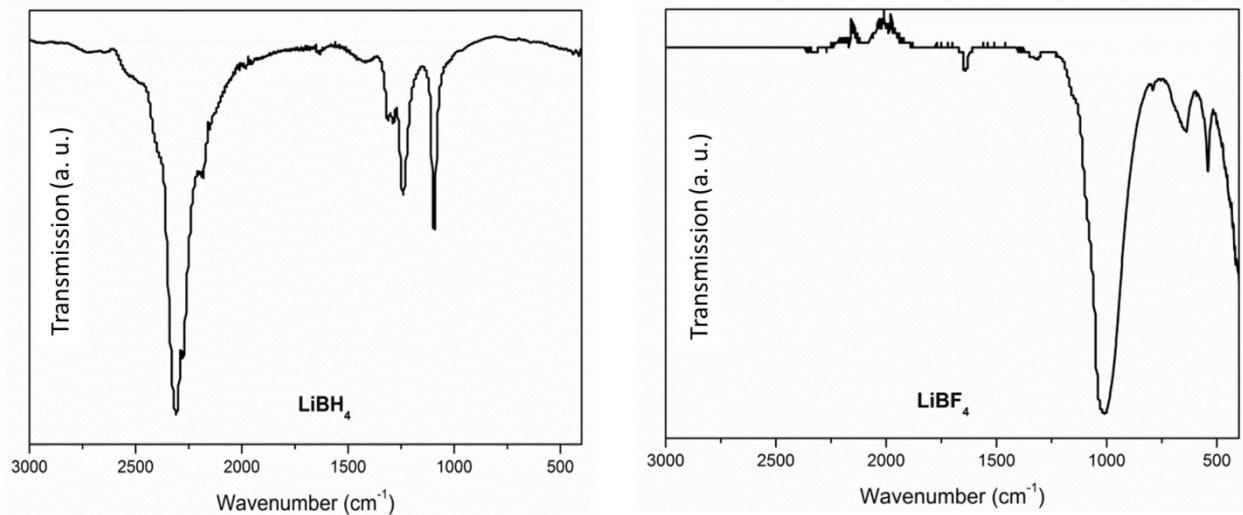


Fig. S5. Reference FTIR spectra for *o*- LiBH_4 and LiBF_4 . For comparison with Fig. S4 and Fig. 4.

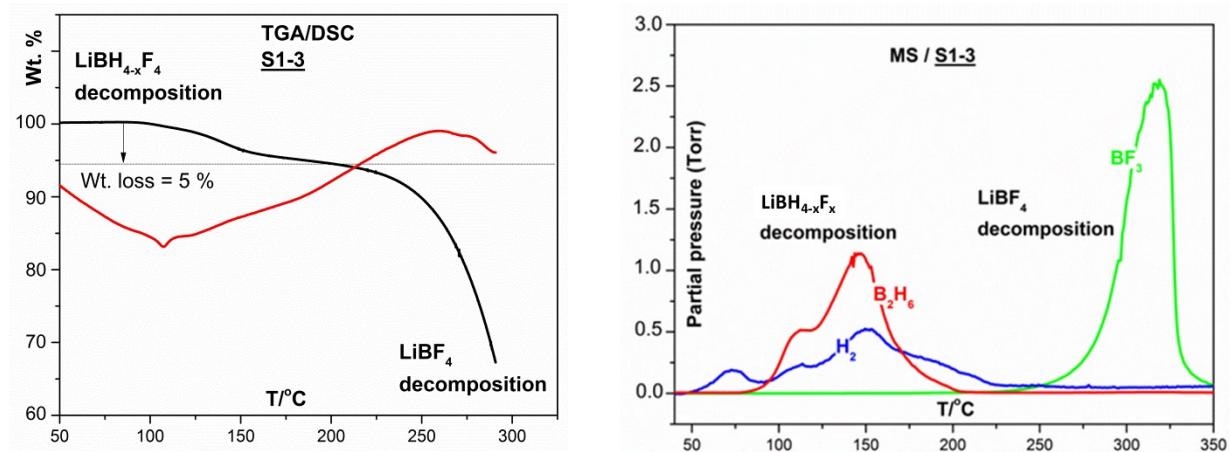


Fig. S6. Thermal analysis of a sample consisting of large excess of LiBF_4 (**S1-3**). Left; TGA/DSC curves from RT - 300 °C. Endothermic peaks are pointed downwards. Right; mass spectroscopy (MS) indicating release of H_2 (blue), B_2H_6 (red) and BF_3 (green) as LiBF_4 decomposes.