

Supplementary information

Hydrogen-fluorine exchange in $\text{NaBH}_4\text{--NaBF}_4$

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Table S1 The optimized distances and angles of the BH_{4-x}F_x⁻ ion.

Species	B-H (Å)	B-F (Å)	HBH (°)	FBH (°)	FBF (°)
BH ₄ ⁻	1.239		109.5		
BH ₃ F ⁻	1.250	1.451	108.0	110.9	
BH ₂ F ₂ ⁻	1.253	1.434	110.0	109.5	108.7
BHF ₃ ⁻	1.244	1.420		110.3	108.6
BF ₄ ⁻		1.410			109.5

Table S2 Assignment of calculated IR-frequencies.

	Freq (cm ⁻¹)	IR Intens	Symm
BH ₄ ⁻	1122.3	44.3	T2
	1239.2	Forbidden	E
	2284.5	497.8	T2
	2291.0	Forbidden	A1
BH ₃ F ⁻	900.5	48.4	A1
	1006.6	35.7	E
	1175.4	56.6	E
	1300.5	222.0	A1
	2190.6	614.9	E
	2248.5	191.7	A1
BH ₂ F ₂ ⁻	448.0	0.1	A1
	933.4	62.2	A1
	939.2	65.2	B2
	1000.8	Forbidden	A2
	1023.3	111.0	B1
	1232.0	143.4	A1
	1309.8	341.3	B2
	2167.1	725.6	B1
BHF ₃ ⁻	2228.1	324.4	A1
	412.8	0.0	E
	593.4	4.4	A1
	966.0	117.2	A1
	974.5	61.5	E
	1229.4	311.6	E
	2277.6	503.3	A1
BF ₄ ⁻	347.5	Forbidden	E
	516.5	2.7	T2
	762.6	Forbidden	A1
	1131.8	346.9	T2

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Table S3: SCF GIAO isotropic magnetic shielding tensor (ppm)

Species	¹¹ B	¹ H	¹⁹ F
BH ₄ ⁻	156.2	32.15	
BH ₃ F ⁻	121.0	28.9	469.4
BH ₂ F ₂ ⁻	108.2	28.3	376.8
BHF ₃ ⁻	109.6	29.0	348.6
BF ₄ ⁻	111.4		360.5

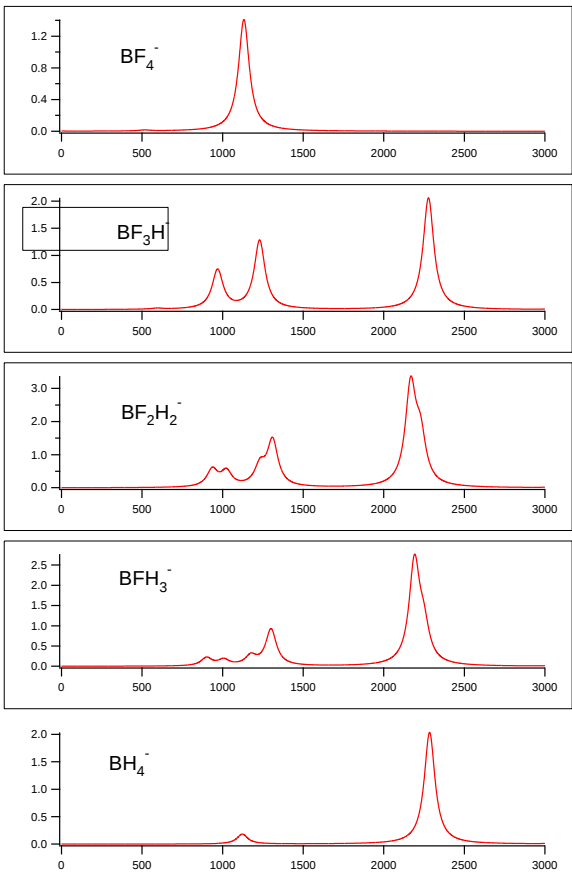


Figure S1. Calculated IR-spectra of the BH_{4-x}F_x⁻ ions, formally calculated at 0 K in the harmonic approximation.

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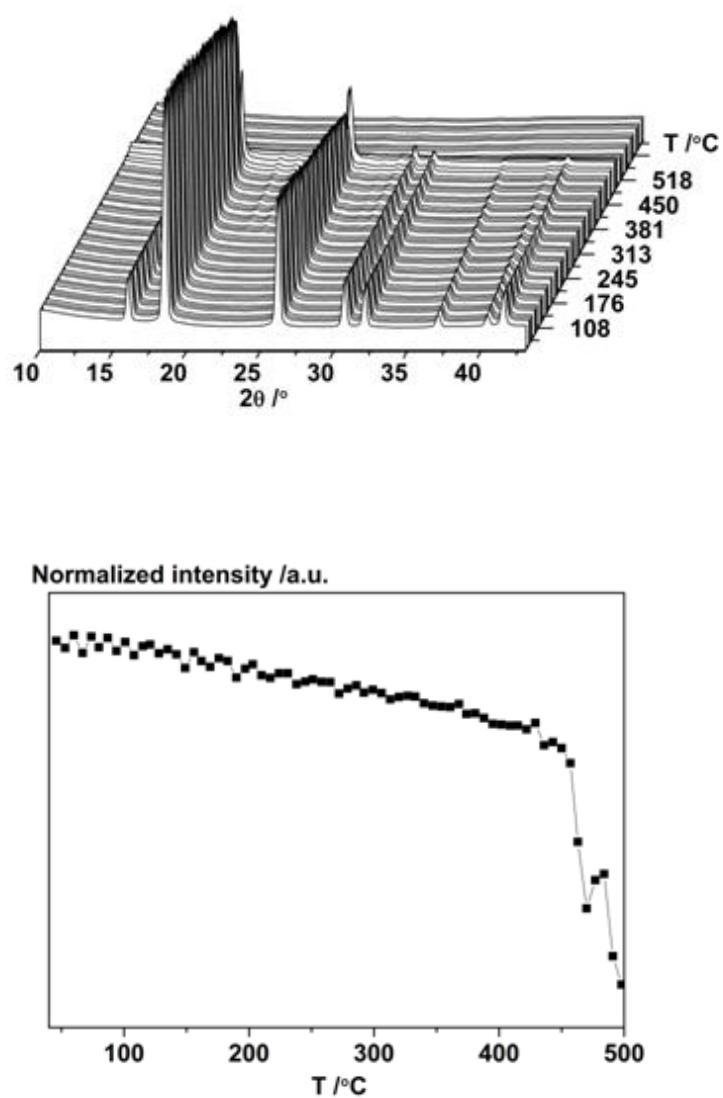


Figure S2. *In situ* SR-PXD data for NaBH₄ measured in the temperature range *RT* to 600 °C ($\Delta T/\Delta t$ = 10 °C/min, $p(\text{Ar})$ = 1 bar, λ = 0.94499 Å, MAX-lab beam line I711). Normalized integrated diffracted intensities for the crystalline compounds in the sample (lower figure).

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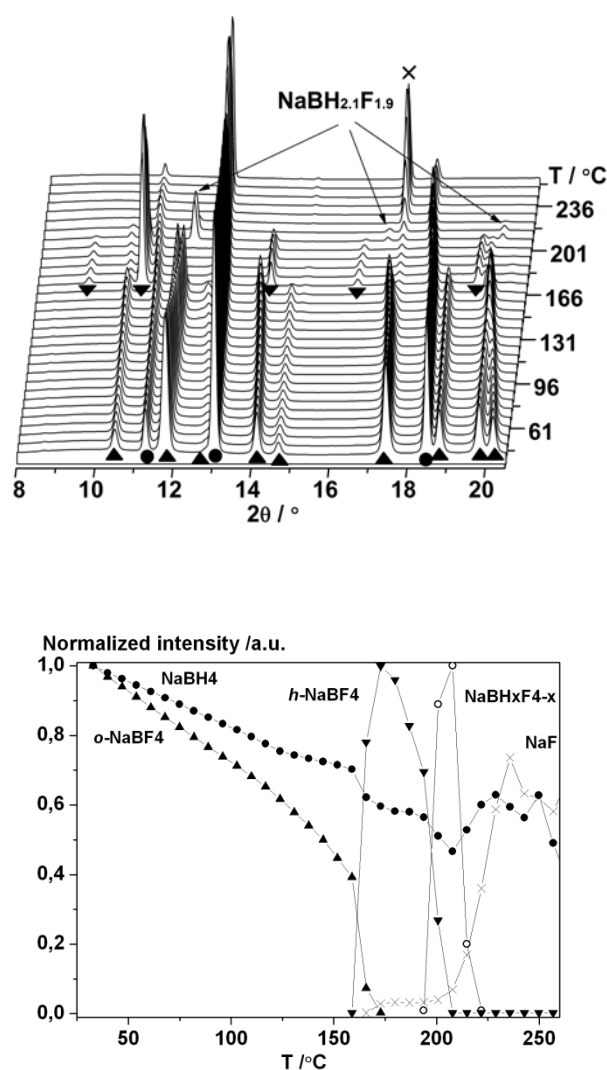


Figure S3. *In situ* SR-PXD data (top) measured for $\text{NaBH}_4\text{-NaBF}_4$ (1:0.5, S2) in the temperature range RT to $450\text{ }^\circ\text{C}$ ($\Delta T/\Delta t = 5\text{ }^\circ\text{C}/\text{min}$, $\lambda = 0.700818\text{ \AA}$, SNBL at ESRF). This data was utilized for Rietveld refinement and revealed a composition of $\text{NaBH}_{2.1}\text{F}_{1.9}$. Normalized integrated diffracted intensities for the crystalline compounds in the sample (lower figure). Symbols: ● NaBH_4 ; ▲ $o\text{-NaBF}_4$; ▼ $h\text{-NaBF}_4$; × NaF .

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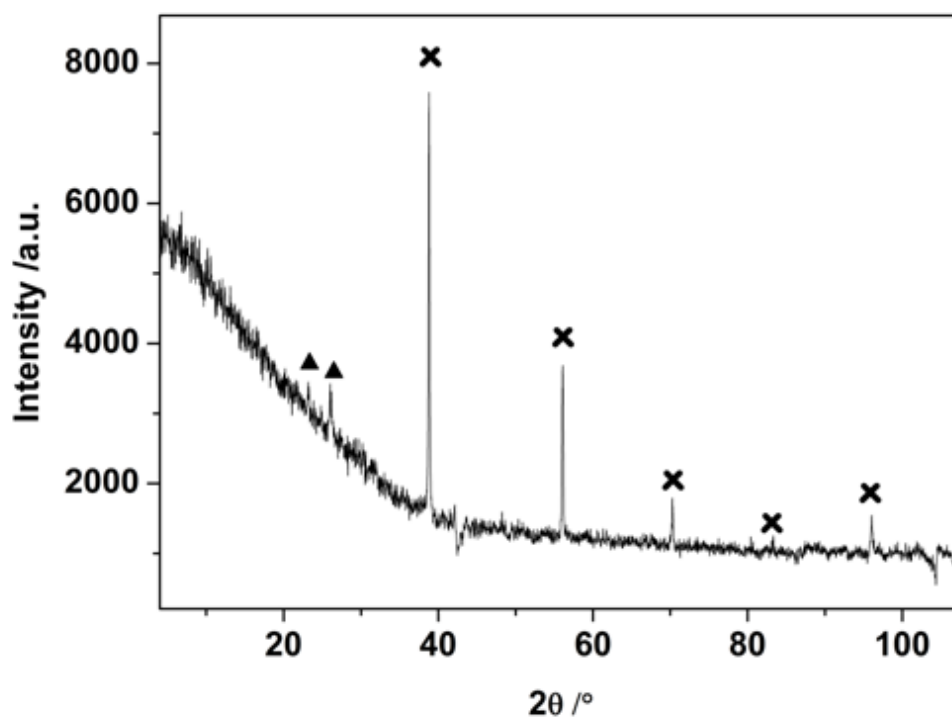


Figure S4. Powder X-ray diffraction ($\lambda = 1.54 \text{ \AA}$) of the $\text{NaBH}_4\text{-NaBF}_4$ (1:0.5, S2-300) sample used for the NMR measurement. Symbols: $\times$ NaF, $\blacktriangle$ LT- NaBF_4 .

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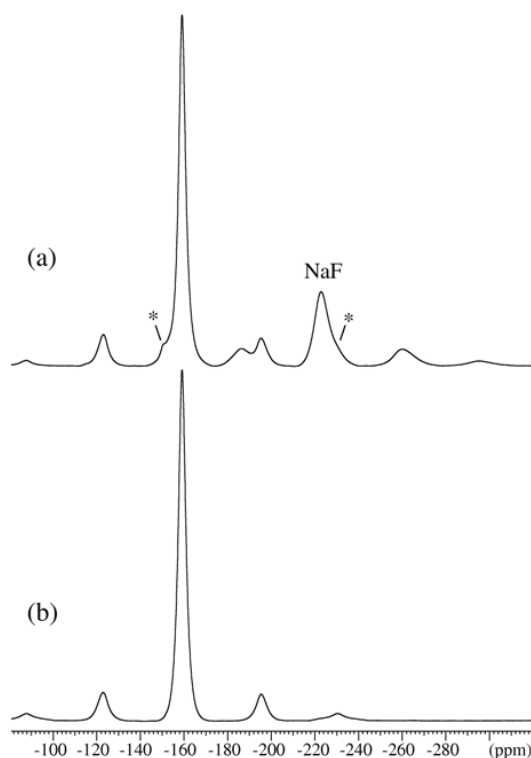


Figure S5. ^{19}F MAS NMR of (a) $\text{NaBH}_4\text{-NaBF}_4$ (1:0.5, S2-300) after heating to $T = 300^\circ\text{C}$ for 1 h and (b) pristine NaBF_4 . Both spectra are obtained at 7.1 T using a spinning speed of $\nu_R = 10.0$ kHz, a $\sim 30^\circ$ excitation pulse, and a relaxation delay of 8 s. The asterisks at -150 ppm and -230 ppm indicate shoulders arising from spinning sidebands from NaF and NaBF_4 , respectively.

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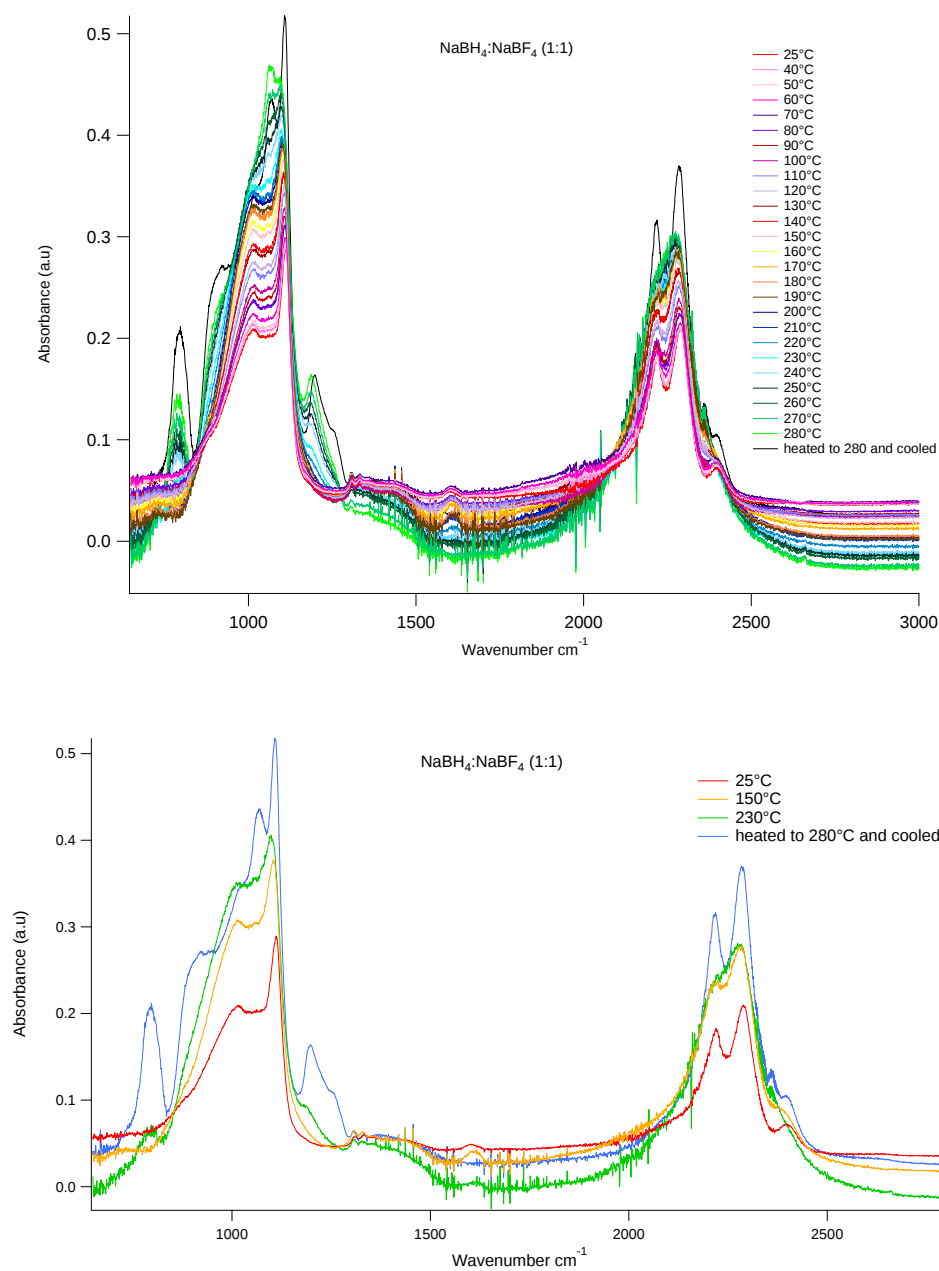


Figure S6. Temperature dependent IR measurement of $\text{NaBH}_4\text{-NaBF}_4$ (1:1, S4). The upper Figure show all spectra and the lower Figure some selected spectra.

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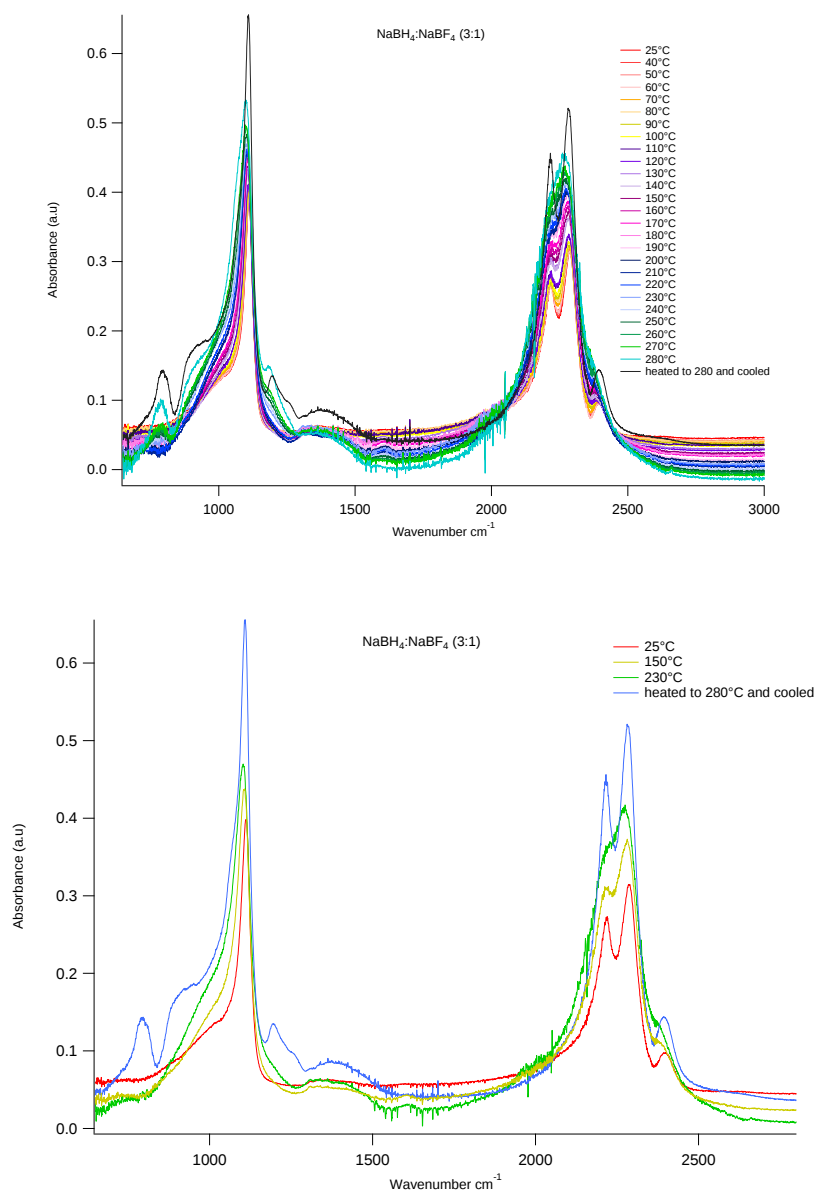


Figure S7. Temperature dependent IR measurement of $\text{NaBH}_4\text{-NaBF}_4$ (1:0.33, S5). The upper Figure show all spectra and the lower Figure some selected spectra.

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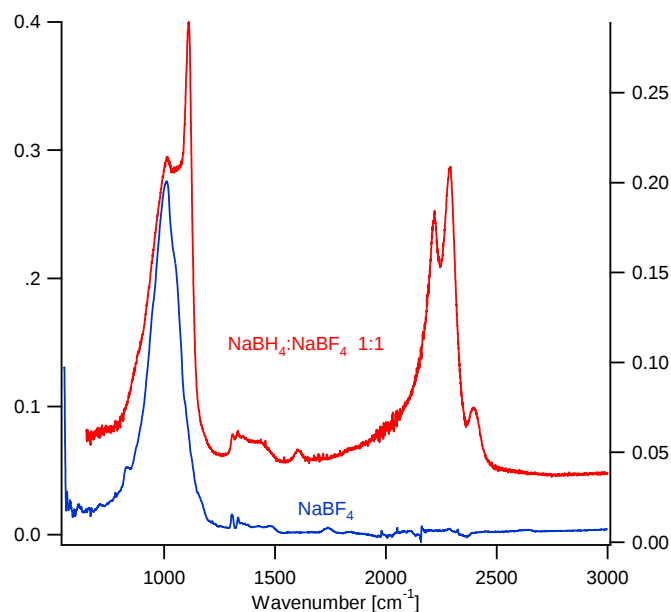


Figure S8. Measured IR spectra of $\text{NaBH}_4\text{-NaBF}_4$ (1:1, S4) shown as red line. IR spectrum of NaBF_4 is shown as reference (blue line).

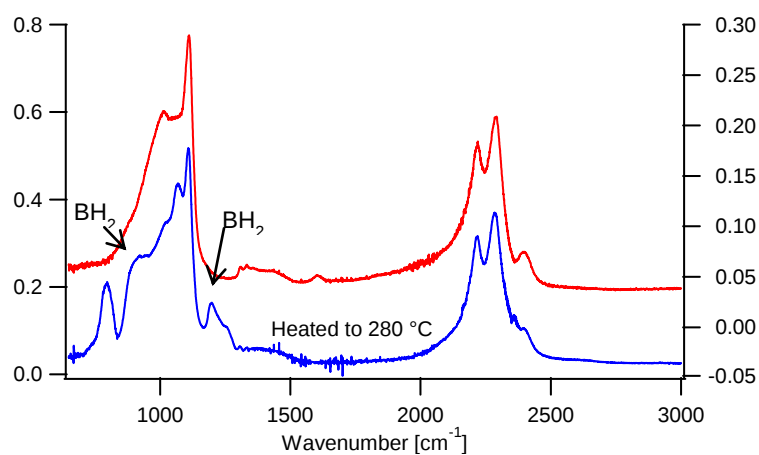


Figure S9. FT-IR spectra of $\text{NaBH}_4\text{-NaBF}_4$ (1:1, S4) measured at room temperature before (red curve) and after heating to 280 °C (blue curve). A tentative assignment of BH_2F_2 is also shown. Notice that the calculated vibrational spectra (Figure S1) show that some of the peaks of BH_2F_2^- , BHF_3^- and BH_3F^- have almost the same frequency values.

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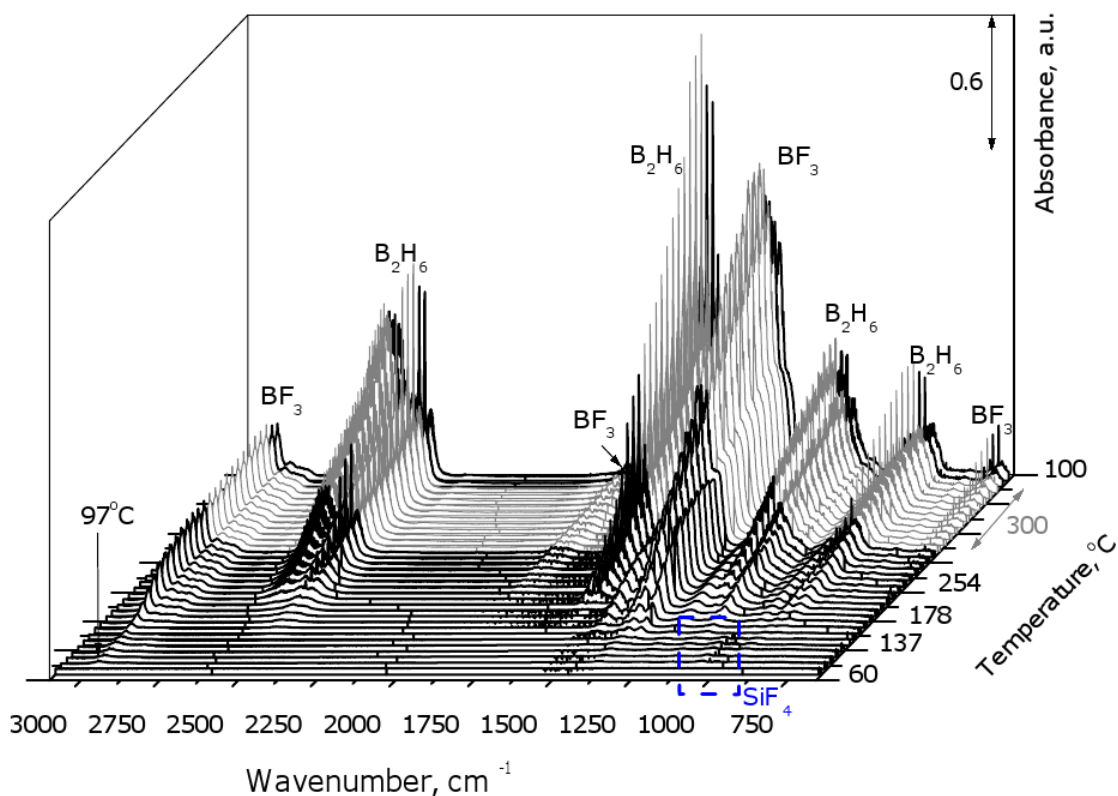


Figure S10. TPD IR of the gaseous species released from $\text{NaBH}_4\text{-NaBF}_4$ (1:0.1, S1) in the temperature region from RT to 300 $^{\circ}\text{C}$. The instrument is not sensitive towards H_2 . A negative signal is recorded in the 1800-1600 cm^{-1} region corresponding to the CO_2 of the background.

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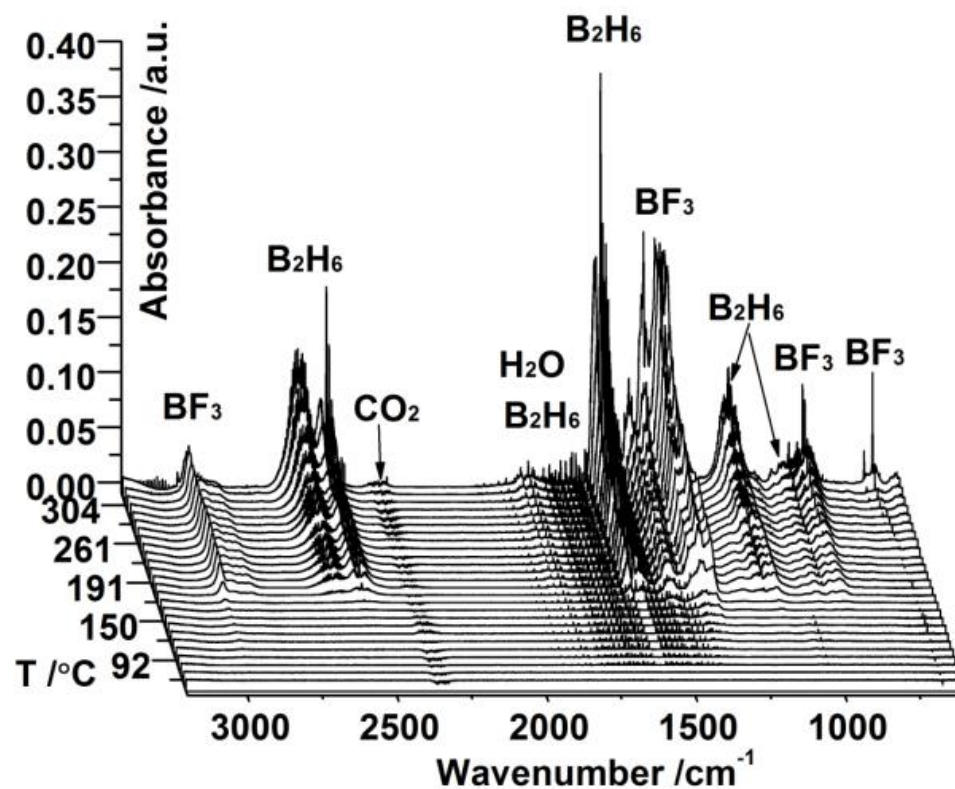


Figure S11. TPD IR of the gaseous species released from $\text{NaBH}_4\text{-NaBF}_4$ (1:0.5, S2) in the temperature region from RT to 300 $^\circ\text{C}$.

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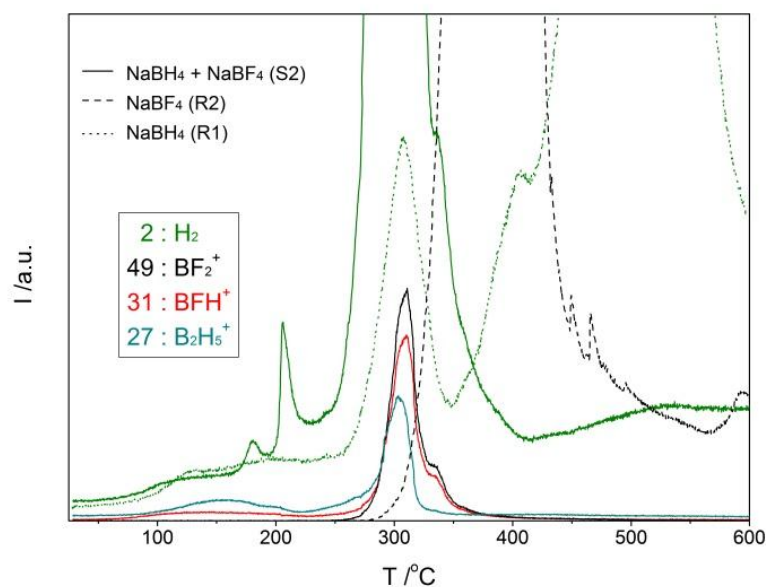


Figure S12 TPD-MS measurements performed in the temperature range from *RT* to 600 °C ($\Delta T/\Delta t = 2$ °C/min) for NaBH₄-NaBF₄ (1:0.1, S1). For comparison, the figure show data for the individual compounds NaBH₄ (R1) and NaBF₄ (R2) as well. The mass fragments detected correspond to H₂, B₂H₆, and BF₃. The range of the intensity axis is reduced by a factor of 10 as compared to the data shown in the article.

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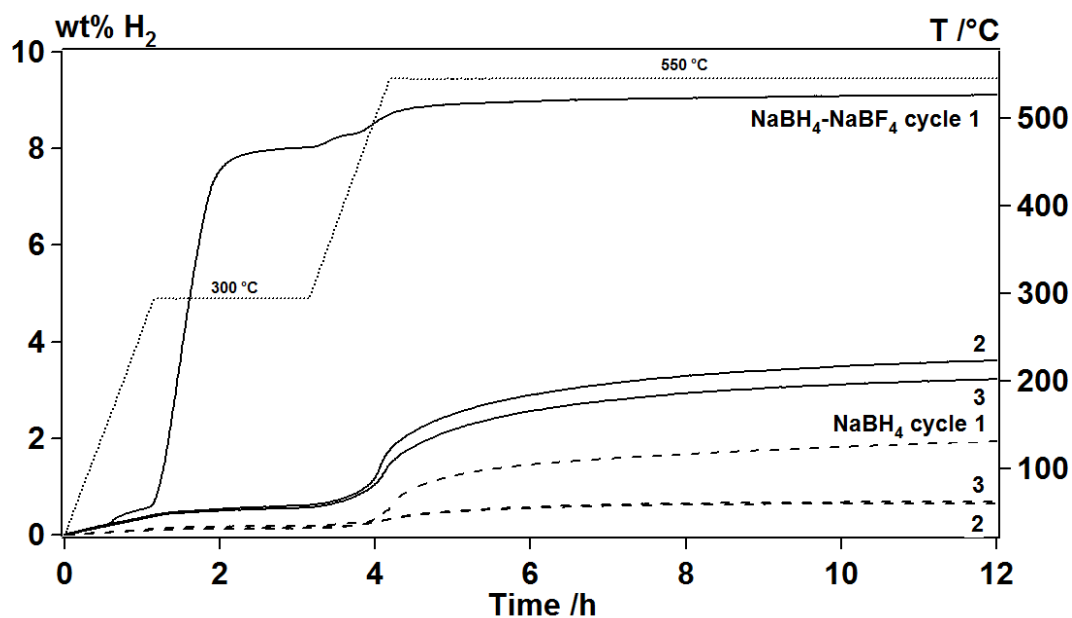


Figure S13. Sieverts measurements showing hydrogen desorption cycles 1 to 3 for samples NaBH_4 (R1, see dashed line) and $\text{NaBH}_4\text{-NaBF}_4$ (1:0.5, S2, solid line). Hydrogen desorption was performed of fixed temperatures of 300 and 550 °C using a heating rate of 4 °C/min and $p(\text{H}_2) = 1$ bar. The temperature profile is shown as dots.

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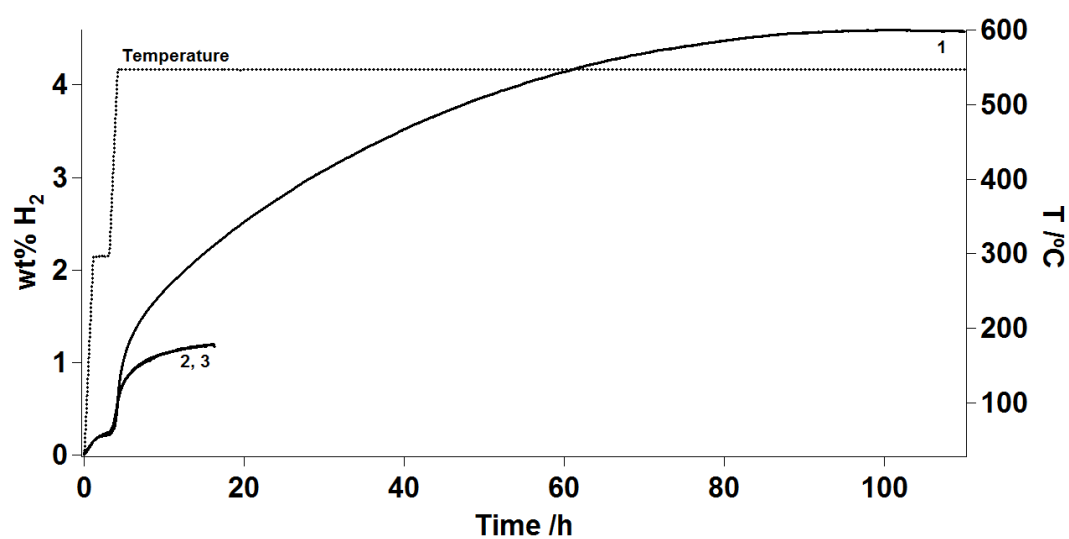


Figure S14. Sieverts measurements showing hydrogen desorption cycles 1 to 3 (2 and 3 are on top of each other) for samples $\text{NaBH}_4\text{-NaF}$ (1:0.25, S6). Hydrogen desorption was performed at fixed temperatures of 300 and 550 °C (heating rate 4 °C/min; the temperature profile is shown as dots).

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Table S4 Thermal analysis. The temperature for the DSC signals and the TGA mass loss are compared for samples S1, S2 and S3 and the reference samples R1 and R2. The calculated gravimetric hydrogen content is denoted $\rho_m(\text{H}_2)$.

Sample	$\rho_m(\text{H}_2)$ /wt%	TGA /wt% (T / °C)	DSC (T / °C) ^b
NaBH ₄ , R1	10.7	-	s (484) s (520)
NaBF ₄ , R2	^a	-	s (246) m (392)
NaBH ₄ -NaBF ₄ 1:0.1, S1	8.3	2.3 (300-320)	w (263) w (278) w (321) s (468)
NaBH ₄ -NaBF ₄ 1:0.5, S2	4.3	7.0 (300-350)	m (245) w (278) m (297) w (314) s(343)
NaBH ₄ -NaBF ₄ 1:0.5, S3	4.3	4.5 (300-350)	m (245) w (278) m (297) w (314) s(338)

^a $\Delta m/m\%(\text{BF}_3) = 61.8$ wt%, ^b s = strong, m = medium, w = weak

Table S5. Sieverts measurements, 3 cycles, compared to the calculated gravimetric hydrogen content $\rho_m(\text{H}_2)$, for NaBH₄ (R1), NaBH₄-NaBF₄ (1:0.5, S2) and NaBH₄-NaF (1:0.25, S6). The gas release for S2 is shown with respect to the amount of NaBH₄ (wt% H₂/NaBH₄) and to the mass of sample (wt% H₂/sample). The amount of released H₂ relative to the full capacity is given in brackets (%).

Sample	$\rho_m(\text{H}_2)$ /wt%	cycle 1 /wt%		cycle 2 /wt%	cycle 3 /wt%
		12h	105h	105h	105h
R1	10.66 ^a	1.9 (18%)	6.0 (56%)	0.69 (6%)	0.65 (6%)
S2 (wt% H₂ / sample)	4.35 ^b	3.7 (85%)	3.7 (85%)	1.5 (34%)	1.3 (30%)
S2 (wt% H₂ / NaBH₄)	10.66 ^b	9.1 (85%)	9.1 (85%)	3.6 (34%)	3.2 (30%)
S6 (wt% H₂ / sample)	6.22 ^a	1.9 (30%)	4.9 (78%)	1.1 (18%)	1.1 (18%)

^a According to reaction (1)

^b Assuming all gas is hydrogen and that all hydrogen is released