

# A thermodynamic investigation of the $\text{LiBH}_4\text{-NaBH}_4$ system

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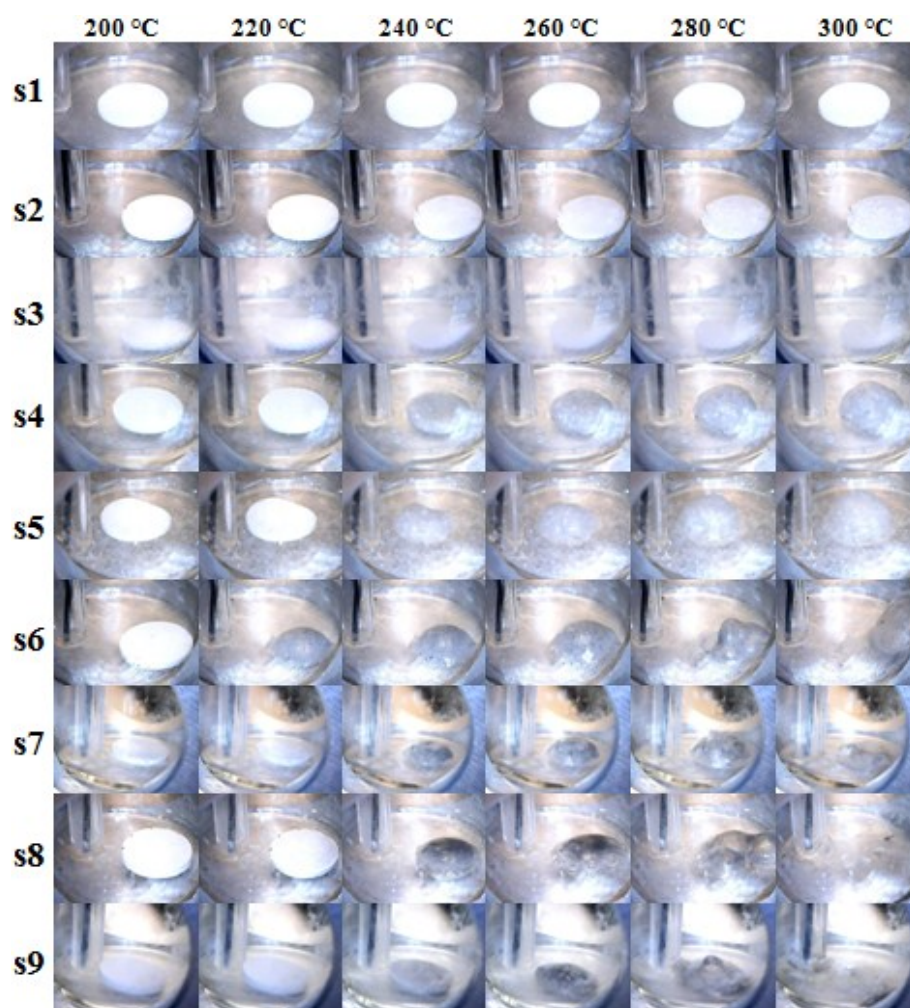
## SUPPLEMENTARY INFORMATION

**Table S1 – ICP (elemental analysis) data for  $\text{LiBH}_4$  (starting material) expressed as the relative contents of B and Li.**

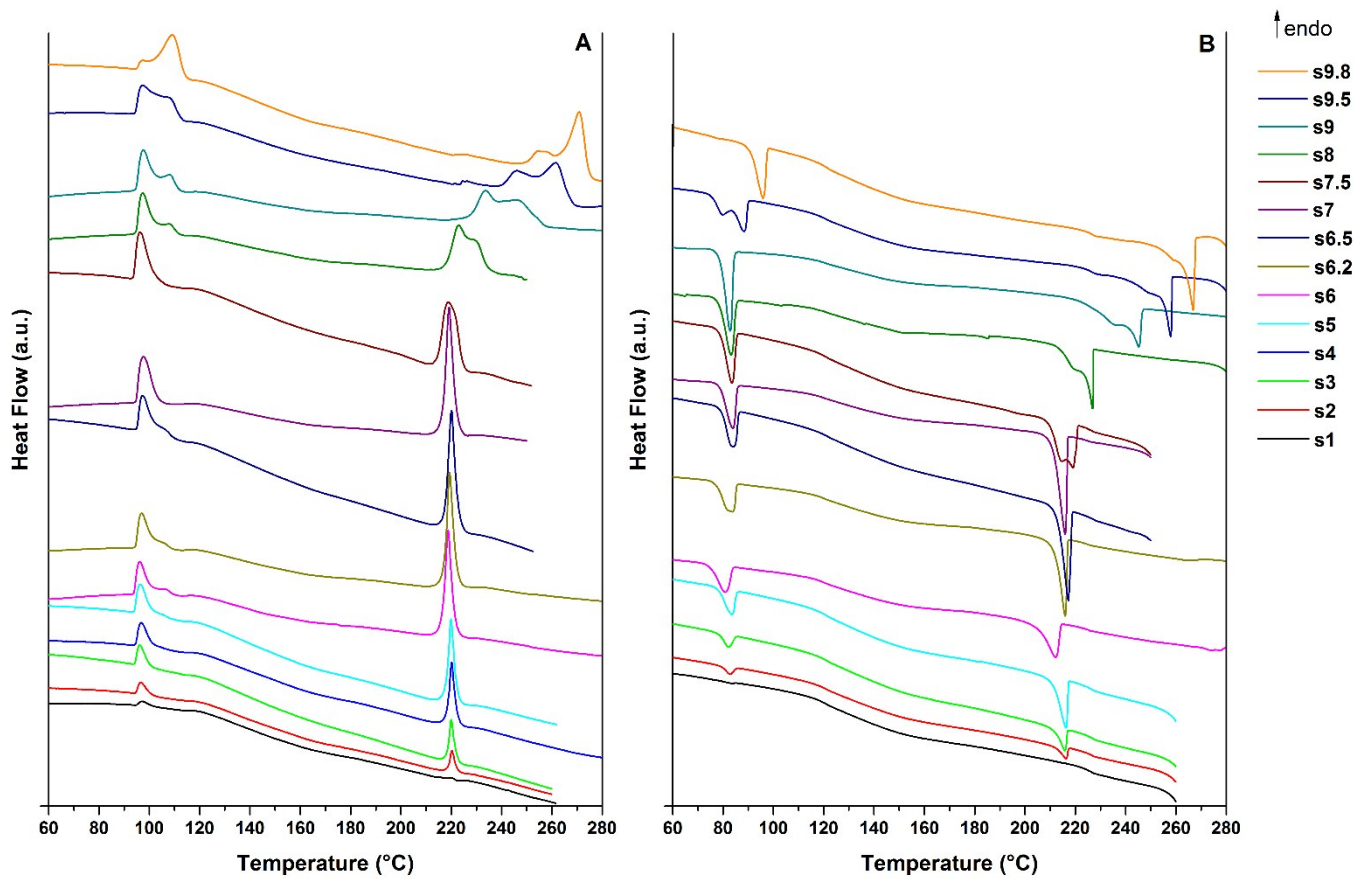
<b>B</b> <b>(mg/kg)</b>	<b>Li</b> <b>(mg/kg)</b>	<b>B</b> <b>(mmol/kg)</b>	<b>Li</b> <b>(mmol/kg)</b>	<b>Purity</b> <b>(ICP)</b>
0.551	0.355	0.0510	0.0511	>99 %

**Table S2 – All DSC data. The area value reported in red were obtained from the integration of the double peak.**

Sample	LiBH <sub>4</sub> mol%	Peak Area (J/g)				Tonset (°C)				
		Phase Transition		Melting		Phase Transition		Melting eutectic		Liquidus
		heating	cooling	heating	cooling	heating	cooling	heating	cooling	cooling
<b>s1</b>	10	13		5		95		215		
<b>s2</b>	20	25	18	24	21	95	85	218	217	
<b>s3</b>	30	39	35	47	46	94	85	217	217	
<b>s4</b>	40	59		75		94		217		
<b>s5</b>	50	69	75	123	125	94	86	216	217	
<b>s6</b>	60	101	101	<b>230</b>	<b>269</b>	94	84	215	214	280
<b>s6.2</b>	62	116	112	<b>254</b>	<b>276</b>	94	86	215	217	270
<b>s6.5</b>	65	109	123	<b>224</b>	<b>213</b>	95	86	216	219	
<b>s7</b>	70	135	133	263	255	95	86	215	217	
<b>s7.5</b>	75	145	151	<b>225</b>	<b>224</b>	94	86	214		221
<b>s8</b>	80	<b>146</b>	<b>168</b>	<b>259</b>	<b>216</b>	94	86	217		227
<b>s9</b>	88	<b>167</b>	<b>212</b>	<b>307</b>	<b>274</b>	95	85	227		247
<b>s9.5</b>	95	<b>171</b>	<b>173</b>	<b>482</b>	<b>338</b>	94	90			259
<b>s9.8</b>	98	<b>203</b>	<b>171</b>	<b>344</b>	<b>389</b>	95	98			268



**Figure S1 – All data from Temperature programmed photographic analysis (TPPA),  $\Delta T/\Delta t = 5$  °C/min, argon atmosphere, temperature range 200-300 °C.**



**Figure S2 – Offset data from DSC measurements,  $\Delta T/\Delta t = 5\text{ }^{\circ}\text{C}/\text{min}$ , 40 mL/minute argon flow, heating (A) and cooling (B).**

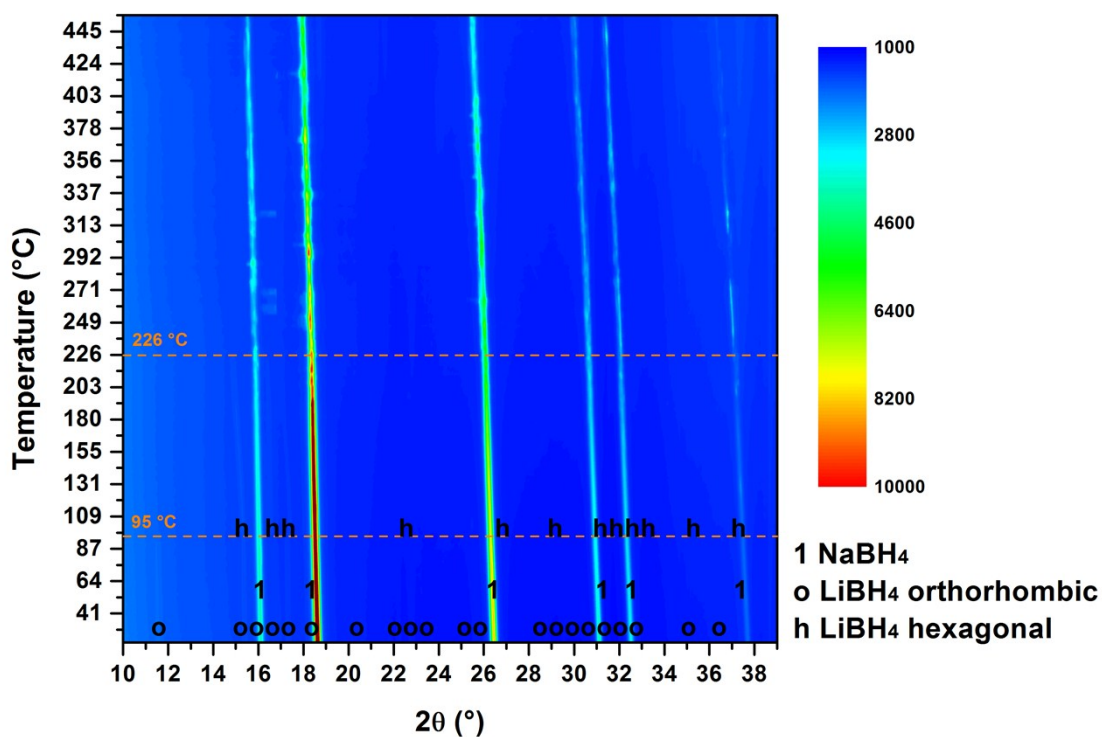


Figure S3 – SR-PXD of s1 ( $\Delta T/\Delta t = 5 \text{ }^\circ\text{C}/\text{min}$ , argon atmosphere, temperature range 25-450  $^\circ\text{C}$ ,  $\lambda=0.9938 \text{ \AA}$ ).

s1 shows the polymorphic transition at 95  $^\circ\text{C}$  and eutectic melting at 226  $^\circ\text{C}$ . Complete melting is not observed, indicating that it happens at temperature higher than 450  $^\circ\text{C}$ .

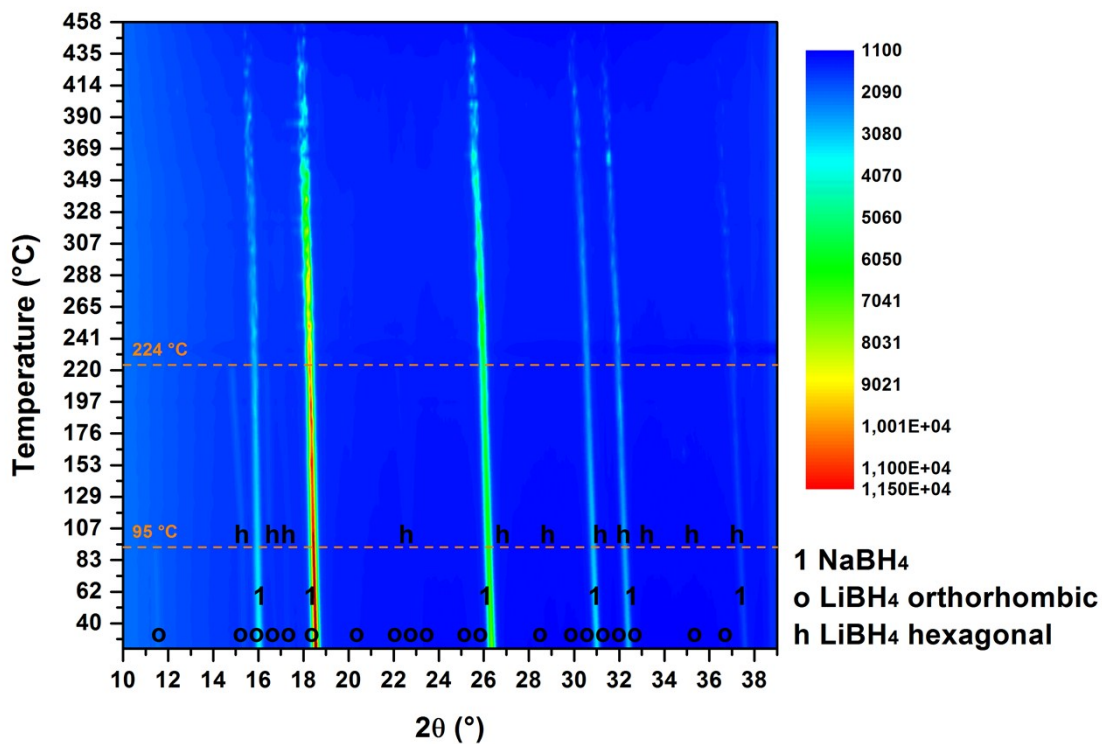


Figure S4 – SR-PXD of s2 ( $\Delta T/\Delta t = 5 \text{ }^\circ\text{C}/\text{min}$ , argon atmosphere, temperature range 25-458  $^\circ\text{C}$ ,  $\lambda=0.9938 \text{ \AA}$ ).

s2 shows the polymorphic transition at 95  $^\circ\text{C}$ , the eutectic melting at 224  $^\circ\text{C}$  and the complete melting at 458  $^\circ\text{C}$ .

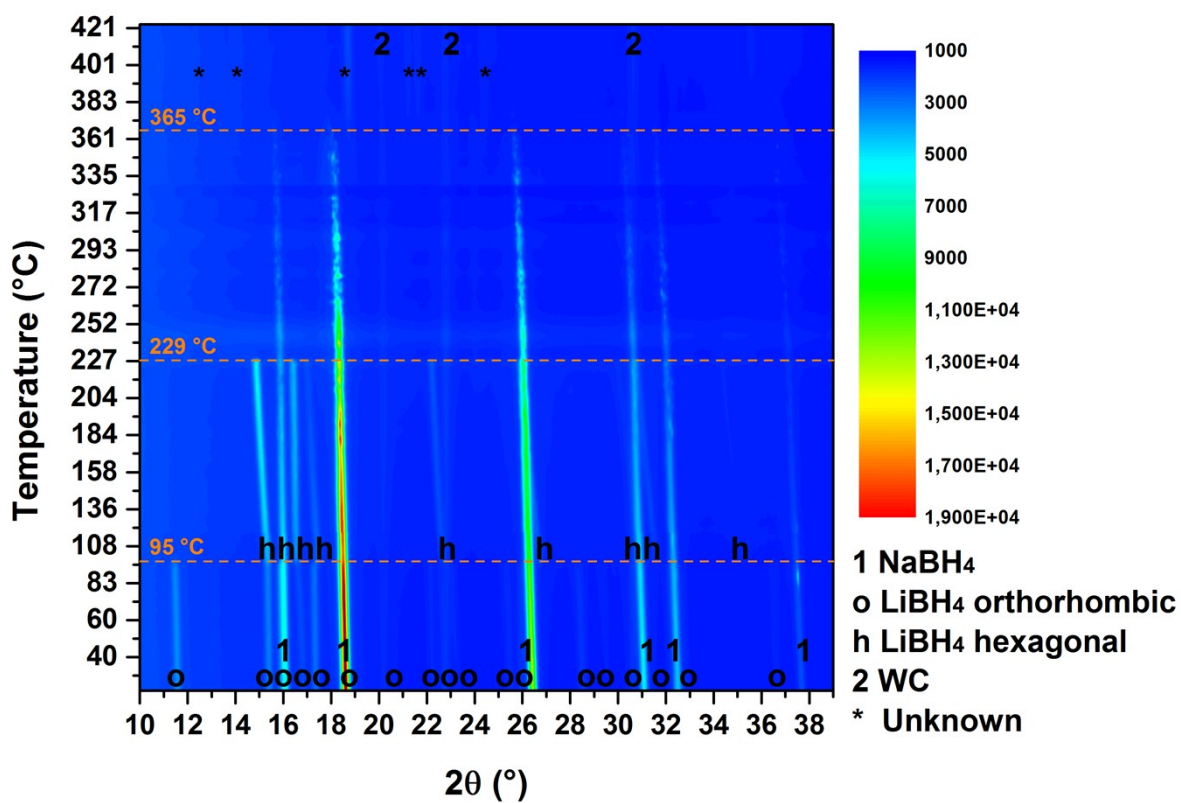


Figure S5 – SR-PXD of s5 ( $\Delta T/\Delta t = 5$  °C/min, argon atmosphere, temperature range 25-425 °C,  $\lambda=0.9938$  Å).

s5 shows the polymorphic transition at 95 °C, the eutectic melting at 229 °C and the complete melting at 365 °C. Above 365 °C s5 decomposes into an unknown phase.

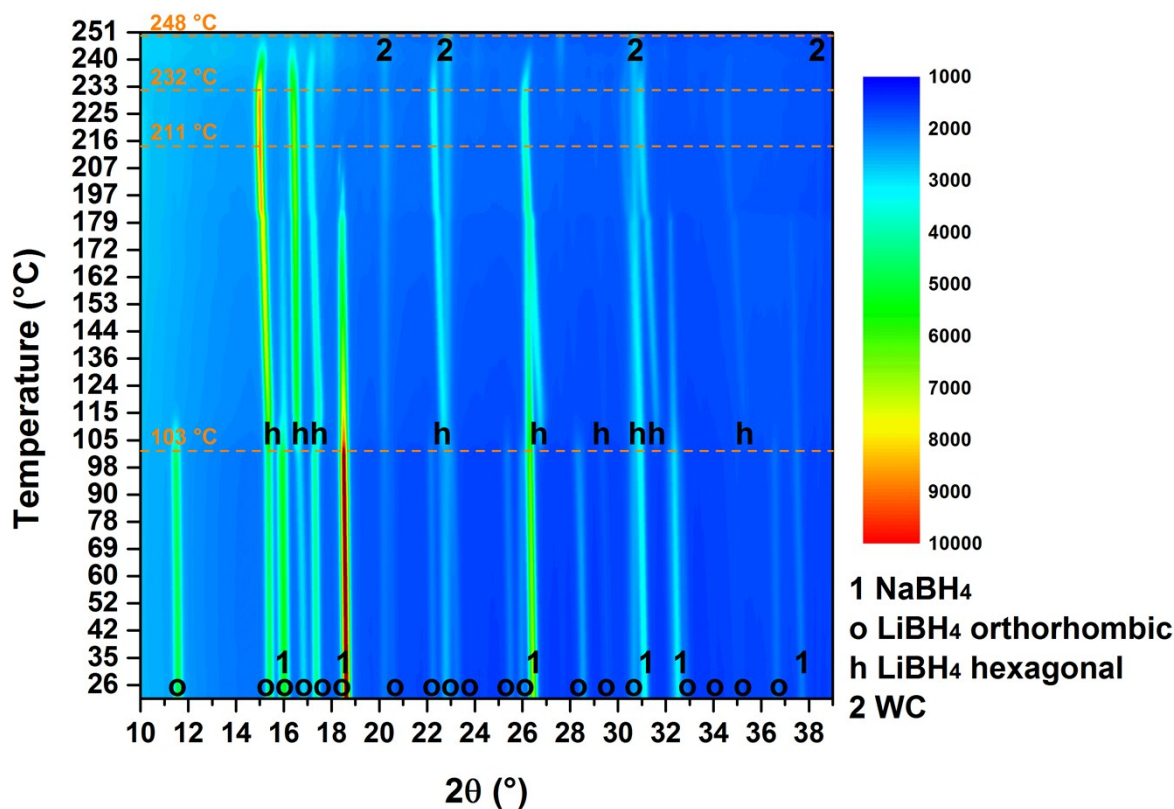
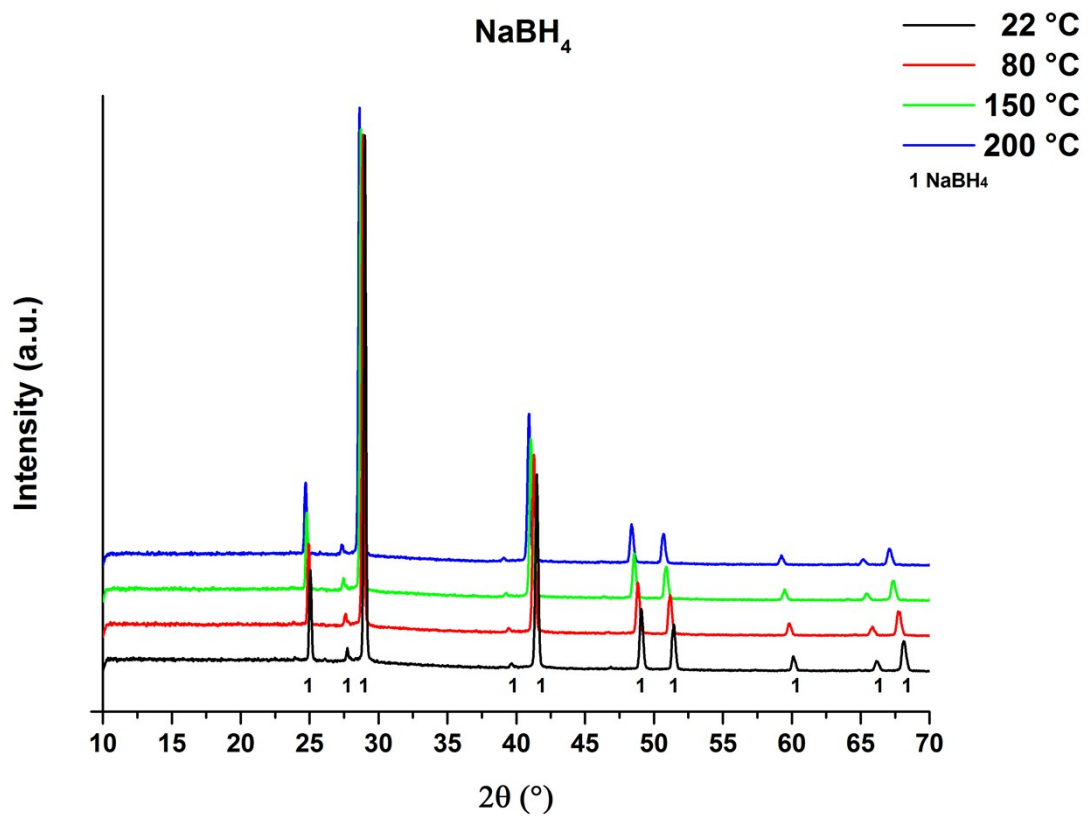


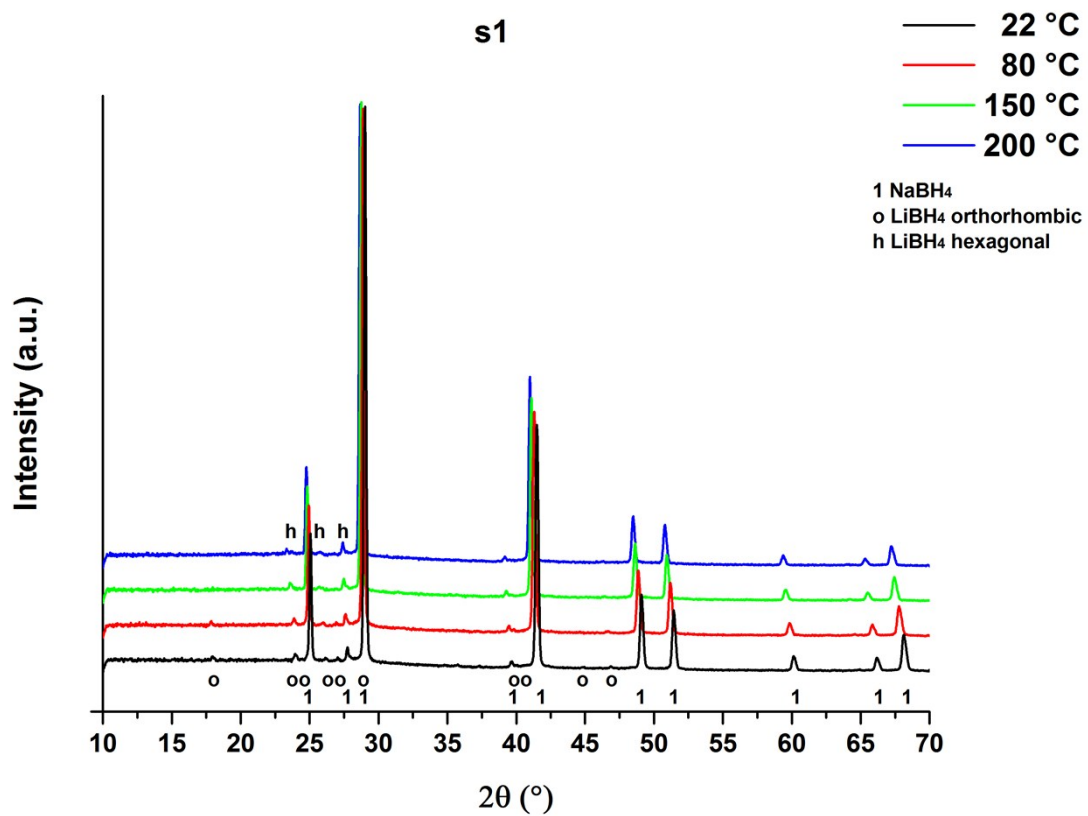
Figure S6 – SR-PXD of s8 ( $\Delta T/\Delta t = 5 \text{ }^\circ\text{C}/\text{min}$ , argon atmosphere, temperature range 25-251  $^\circ\text{C}$ ,  $\lambda=0.9938 \text{ \AA}$ ).

s8 shows the polymorphic transition at 103  $^\circ\text{C}$ . The reflections from NaBH<sub>4</sub> vanish at 211  $^\circ\text{C}$ , significantly before the melting of the eutectic, indicating the formation of a hexagonal solid solution. Upon further heating, the release of Na from the solid solution is observed at 232  $^\circ\text{C}$ , just before the complete melting at 248  $^\circ\text{C}$ . The unit cell parameter of hexagonal solid solution decreases significantly, as NaBH<sub>4</sub> is expelled from the structure, due to a reduced solubility during the melting of the mixture.

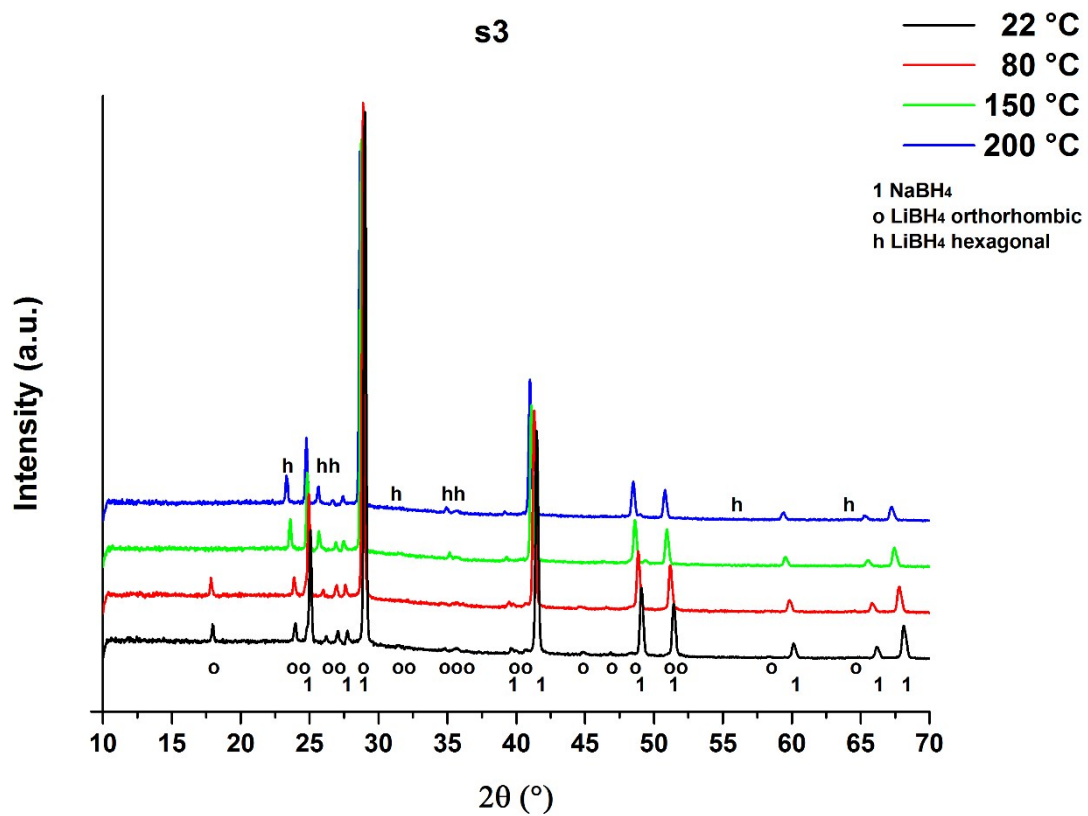




**Figure S7 – HT-PXD of NaBH<sub>4</sub> at different temperatures in equilibrium condition ( $\lambda=1.54059$  Å).**



**Figure S8 – HT-PXD of s1 at different temperatures in equilibrium condition ( $\lambda=1.54059 \text{ \AA}$ ).**



**Figure S9 – HT-PXD of s3 at different temperatures in equilibrium condition ( $\lambda=1.54059 \text{ \AA}$ ).**

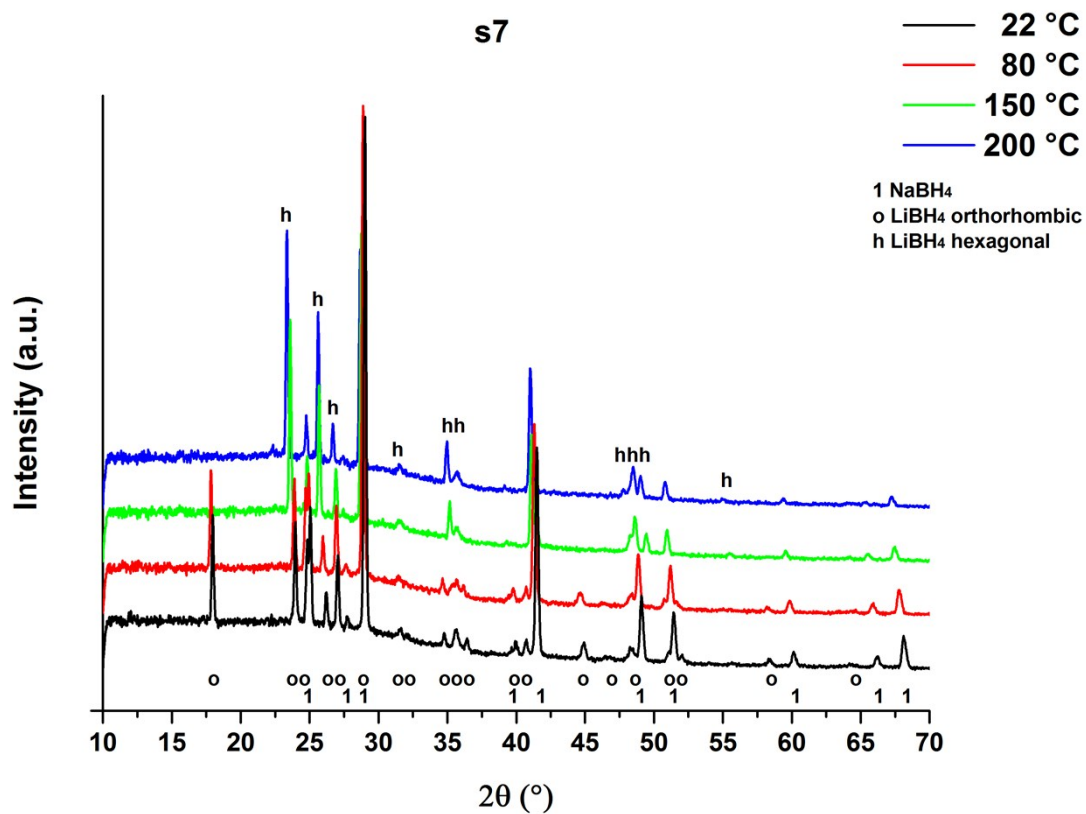


Figure S10 – HT-PXD of s7 at different temperatures in equilibrium condition ( $\lambda=1.54059 \text{ \AA}$ ).

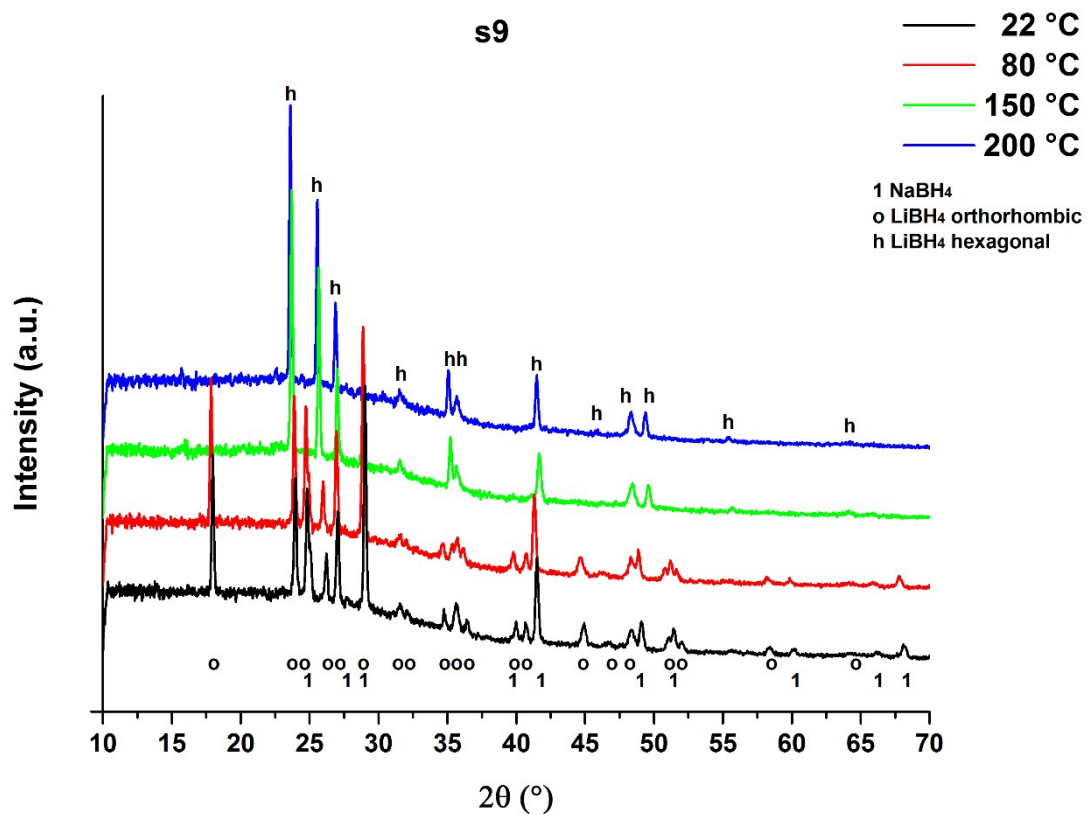


Figure S11 – HT-PXD of s9 at different temperatures in equilibrium condition ( $\lambda=1.54059 \text{ \AA}$ ).

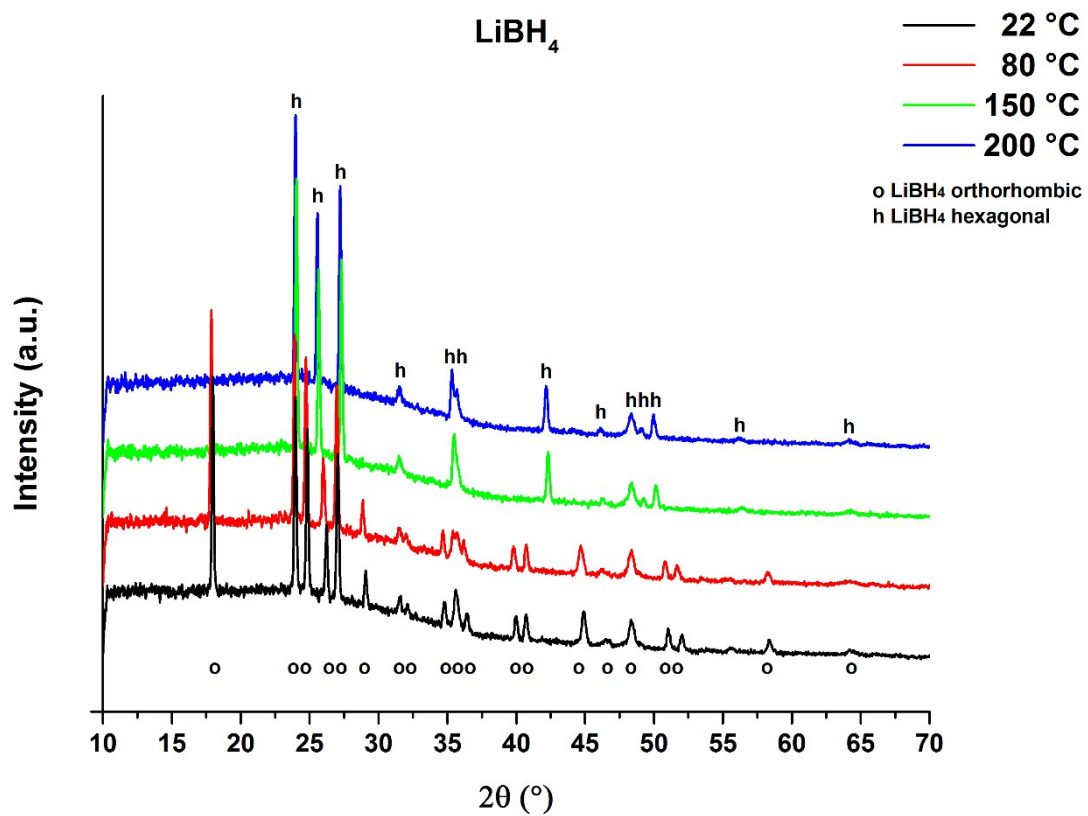


Figure S12 – HT-PXD of  $\text{LiBH}_4$  at different temperatures in equilibrium condition ( $\lambda=1.54059 \text{ \AA}$ ).