

Phase diagrams in the $\text{LiBH}_4\text{-NaBH}_4\text{-KBH}_4$ system

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SUPPLEMENTARY INFORMATION

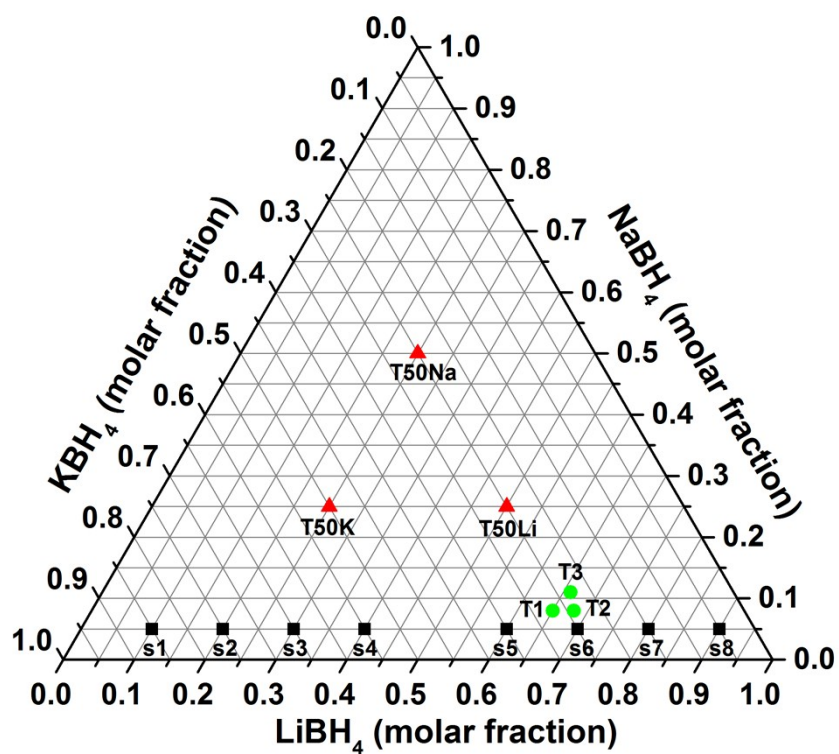


Figure S1 – Investigated compositions in the ternary system. For more details, see Table 1.

Table S1 – List and details of synchrotron facilities.

Facility	Beam Line	Wavelength (Å)	Exposure Time (s)	Sample
MAXLAB laboratories, MAX-II Lund, Sweden	I711	0.9938	30	T50Li, T50Na, T50K
Dimond Light Source Didcot, UK	I11	0.8259	5	T1
DESY Hamburg, Germany	PETRA III	0.2072	5	T2
ESRF Grenoble, France	BM01	0.7129	5	T3

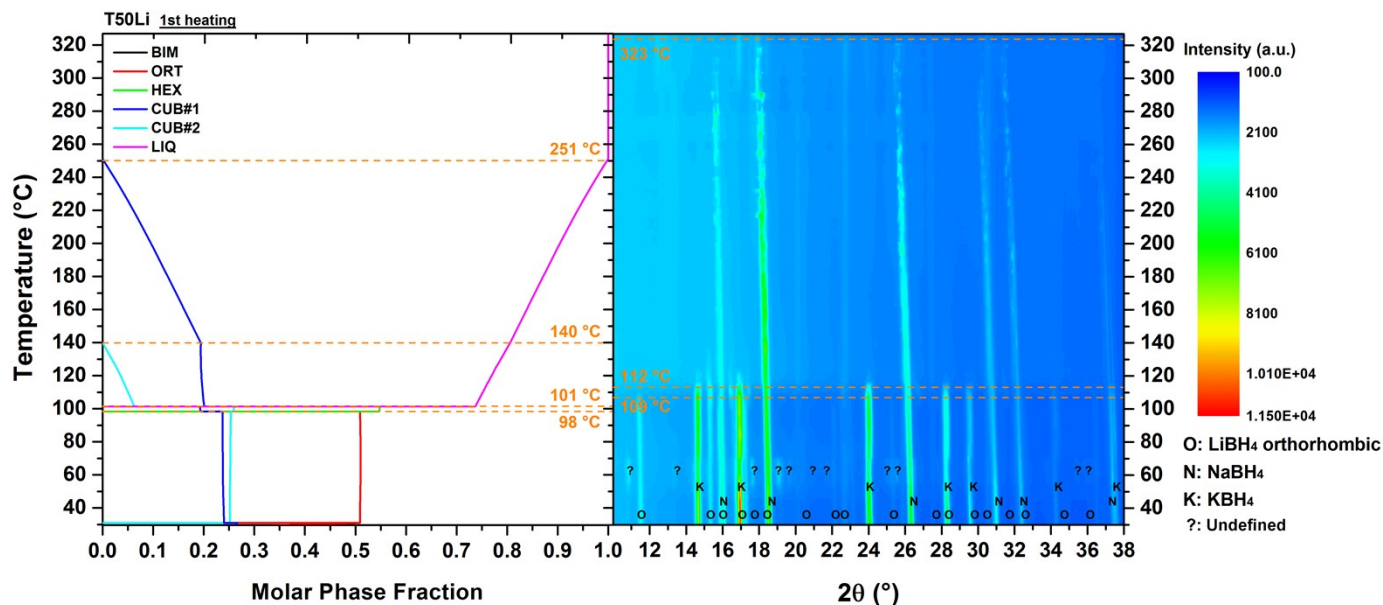


Figure S2 - Amount of calculated phases (CALPHAD, left) and SR-PXD (right) of T50Li, 0.50LiBH₄-0.25NaBH₄-0.25KBH₄ ($\lambda = 0.9938$ Å, $\Delta T/\Delta t = 5$ °C/min, argon atmosphere).

Polymorphic transition of LiBH₄ is observed at 109 °C (calculated temperature 98 °C), followed by eutectic melting at 112 °C (calculated temperature 101 °C). At 140 °C the calculations reveals the complete melting of the cubic phase two (KBH₄) that is no more visible in the *in-situ* data after the eutectic melting. Experimental temperatures are higher with respect to calculated one probably because of kinetic reasons. Liquidus temperature is recorded at 323 °C (calculated temperature 251 °C).

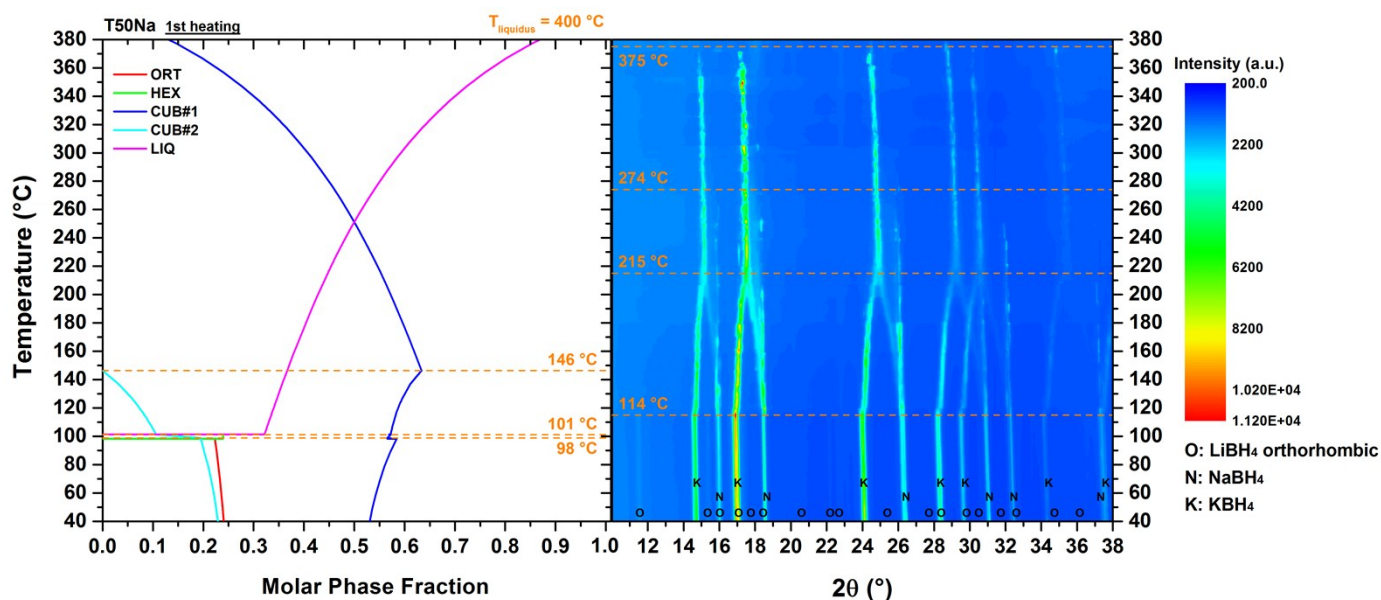


Figure S3 - Amount of calculated phases (CALPHAD, left) and SR-PXD (right) of T50Na, 0.25LiBH₄-0.50NaBH₄-0.25KBH₄ ($\lambda = 0.9938 \text{ \AA}$, $\Delta T/\Delta t = 5 \text{ °C/min}$, argon atmosphere).

At 98 °C and 101 °C calculated temperature, polymorphic transition of LiBH₄ and eutectic melting are taking place respectively, but they are not clearly revealed by the *in-situ* investigation. At 185 °C (174 °C calculated temperature), the cubic phase two (KBH₄) disappears because of the formation of a single-phase cubic solution. In the experiment, the solid solution between NaBH₄ and KBH₄ starts to form at 114 °C and one phase solid solution is observed at 215 °C. Liquidus temperature is recorded at 375 °C (calculated temperature 400 °C).

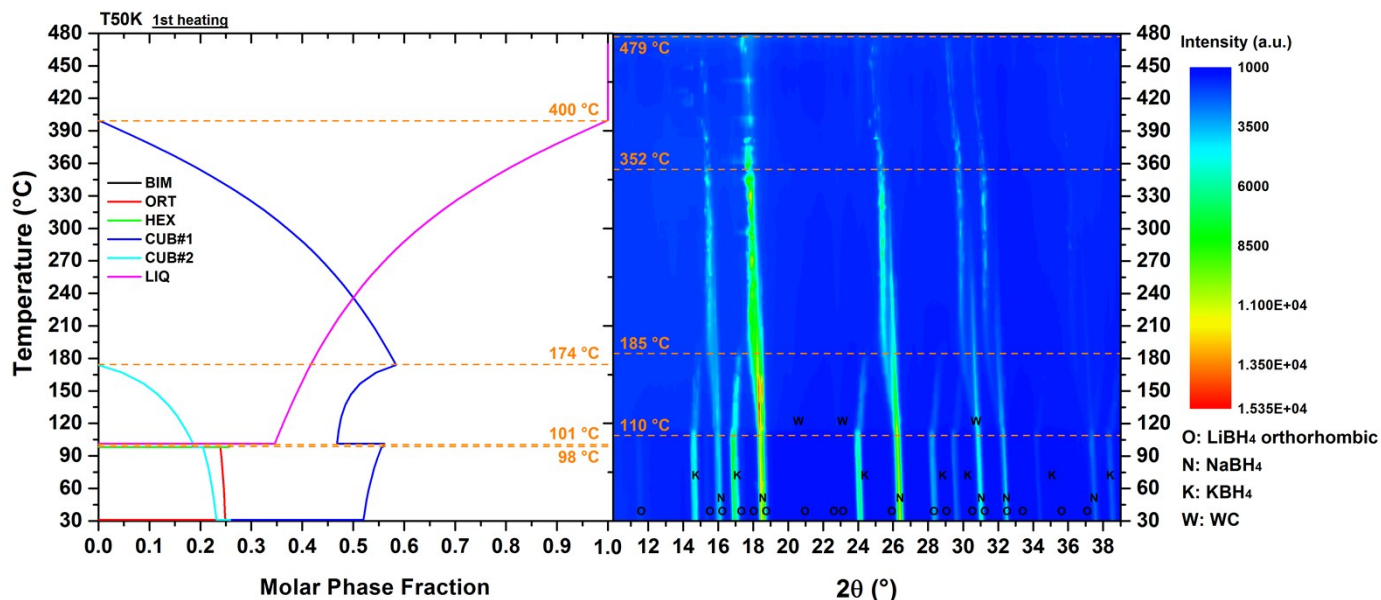


Figure S4 - Amount of calculated phases (CALPHAD, left) and SR-PXD (right) of T50K, 0.25LiBH₄-0.25NaBH₄-0.50KBH₄ ($\lambda = 0.9938 \text{ \AA}$, $\Delta T/\Delta t = 5 \text{ °C/min}$, argon atmosphere).

As reported before, at 98 °C and 101 °C calculated temperature, polymorphic transition of LiBH₄ and eutectic melting are taking place respectively, from *in-situ* investigation the eutectic melting can be observed at 110 °C. At 185 °C (174 °C calculated temperature), the cubic phase two (KBH₄) disappear because of the formation of a single-phase cubic solution. Liquidus temperature is recorded at 352 °C (calculated temperature 400 °C).

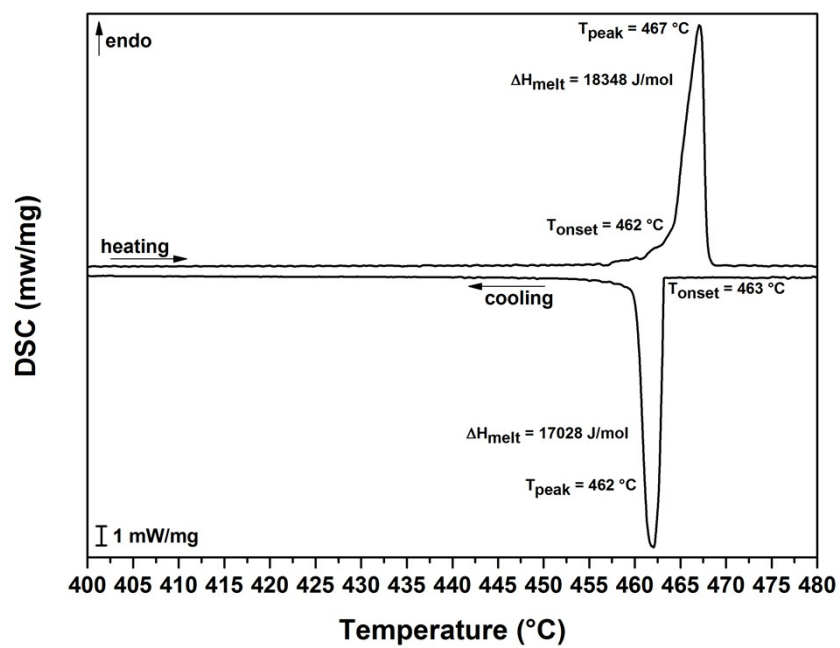


Figure S5 – DSC of 0.682NaBH₄-0.318KBH₄ mixture, heating and cooling at 5 °C/min under 10 bars of H₂.

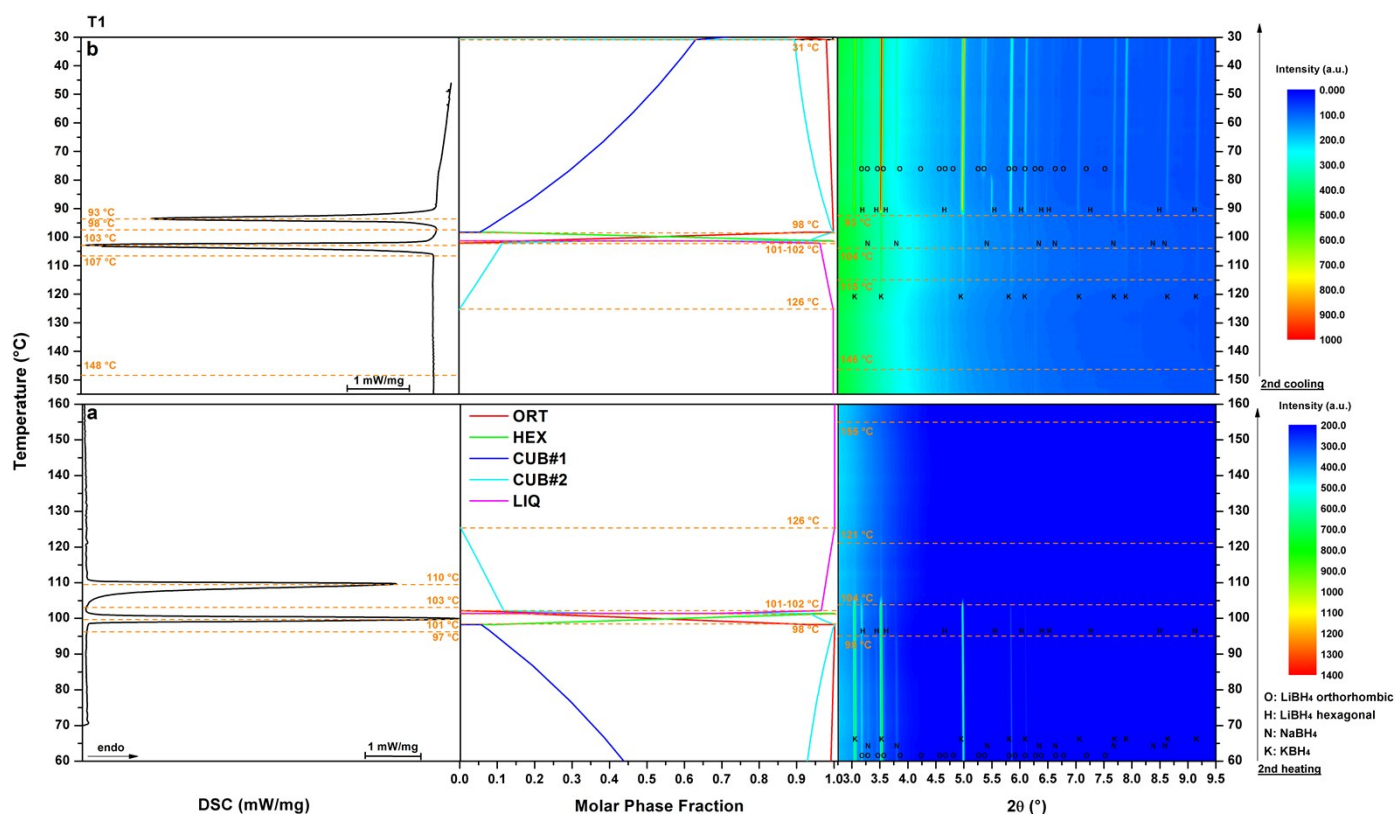


Figure S6 – DSC (left), amount of calculated phases (CALPHAD, middle) and SR-PXD (right) of T1, $0.65\text{LiBH}_4-0.08\text{NaBH}_4-0.27\text{KBH}_4$ ($\lambda = 0.2072 \text{ \AA}$, $\Delta T/\Delta t = 5 \text{ }^\circ\text{C}/\text{min}$, argon atmosphere, 2nd cycle of heating (a) and cooling (b)).

As reported before, at 98 °C and 101 °C calculated temperature, polymorphic transition of LiBH_4 and eutectic melting are taking place respectively. From *in-situ* investigation, the transitions can be observed at 95 °C and 104 °C respectively, in good agreement also with DSC measurement (start of DSC peak at 97 °C and 103 °C, on heating, respectively). At 121 °C NaBH_4 disappears (melting), and the liquidus temperature is recorded at 155 °C (calculated temperature 125 °C) but it cannot be clearly reveal by DSC measurements, only a noisy baseline is recorded after the eutectic melting. On cooling, the same transitions can be observed under undercooled conditions.

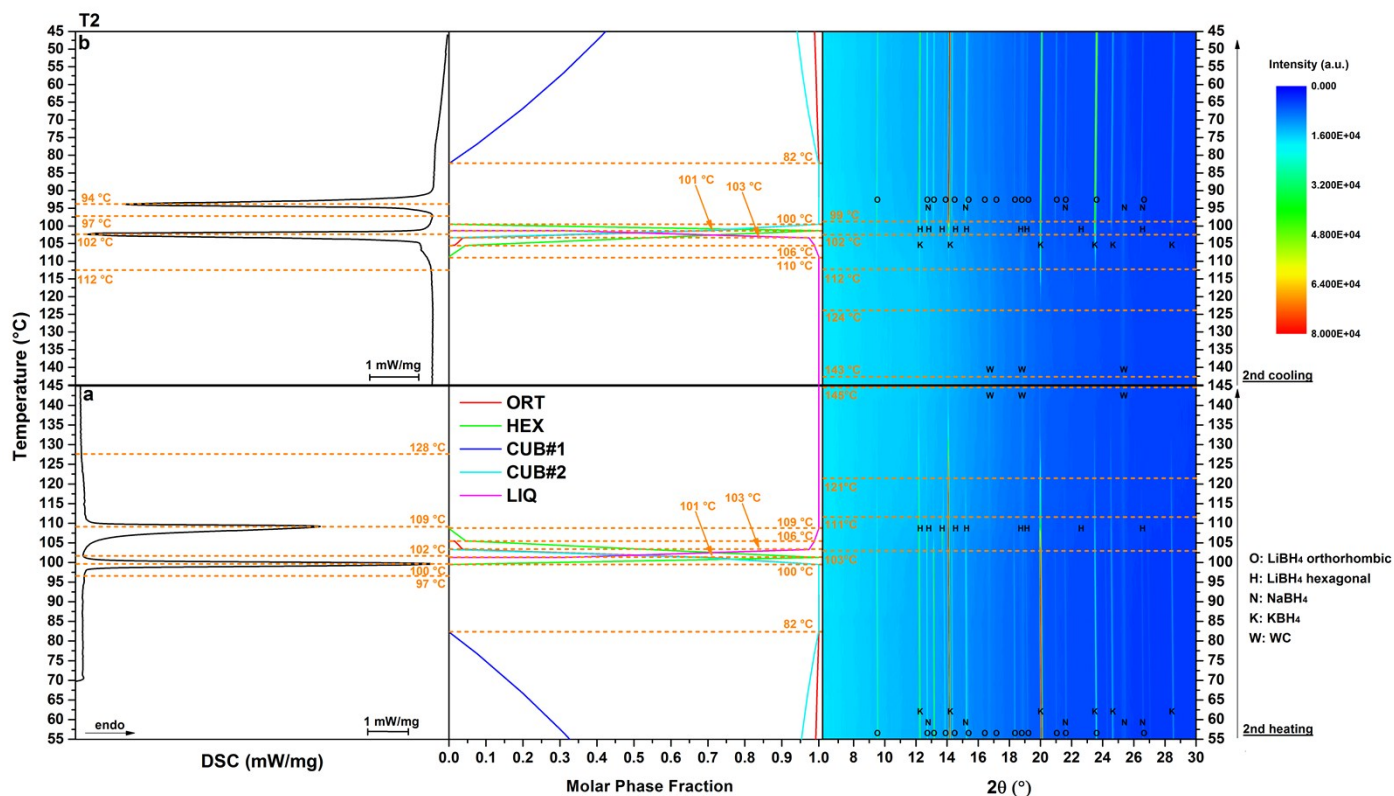


Figure S7 – DSC (left), amount of calculated phases (CALPHAD, middle) and SR-PXD (right) of $T2$, $0.68\text{LiBH}_4\text{-}0.08\text{NaBH}_4\text{-}0.24\text{KBH}_4$ ($\lambda = 0.8259 \text{ \AA}$, $\Delta T/\Delta t = 5^{\circ}\text{C}/\text{min}$, argon atmosphere, 2nd cycle of heating (a) and cooling (b)). Presence of WC due to ball milling.

At 82°C calculated temperature, a single cubic solid solution phase is formed, but it is not revealed by *in-situ* investigation. At 100°C and 101°C calculated temperature, polymorphic transition of LiBH_4 and eutectic melting are taking place respectively, while from *in-situ* investigation from 103°C to 111°C both orthorhombic and hexagonal LiBH_4 are present and then melt. Calculations predict that the cubic phase is the first to melt (103°C), followed by the orthorhombic (106°C) and hexagonal phase (109°C). Experimentally orthorhombic and hexagonal phase are completely melted at 111°C , followed by the melting of NaBH_4 (121°C) and KBH_4 (145°C , liquidus temperature, 109°C calculated liquidus temperature). On cooling, the same transitions can be observed under undercooled conditions.