Phase diagrams in the LiBH$_4$-NaBH$_4$-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.

<table>
<thead>
<tr>
<th>Facility</th>
<th>Beam Line</th>
<th>Wavelength (Å)</th>
<th>Exposure Time (s)</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAXLAB laboratories, MAX-II Lund, Sweden</td>
<td>I711</td>
<td>0.9938</td>
<td>30</td>
<td>T50Li, T50Na, T50K</td>
</tr>
<tr>
<td>Dimond Light Source Didcot, UK</td>
<td>I11</td>
<td>0.8259</td>
<td>5</td>
<td>T1</td>
</tr>
<tr>
<td>DESY Hamburg, Germany</td>
<td>PETRA III</td>
<td>0.2072</td>
<td>5</td>
<td>T2</td>
</tr>
<tr>
<td>ESRF Grenoble, France</td>
<td>BM01</td>
<td>0.7129</td>
<td>5</td>
<td>T3</td>
</tr>
</tbody>
</table>
Polymorphic transition of LiBH$_4$ 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 (KBH$_4$) 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).
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) disappear 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 (λ = 0.9938 Å, ΔT/Δt = 5 °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 0.682NaBH$_4$-0.318KBH$_4$ mixture, heating and cooling at 5 °C/min under 10 bars of H$_2$. 
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 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 NaBH₄ 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, 0.68LiBH$_4$-0.08NaBH$_4$-0.24KBH$_4$ ($\lambda = 0.8259$ Å, $\Delta T/\Delta t = 5$ °C/min, argon atmosphere, 2$^{nd}$ 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.