Electronic Supplementary Information (ESI)

Eutectic melting of $LiBH_4$ – KBH_4

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Experimental

Synthesis

An overview of produced samples along with preparation and characterisation methods is given in Table S1. Mechanochemical treatment i.e. ball milling (BM) of samples **s12-s14** was performed in a Fritsch Pulverisette 6 planetary mill under inert conditions (argon atmosphere) in 80 mL tungsten carbide containers and balls (o.d. 6 mm). Ball milling was conducted applying 5 min milling followed by 2 min pause for repeated sequences using a speed of 400 rpm for the total milling time given in Table 1. Ball milling was stopped for **s13** and **s14** after 5, 10, 20, 30, 45, 60, 90, 120 and 240 min and after 12, 24 and 36 h. At these times small amounts of sample were taken out and a PXD pattern was obtained for each sample. All ball milling times are total milling time.

Table S1 - Overview of produced samples, synthesis and characterisation.

Sample	x$LiBH_4$	1-xKBH_4	Synthesis	Characterisation
s1	0.9	0.1	Hand mixing	DSC/TGA, TPPA
s2	0.8	0.2	Hand mixing	DSC/TGA, TPPA
s3	0.7	0.3	Hand mixing	*In situ* SR-PXD, DSC/TGA, TPPA
s4	0.6	0.4	Hand mixing	DSC/TGA, TPPA
s5	0.5	0.5	Hand mixing	DSC/TGA, TPPA
s6	0.4	0.6	Hand mixing	DSC/TGA, TPPA
s7	0.3	0.7	Hand mixing	DSC/TGA, TPPA
s8	0.2	0.8	Hand mixing	DSC/TGA, TPPA
s9	0.1	0.9	Hand mixing	DSC/TGA, TPPA
s10	0.75	0.25	Hand mixing	*In situ* SR-PXD, DSC/TGA, TPPA
s11	0.725	0.275	Hand mixing	DSC/TGA, TPPA
s12	0.725	0.275	Ball milling, 240 min	DSC/TGA
s13	0.5	0.5	Ball milling, 36 h	PXD
s14	0.665	0.335	Ball milling, 36 h	PXD

Samples **s1**-**s11** were made by manual mixing of $LiBH_4$ and KBH_4 in selected ratios using a mortar, pestle and pre-ball milled $LiBH_4$.

All preparation and manipulation of samples was performed in a glove box with a circulation purifier maintained under an argon atmosphere with <1 ppm of O_2 and H_2O or using Schlenk techniques utilizing a Schlenk line in a fume hood. The chemicals used were lithium borohydride, $LiBH_4$ (Sigma-Aldrich, 95 %) and potassium borohydride, KBH_4 (Sigma-Aldrich, 97 %). All chemicals were used as received.

Laboratory powder X-ray diffraction

In house powder X-ray diffraction (PXD) was performed using a Rigaku Smart Lab X-ray diffractometer configured with a Cu X-ray source and a parallel beam multilayer mirror (Cu Kα radiation, λ = 1.540593 Å). Data were collected at RT between 5 and 55° 2θ at 2°/min. Air-sensitive samples were mounted in 0.5 mm borosilicate glass capillaries in a glove box and sealed with glue.

In situ time resolved synchrotron radiation powder X-ray diffraction

In situ SR-PXD data were collected for $0.7LiBH_4 – 0.3KBH_4$ (**s3**), $0.75LiBH_4 – 0.25KBH_4$ (**s10**) and $0.725LiBH_4 – 0.275KBH_4$ (**s12**) during two beam times at beam line I711 at the MAX IV laboratories in Lund, Sweden with a MAR165 CCD detector system and selected wavelength of $\lambda = 0.9910$ and 0.9919 Å with X-ray exposure times of 10 s. The *in situ* sample cell is specially developed for gas/solid reactions studies and allows high pressure and temperature to be applied.[1] The powdered samples were mounted in a sapphire (Al_2O_3) single-crystal tube (o.d. 1.09 mm, i.d. 0.79 mm) in an argon-filled glovebox $p(O_2, H_2O) < 1$ ppm. The temperature was controlled with a thermocouple placed in the sapphire tube less than 1 mm from the sample.

All raw 2D diffraction data sets were transformed to 2D powder patterns using the FIT2D program,[2] incorporating wavelength calibration using a standard NIST 660a LaB_6 sample, and masking single-crystal diffraction spots from the sapphire sample holder. Uncertainties of the integrated intensities were calculated at each 2θ point by applying Poisson statistics to the intensity data, considering the geometry of the detector.[3]

Thermal analysis

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained simultaneously using a PerkinElmer STA 6000 apparatus. The samples (approx. 3 mg) were placed in an Al crucible and heated (5 °C/min) in an argon flow of 65 mL/min. The eutectic samples exhibit vigorous frothing above 400 °C, inhibiting us to heat the samples further during the thermal analysis experiment.

Temperature programmed photographic analysis

Temperature programmed photographic analysis (TPPA) was performed using a setup previously described.[4] Photographs were collected using a digital camera whilst heating the samples from RT to 300 °C ($\Delta T/\Delta t$ = 5 °C/min). Samples were sealed under argon in a glass vial connected to an argon filled balloon to maintain an inert atmosphere. A thermocouple was in contact with the sample within the glass vial to monitor the temperature during thermolysis. The glass vial was encased within an aluminium block with open viewing windows for photography, to provide near-uniform heating by rod heaters, interfaced to a temperature controller. The aluminium block was in some experiments painted black with a magic marker to improve the optical contrast. Additional experiments for **s5** and **s11** were performed in the TPPA setup, in order to determine the composition in the samples after melting at 125 °C and then cooling at rates of $\Delta T/\Delta t$ = 1 and 20 °C/min. The samples were analysed by PXD after cooling. Additionally, **s5** and **s11** were packed in borosilicate capillaries and annealed at 125 °C for 30 min and cooled at $\Delta T/\Delta t$ = 1 °C/min to RT. Subsequently, the samples were analysed with PXD. The samples were then crushed together with the capillaries and repacked in new capillaries. It was not possible to get the melted samples out of the capillaries after melting.

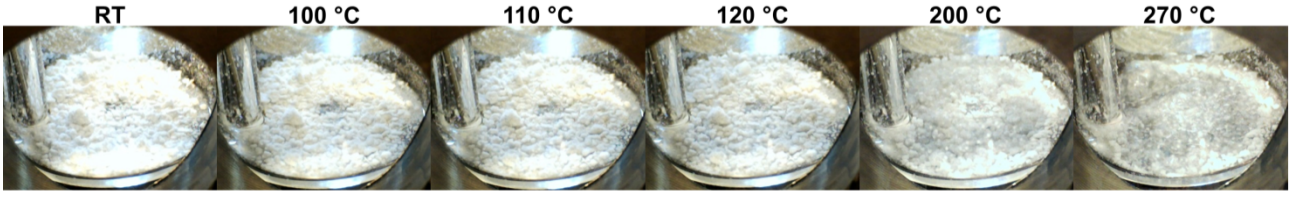

Figure S1 Temperature programmed photographic analysis of $0.9LiBH_4 – 0.1KBH_4$ (**s1**) ($\Delta T/\Delta t$ = 5 °C/min, argon atmosphere).

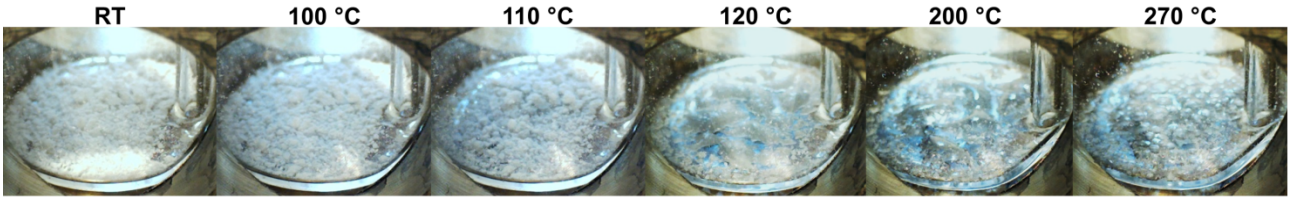

Figure S2 Temperature programmed photographic analysis of $0.8LiBH_4$ – $0.2KBH_4$ (**s2**) ($\Delta T/\Delta t$ = 5 °C/min, argon atmosphere).

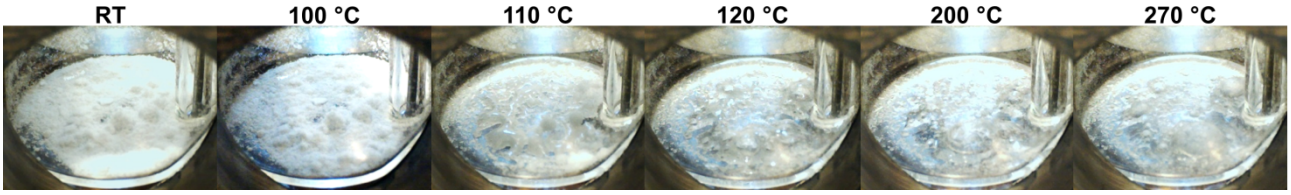

Figure S3 Temperature programmed photographic analysis of $0.6LiBH_4$ – $0.4KBH_4$ (**s4**) ($\Delta T/\Delta t$ = 5 °C/min, argon atmosphere).

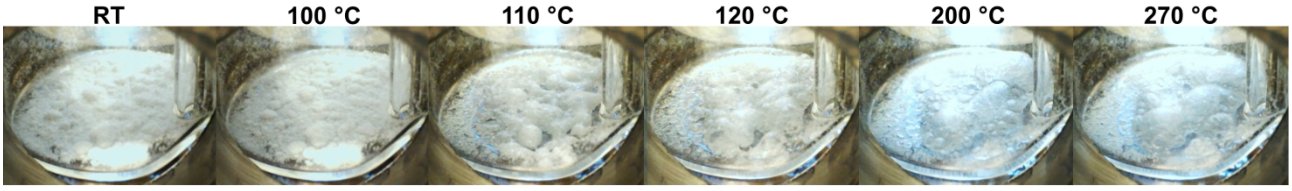

Figure S4 Temperature programmed photographic analysis of $0.5LiBH_4$ – $0.5KBH_4$ (**s5**) ($\Delta T/\Delta t$ = 5 °C/min, argon atmosphere).

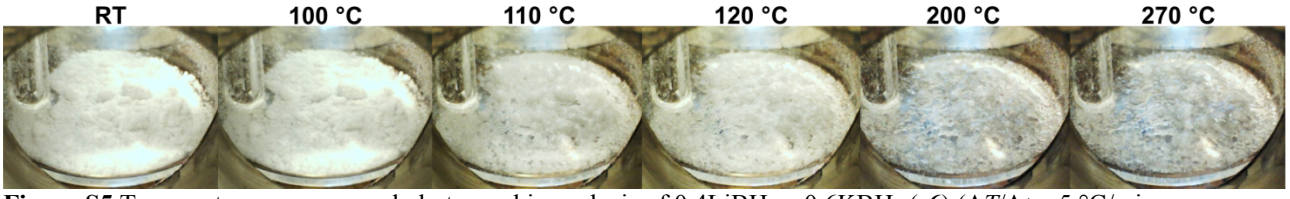

Figure S5 Temperature programmed photographic analysis of $0.4LiBH_4$ – $0.6KBH_4$ (**s6**) ($\Delta T/\Delta t$ = 5 °C/min, argon atmosphere).

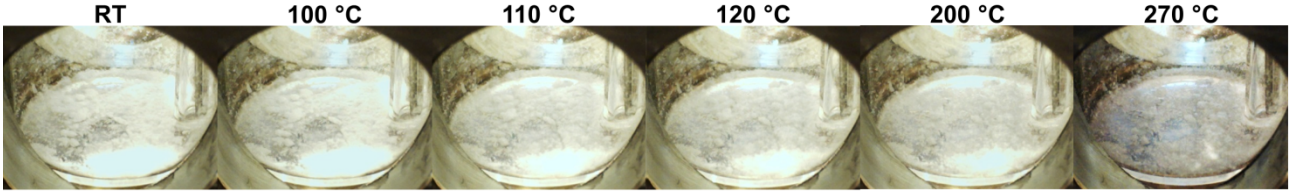

Figure S6 Temperature programmed photographic analysis of $0.3LiBH_4$ – $0.7KBH_4$ (**s7**) ($\Delta T/\Delta t$ = 5 °C/min, argon atmosphere).

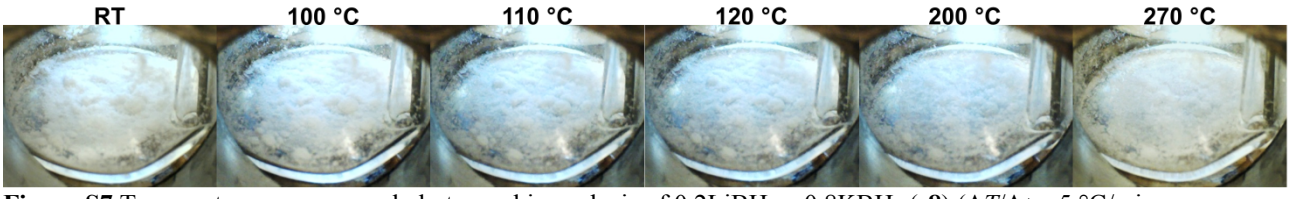

Figure S7 Temperature programmed photographic analysis of $0.2LiBH_4$ – $0.8KBH_4$ (**s8**) ($\Delta T/\Delta t$ = 5 °C/min, argon atmosphere).

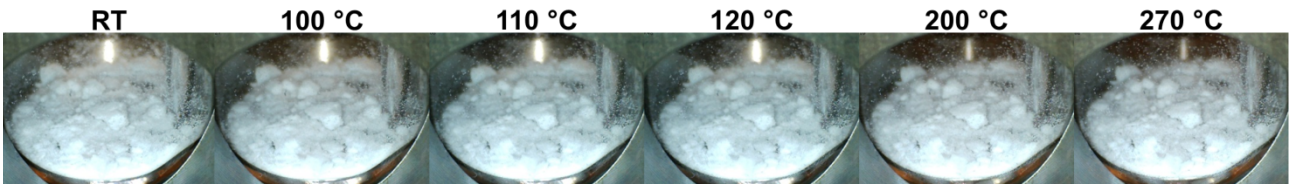

Figure S8 Temperature programmed photographic analysis of $0.1LiBH_4 – 0.9KBH_4$ (**s9**) ($\Delta T/\Delta t$ = 5 °C/min, argon atmosphere).

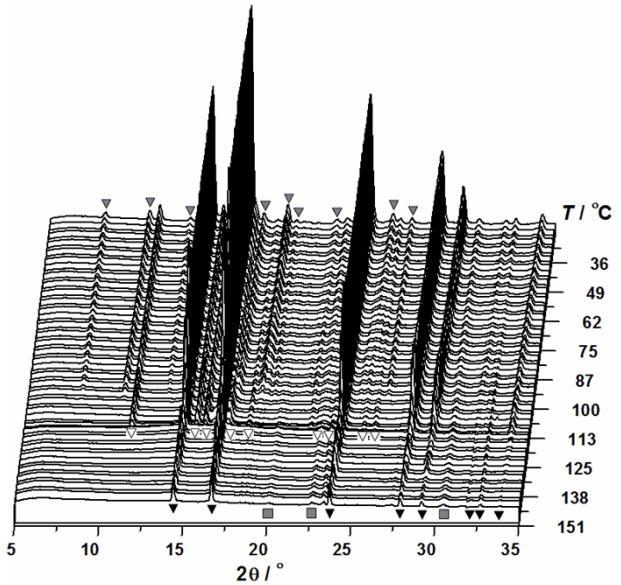

Figure S9 *In situ* SR-PXD data for $0.7LiBH_4 – 0.3KBH_4$ (**s3**) from RT to 150 °C ($\Delta T/\Delta t$ = 5 °C/min, p(Ar) = 1 bar, λ = 0.99102 Å). Symbols: white triangle $LiBH_4$, black triangle KBH_4, grey triangle $LiK(BH_4)_2$ and grey square WC.

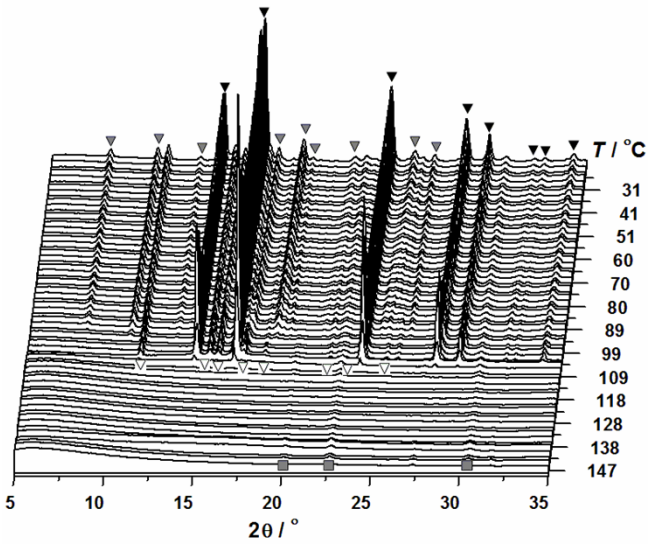

Figure S10 *In situ* SR-PXD data for $0.75LiBH_4 – 0.25KBH_4$ (**s10**) from RT to 150 °C ($\Delta T/\Delta t$ = 5 °C/min, p(Ar) = 1 bar, λ = 0.99102 Å). Symbols: white triangle $LiBH_4$, black triangle KBH_4, grey triangle $LiK(BH_4)_2$ and grey square WC.

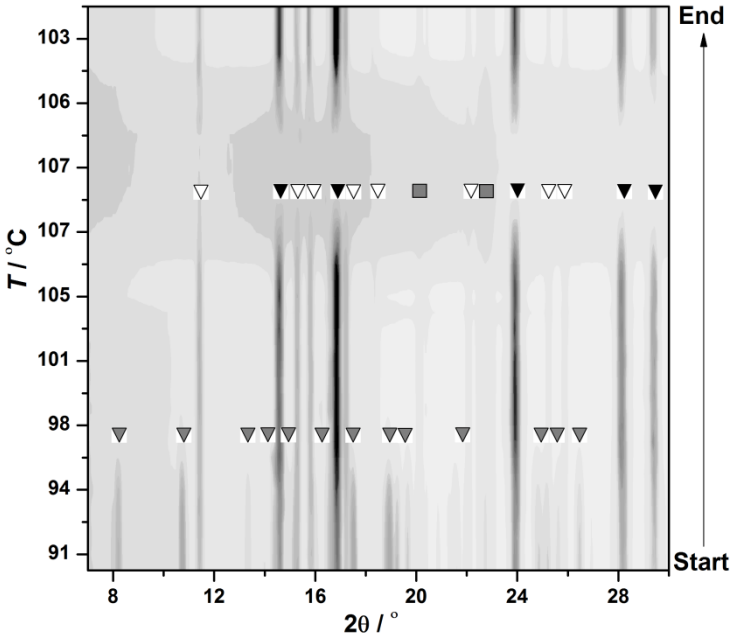

Figure S11 Enlargement of selected area of Figure 4 of *in situ* SR-PXD data for 0.725$LiBH_4$ – 0.275KBH_4 (**s12**) showing the temperature interval 90 to 107 to 100 °C ($\Delta T/\Delta t$ = 5 °C/min, p(Ar) = 1 bar, λ = 0.9919 Å). Symbols: white triangle $LiBH_4$, black triangle KBH_4, grey triangle $LiK(BH_4)_2$ and grey square WC.

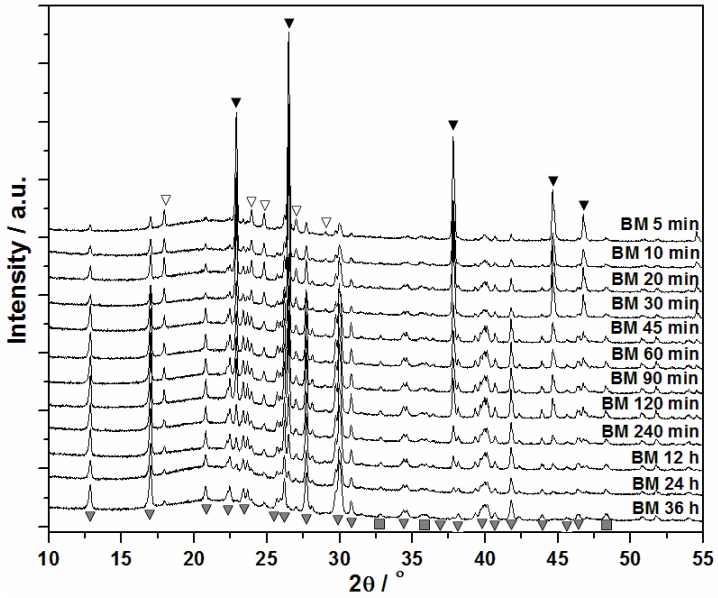

Figure S12 PXD patterns of 0.665$LiBH_4$ – 0.335KBH_4 ball milled for up to 36 h (λ = 1.540593 Å). Symbols: white triangle $LiBH_4$, black triangle KBH_4, grey triangle $LiK(BH_4)_2$ and grey square WC.

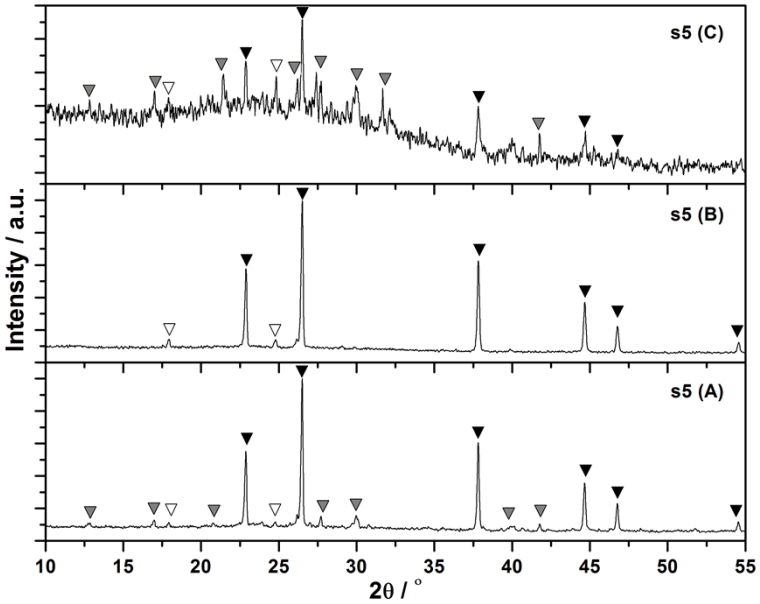

Figure S13 PXD patterns of $0.5LiBH_4$ – $0.5KBH_4$ (**s5**) (**A**) melted at 125 °C and cooled at $\Delta T/\Delta t$ = 1 °C/min in a capillary (**B**). After cooling the capillary was crushed and the sample was hand mixed in a mortar and pestle and repacked in a new capillary (**C**) (λ = 1.540593 Å). Symbols: white triangle $LiBH_4$, black triangle KBH_4 and grey triangle $LiK(BH_4)_2$.

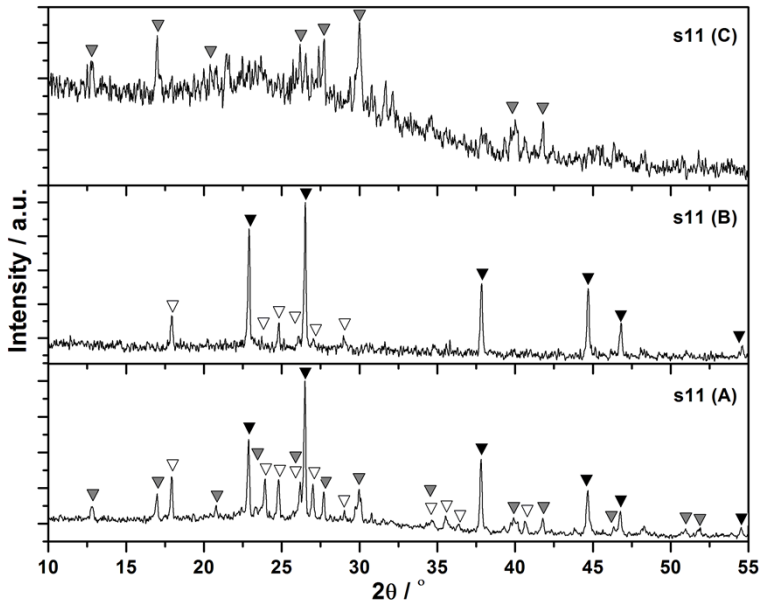

Figure S14 PXD patterns of $0.725LiBH_4$ – $0.275KBH_4$ (**s11**) (**A**) melted at 125 °C and cooled at $\Delta T/\Delta t$ = 1 °C/min in a capillary (**B**). After cooling the capillary was crushed and the sample was hand mixed in a mortar and pestle and repacked in a new capillary (**C**) (λ = 1.540593 Å). Symbols: white triangle $LiBH_4$, black triangle KBH_4 and grey triangle $LiK(BH_4)_2$.

In order to study the effect of melting and of the cooling rate on formation of $LiK(BH_4)_2$, we investigated $0.5LiBH_4$ – $0.5KBH_4$ (**s5**) and $0.725LiBH_4$ – $0.275KBH_4$ (**s11**). Both samples were

annealed at 125 °C and cooled at $\Delta T/\Delta t$ = 1 or 20 °C/min in the TPPA vial. It should be noted, that to obtain a powder sample for packing in a capillary after the melting experiment, the samples had to be crushed with a morter and pestle. This treatment may by itself facilitate the formation $LiK(BH_4)_2$, as observed in the PXD study of **s3** and **s6**. The PXD patterns of the samples after cooling (Figure S13) show $LiK(BH_4)_2$ is present is **s5** after cooling at both a fast and slow rate. In $0.725LiBH_4 – 0.275KBH_4$ (**s11**), $LiK(BH_4)_2$ is present after slow cooling at $\Delta T/\Delta t$ = 1 °C/min, but not after fast cooling. Therefore, there seems not to be a direct correlation between the cooling rate and the formation of $LiK(BH_4)_2$ and the formation is most likely facilitated by the hand grinding after the melting.

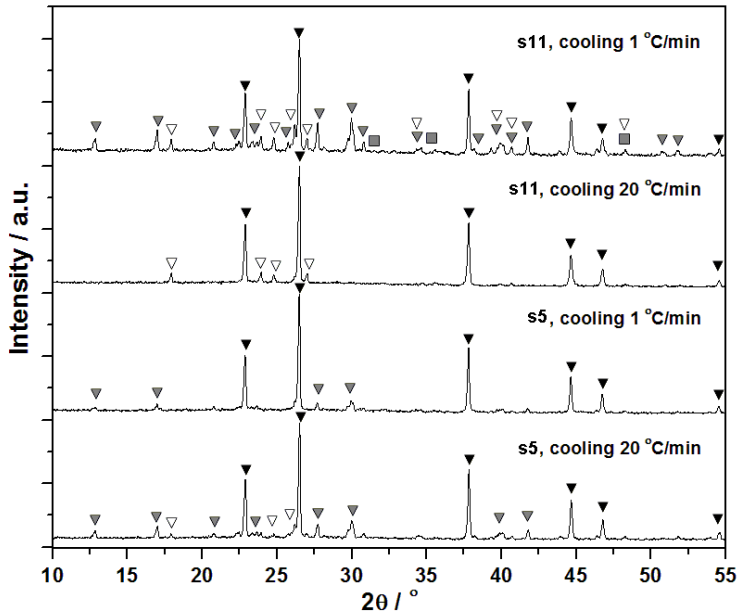

Figure S15 PXD patterns of $0.5LiBH_4 – 0.5KBH_4$ (**s5**) and $0.725LiBH_4 – 0.275KBH_4$ (**s11**) melted at 125 °C, before cooled at either $\Delta T/\Delta t$ = 20 or 1 °C/min (λ = 1.540593 Å). Symbols: white triangle $LiBH_4$, black triangle KBH_4, grey triangle $LiK(BH_4)_2$ and grey square WC.

References

1. T. R. Jensen, T. K. Nielsen, Y. Filinchuk, J. E. Jørgensen, Y. Cerenius, E. M. Gray, and C. J. Webb, *J. Appl. Cryst.*, 2010, **43**, 1456–1463.
2. A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Hausermann, *High Pressure Res*, 1996, **14**, 235–248.
3. S. Vogel, L. Ehm, K. Knorr, and C. Braun, *Adv. X-ray Anal.*, 2002, **45**, 31–33.
4. M. Paskevicius, M. B. Ley, D. A. Sheppard, T. R. Jensen, and C. E. Buckley, *Phys. Chem. Chem. Phys.*, 2013, **15**, 19774–19789.