

STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE

Final report – In-situ SR-PXD: 01-02-862 Beamline BM01A

Initial comment

The Physics Department at Institute for Energy Technology has a strong activity on hydrogen storage materials, involving many national and international collaborators. The strong position of the group is to a high degree owing to the good access to neutrons for powder neutron diffraction (PND) using the diffractometer PUS at the Institute's research reactor JEEP II.

Synchrotron power X-ray diffraction (SR-PXD) is an invaluable supplement to PND due to the superior speed and resolution. The data acquisition times are typically 3 orders of magnitude shorter using the MAR345 image plate at BM01A compared to PUS. This allows in-situ investigations of chemical reactions that we cannot possibly follow with PND. The very high resolution offered at BM01B allows indexing and space group determination from complex structures where the problem with peak overlapping makes the task unmanageable with PND- or laboratory PXD data.

Thus, the predictable, long-term access to the beam lines at SNBL through the long-term projects 01-01-805 and 01-02-862, has been an invaluable supplement to our neutron diffraction facilities and the rest of our experimental activity.

This final report summarizes the obtained results on long-term project 01-02-862.

Formation and decomposition of CaB_2H_x

A CaB_2H_x phase has previously been identified as an intermediate phase in the decomposition scheme of $\text{Ca}(\text{BH}_4)_2$ (see final report for long-term project 01-01-805). The phase has previously never been observed to form in *in-situ* experiments, and thus the details of formation and thermal decomposition has not been studied.

In the present investigation a sample prepared ex-situ containing prepared CaB_2H_x was measured by in-situ SR-PXD at BM01A. The phase transformation as a function of temperature is shown in Figure 1. The diffraction data at 130 °C shows the presence of CaB_2H_x , CaH_2 and CaO . Bragg peaks from $\beta\text{-Ca}(\text{BH}_4)_2$ grow in the temperature range 165 to 305 °C, and from 320 °C, a weak double peak corresponding to the strongest Bragg reflections from the recently identified $\text{Ca}_3(\text{BH}_4)_3(\text{BO}_3)$ (see report from long-term project 01-01-805) as well as weak peaks corresponding to an unknown decomposition product are observed. The growth of these crystalline phases is not accompanied by any apparent decrease in the Bragg intensities of the other crystalline phases. They therefore appear to crystallize from the amorphous components of the sample. At 335 °C the crystalline phases present are CaB_2H_x (47 mol %), $\beta\text{-Ca}(\text{BH}_4)_2$ (24 mol %), CaH_2 (13 mol %), CaO (16 mol %), and small amounts of $\text{Ca}_3(\text{BH}_4)_3(\text{BO}_3)$ and the unknown decomposition product. CaB_2H_x decompose in the temperature range from 390 to 440 °C. The decomposition is accompanied by a large increase in the CaH_2 Bragg peak intensities. The formation of CaH_2 starts already from 370 °C, indicating that also some amorphous phase(s) decompose above this temperature. No formation of

amorphous products can be detected, and the background level drops significantly during decomposition of CaB_2H_x (Figure 2).

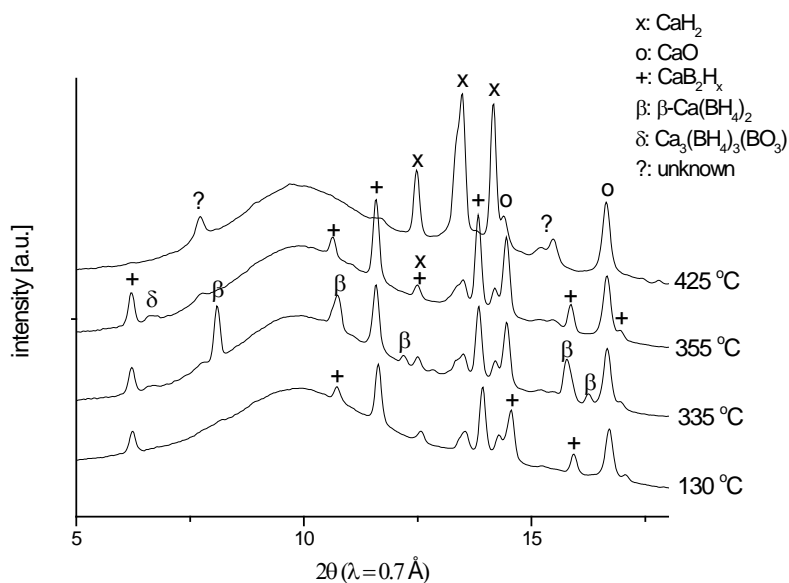


Figure 1 Diffraction patterns at selected temperatures showing details from the different transition steps. The background around 10° is due to scattering from the quartz capillary.

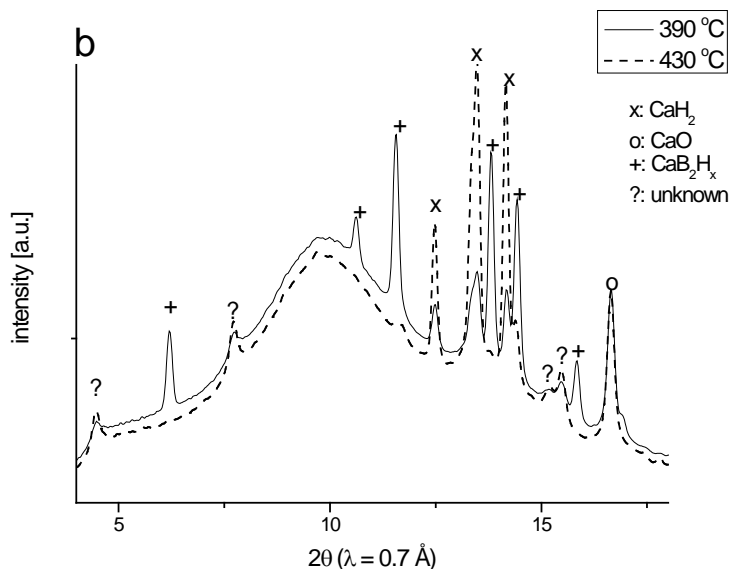


Figure 2 Diffraction pattern showing the decomposition of CaB_2H_x in the temperature range 390 to 430 °C. The decomposition is accompanied by a huge increase in CaH_2 and decreased diffuse scattering. The data are corrected for the decay in beam intensity during the measurement.

Previous *in-situ* measurements of thermal decomposition of $\text{Ca}(\text{BH}_4)_2$ has not shown formation of CaB_2H_x . In the present study, CaB_2H_x is present in the starting material,

and a clear increase in amount of CaB_2H_x is observed during decomposition of $\beta\text{-Ca}(\text{BH}_4)_2$. This could indicate that nucleation is a limiting factor for formation of this phase.

Only CaH_2 could be clearly identified as a decomposition product of CaB_2H_x and no information about the boron containing phases could be obtained from the present data. A significant drop in background during decomposition of CaB_2H_x could indicate a high degree of disorder in the phase. A high degree of disorder could explain why a stable CaB_2H_x phase based on the proposed CaB_2 sub lattice can not be found from DFT calculations. However, as also amorphous phases take part in the decomposition, no conclusions can be drawn about the source for the reduced background in the last decomposition step.

The results were included in the PhD thesis of Marit Riktor which was publicly defended on March 17 2011 and are submitted for publication to Journal of Physical Chemistry C.

Thermal decomposition of a NaBH₄ – YCl₃ mixture

A sample consisting of a NaBH₄-YCl₃ mixture (4:1 molar ratio) obtained after cryo-milling was heated from room temperature (RT) to 450°C with a constant heating rate of 2 °C/min under dynamic vacuum in a quartz capillary fitted in a “Nordby-cell” at BM01A. Diffraction data were collected every 2 minutes on a MAR345 image plate. Between RT and approximately 100°C, the X-ray diffraction pattern shows an increase in crystallinity for the milled material, which is revealed by an increase in peak intensity and narrowing of the peak-widths (Figure 3).

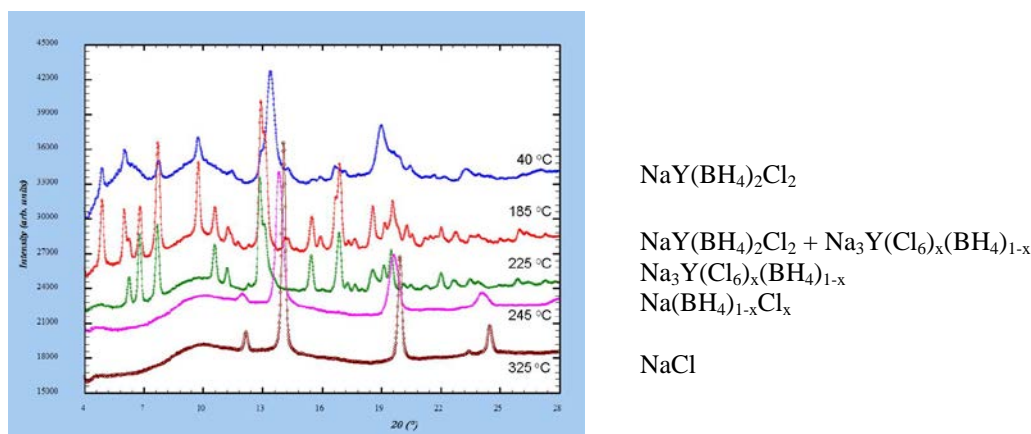


Figure 3 Selected X-ray powder patterns for a NaBH₄-YCl₃ mixture in the temperature range 40-325°C (left) with indication of present phases (right).

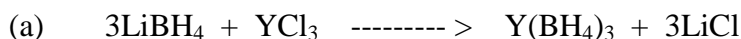
The dominant phase between RT and 150°C could be identified as NaY(BH₄)₂Cl₂, a recently reported rare example of a mixed-metal mixed-anion borohydride. Between 150°C and 200°C this phase co-exists with another phase that has a Na₃YCl₆-type structure ($a = 7.06 \text{ \AA}$, $c = 19.1 \text{ \AA}$, space group $R\bar{3}$), albeit with enlarged lattice constants compared to published data (ICSD database entry 300258: $a = 6.973(1) \text{ \AA}$, $c = 18.684(1) \text{ \AA}$). This could indicate the formation of a mixed anion compound Na₃Y(Cl₆)_x(BH₄)_{1-x} instead of the pure halide. This material decomposes between 225-245°C into another mixed anion phase, Na(BH₄)_{1-x}Cl_x, which finally forms pure NaCl at temperatures above 350°C.

The results will be included in a planned publication on transition metal- and rare earth-borohydrides.

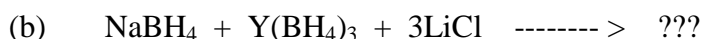
Reactions and thermal decomposition of mixtures containing NaBH₄ and Y(BH₄)₃

Mixed-metal borohydrides are a new class of materials that allow the tuning of thermodynamic properties (e.g. decomposition temperature) via combination of several metals with different Pauling electronegativity. The two major strategies for obtaining these materials are a) via metathesis reaction between a borohydride and a metal halide or b) through physically mixing of two different metal borohydrides.

The material was prepared in a two-step process: starting from LiBH₄ and YCl₃ in a 3:1 molar ratio, yttrium borohydride, Y(BH₄)₃, was first prepared by ball-milling according to:



In a second step, one equivalent of NaBH₄ was added and ball-milled again.



DSC studies on this newly formed material showed the presence of a first endothermic event at about 160°C, which is about 50°C lower than the corresponding event in pure yttrium borohydride. Laboratory X-ray data obtained from as-milled material showed only the presence of yttrium borohydride and small amounts of NaBH₄, and gave no indication for a new mixed-metal borohydride after milling.

In order to study the thermal behavior of this mixture and to analyze possible decomposition products, in-situ experiments at BM01A were performed between RT and 450°C, with a constant heating rate of 2°C/min under dynamic vacuum.

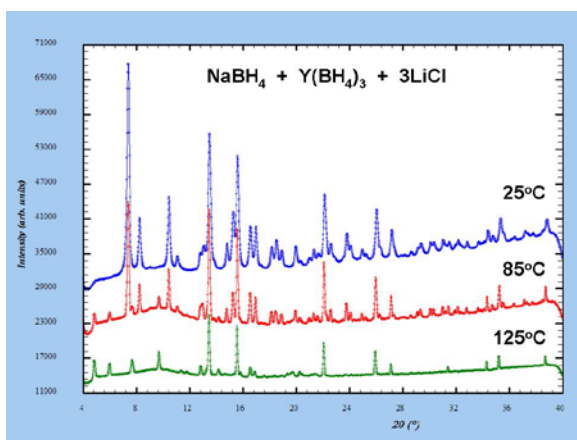


Figure 4 Selected in-situ X-ray patterns obtained from heating a NaBH₄-Y(BH₄)₃-3LiCl mixture with a heating rate of 2 °C/min at BM01A.

The RT pattern shows the presence of 3 different phases: Y(BH₄)₃, LiCl and NaBH₄. Between 50-60°C, an additional phase appears and is clearly visible at 85°C (Figure 3). At about 125°C, the initial Y(BH₄)₃ has completely disappeared and the pattern only shows contributions from this new phase and LiCl.

The 10 strongest peaks of the pattern measured at 125°C were indexed in *DICVOL*, resulting in an orthorhombic unit cell with lattice parameters $a = 8.235(27) \text{ \AA}$, $b = 6.780(12) \text{ \AA}$ and $c = 6.697(21) \text{ \AA}$. Interestingly, the relative intensities of the peaks belonging to this phase as well as the unit cell dimensions suggested by the indexing routine show a striking resemblance to the NaY(BH₄)₂Cl₂ phase, that was obtained

through a metathesis reaction between NaBH_4 and YCl_3 (4:1) ratio. This leads to the conclusion that a solid-state reaction between the two borohydrides and lithium chloride not only results in the formation of a mixed-metal borohydride but also to anion substitution resulting in a rare example of a mixed-metal mixed-anion borohydride.

The results will be included in a planned publication on transition metal- and rare earth-borohydrides.

Reactions and thermal decomposition of mixtures containing LiBH_4 and YbCl_3

Mixtures of LiBH_4 and YbCl_3 in a molar ratio of (3:1) were ball-milled for 2 hours in order to obtain $\text{Yb}(\text{BH}_4)_3$ or a related compound. The reaction was followed by a pressure monitoring system and it was found that the reaction proceeded without gas evolution. This indicates that the ytterbium remains in its trivalent state and is not reduced by the BH_4 group. The structural evolution of new phases and possible reactions in the solid state were then investigated at BM01A in the temperature region between RT and 425°C under dynamic vacuum at a constant heating rate of $2^\circ\text{C}/\text{min}$.

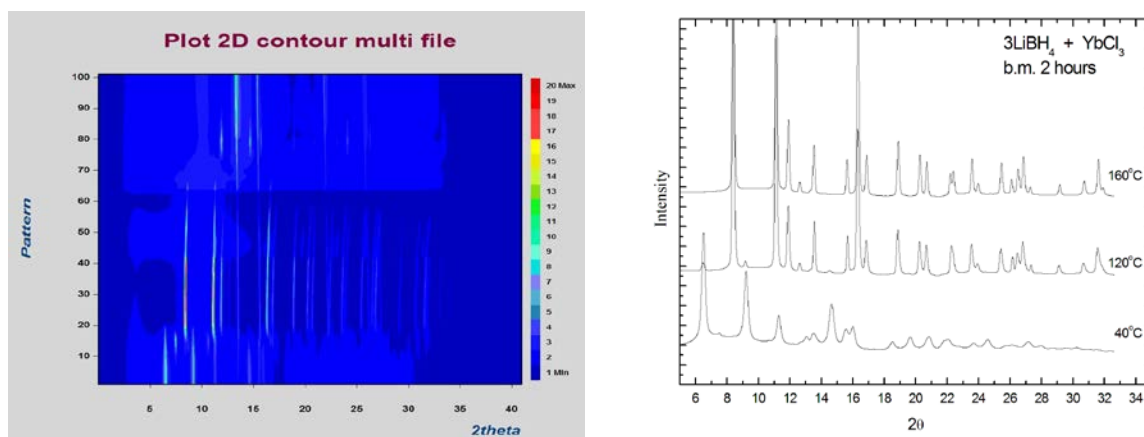


Figure 5 Colour contour plot ranging from RT to 425°C (left) and selected X-ray patterns (right) for a mixture of LiBH_4 and YbCl_3 ball-milled for 2 hours.

The RT pattern shows very broad peaks as a result of the ball-milling procedure. The exact nature of this initial phase remains unknown but indexing revealed a cubic unit cell with dimensions $6.2008(1) \text{ \AA}$ and no special conditions for reflections.

At about 100°C this phase transforms into another phase and the transformation is fully completed at 160°C (top pattern Figure 5 right).

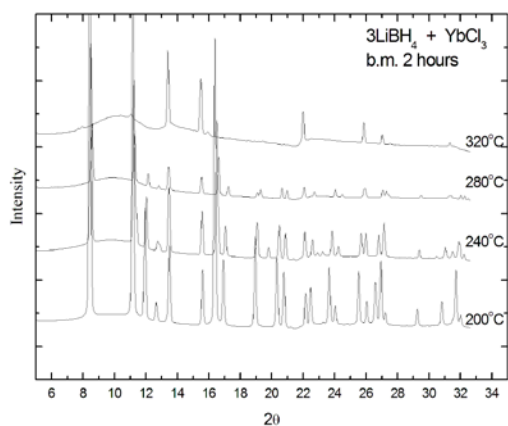


Figure 6 Selected X-ray patterns for the stability range of an unknown phase observed during annealing of a LiBH₄ – YbCl₃ mixture (3:1). At 320°C the only crystalline component is LiCl.

Indexing of this unknown phase resulted in a tetragonal unit cell with lattice parameters $a = 6.745(1) \text{ \AA}$ and $c = 4.282(1) \text{ \AA}$. This phase remains visible up to about 300°C. At higher temperatures the only crystalline component is identified as LiCl.

The system is currently still under investigation and the results will be published later in 2012.

The thermal decomposition of yttrium borohydride $Y(BH_4)_3$.

Yttrium borohydride has been prepared by cryo-milling and ball-milling and the structure of two polymorphic forms (alpha and beta) has been solved by a combination of HR-SR-PXD and PND (see preliminary report for long-term project 01-01-805). To study the thermal decomposition of this material, a 0.5 mm quartz capillary was heated under dynamic vacuum at a constant heating rate of $2^\circ\text{C}/\text{min}$ and SR-PXD patterns recorded every 4°C .

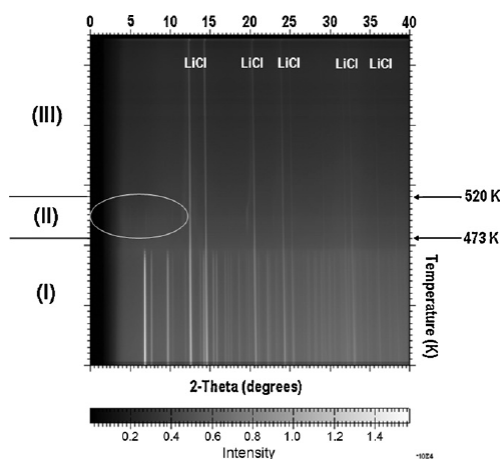


Figure 7 SR-PXD pattern of $Y(BH_4)_3$ in the temperature range of 295 – 723 K. Three distinct regions have been highlighted and the temperature region for the appearance of an intermediate phase has been encircled.

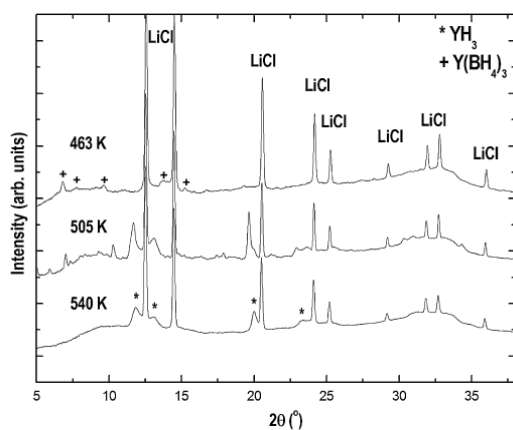


Figure 8 Representative XRD patterns at selected temperatures: the top pattern shows traces of α - $Y(BH_4)_3$, the bottom pattern shows YH_3 , and the middle pattern exhibits YH_3 and an additional intermediate phase.

In region I (Figure 7) the PXD pattern shows the presence of the low-temperature phase of α - $Y(BH_4)_3$ together with peaks from LiCl. At about 455 K the intensity of the peaks associated with α - $Y(BH_4)_3$ decreases significantly, but traces of this phase were observed up to 468 K. The transformation from α - $Y(BH_4)_3$ into the high-temperature β -polymorph was not observed under these experimental conditions. This suggests that the heating rate of 2 K/min is too fast compared to the rate at which the phase

transformation proceeds. In region III (Figure 7), above 535 K, the pattern consists solely of peaks originating from LiCl and YH₃ as the only crystalline materials present. In region II (Figure 7) which stretches from approximately 468 K to 535 K, the pattern shows contributions from YH₃ and LiCl as major phases. In addition, weaker peaks of a new crystalline phase start to emerge at around 473 K, gain in intensity up to a temperature of about 505 K, and diminish again until they finally disappear at temperatures above 520 K. The region where this intermediate phase is visible has been highlighted by a circle in Figure 7. Furthermore, Figure 8 shows three SR-PXD patterns for the regions I, II and III in the temperature range from 463 K to 540 K. The middle pattern in Figure 7 recorded at 505 K exhibits LiCl and YH₃, and in addition to that clearly shows a number of peaks that can be attributed to this intermediate phase. Based on 17 non-overlapping reflections in a two-theta range from 5° to 20°, peak indexing and unit cell determination have been performed using the program *DICVOL*. This resulted in an orthorhombic unit cell with lattice parameters $a = 12.170(14) \text{ \AA}$, $b = 7.670(5) \text{ \AA}$, and $c = 7.478(6) \text{ \AA}$. Inspection of the assigned peak indices as well as visual comparison of possible space groups in *CHEKCELL* indicated the absence of centering and hence a primitive-type unit cell. Due to only minor amounts of this intermediate phase and the small number of resolved reflections no attempts to solve the crystal structure has been successful. Further attempts to generate this intermediate phase ex-situ by post-annealing the material under hydrogen back-pressure were unsuccessful.

*The results have been published in journal of Alloys and Compounds*¹

Decomposition path of $\text{Ca}(\text{BH}_4)_2$ polymorphs

A study of the decomposition behaviors of the best known polymorphs of $\text{Ca}(\text{BH}_4)_2$ was carried out at BM01A. By increasing temperature, both the α and β modifications transform into the high-temperature phase γ - $\text{Ca}(\text{BH}_4)_2$, in agreement with the calculated free energies in the literature (Figure 9). The transition is heterogeneous and few phases co-exist below 305 °C. The borate $\text{Ca}_3(\text{BH}_4)_3(\text{BO}_3)$ forms before 275 and 325 °C for γ and α , respectively, and increases its intensity between 340 and 370 °C, for the β - $\text{Ca}(\text{BH}_4)_2$ sample. These values agree with the observed TPD bump at ca. 283 °C for the α and mixed samples. The compound disappears before 400 °C. At 400 °C the high-temperature phase has decomposed completely giving rise to CaH_2 . The decomposition of $\text{Ca}_3(\text{BH}_4)_3(\text{BO}_3)$ leads to a series of oxygen-containing compounds such as pricelite, hexahydroborite or calcium borate hydroxide. These mostly form and decompose in the 400 – 500 °C range, but some appear as final products together with CaH_2 and CaO .

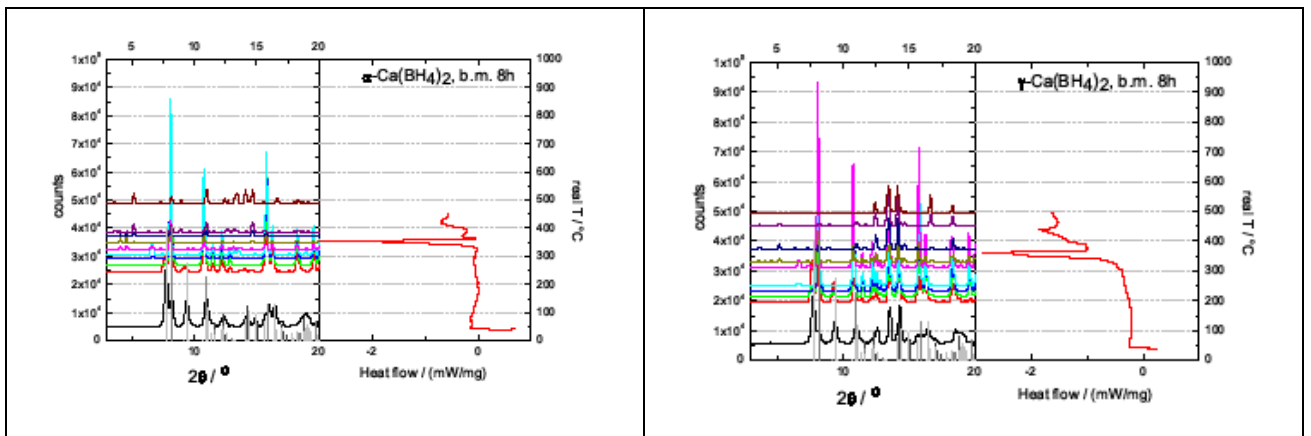


Figure 9 In-situ SR-PXD data for thermal decomposition of α - (left) and γ - $\text{Ca}(\text{BH}_4)_2$ (right) and corresponding DSC data.

The results are in process of being submitted for publication.

Decomposition of mixed-metal borohydrides containing one light cation and one transition metal cation, $MM'(BH_4)_n$ with $M = Na$ and $M' = Ti, Fe$

The thermal stability and phase formation of the systems produced by ball milling $NaBH_4$ with either TiF_3 , or FeF_3 was examined by *in situ* SR-PXD (see Figure 10 and Figure 11).

The as-milled phases remain stable up to 225 °C when the formation of NaH takes place. The fraction of $NaBH_4$ decreases upon the formation of NaH. Another unknown phase is present in the intermediate zone of 225 – 300 °C. After 300 °C NaH has been decomposed and NaF is the predominant phase.

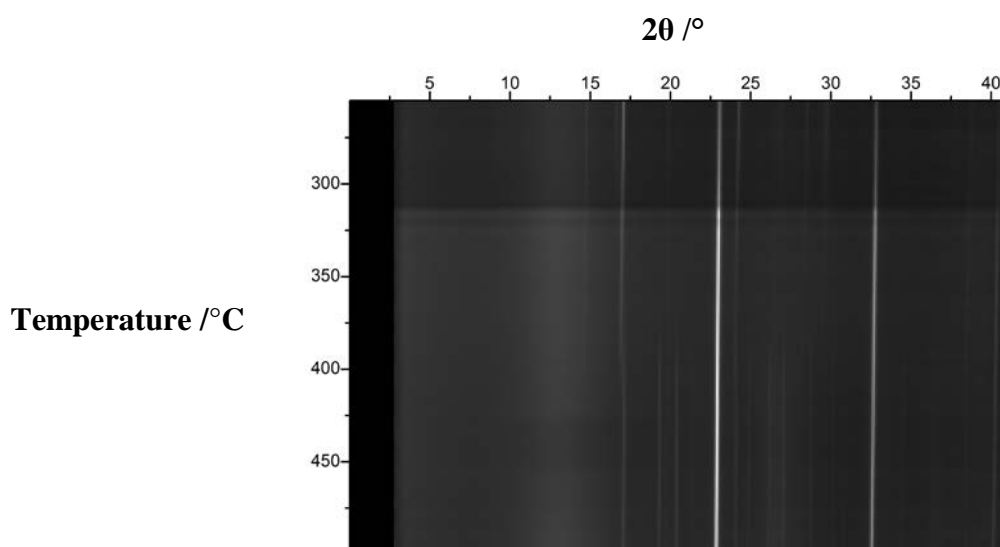


Figure 10. *In-situ* PXD in the temperature region of 175 – 600 °C of the $0.8NaBH_4 + 0.2TiF_3$, as-milled.

The mixture of $0.8NaBH_4 + 0.2FeF_3$ shows a different behavior upon heating. Due to the excellent signal-to-noise ratio offered by, unreacted FeF_3 and Fe can be detected in the as-milled powder. As the temperature increases there is no formation of intermediate phases and $NaBH_4$ and FeF_3 are consumed to form NaF.

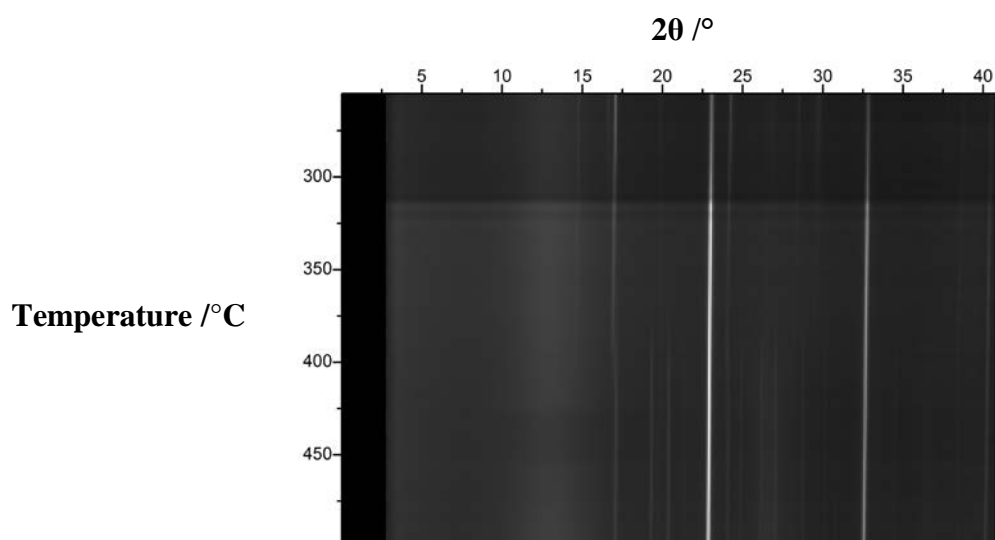


Figure 11. *In-situ* SR-PXD in the temperature region of 200 – 500 °C of the $0.8\text{NaBH}_4 + 0.2\text{FeF}_3$, as-milled.

The results have been included in the 1st year research report of the E.U project SSH2S and they are in the process to be submitted for publication

Anion substitution with halides in $\text{Mg}(\text{BH}_4)_2$

$\text{Mg}(\text{BH}_4)_2$ which contains large amount of hydrogen with 14.9 mass % is one of the most promising hydrogen storage materials for mobile use. The material undergoes a polymorphic phase transition at around 190 °C and desorbs hydrogen at around 300 °C. In order to reduce the temperature for hydrogen release, substitution of BH_4^- by halide anion has been studied to change stability and thermodynamics of mixed phase $\text{Mg}(\text{BH}_4)_{2-x}\text{X}_x$.

Mixtures of $\text{Mg}(\text{BH}_4)_2 + \text{MgX}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were prepared by ball milling using different milling times/speeds. $\text{Mg}(\text{BH}_4)_2$ was synthesized by wet chemistry methods and MgX_2 were commercially obtained (MgCl_2 : 98%, MERCK, MgBr_2 and MgI_2 : 98%, Aldrich). Samples of the milled mixtures were annealed under hydrogen back pressure at below (160 °C) and above (200 °C) the temperature of phase transition of $\text{Mg}(\text{BH}_4)_2$.

The milled mixture was heated from room temperature to 300 °C with a heating rate of 2 °C/min under 5 bar H_2 atmosphere in a boron-silica glass capillary at BM01A. Figure 12 shows selected in-situ SR-PXD patterns of $\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2$ milled for 12 h with milling speed of 505 rpm. During heating, α - $\text{Mg}(\text{BH}_4)_2$ transformed to an unidentified intermediate phase at 123 °C, and then, to β modification at 162 °C. β - $\text{Mg}(\text{BH}_4)_2$ disappeared at 274 °C. The intermediate phase has not been observed to form from pure α - $\text{Mg}(\text{BH}_4)_2$ and could be due to anion substitution. The samples of $\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2 / \text{MgBr}_2$ milled with slower milling speed (280 rpm, 12 h), showed α to β phase transition at around 200 °C, and disappearance of β phase at around 260 °C, however, no intermediate phase appeared.

In-situ SR-PXD profiles of $\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2$ milled for 12 h with milling speed of 360 rpm (as shown in Figure 13) and $\text{Mg}(\text{BH}_4)_2 + \text{MgBr}_2$ milled for 12 h with milling speed of 505 rpm were measured under the same conditions. The peak from the same intermediate phase is observed in the diffraction patterns at around 190 °C and 170 °C for the samples of $\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2$ milled at 360 rpm and $\text{Mg}(\text{BH}_4)_2 + \text{MgBr}_2$ milled at 505 rpm, respectively.

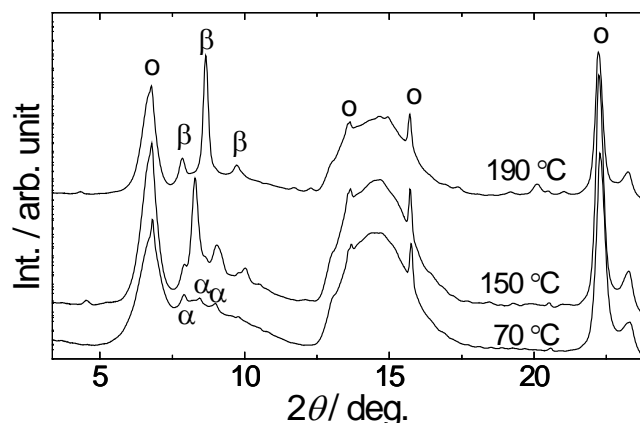


Figure 12 In-situ SR-PXD for $\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2$ milled for 12h at 505 rpm. The sample was heated with a rate of 2 °C/min ($\lambda = 0.70947 \text{ \AA}$). Symbols: (o) MgCl_2 , (α) α - $\text{Mg}(\text{BH}_4)_2$, (β) β - $\text{Mg}(\text{BH}_4)_2$.

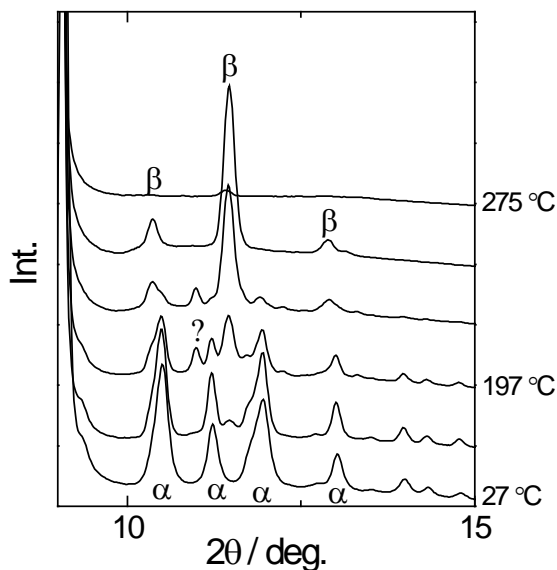


Figure 13 In situ SR-PXD profile of $\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2$ milled for 12h at 360 rpm. The sample was heated with a rate of $2^\circ\text{C}/\text{min}$ ($\lambda = 0.93388 \text{ \AA}$).

The mixture of $\text{Mg}(\text{BH}_4)_2 + \text{MgX}_2$ ($X = \text{Cl}, \text{Br}$) was ball-milled for 12h (280 rpm) and then annealed at 200°C for 10 h under 10 bar H_2 . High resolution SR-PXD data were collected at BM01B ($\lambda = 0.50123 \text{ \AA}$, Dec. 2010) at room temperature. SR-PXD data (Fig. 2) shows that position of peaks from $\beta\text{-Mg}(\text{BH}_4)_2$ in the mixtures is shifted to higher angle about 0.05° compared to pure $\beta\text{-Mg}(\text{BH}_4)_2$. The unit cell dimensions for $\beta\text{-Mg}(\text{BH}_4)_2$ were refined by according to Rietveld method. The pure $\beta\text{-Mg}(\text{BH}_4)_2$ phase in sample (a) (see caption Figure 14 for sample details) shows $a = 37.103$, $b = 18.6328$, $c = 10.9048$, and these values are agree with the ICSD database. The unit cell parameters of $\beta\text{-Mg}(\text{BH}_4)_2$ in the mixtures are $a = 36.878$, $b = 18.5185$, $c = 10.8145$ for sample (b) and $a = 36.891$, $b = 18.5100$, $c = 10.8028$ for sample (c), respectively. These smaller unit cell dimensions could be due to substitution of BH_4^- (ionic radius $r = 2.05 \text{ \AA}$) by Cl^- ($r = 1.81 \text{ \AA}$) or Br^- ($r = 1.96 \text{ \AA}$).

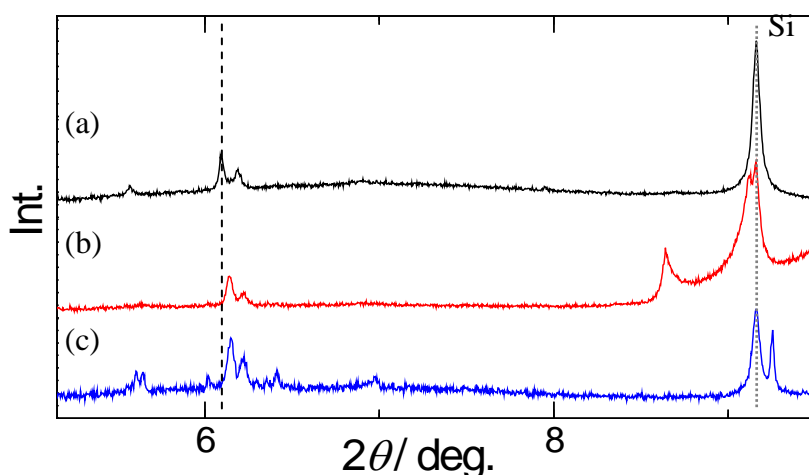


Figure 14 SR-PXD data ($\lambda = 0.50123 \text{ \AA}$) for (a) $\text{Mg}(\text{BH}_4)_2$ heated up to 300°C under 10 bar H_2 atmosphere, (b) $\text{Mg}(\text{BH}_4)_2 + \text{MgBr}_2$ and (c) $\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2$ milled for 12h at 280 rpm and annealed at 200°C for 10 h under 10 bar H_2 atmosphere. The samples contained Si powder as an inner standard from preliminary lab-PXD measurements.

$\text{Mg}(\text{BH}_4)_2$ was ball milled with MgI_2 in a 1:1 molar ratio under various conditions. The mixture was hand grind for 10 min or ball milled for 30 min, 1h, 2h and 12h to see possible substitution. In-situ SR-PXD data of the samples was measured from RT to 300°C at a hydrogen back pressure of 5 bar. α - $\text{Mg}(\text{BH}_4)_2$ and MgI_2 was observed at the start of each measurement, but no clear sign of substitution, see Figure 15. The transition from α - to β - $\text{Mg}(\text{BH}_4)_2$ was observed at $\sim 190^\circ\text{C}$ and the decomposition of β - $\text{Mg}(\text{BH}_4)_2$ was finished at 250 - 270°C in all the samples, showing no significant deviation from the expected decomposition temperatures. Selected samples has also been measured by High Resolution SR-PXD at beamline BM01B to clarify possible peak shift as a sign of substitution.

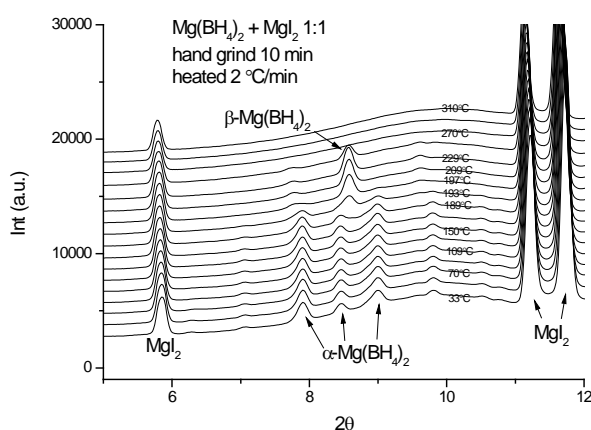


Figure 15: In-situ SR-PXD of $\text{Mg}(\text{BH}_4)_2 + \text{MgI}_2$ hand grind for 10 min.

A manuscript is in the final stage of preparation.

Chlorine substituted NaBH_4

Cl^- to BH_4^- ion substitution was induced into NaBH_4 samples through mechano-chemical reactions with a variety of transition metal (TM) chlorides (TM = Ti, V, Ni, Cu, and Cd). The result is a series of $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$ borohydrides, with x ranging from 0.65 to 0.76 depending on the transition metal involved. In-situ synchrotron radiation (SR-PXD) data collected while heating using a MAR345 image plate detector show a similar decomposition behavior for all the samples, with a small shift of the $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$ diffraction peaks towards smaller angles due to thermal expansion and then a gradual shift towards larger angles during decomposition (Fig xx).

This shift is a consequence of the loss of BH_4^- units and the subsequent contraction of the crystalline lattice towards that of NaCl . Other phases are observed to appear in small amounts at temperatures between 500 and 650°C for most of the samples. The formation of oxides is evidenced for Na-Cu by a decrease of the Cu contribution and appearance of CuO and Cu_2O while the corresponding $\text{Na}(\text{BH}_4)_{0.35}\text{Cl}_{0.65}$ diffraction peaks shift towards larger angles until NaCl is formed.

In the case of Na-Ti and Na-Ni, where only $\text{Na}(\text{BH}_4)_{0.31}\text{Cl}_{0.69}$ and $\text{Na}(\text{BH}_4)_{0.34}\text{Cl}_{0.66}$ are observed initially, increasing the temperature leads to a gradual decomposition and formation of NaCl . For Na-Ni the formation of unidentified phases and metallic Ni is also observed. Comparison with temperature programmed decomposition (TPD) data

confirms the correlation between the shift of the peaks and a strong release of gas with maximum at approximately 400 °C for these two samples.

Pure, transition metal-free samples of $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$ with x in the range 0-0.9, were made for ball milling of NaBH_4 and NaCl in the proper ratios.

Samples of $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$ was heated to 600°C with a heating rate of 8°C/min to 400°C continuing with 2°C/min under dynamic vacuum in a sapphire capillary fixed in a Swagelok fitting at BM01A. Diffraction data were collected every 2 minutes on the MAR345 image plate.

The pure NaBH_4 sample show a clear melting at about 545 °C, and the Cl-containing samples show a gradual shift to higher angles for the Bragg peak around the melting point, and the end product is identified as NaCl .

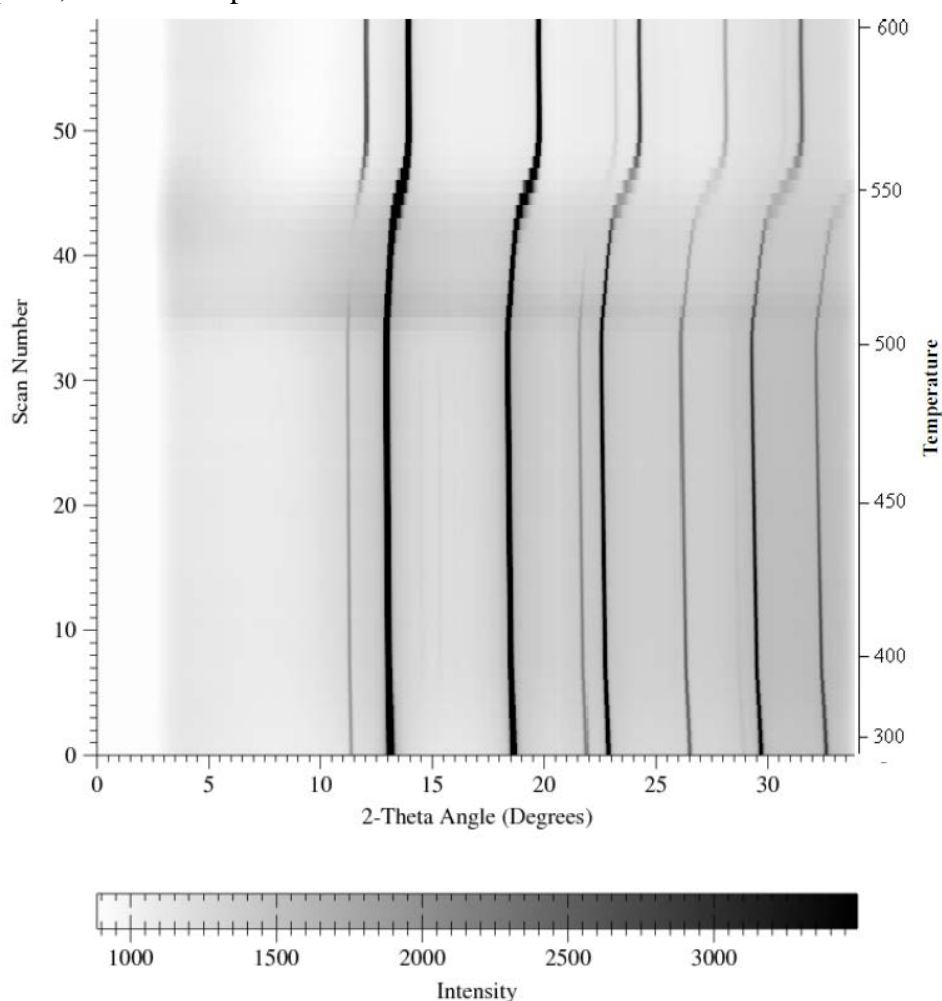


Figure 16 In-situ SR-PXD of sample with $x = 0.25$

The results are published in Journal of Alloys and Compounds²

Thermal decomposition of $\text{LiCe}(\text{BD}_4)_3\text{Cl}$

$\text{LiCe}(\text{BD}_4)_3\text{Cl}$ is formed from ball milling of LiBD_4 and CeCl_3 and the crystal structure has been solved by combined high-resolution SR-PXD (BM01B) and PND (IFE) (see final report for project 01-01-805)

To study the thermal decomposition in detail and to obtain information about decomposition products and possible inter-mediate, in-situ SR-PXD experiments were conducted at BM01B. Figure 17a shows the evolution of powder patterns as a function of temperature between 80 and 600 °C, whereas Figure 17b displays powder patterns at selected temperatures in more detail. The experiments were performed with a constant heating rate of 2 °C/min under dynamic vacuum for a $(3\text{LiBD}_4\text{-CeCl}_3)$ mixture obtained after ball-milling (6 h). In the low-temperature region between 80 and 150 °C, the X-ray profiles become narrower and the overall intensity of the peaks increases (Figure 17a). This indicates that the crystallinity of the material increases during annealing. A similar finding was made by ex-situ post annealing of a ball-milled mixture under deuterium back pressure. The only crystalline phases present after ball-milling are LiCl and $\text{LiCe}(\text{BD}_4)_3\text{Cl}$, respectively, and the latter is stable up to its decomposition temperature of ~240 °C (Figure 17a). At this temperature, peaks belonging to this phase vanish and the SR-PXD pattern exhibits only peaks belonging to LiCl . Going to higher temperatures, between 270 and 450 °C, the data exhibit a broad and featureless region around $2\theta = 15^\circ$. This is characteristic of some amorphous boron containing compounds in addition to LiCl , which could either be boron itself or a Ce-B containing species. Above 450 °C, new peaks start to appear, sharpen up, and gain in intensity up to the final temperature of 600 °C. They have been assigned to cerium hydride, CeH_2 , and are highlighted in Figure 17b.

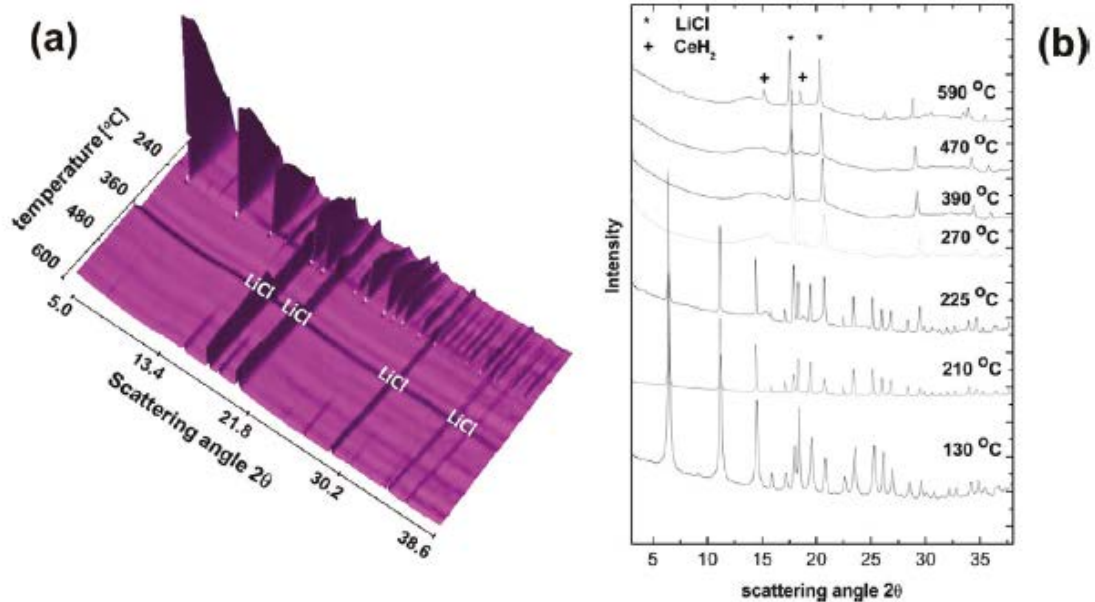


Figure 17: (a) In situ SR-PXD data obtained in the temperature region between 80 and 600 °C. (b) Selected powder patterns between 130 and 590 °C. The heating rate was 2 °C/min. Peak positions of the major phases have been indicated in the plots.

The results have been published in Journal of Physical Chemistry C³.

Substitution of fluorides in AlD₃

AlD₃, alane, is regarded as an interesting material for hydrogen storage due to its high gravimetric hydrogen content (10.8 wt%). In this study alane was mixed with selected fluorides to investigate a possible substitution by the formation of a mixed solid solution phase like AlD_{3(1-x)}F_x. Such anion substitution could change the stability and thermodynamics of alane.

Both hydrided and deuterated alane was investigated. AlD₃ was made by cryomilling a mixture of $3\text{LiAlD}_4 + \text{AlCl}_3 \rightarrow 4\text{AlD}_3 + 3\text{LiCl}$. After this synthesis either AlF₃ or NaF was added to the mixture of AlD₃ and LiCl in a molar ratio 1:1 of D and F in the sample. The samples were cryomilled for 2 h in a Spex Freezer mill.

AlH₃ was made by cryomilling a mixture of $3\text{NaAlH}_4 + \text{AlCl}_3 \rightarrow 4\text{AlH}_3 + 3\text{NaCl}$. AlF₃ was either included among the mixture of starting materials and cryomilled for 1h or added to a synthesized mixture of AlH₃ and NaCl, and cryomilled for 15 minutes.

In situ SR-PXD data for all samples was collected at SNBL station A. In general, no fluorine substitution was observed in any of the samples:

AlD₃ + AlF₃

For a sample of AlD₃ + AlF₃ the data show no content of AlD₃. The prolonged time of cryomilling was used to facilitate mix of AlD₃ and AlF₃, but probably resulted in decomposition of AlD₃ during milling, giving an increased content of Al than what was expected from the synthesis of alane.

AlD₃ + 3NaF

The data show no content of AlD₃ also for this sample. As seen in Figure 18, there is a significant amount of NaAlD₄ showing that the mixing of AlD₃ and NaF favours formation of NaAlD₄ instead of AlD₃. No LiCl is found, showing that the LiCl from the synthesis of AlD₃ together with the added NaF forms NaCl and probably LiF. In addition Na₃AlF₆ is present and the content increases during heating.

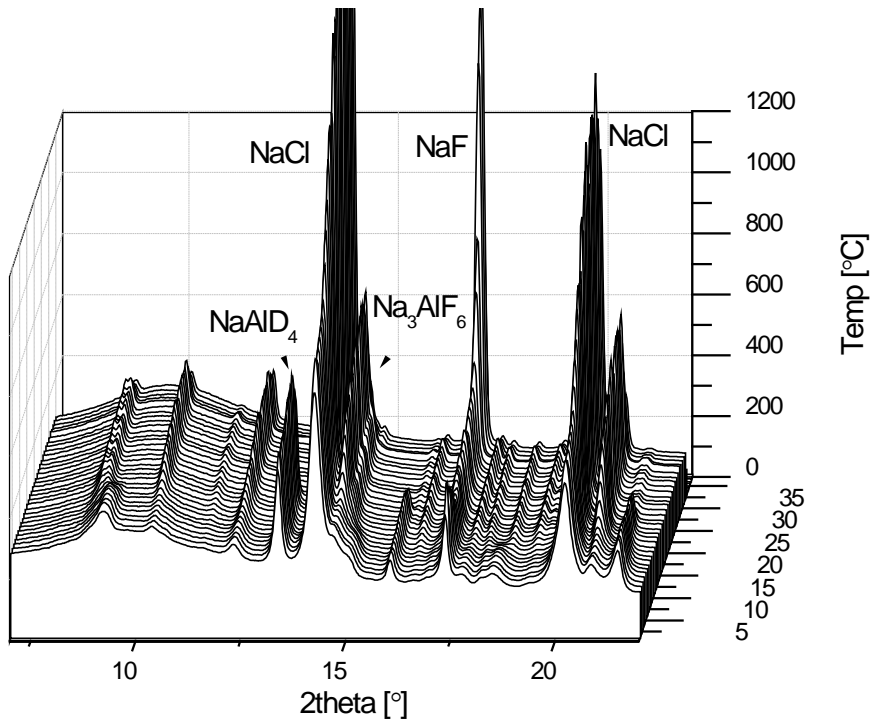


Figure 18: In situ SR-PXD of $\text{AlD}_3 + 3\text{NaF}$

$\text{AlH}_3 + \text{AlF}_3$

Adding AlF_3 to the starting materials in the synthesis of AlH_3 gave no substitutional effect. AlH_3 was formed during cryomilling, but no change in the unit cell parameters was observed neither after cryomilling nor during heating in the in-situ measurement. Mixing of premade AlH_3 with AlF_3 led to no change in unit cell parameters of AlH_3 . In both samples the AlF_3 stayed unreacted during heating. In addition a significant content of Al was observed already at the start of the in-situ measurement, indicating that a larger amount of AlH_3 had possibly formed and partly decomposed in the synthesis before the in-situ heating.

*The results are published in Journal of Alloys and Compounds*⁴.

Hydride formation in Mg-based systems processed by reactive milling

The Mg-Mn-Fe-D systems described in the preliminary report for project 01-01-805 were also investigated by in-situ SR-PXD performed at SNBL (BM01A) in October 2009. Both systems were heated up to study the deuterium desorption. The results show that the desorption products are Mg, Fe and an unidentified Mn-based phase with an orthorhombic unit cell.

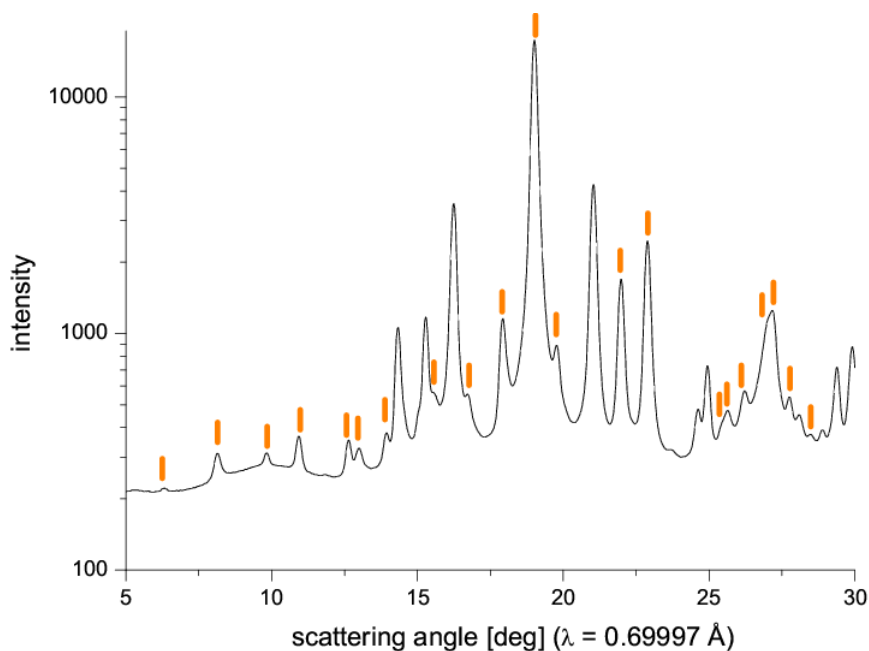


Figure 19 In-situ SR-PXD for $\text{Mg}_2\text{Mn}(\text{Fe})$ ball milled in D_2 after desorption. The pattern was acquired at about 390°C . The orange bars indicate the peaks for the unidentified Mn-based phase.

These results will be part of a forthcoming publication.

Concluding remarks

The long-term project has so far resulted in 4 publications and 1 submitted manuscript. The already collected data are expected to result in another 6 manuscripts in 2012.

Published papers with results from the long-term project

1. C. Frommen, N. Aliouane, S. Deledda, J. E. Fonnelop, H. Grove, K. Lieutenant, I. Llamas-Jansa, S. Sartori, M. H. Sorby and B. C. Hauback, *J. Alloys Comp.*, 2010, **496**, 710-716.
2. J. E. Olsen, M. H. Sorby and B. C. Hauback, *J. Alloys Comp.*, 2011, **509**, L228-L231.
3. C. Frommen, M. H. Sorby, P. Ravindran, P. Vajeeston, H. Fjellvag and B. C. Hauback, *J. Phys. Chem. C*, 2011, **115**, 23591-23602.
4. J. E. Fonnelop, M. Corno, H. Grove, E. Pinatel, M. H. Sorby, P. Ugliengo, M. Baricco and B. C. Hauback, *J. Alloys Comp.*, 2011, **509**, 10-14.