

STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE

Final report (preliminary^a) – In-situ SR-PXD measurement: 01-02-772 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 01-01-745 and 01-02-772, has been an invaluable supplement to our neutron diffraction facilities and the rest of our experimental activity.

Phase transformations and thermal decomposition of Mg(BH₄)₂ and Ca(BH₄)₂

Mg(BH₄)₂ and Ca(BH₄)₂ are among the most promising materials for mobile hydrogen storage with 14.9 and 11.6 w% H, respectively, and predicted favorable thermodynamics. However, their decomposition pathways have not been experimentally determined.

A sample of α -Mg(BH₄)₂ was heated from room temperature (RT) to 500°C with 2°C/min under dynamical vacuum in a quartz capillary fitted in a "Nordby-cell" at BM01A. Diffraction data were collected every 2 minutes on the MAR345 image plate.

Between 180 and 190 °C, most of the α -Mg(BH₄)₂ is transformed to β -Mg(BH₄)₂. However, about 20% of the sample remains as α -Mg(BH₄)₂ which only disappears slowly between 190 and 245°C without any further increase in the amount of β -Mg(BH₄)₂. Thus, this fraction of the α -Mg(BH₄)₂ appears to decompose without prior transformation to the β -modification.

β -Mg(BH₄)₂ decomposes from about 245 °C under formation of MgO, Mg and traces of MgH₂. The formation of MgO, which becomes significant above 280°C, indicates a leak in the system or reaction with the capillary. This unfortunately obscures the investigation of the pure decomposition reaction. No boron-containing phases are observed at any point.

The Bragg peaks from MgH₂ starts to increase above 360°C which is remarkable since it is well over the expected decomposition temperature. It may be explained by crystal size growth of nanosized MgH₂ which may be stabilized by encapsulation in MgO. The MgH₂ starts to decompose at 440°C.

^a One experimental session (12 shifts) for the long-term project 01-02-772 remains and will be performed in 22-25 April 2009

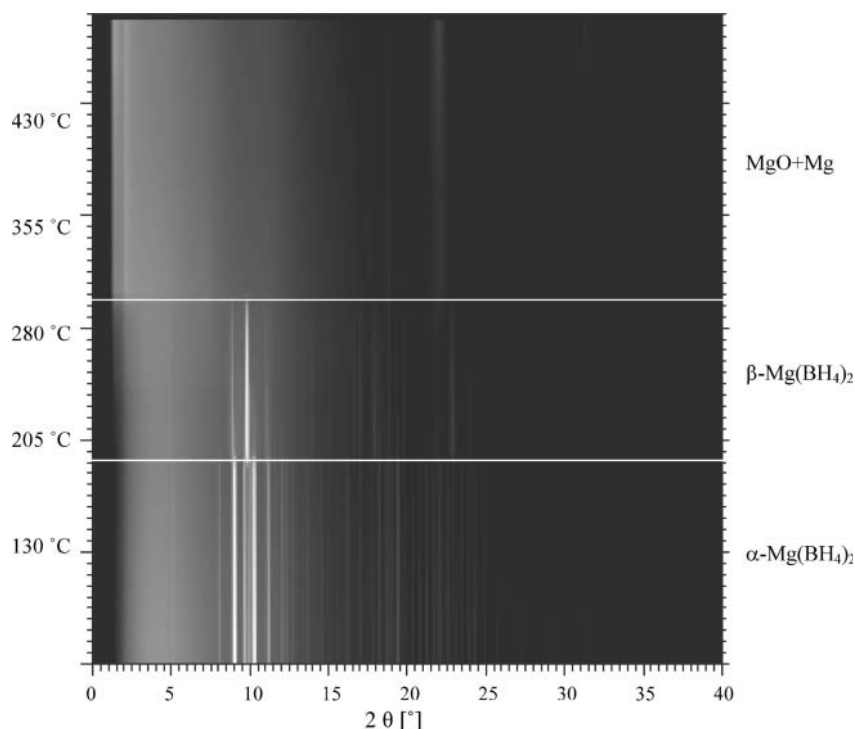


Figure 1 In-situ SR-PXD data of the thermal decomposition of $\text{Mg}(\text{BH}_4)_2$.

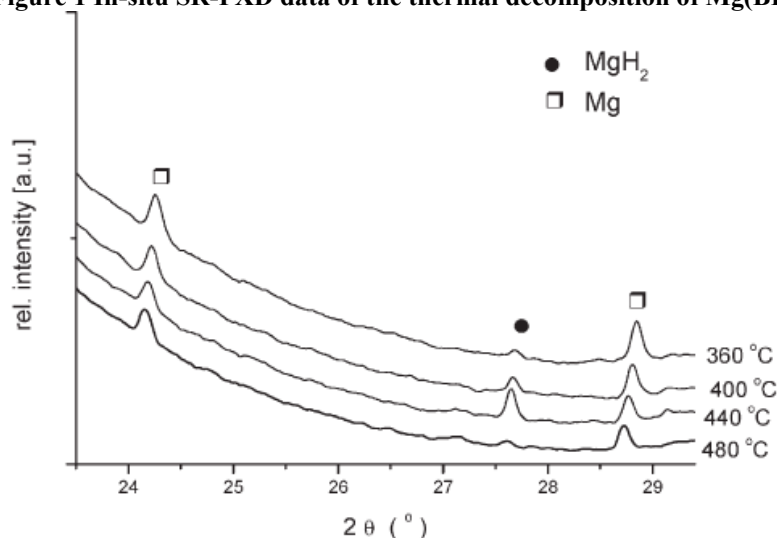


Figure 2 Formation and decomposition of MgH_2 at unusually high temperature.

A sample containing the β - and γ -modification of $\text{Ca}(\text{BH}_4)_2$ was investigated in the same way.

Parts of the γ - $\text{Ca}(\text{BH}_4)_2$ is slowly and gradually transformed to β - $\text{Ca}(\text{BH}_4)_2$ between 40°C and 290°C (Figure 3a). From 290°C to 330°C there is a faster transformation of the remaining γ - $\text{Ca}(\text{BH}_4)_2$ to a new phase. This occurs without any change in the amount of β - $\text{Ca}(\text{BH}_4)_2$ (Figure 3b) and in a temperature range where no gas desorption is detected by Temperature-Programmed Desorption (TPD). Thus, it is assumed that the phase is a new modification of $\text{Ca}(\text{BH}_4)_2$, tentatively named δ - $\text{Ca}(\text{BH}_4)_2$.

β - $\text{Ca}(\text{BH}_4)_2$ starts to decompose at 330°C and the decomposition is completed at 380°C . This correspond to the temperature range of the main gas desorption event measured by TPD. The disappearance of β - $\text{Ca}(\text{BH}_4)_2$ is accompanied by a small increase in the amount of the new “ δ - $\text{Ca}(\text{BH}_4)_2$ ” phase, formation of a second unidentified phase, and an increased amount of CaO .

The new “ δ - $\text{Ca}(\text{BH}_4)_2$ ” phase decomposes in the temperature range 400–480 °C. This decomposition also involves gas release according to the TPD measurement.

The final crystalline products at 500 °C are CaO (again indicating leak or reaction with capillary), CaH_2 and the unidentified phase that was formed on decomposition of “ δ - $\text{Ca}(\text{BH}_4)_2$ ”. No crystalline boron-containing phases were observed. However, EDS/SEM show that the Ca:B-ratio is unchanged in the fully desorbed sample. Thus, the boron does not disappear as diborane gas but must be present in an amorphous state.

The intermediate phase CaB_2H_2 (see ref. [1] and final report for long-term project 01-01-745) is not observed in the in-situ measurement. This is probably due to its very high reactivity towards air. The formation of CaO indicates a leak and the CaB_2H_2 may be oxidised immediately after it is formed.

The results are published in Journal of Materials Chemistry.[2]

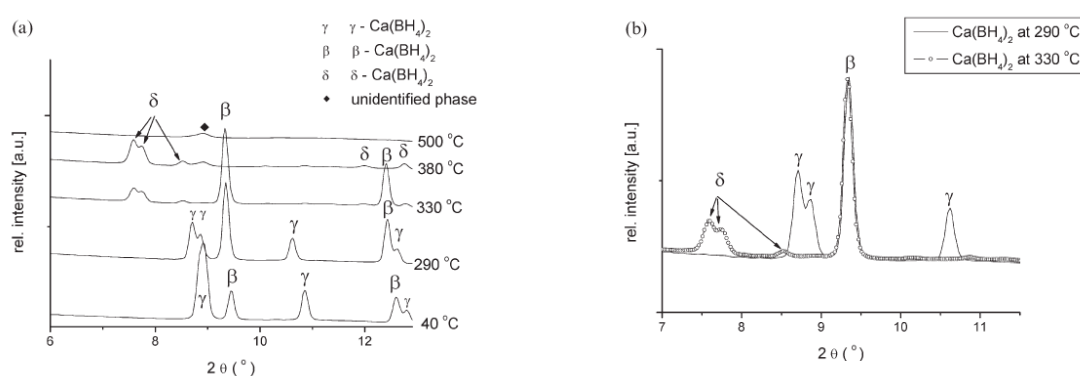


Figure 3 a) Selected integrated SR-PXD patterns during thermal decomposition of $\text{Ca}(\text{BH}_4)_2$ (see text for discussion). b) formation of “ δ - $\text{Ca}(\text{BH}_4)_2$ ” from γ - $\text{Ca}(\text{BH}_4)_2$.

Phase transformations and thermal decomposition of alane

Alane, AlH_3 , is interesting for hydrogen storage due to the very high hydrogen capacity (10.1 w%H) which is released at a moderate temperature (~120 °C).

Six structure modifications of AlH_3 are reported, but only four of them, α -, α' - β - and γ - AlD_3 , have been synthesised reproducibly. The crystal structures of α' - β - and γ - AlD_3 were determined from PND and high-resolution SR-PXD data from an earlier long term project at BM01B. It has been debated in the literature which modification is the most stable.

Experimental studies indicate that α - AlD_3 is the most stable modification but DFT calculations indicate that β - is more stable than α - AlD_3 .

In the present investigation, the phase transformation and thermal decomposition of the modifications α -, α' - β - and γ - AlD_3 are investigated by in-situ SR-PXD at BM01B. Heating rates of 1 °C/min were used. Quantitative phase analysis was performed for every recorded diffraction pattern see the phase evolution.

The phase evolution on heating for a sample containing a mixture of α - and α' - AlD_3 is shown in Figure 4. Decomposition of the α' -phase starts around 80 °C as seen from a decrease its relative phase proportion and onset of Al formation. The α -phase starts to decompose around 95 °C. The α' and α are fully decomposed at 140 and 160 °C, respectively. There is no indication of phase transformation from α - AlD_3 to α' - AlD_3 or visa versa.

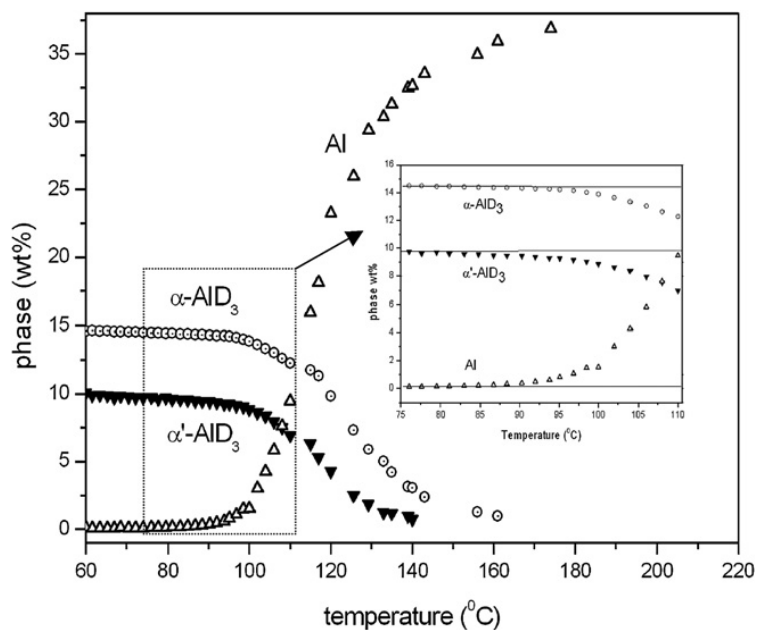


Figure 4 Phase evolution on heating for a sample containing α - and α' -AlD₃ as found from in-situ SR-PXD and quantitative phase analysis.

The thermal decomposition of γ -AlD₃ proceeds differently. Figure 5 shows the phase evolution for a sample of 90% γ - and 10% α -AlD₃. From about there is clearly a transformation from γ - to α -AlD₃ as the amount of the former decrease while the latter increase correspondingly. From about 105°C, the rate of reduction of the γ -AlD₃ decrease, but it increases again from 115°C (see inset Figure 5) which coincide with the onset of Al formation. Thus, γ -AlD₃ decomposes directly to Al and D₂ from this temperature. All γ -AlD₃ has disappeared at 120°C where the α -AlD₃ starts to decompose. The decomposition is complete at 150 °C. The reason for the different in the temperature range for decomposition of α -AlD₃ in the two measurements, are not clear.

The phase evolution of β -AlD₃ (90% purity, 10% γ -AlD₃) is shown in Figure 6. The β -phase shows a complete transformation to α -AlD₃ and no direct decomposition is observed. The α -phase decomposes in a similar way as in the γ + α -sample. Interestingly, the γ -AlD₃ impurity shows a similar features as for the γ -AlD₃ sample above, with an initial rapid conversion to α -AlD₃ which slows down before a direct decomposition to Al and D₂ starts. Thus, this peculiar behaviour seems to be a characteristic feature for γ -AlD₃.

From these investigations, it is clear that α -AlD₃ is the most stable modification among α -, α' - β - and γ -AlD₃.

The results are published in two papers in Journal of Physical Chemistry C[3] and Journal of Materials Science.[4]

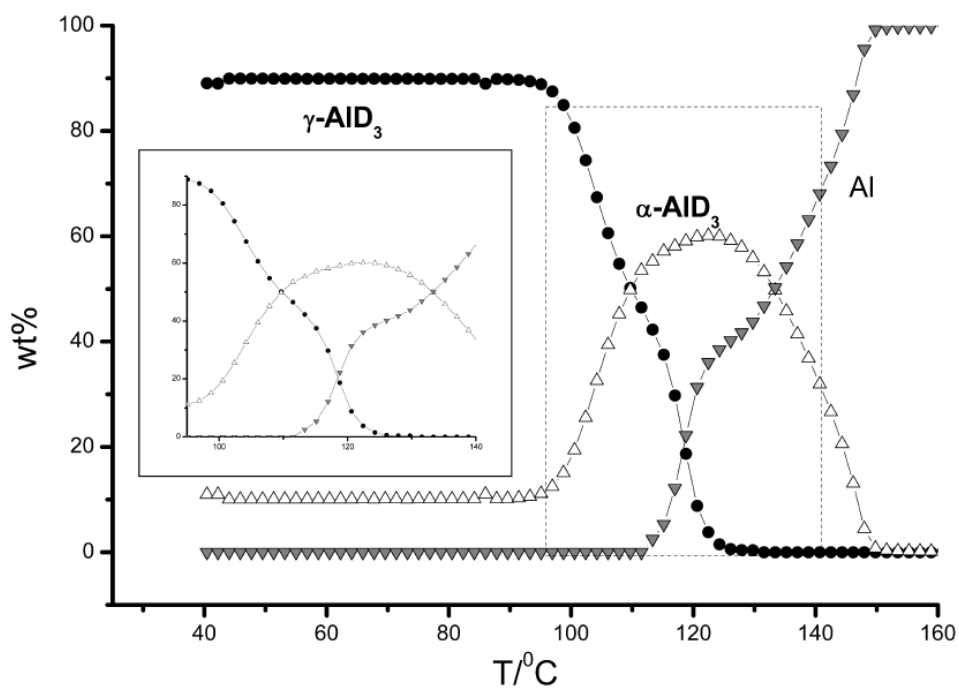


Figure 5 Phase evolution on heating a sample of 90% γ -AID₃ and 10% α -AID₃ as found from in-situ SR-PXD and quantitative phase analysis.

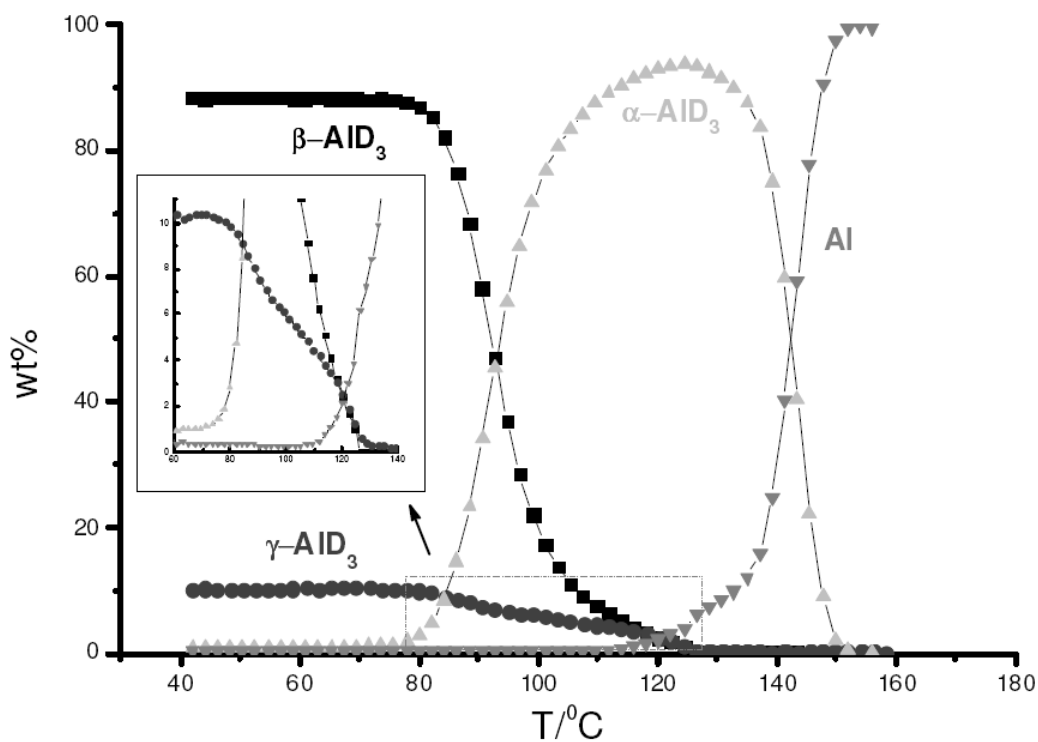


Figure 6 Phase evolution on heating a sample of 90% β -AID₃ and 10% γ -AID₃ as found from in-situ SR-PXD and quantitative phase analysis.

Thermal decomposition of Na₂LiAlH₆

The thermal decomposition of the pure and TiF₃-doped Na₂LiAlH₆ was investigated by in-situ SR-PXD at BM01A.

Pure $\text{Na}_2\text{LiAlH}_6$ and $\text{Na}_2\text{LiAlH}_6$ doped with 2mol% TiF_3 decompose in a similar manner to LiH , NaH and Al from around 200 to 250°C. Samples with 10mol% TiF_3 behave quite differently. Firstly, a significant proportion (20mol%) of the $\text{Na}_2\text{LiAlH}_6$ is decomposed when the TiF_3 is added, yielding Na_3AlH_6 and Al . Moreover, the parts of remaining $\text{Na}_2\text{LiAlH}_6$ decompose to Na_3AlH_6 and Al before the final decomposition to NaH , LiH and Al . This is particularly pronounced in a sample that has been dehydrogenated and rehydrogenated (cycled).

A manuscript for publication of the results are in the final stage of preparation and will be submitted to Journal of Alloys and Compounds.

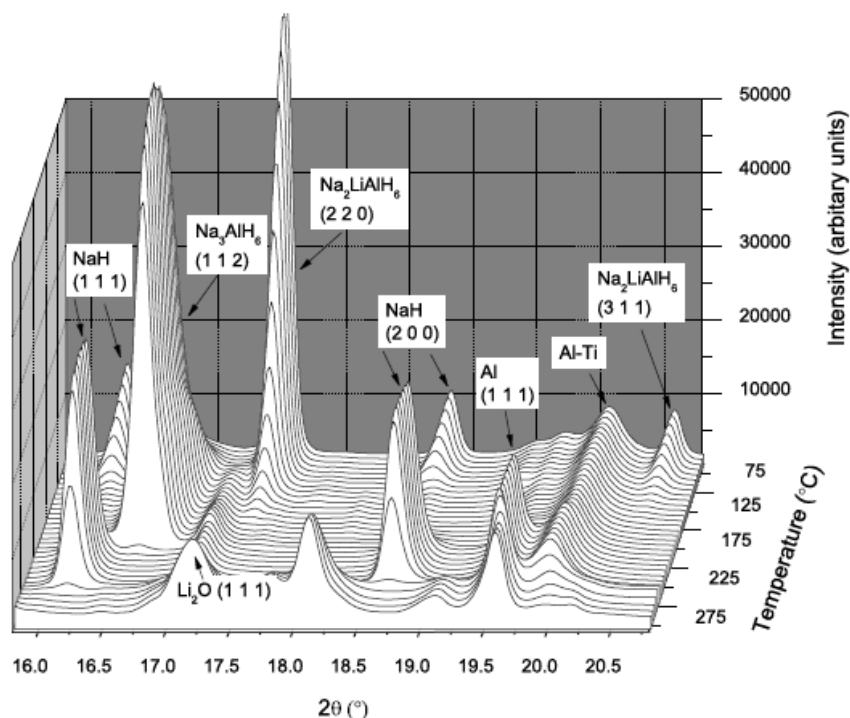


Figure 7 In-situ SR-PXD data for thermal decomposition of cycled $\text{Na}_2\text{LiAlH}_6 + 10 \text{ mol}\% \text{ TiF}_3$. Note the substantial increase in the Na_3AlH_6 amount prior to decomposition.

Thermal decomposition of $\text{NaAl}(\text{NH}_2)_4$

Amides, NH_2^- - containing salts, have been considered for hydrogen storage since the discovery of reversible hydrogen uptake in Li_3N under formation of LiNH_2 and LiH .

The amide $\text{NaAl}(\text{NH}_2)_4$ was prepared by direct reaction of NaAlH_4 and NH_3 under ball milling. SR-PXD at BM01A at ambient temperature showed a sample of high purity, as shown in the Rietveld fit in Figure 8 (the structure model was taken from literature).

The in-situ SR-PXD (Figure 9) was performed simultaneously with Raman spectroscopy (Figure 10). There are no changes in the SR-PXD patterns, besides peak shift due to thermal expansion, until 110°C which correspond to the first where approximately $\frac{1}{2}$ NH_3 pr. formula unit is desorbed (measured separately with thermogravimetry (TG) and mass spectroscopy (MS)). This leads to a complete amorphisation of the sample, as seen by the absence of Bragg peaks. However, the Raman signal barely change as a result of the amorphisation which means that the amorphous decomposition product also contain amide ions.

According to the TG/MS measurements, there is a steady loss of NH_3 (reflected by a gradual decrease in the NH_2 Raman signal) from the first desorption event up to 230°C where a new peak in the NH_3 desorption is observed. This desorption event is reflected in both the SR-PXD and the Raman data. The diffuse scattering measured by SR-PXD change its characteristics, indicating formation of a different amorphous substance. At the same time, the Raman signal corresponding to NH_2 -bending and stretching is lost. The TG/MS indicate that 2 NH_3 pr. formula unit are lost at this point. The amorphous phase above 230°C is thus probably Na-Al imide, $\text{NaAl}(\text{NH}_2)_2$.

A manuscript for publication of the results is under preparation.

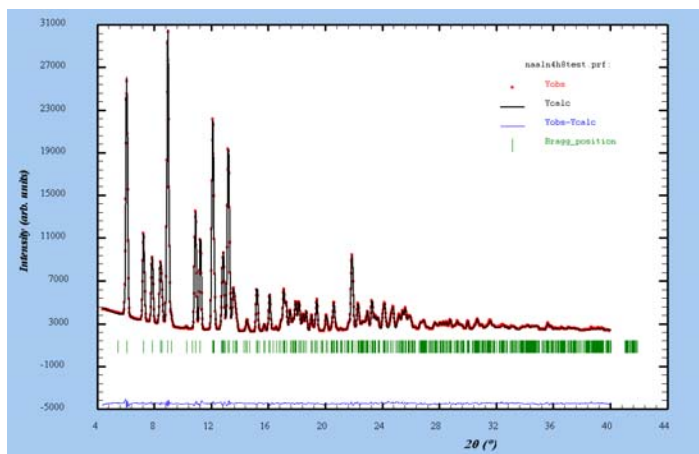


Figure 8 Rietveld fit of SR-PXD data (RT) showing a $\text{NaAl}(\text{NH}_2)_4$ sample of high purity.

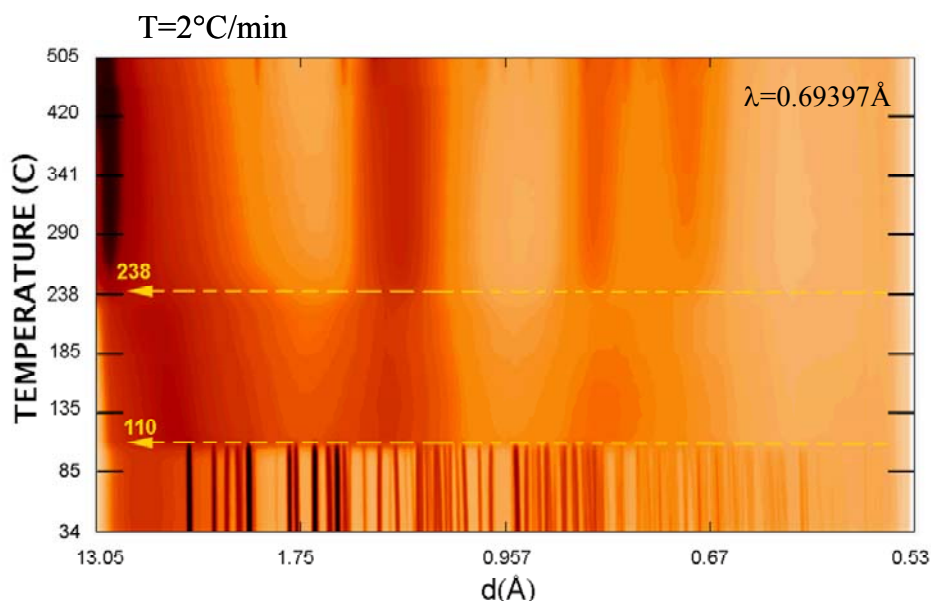


Figure 9 In-situ SR-PXD data for thermal decomposition of $\text{NaAl}(\text{NH}_2)_4$.

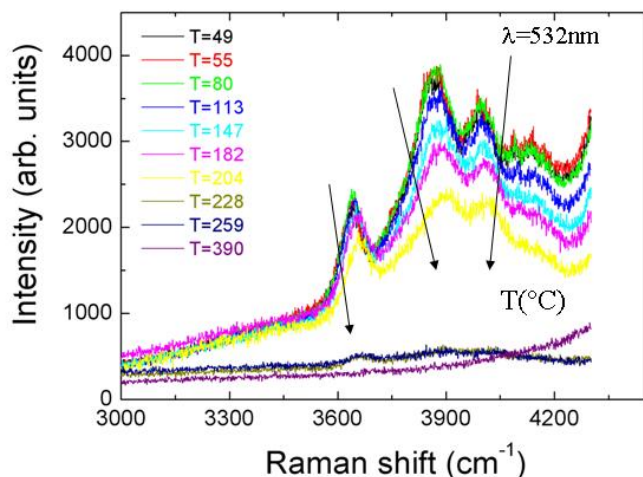


Figure 10 In-situ Raman data for thermal decomposition of $\text{NaAl}(\text{NH}_2)_4$. The signals above 228 °C are associated to bending and stretching modes of NH_2 .

Thermal decomposition of $\text{Mg}_2(\text{Fe}_{0.5}\text{Co}_{0.5})\text{D}_{5.5}$

The synthesis and structural characterization of the quaternary deuteride $\text{Mg}(\text{Fe}_{0.5}\text{Co}_{0.5})\text{D}_{5.5}$ is described in the report for long-term project 01-01-745.

The thermal decomposition of the phase was investigated by in-situ SR-PXD at BM01B. The raw data are shown in Figure 11. Bragg peaks from Mg, which indicate the onset of decomposition, start to appear around 500K (230°C). Around 600 K (330°C) the peaks from the quaternary deuteride start to disappear quickly and they have completely disappeared at 610 K. The decomposition products are Mg and FeCo solid solution.

The result is accepted for publication in Nanotechnology.[5]

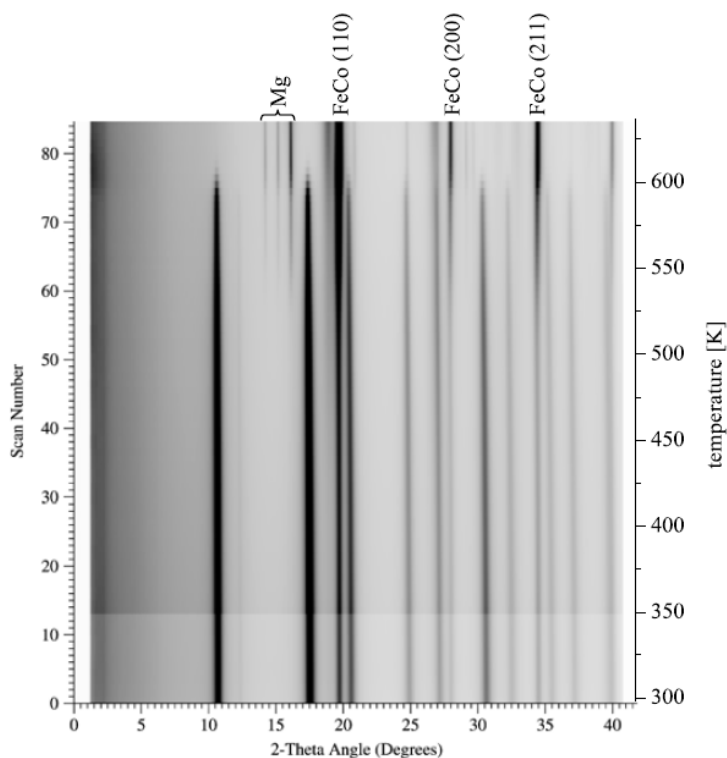


Figure 11 In-situ SR-PXD data for thermal decomposition of $\text{Mg}_2(\text{Fe}_{0.5}\text{Co}_{0.5})\text{D}_{5.5}$

References to publications from long-term project 01-02-772

- [1] Riktor, M.D.; Sørby, M.H.; Chłopek, K.; Fichtner, M.; Hauback, B.C.: The identification of an hitherto unknown intermediate phase CaB_2H_x from decomposition of $\text{Ca}(\text{BH}_4)_2$. *Journal of Materials Chemistry* DOI: **10.1039/B818127F** (2009)
- [2] Riktor, M.D.; Sorby, M.H.; Chlopek, K.; Fichtner, M.; Buchter, F.; Zuetzel, A.; Hauback, B.C.: In situ synchrotron diffraction studies of phase transitions and thermal decomposition of $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$. *Journal of Materials Chemistry* **17** (2007) 4939-4942
- [3] Grove, H.; Sorby, M.H.; Brinks, H.W.; Hauback, B.C.: In situ synchrotron powder X-ray diffraction studies of the thermal decomposition of beta- and gamma-A1D3. *Journal of Physical Chemistry C* **111** (2007) 16693-16699
- [4] Sartori, S.; Opalka, S.M.; Lovvik, O.M.; Guzik, M.N.; Tang, X.; Hauback, B.C.: Experimental studies of alpha-A1D(3) and alpha '-A1D(3) versus first-principles modelling of the alane isomorphs. *Journal of Materials Chemistry* **18** (2008) 2361-2370
- [5] Deledda, S.; Hauback, B.C.: Formation mechanism and structural characterization of the mixed transition-metal complex hydride $\text{Mg}_2(\text{FeH}_6)_{0.5}(\text{CoH}_5)_{0.5}$ obtained by reactive milling. *Nanotechnology* **accepted** (2009)

Additional publications where measurements from long-term project 01-02-772 plays a minor role

- a) Riktor, M.D.; Deledda, S.; Herrich, M.; Gutfleisch, O.; Fjellvåg, H.; Hauback, B.C.: Hydride formation in ball-milled and cryomilled Mg-Fe powder mixtures. *Materials Science and Engineering B* **accepted** (2009)