

STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE

Report – In-situ SR-PXD measurement: 01-02-772 (December 2007) Beamline BM01A

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α -, β - and λ -Ca(BH₄)₂

Ca(BH₄)₂ is considered as an attractive hydrogen storage material due to high gravimetric capacity and expected thermodynamic properties suitable for mobile hydrogen storage applications. However, the decomposition route is still unclear. In this investigation, Ca(BH₄)₂ synthesized by two different wet-chemical methods giving different modifications in the as-synthesized powder, were studied. One sample contained α -Ca(BH₄)₂ and the other contained a mixture of β - and λ -Ca(BH₄)₂. Due to earlier observed reaction between glass capillary and powder at elevated temperatures, the measurements were done using quartz capillaries, and the thermal decomposition of the two samples (α -Ca(BH₄)₂ and γ/β -Ca(BH₄)₂) were investigated using a heating rate of 2K/min. Bragg peaks from the previously observed intermediate phase, believed to be an unknown Ca(BH₄)₂-modification (“ δ ”-Ca(BH₄)₂), were observed in both measurements, but in significantly different amounts. Another previously observed unknown phase, believed to be a contamination phase, was not observed in this experiment.

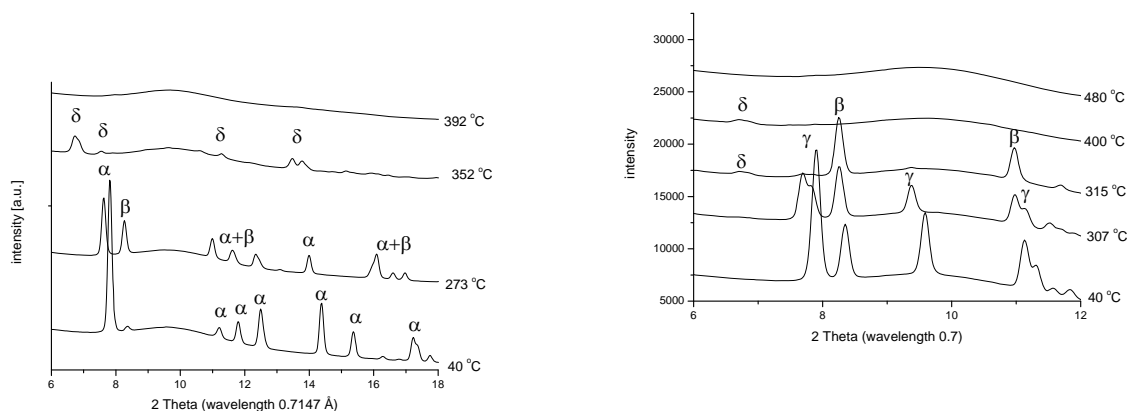


Fig. 1 α -Ca(BH₄)₂ (left) and γ/β -Ca(BH₄)₂ (right) heated under dynamical vacuum at 2K/min.

Ca(BH₄)₂ from ball milling

A previously unknown modification of Ca(BH₄)₂ was obtained by ball milling CaCl₂ and LiBH₄. LiCl is formed as a side product which indicates that the reaction proceeds till completion. Fig 2 shows comparison between diffraction patterns of β-Ca(BH₄)₂ and the unknown modification. Thermal decomposition of this material was studied at MAR. The heating rate was 2°C/min the phase undergoes decomposition at about 350°C (Fig. 2). Preliminary temperature-programmed desorption (TPD) measurements are showing that hydrogen release occurs at that temperature. 2D plot shows that in one stage of decomposition there is reaction with LiCl, as the LiCl peaks disappear. Also several phase transitions are observed. The work in determining the structure and the phase transition is in progress.

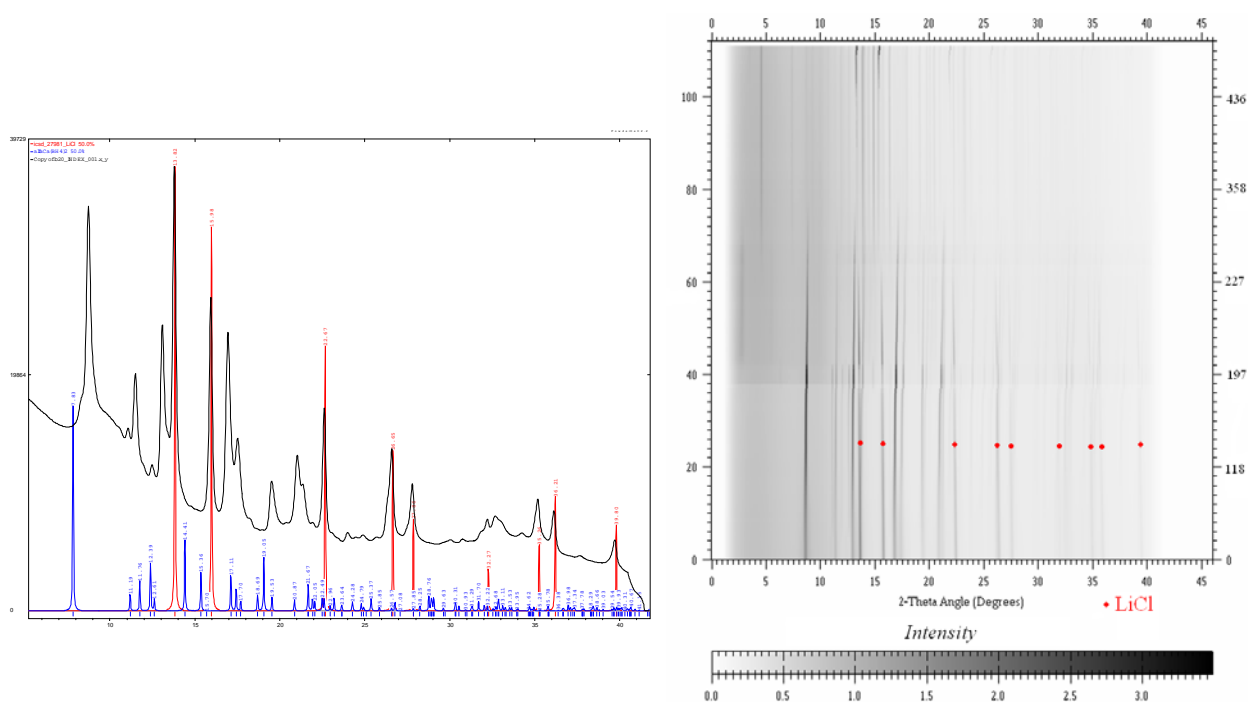
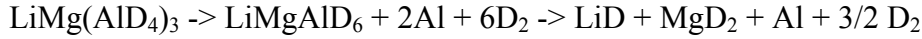


Fig. 2 (left) MAR data for the as-milled material, red lines – LiCl, blue – simulated pattern of β Ca(BH₄)₂
(right) 2D plot of thermal decomposition of unknown Ca(BH₄)₂ phase

LiMg(AlD₄)₃

The first thermal decomposition step of LiMg(AlD₄)₃ has been investigated earlier and it was found that it decomposes to lithium deuteride and magnesium deuteride:



In the present study, the sample was heated to higher temperature (400°C) than earlier to investigate how the decomposition of magnesium hydride (MgD₂ → Mg + D₂) is affected by the presence of Li and Al. When MgD₂ is decomposing, the expected Mg-phase is not seen, instead several different Al_xMg_y phases are appearing. This indicates that the presence of Al can affect the decomposition of MgD₂. The figure shows the decomposition of purified LiMg(AlD₄)₃. The circled area shows the decomposition of MgD₂; the diffraction peaks from MgD₂ are disappearing and Al_xMg_y phases are appearing

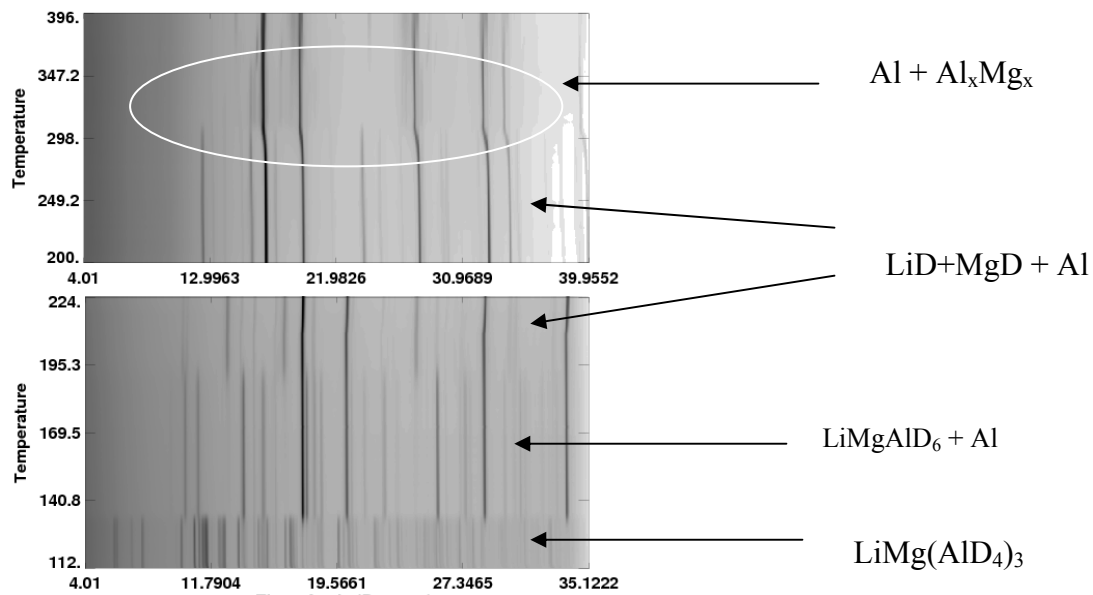


Fig. 3 Decomposition of pure LiMg(AlD₄)₃.

$\text{Na}_3\text{AlF}_x\text{H}_{6-x}$

We have recently found that fluorine can partly substitute hydrogen in Na_3AlH_6 to form the isostructural phase $\text{Na}_3\text{AlF}_x\text{H}_{6-x}$.

$\text{Na}_3\text{AlF}_x\text{H}_{6-x}$ with $x \sim 2$ was synthesised by ball milling NaF and Al and applying hydrogen pressure. The thermal decomposition was studied on MAR. The substitution of hydrogen atoms with fluorine changes the thermodynamic properties of the compound. The diffraction pattern shows that the product after ball milling consists of $\text{Na}_3\text{AlF}_x\text{H}_{6-x}$ mixed with NaF and Al. Heating the sample to 400°C reverse the reaction completely. No other phases than NaF, Al and $\text{NaAlF}_x\text{H}_{6-x}$ are seen during decomposition. Close comparison with the decomposition of undoped $\text{Na}_3\text{AlF}_x\text{H}_{6-x}$ and doped Na_3AlH_6 will be performed.

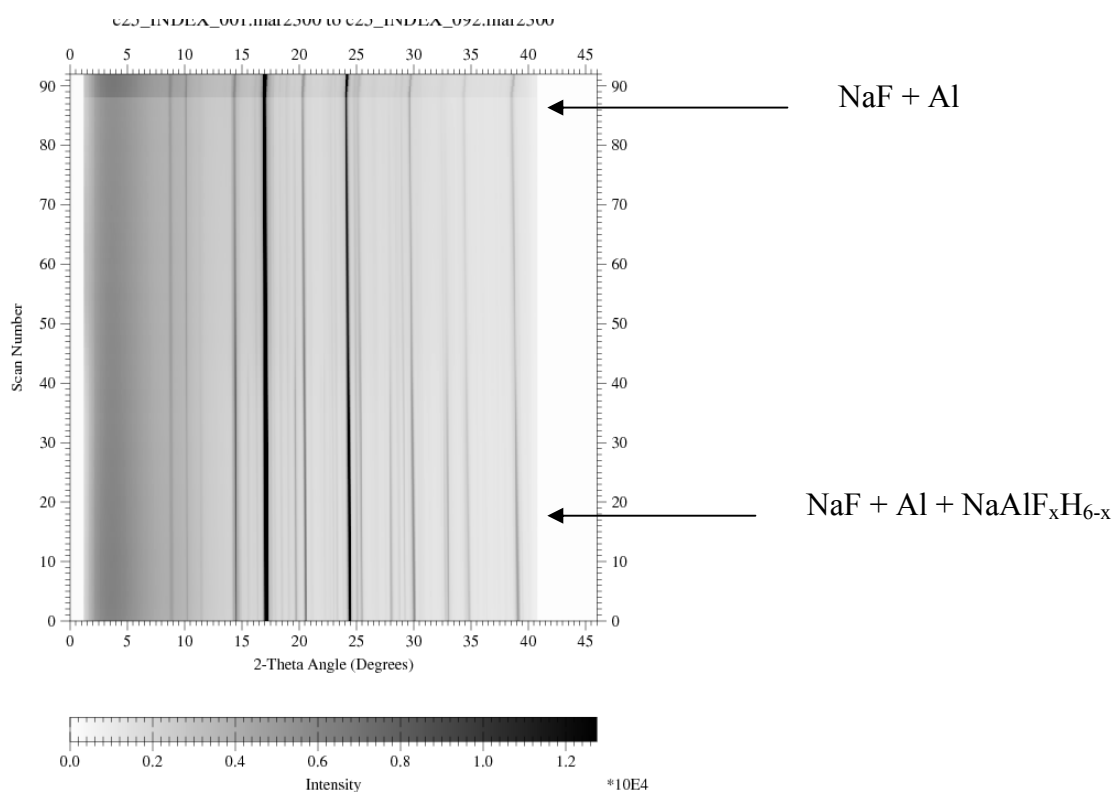


Fig. 4 Decomposition of $\text{Na}_3\text{AlF}_x\text{H}_{6-x}$

Hydrogenation and dehydrogenation of ball-milled Mg-Zn alloys

Further investigations on ball milled Mg-Zn alloys were carried out. In-situ SR-PXD was performed under 18 bar H₂ up to 225 °C (heating rate 2K/min). This was done to see if the amorphous/nanocrystalline MgZn phase that forms upon ball milling absorbs hydrogen before precipitation of Mg₂₁Zn₂₅ occurs (see previous report and [Deledda, S. et al. (2007). "H-sorption behaviour of mechanically activated Mg-Zn powders." *Journal of Alloys and Compounds* **446**: 173-177]). As shown in the figure below, crystallization of the amorphous/nanocrystalline phase sets in below 200 °C, with no indication of any hydride phases precipitating.

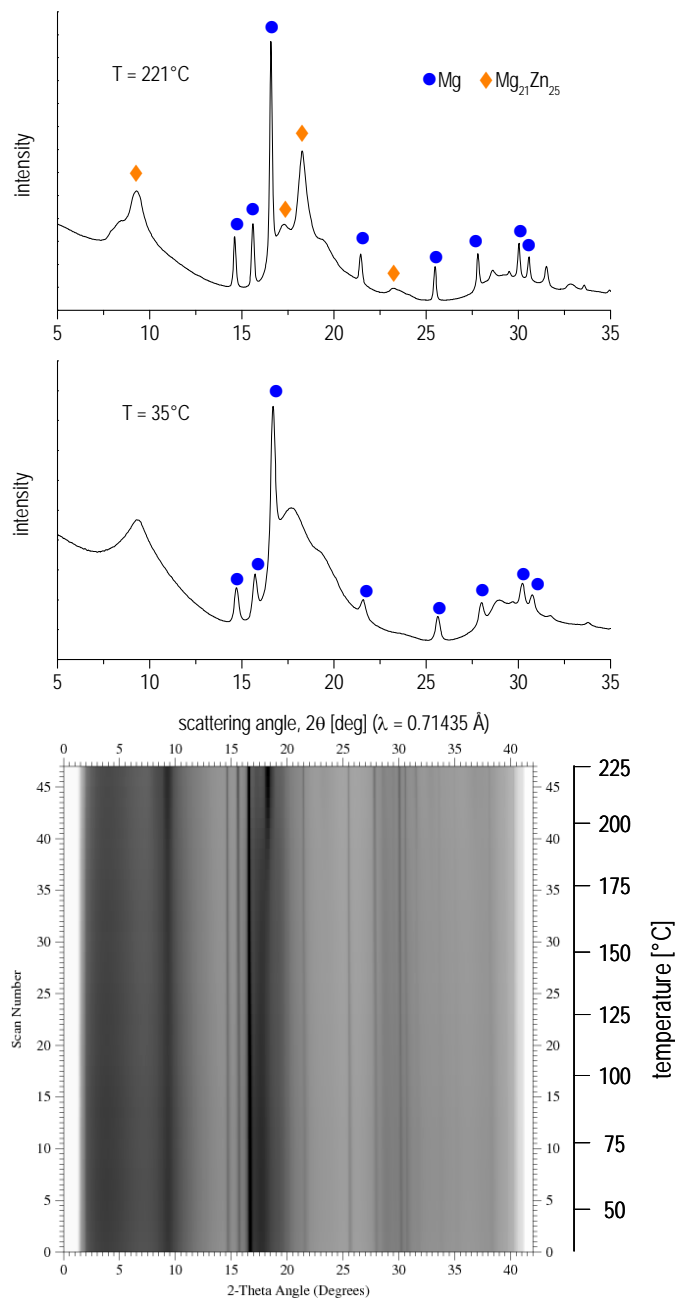


Fig. 5 Crystallization of Mg₂₁Zn₂₅