

**STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE –
desorption experiments – 01-02-631 (February-March 2005). Beamline BM01A**

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The present time-resolved in situ diffraction experiments aim on detailed studies of the desorption process of undoped and doped samples. The following materials were investigated during the experiment carried out in February-March 2005:

- (a) $LiAlD_4$ doped with VCl_3 .
- (b) K_2NaAlH_6
- (c) K_2LiAlH_6
- (d) $NaAlH_4$ pure and doped with TiF_3
- (e) Zr_2CuD_x
- (f) Na_2LiAlH_6 pure and doped with TiF_3

Not all the data have been fully analysed yet. Herein we present some of the first conclusions drawn from the preliminary analysis on the integrated diffraction patterns.

(a) Decomposition of $LiAlD_4$ doped with VCl_3

The sample was made of $LiAlD_4 + 5\%VCl_3$ ball milled for 20 min. It was heated at a constant heating rate of $2^\circ C/min$. from $25^\circ C$ up to $235^\circ C$ in vacuum.

The effect of VCl_3 as doping agent in the complex hydride $LiAlD_4$ is still unclear. After the ball-milling process the state and location of the V remains uncertain. In some of our ball-milled samples a new phase has been observed. Despite this phase has not been yet clearly identified we believe that it is a product of the reduction

reaction between Li and VCl_3 , probably in the form of a $Li_xV_yCl_z$ phase. The aim of this measurement was to follow the evolution and development of this phase and the formation of some possible Al-V phases.

During milling the $LiAlD_4$ vanished, from the reduction of VCl_3 and thermal decomposition giving $Li_3AlD_6 + Al$. These phases are observed in the pattern at room temperature, see Fig. 1.

On this figure one can see that the “unknown” phase vanishes at around $210^\circ C$ and that the $LiCl$ phase is growing up at the same time. This shows that “unknown” phase must include Li and Cl.

Furthermore the decomposition of lithium hexahydride is also observed. A careful analysis has to be carried out in order to check if any Al-V solid solution can be seen.

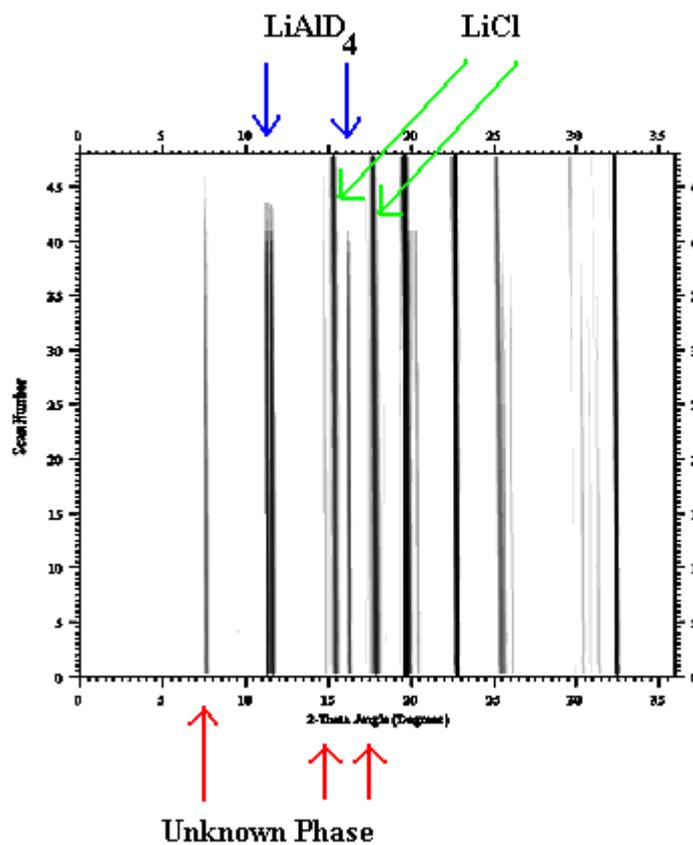


Figure 1 – Integrated intensities of the measured diffractograms for $LiAlD_4 + 5 \text{ mol\% } VCl_3$. Heating rate $2^\circ C/min$ from $25^\circ C$ to $235^\circ C$.

b) K_2NaAlH_6

The mixed alanate, K_2NaAlH_6 is a new compound that has been synthesized by ball milling in our laboratory. Nothing is known about the decomposition and release hydrogen upon heating.

The decomposition was investigated by heating the sample up to 400°C with a rate of 2°C/min, (see Fig.2). The decomposition starts around 80°C as the strongest peaks from KH start to develop. The sample starts to melt around 165°C while it is still not decomposed. The melt at first contain Al particles and complete melting is achieved at about 225°C. Interestingly, the melt reacts very abruptly with the capillary at around 275°C to form a well-crystalline silicate phase, which is isostructural with K_2MgSiO_4 .

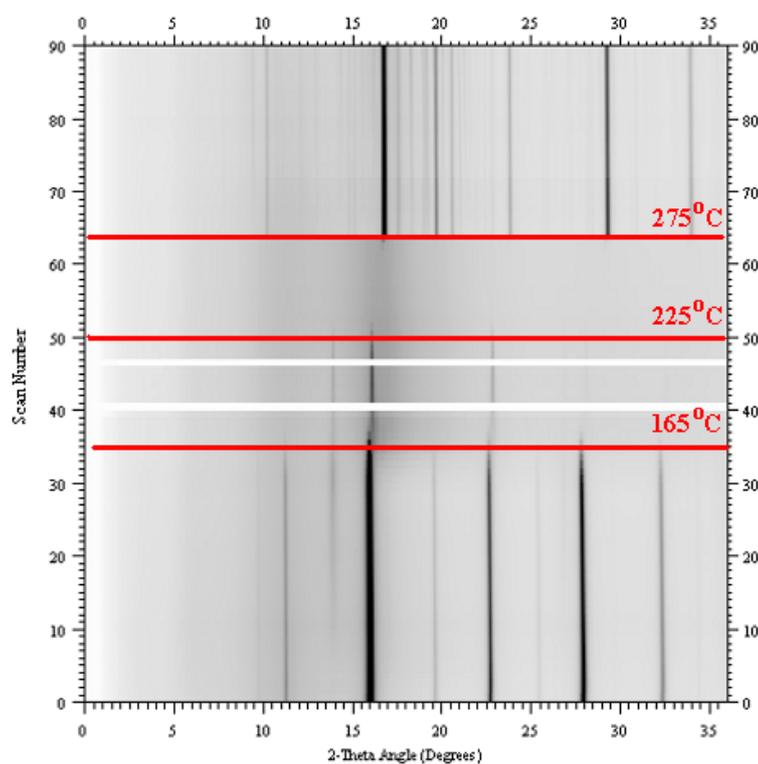


Figure 2 – Integrated intensities of the measured diffractograms for K_2NaAlH_6 .
Heating rate 2 °C/min from 25°C to 400°C.

c) K_2LiAlH_6

The mixed alanate, K_2LiAlH_6 is another new compound that has been synthesized in our laboratory. The decomposition is also unknown for this compound.

The sample was heated in vacuum with a heating rate of $2^\circ\text{C}/\text{min}$ up to 290°C , (See Fig.3). The Decomposition starts at around 100°C and finished at around 270°C where the starting phase vanishes. During the decomposition a new phase is formed at 170°C , and it vanishes at 245°C when two new phases are created. One of them disappears at the same temperature as K_2LiAlH_6 . No attempts to identify the different phases have been made yet. The data will be analysed in detail.

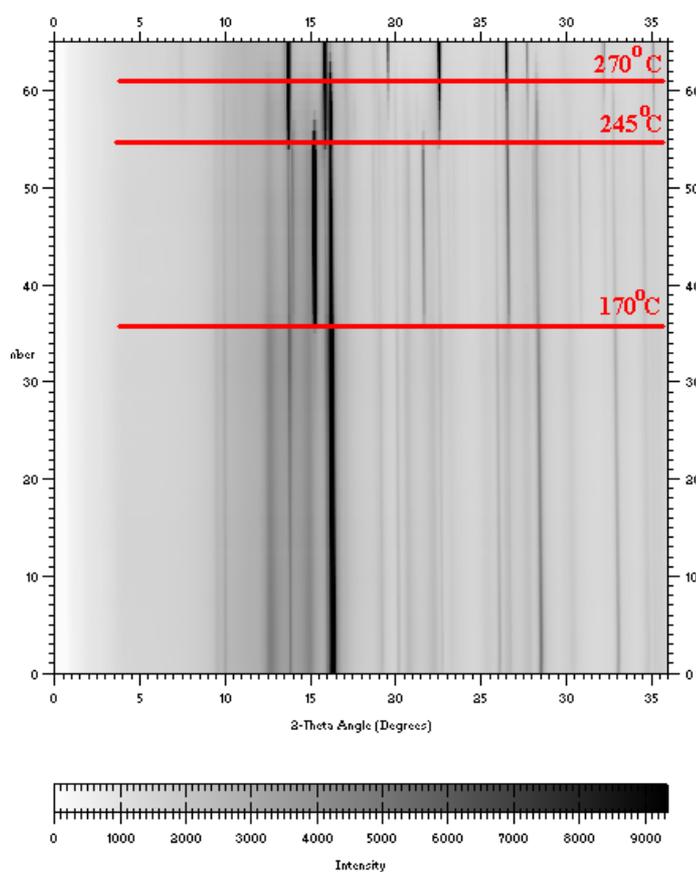


Figure 3 – Integrated intensities of the measured diffractograms for K_2LiAlH_6 .

Heating rate $2^\circ\text{C}/\text{min}$ from 25°C to 400°C .

d) Isothermal Decomposition of NaAlH₄ pure and doped with 2%TiF₃

The measurements were done for both samples at a constant temperature (158°C). The aim of this experiment is to obtain further information about the effect of the additive on the nucleation and diffusion of the species. The John-Mehl and Avramy relation has been successfully applied to the same kind of experiments, performed with doped Lithium alanate. It has been shown that the process of nucleation is affected by the presence of the additives. The collected data will be analysed based on this.

e) Zr₂CuD_x

The time-resolved in situ diffraction experiment aimed to study the phase transformations in Zr₂Cu hydrides upon heating.

The structure of Zr₂CuH_x has not been yet accurately solved for $x > 2$. In this experiment saturated Zr₂Cu hydride was heated from 50 to 430°C at a rate of 2°C/min. Fig. 4 indicates two different structures, the higher hydride (nearly saturated) (bottom) and the lower hydride (with less hydrogen) (top). The phase transition occurs at around 200°C. Both phases are distinctly different from the original Zr₂Cu compound structure. High-resolution diffraction data will be collected in May 2005. The goal is to solve the structure of the lower hydride.

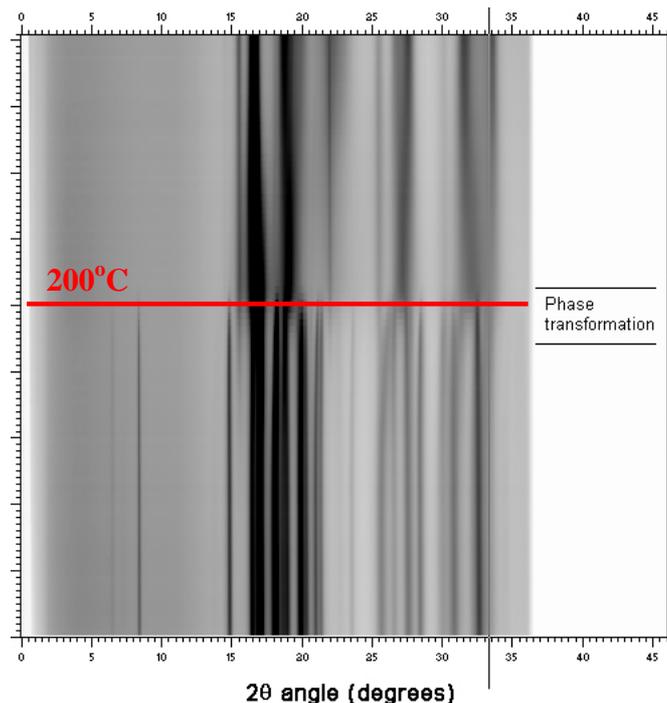


Figure 4 - Integrated intensities of the measured diffractograms for Zr_2Cu hydride.
Heating rate $2\text{ }^\circ\text{C}/\text{min}$ from $50\text{ }^\circ\text{C}$ to $430\text{ }^\circ\text{C}$.

f) Na_2LiAlH_6 , pure and doped.

Na_2LiAlH_6 is believed to decompose through the following reactions:



Four samples were measured to investigate the decomposition routes and the effect of additives:

- (i) Pure Na_2LiAlH_6
- (ii) $Na_2LiAlH_6 + 2\% TiF_3$ (heat treated)
- (iii) $Na_2LiAlH_6 + 10\% TiF_3$ (heat treated)
- (iv) $Na_2LiAlH_6 + 10\% TiF_3$

All samples were heated from room temperature, $25\text{ }^\circ\text{C}$, to approx. $400\text{ }^\circ\text{C}$, (ii) at heating rate $1\text{ }^\circ\text{C}/\text{min}$, the others at $2\text{ }^\circ\text{C}/\text{min}$.

The three reactions are clearly identified from the analyses of the integrated diffraction patterns (see Fig. 5 and 6). Comparing the decomposition of pure (i) Fig. 5,

and of one of the doped samples (iv) Fig.6, the decomposition reactions occur at lower temperatures for the doped sample (iv). R1 occurs at 200°C versus 250°C and R2 at 325°C versus 345°C, for respectively (iv) and (i). This clearly proves the effect of the additives to decrease the activation energy of the reactions. The data from the measurements are not fully analyzed; further investigation has to be performed to identify all the phases involved in the different reactions and to get a better understanding of the effect of the additive and on the heat treatment performed on some of the samples before the measurements.

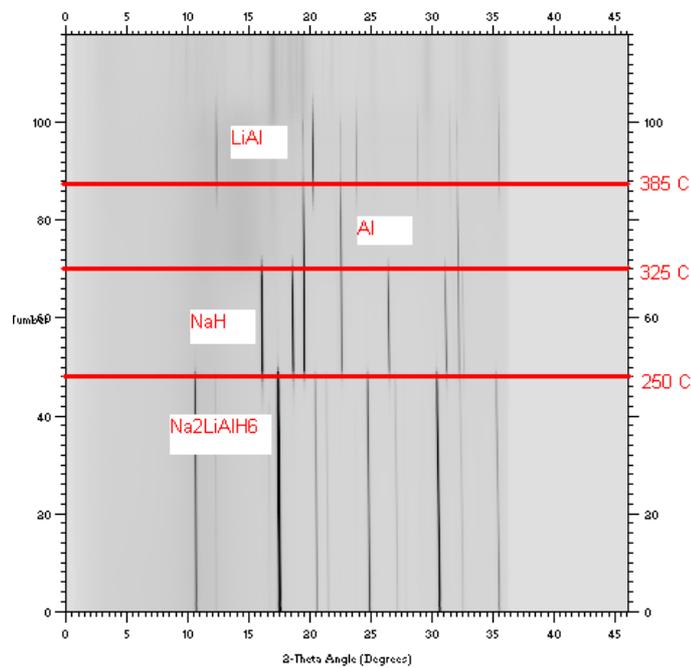


Figure 5 - Integrated intensities of the measured diffractograms for pure $\text{Na}_2\text{LiAlH}_6$. Heating rate 2 °C/min from 25°C to 430°C.

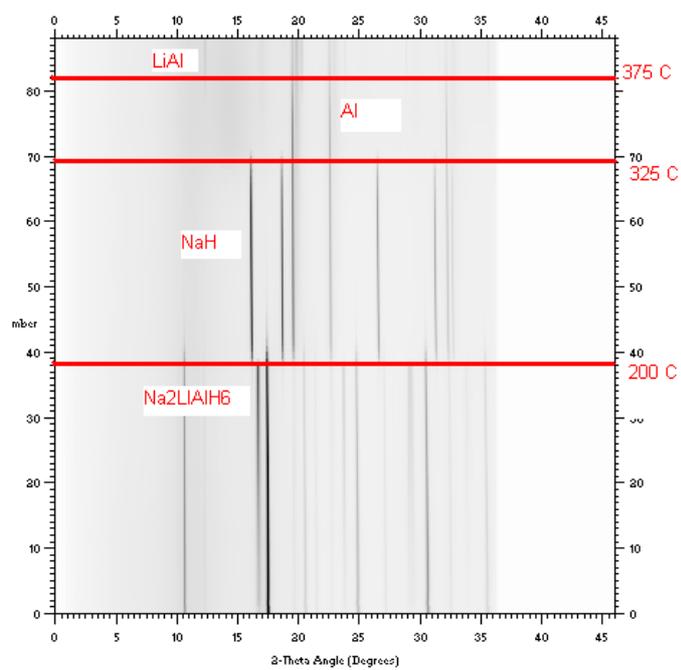


Figure 6 - Integrated intensities of the measured diffractograms for $\text{Na}_2\text{LiAlH}_6 + 10\% \text{TiF}_3$. Heating rate $2^\circ\text{C}/\text{min}$ from 25°C to 430°C