STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE – desorption experiments – 01-02-631.

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The time-resolved in situ diffraction experiments aim on detailed studies of the desorption process of undoped and doped alanate samples. The following materials were investigated during the experiment carried out in April 2004:

(a) Li_3AlD_6 both pure and 2 samples with different VCl_3 and $(Ti,Al)Cl_3$ doping.
(b) $KAlD_4$.
(c) $NaAlH_4$+10mol% TiF_3
(d) $Mg(AlH_4)_2$
(e) $BaMgNiD_4$
(f) $TbNiAlD_x$

(a)Decomposition of doped and undoped Li_3AlD_6

It as been found from previous measurements that even at rather low temperatures the hexahydride phase (Li_3AlD_6), from the decomposition of $LiAlD_4$, was partially decomposed, see Eq. 1 and 2.

$3LiAlD_4 \rightarrow Li_3AlD_6 + 2Al + D_2$ (1)
$Li_3AlD6 \rightarrow 3LiD + Al + 3/2D_2$ (2)

For this reason, the isothermal decomposition of (i) pure Li_3AlD_6, (ii) Li_3AlD_6 added with 2 mol% VCl_3, and (iii) Li_3AlD_6 added with 2 mol% $3TiCl_3.AlCl_3$ has been studied. The purposes of these measurements were to get quantitative measurements of these second decompositions as well as clear insight on this reaction.
For all samples diffraction diagrams were collected at five temperatures, for the undoped sample: 136, 138, 140, 144, 148, 207 °C and for the two doped samples: 122, 126, 130, 134 138 and 207°C.

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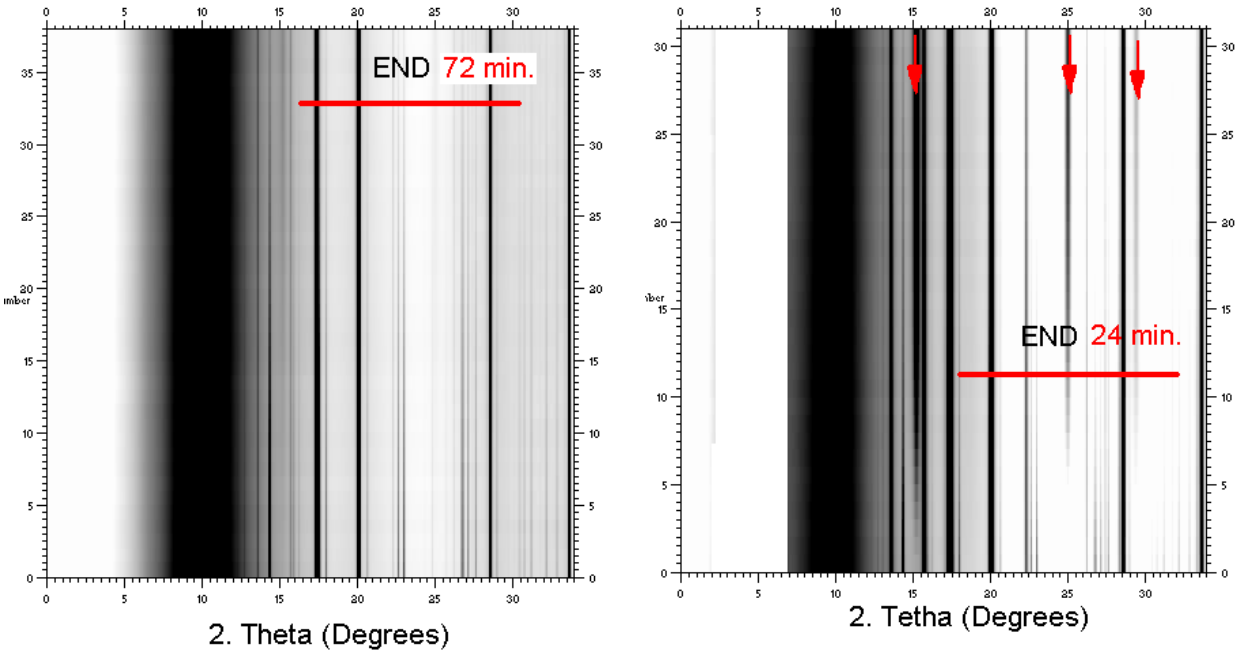
Fig 1 shows the results obtained for the decomposition of pure and doped Li_3AlD_6 with VCl_3 at 207°C. The figure shows the integrated intensities of the measured diffractograms plotted as a function of 2θ and scan number. The total decomposition of the hexahydride is completed, after 72 min. and 24 min for the pure and doped sample, respectively. The efficiency of the VCl_3 to promote the second step reaction is then clearly shown. For the doped sample a new phase is coming up after the completion of the reaction. This phase has never been observed and is certainly due to the presence of the V phase in the sample. It has to be identified.



a) T= 207 °C – End of decomposition 72 min

b) T= 207 °C-End of decomposition 24 min

Figure 1 – Isothermal decomposition of a)Li_3AlD_6 and b)Li_3AlD_6 mixed with 2 mol% VCl_3.

For the measurements made at lower temperatures no clear trend can be observed directly from the Fid2D integrated plots. Thus, further analyses in term of phase composition using Rietveld refinements have to be done to get clear insight and quantitative data.

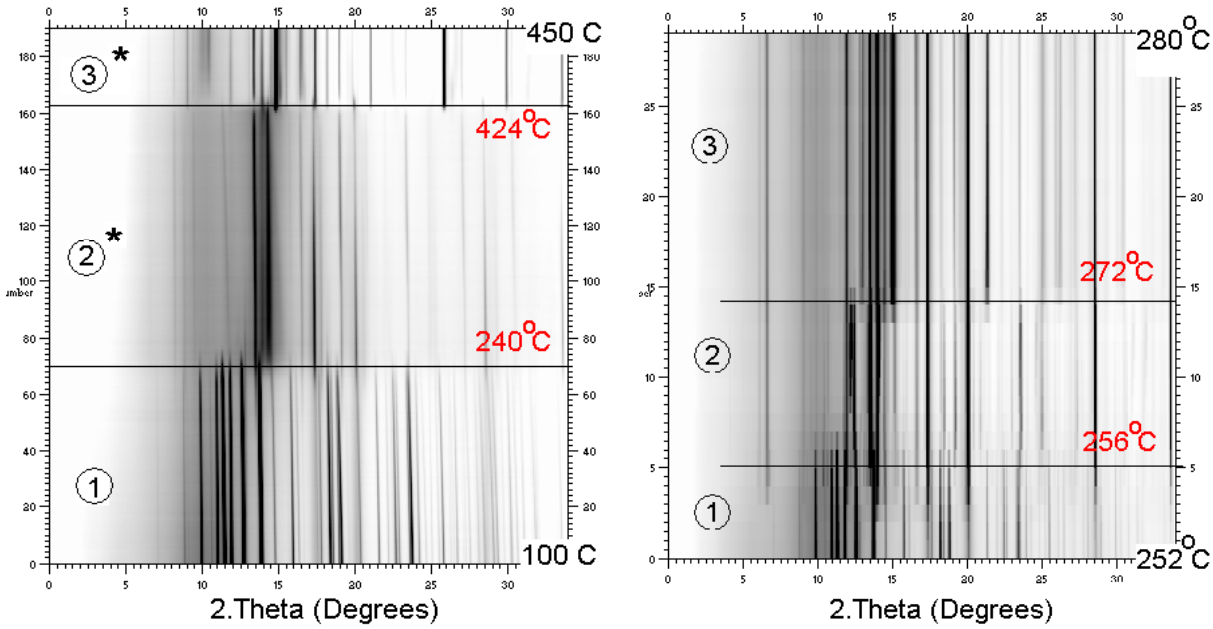
b) Decomposition of $KAlD_4$

The decomposition of $KAlD_4$ has been previously studied with a constant heating rate of 2°K/min. The decomposition follow the two steps described in the following set of equations:

$$3\ KAlD_4 \rightarrow K_3AlD_6 + 2Al + 3D_2 \quad (3)$$

$$K_3AlD_6 \rightarrow 3KD + Al + 3/2D_2 \quad (4)$$

The obtained results were not clear. Both decompositions were found to be fast and a possible melting of $KAlD_4$ was suspected to occur during the first decomposition step. In this new set of experiments the decomposition was studied at lower heating rates: 1°K/min, with a starting temperature of 100 °C. From these data it is clear that no melting occurs. The first reaction occurs at around 240 °C (Phase 1 to 2*), a second at around 424°C (Phase 2* to 3*), see Fig 2.a). Furthermore, together with the second crystalline phase a large proportion of amorphous compounds is found, seen by a significant increase in the background level. At 0.5°K/min, see Fig 2.b), starting at 252°C, again no melting seems to occur. Nevertheless, the decomposition does not follow the same route. The first reaction occurs at around 256 °C (Phase 1 to 2), a second at 272°C (Phase 2 to 3). Further investigation has to be performed to identify all the phases involved in the different reactions.



a)1°K/min-Starting temperature 100°C

b)0.5°K/min – Starting temperature 252°C

Figure 2 – $KAlD_4$ decomposition at several heating rates.

Isothermal measurements have also been performed. Analysis of the data is in progress.

c) Decomposition of $NaAlH_4$ with 10% TiF_3 additive

The thermal decomposition of sodium alanate, $NaAlH_4$ added with 10 mol% TiF_3, at constant heating rate of 1 °K/min has been measured. The starting temperature was 50 °C. As the other alanates, sodium alanate is supposed to decompose in a two steps reaction. On the following picture one can easily see that the decomposition does not follow this "simple route". At least five different composition can be seen.

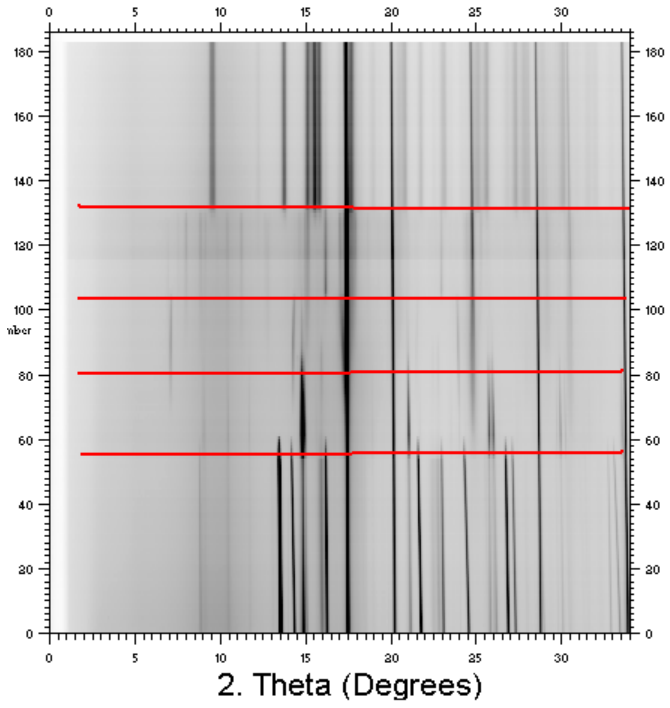


Figure 3 - Integrated intensities of the measured diffractograms for $NaAlH_4$ + 10 mol% TiF_3. against 2θ and the scan number. Heating rate 0.5 ^oK/min from 50oC to 420 ^oC.

d) Decomposition of $Mg(AlH_4)_2$

The thermal decomposition of magnesium alanate, $Mg(AlH_4)_2$, at constant heating rates of 2, 5 and 10 K/min has previously been investigated by our research group. Supplementary constant heating rate experiments, as well as five constant temperature decomposition experiments were performed on this occasion. Analysis of the data is in progress.

e) Decomposition of $BaMgNiD_4$

The thermal decomposition of the complex deuteride $BaMgNiD_4$ was studied during heating at a constant heating rate of 1 K/min. Decomposition was only observed at temperatures > ~300°C. Analysis of the data is in progress.

f) Decomposition of $TbNiAlD_{\sim 1.1}$

Thermal desorption measurements on $TbNiAlD_{\sim 1.1}$ were performed with a constant heating rate of 0.5 K/min. Two phase transitions could be seen in the measured temperature region. The first phase transition is thought to correspond to the transition from orthorhombic Amm2 to hexagonal P62m at a D content of ~0.67, whereas the second phase transition most likely is the transition from hexagonal P62m to hexagonal P62c at a D content of ~0.33 by comparison with literature data. Analysis of the data is in progress.

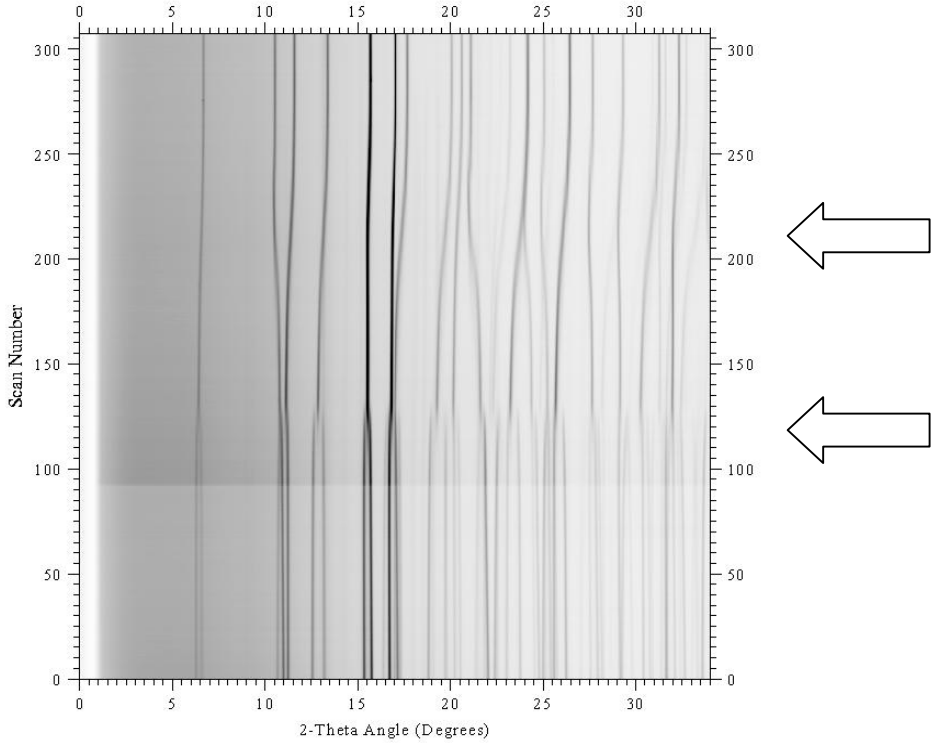


Figure 4 - Integrated intensity of the measured diffractograms for $TbNiAlD_x$ plotted against 2θ and the scan number. The phase transitions are shown with arrows.