

B. C. Hauback, M.H. Sørby, Y. Nakamura, J. Höwing, H. Grove and I.J.T. Jensen
*Department of physics, Institute for Energy Technology, P. O. Box 40, NO-2027 Kjeller,
Norway*

Time-resolved *in-situ* diffraction experiments were carried out on the MAR-instrument at station BM01A to investigate thermal decomposition behaviour of hydrogen storage materials. The following materials were investigated during the experiment carried out in December 2005:

- (a) $3\text{Mg}(\text{NH}_2)_2 + 8\text{LiH}$
- (b) $\text{LiND}_2 + 2\text{LiD}$
- (c) Sr-Al-D
- (d) $\text{LiMg}(\text{AlD}_4)_3$ and LiMgAlD_6
- (e) Zr_2Pd_x

(a) $3\text{Mg}(\text{NH}_2)_2 + 8\text{LiH}$

A mixture of $\text{Mg}(\text{NH}_2)_2$ with LiH in a molar ratio of 3:8 can be release about 7wt% of hydrogen. The details of the dehydrogenation reaction have not been investigated yet. The sample was heated in vacuum with a heating rate of 1 °C/min up to 500 °C (see Fig. 1). With increasing temperature, intensities for $\text{Mg}(\text{NH}_2)_2$ and LiH decreased and the pattern of a new phase appeared. This transformation was accelerated from around 150 °C and completed at around 200 °C. This new pattern started to split above 200 °C. Unfortunately the boron glass capillary was broken during the reaction, probably because of a small emission of NH_3 . The sample was quickly oxidized above around 300 °C.

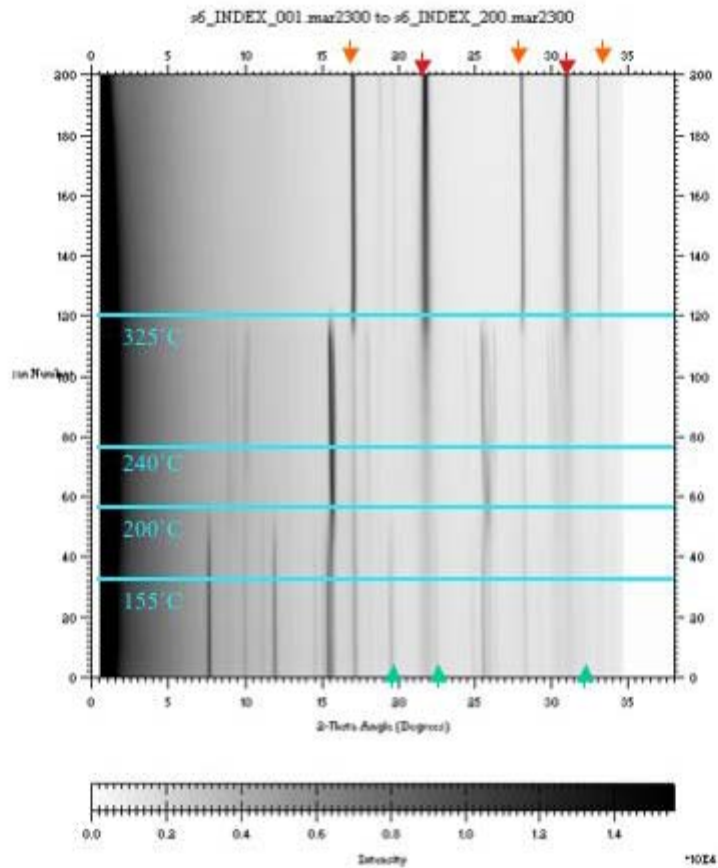


Figure 1 Integrated intensities of the measured diffractograms for a mixture of $\text{Mg}(\text{NH}_2)_2$ and LiH . Heating rate $1^\circ\text{C}/\text{min}$ from 100°C to 500°C . Blue arrows: LiH , red arrows: MgO , orange arrows: Li_2O .

(b) $\text{LiND}_2 + 2\text{LiD}$

A mixture of LiND_2 and LiD in a molar ratio of 1:2 can release about 6wt% of hydrogen. Some reaction mechanisms have been proposed, but they are still not clear. The sample was heated in vacuum with a heating rate of $1^\circ\text{C}/\text{min}$ up to 315°C (see Fig.2). The pattern of Li_2O appeared and rapidly grew up above 150°C . It is because the boron glass capillary was broken in the same way as the reaction of $\text{Mg}(\text{NH}_2)_2$ with LiH described above.

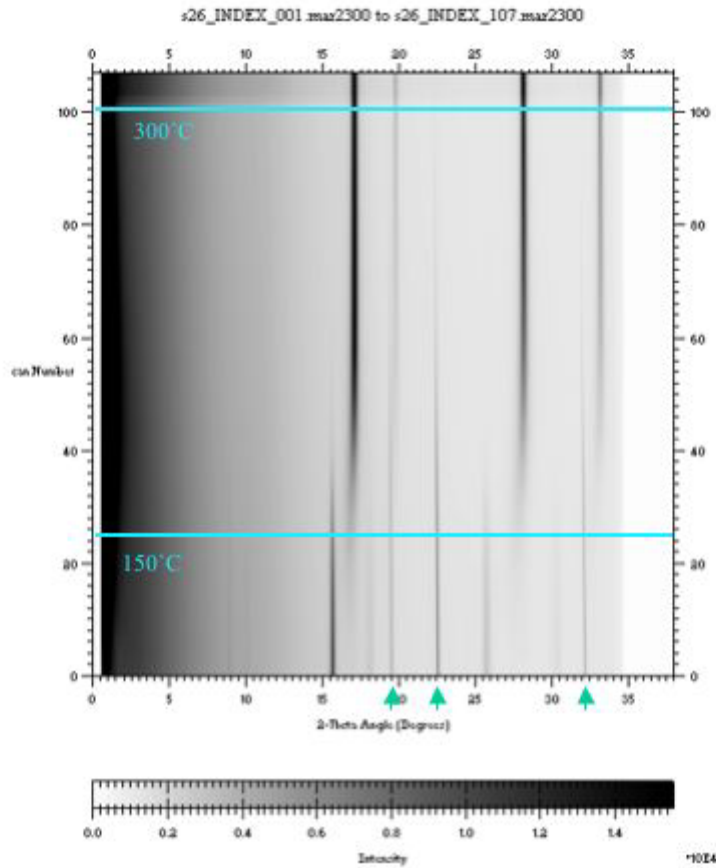


Figure 2 Integrated intensities of the measured diffractograms for a mixture of LiND₂ with 2LiD. Heating rate 1 °C/min from 100 °C to 315 °C. Blue arrows: LiH

(c) *Sr-Al-D*

The sample was synthesized from SrCl₂ and LiAlD₄ by ball milling and annealing in a hydrogen atmosphere aiming for a new Sr-Al-D compound. The reaction expected is:

$$\text{SrCl}_{2(s)} + 2\text{LiAlD}_{4(s)} \rightarrow \text{Sr}(\text{AlD}_4)_{2(s)} + \text{LiCl}_{(s)}$$

The sample was heated in vacuum with a heating rate of 2°C/min up to 400°C (see Fig. 3). At the starting temperature, a pattern corresponding to a new Sr-Al-D phase with relatively broad peaks is seen, in addition to LiCl (blue arrows) and Al (red arrows). This phase began to transform to another phase at around 200 °C and remained up to 340 °C. Above this temperature, a further decomposition proceeded. Structure analysis of the observed phase has not yet been done.

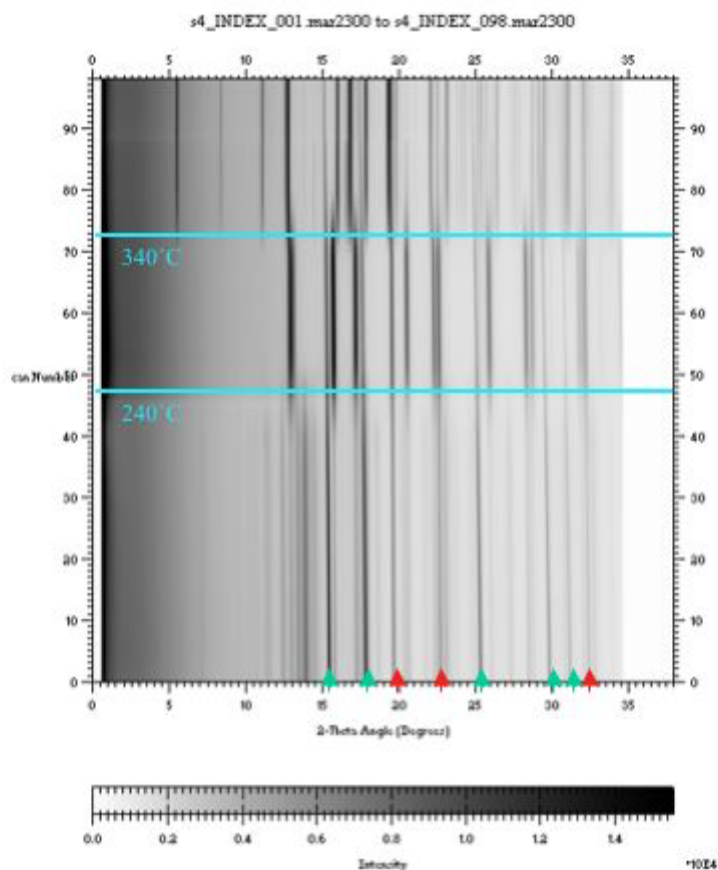


Figure 3 Integrated intensities of the measured diffractograms for a Sr-Al-D sample. Heating rate 2 °C/min from 50°C to 400°C.

(d) $\text{LiMg}(\text{AlD}_4)_3$ and LiMgAlD_6

$\text{LiMg}(\text{AlD}_4)_3$ was measured under dynamic vacuum from 70 °C to 220 °C at a constant heating rate of 0.5 °C/minute. Several phases are observed during the temperature increase. The reaction occurring is: $\text{LiMg}(\text{AlD}_4)_3(\text{s}) \rightarrow \text{LiMgAlD}_6(\text{s}) + 2\text{Al}(\text{s}) + 3\text{D}_2(\text{g}) \rightarrow \text{LiD}(\text{s}) + \text{MgD}_2(\text{s}) + 3\text{Al}(\text{s}) + 3/2\text{D}_2(\text{s})$. LiCl, a biproduct in the synthesis, is present at all temperatures. The data are difficult to interpret because $\text{LiMg}(\text{AlD}_4)_3$ and LiMgAlD_6 diffract weakly; probably due to a high degree of amorphous character. In addition, a LiMgAlD_6 sample prepared by thermal decomposition of $\text{LiMg}(\text{AlD}_4)_2$ prior to the experiments, was measured ex-situ. Structure determination of LiMgAlD_6 is in progress.

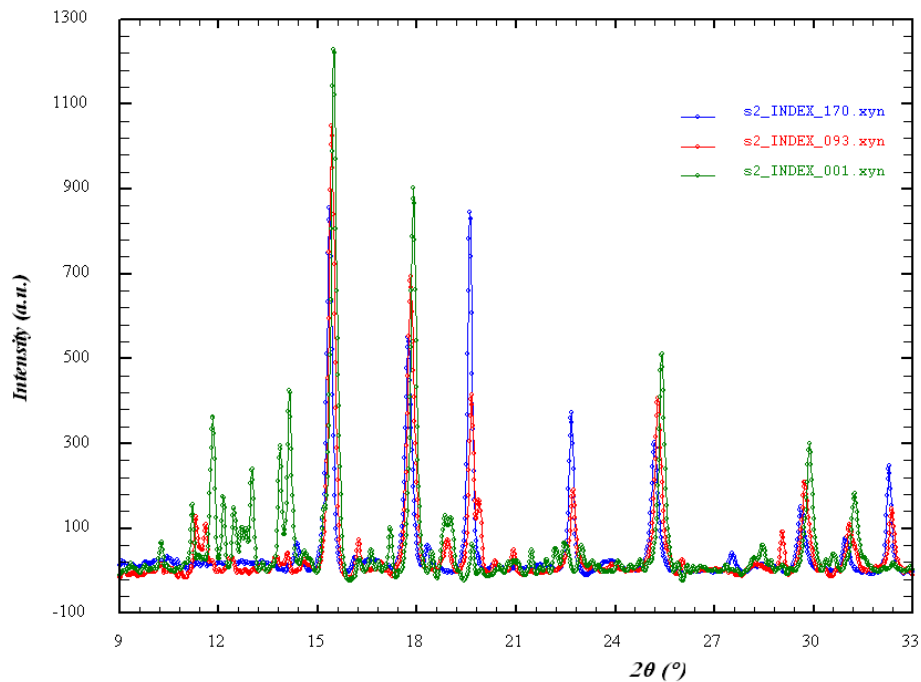


Figure 4 The figure shows the diffraction pattern at three different temperatures for the $\text{LiMg}(\text{AlD}_4)_3$ system. Index_001 was collected at 68 °C; Index_073 was collected at 151 °C; Index_170 was collected at 217 °C.

(e) Zr_2PdD_x

Zr_2Pd (tetragonal, space group, $I4/mmm$, MoSi_2 -type structure) absorbs deuterium to the composition Zr_2PdD_5 . The crystal structure of Zr_2PdD_2 is known to be an expanded version of the intermetallic structure, however the structure at both higher and lower deuterium content is unclear. A sample with composition Zr_2PdD_3 was measured *in-situ* from ambient temperature to 600 °C under dynamical vacuum. Peak splitting was observed for deuterium contents $\text{Zr}_2\text{PdD}_{>2}$ indicating symmetry lower than that for the intermetallic. An expanded tetragonal MoSi_2 -type structure was observed for $\text{Zr}_2\text{PdD}_{<2}$ (Fig. 5), thus disproving earlier indications of an orthorhombic phase in that composition range.

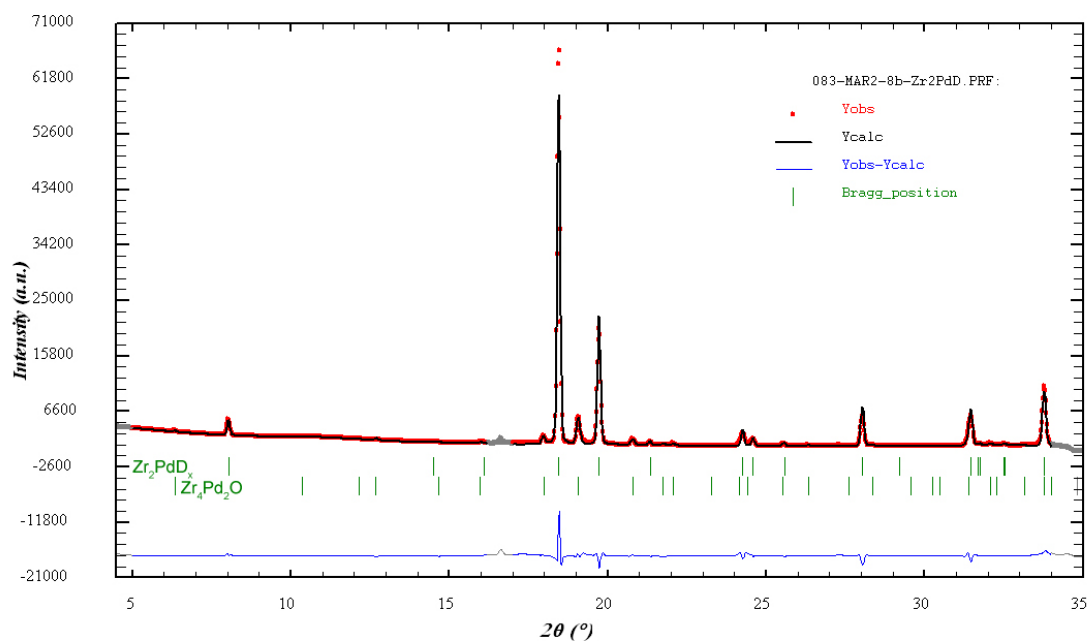


Figure 5 Rietveld refinement of $\text{Zr}_2\text{PdD}_{2.2}$ at 674 °C revealing a MoSi_2 -type structure.

General remarks

There were few, if any, problems with the instrument and the supporting equipment during the experiments. The hot air blower worked beautifully and gave very stable heating rates from room temperature up to 850 °C. All the software was stable, and the beam was only lost for one short period.

We did learn that boron glass capillaries are corroded quickly by ammonia at elevated temperatures. Thus, other kind of capillaries will be used in future in-situ experiments involving amides and imides.