Experimental Report

03/03/2015

Proposal:	**5-25-235**	**Council:**	4/2014

Title: Real-time study of the deuterationof reactive hydride composites in the Li-Mg-N-D system (Li3N-MgD2)

This proposal is a new proposal

Researh Area: Chemistry

Main proposer: **KOHLMANN Holger**

Experimental Team:
AUER Henry
GOETZE André
BEHRENDT Gereon
KOHLMANN Holger

Local Contact: HANSEN Thomas

Samples:
MgH2
Li3N

Instrument	**Req. Days**	**All. Days**	**From**	**To**
D20	3	3	03/10/2014	06/10/2014

Abstract:

In situ neutron powder diffraction shall be performed on potential hydrogen storage materials in the system Li-Mg-N-D. The mixture Li3N+MgD2 yields LiND2+MgD2 by heating under deuterium gas. The desorption yielding mixtures of magnesium nitride, lithium magnesium nitride and lithium deuteride, and the redeuteration of this mixture follows different pathways, depending on the deuterium gas pressure. These reactions will be investigated by using a sapphire single crystal based gas pressure cell on D20 with a time resolution of 1 minute in two experiment: At a deuterium pressure of 1 bar, Li3N+MgD2 will be deuterated at 500 K, the reaction product dedeuterated at 700 K under argon as protective gas and then redeuterated at 500 K. The same experimental protocol will be followed for a deuterium gas pressure of 10 bar. These in situ investigations will reveal the different reaction pathways and help understanding reversibility of hydrogenation-dehydrogenation cycles in this system. To allow for an accurate temperature measurement and the best possible instrumental setting, new temperature calibration and testing of the sapphire crystals by omega scans will be performed beforehand.

Report to experiment 5-25-235:

Real-time study of the deuteration of reactive composites in the Li-Mg-N-D system (Li_3N-MgD_2)

Holger Kohlmann, Gereon Behrendt, Universität Leipzig, Germany

The topic of the experiment was the investigation of reaction pathways of the deuteration of Li_3N-MgD_2 mixtures for hydrogen storage. Li_3N can be hydrogenated at mild conditions and this reaction may be further facilitated by adding Mg to the system [1-3]. While the hydrogenation (deuteration) of pure Li_3N has been studied in detail [1, 4], little information is available on the reaction pathway of Li_3N+MgH_2 with hydrogen gas, especially when reactants were not ball-milled beforehand [2]. We studied this reaction on the deuterides using two different deuterium gas pressures (15 and 90 bar), because preliminary *ex situ* and *in situ* differential scanning calorimetry suggest different pathways [1, 4].

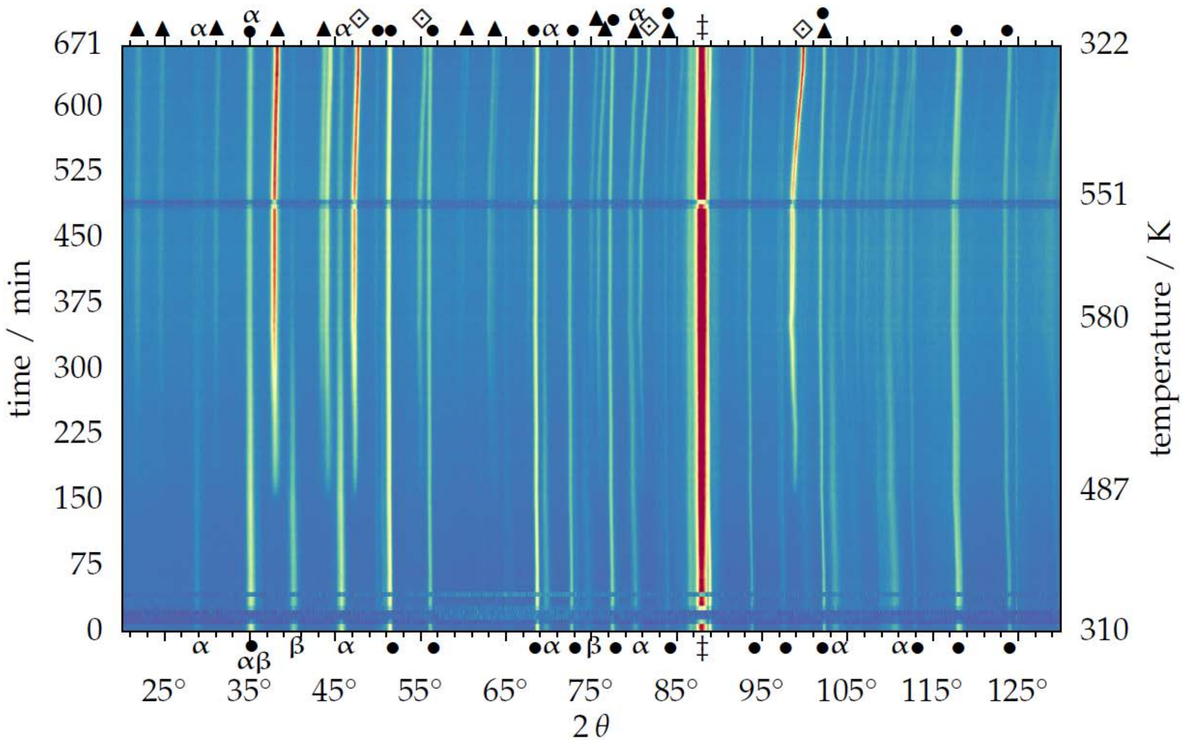

Figure 1: *In situ* neutron powder diffraction on equimolar mixtures of Li_3N and MgD_2 under 1.5 MPa deuterium gas pressure. Phases: α-Li_3N (*P*6/*mmm*), β-Li_3N (*P*6_3/*mmc*), ●MgD_2, ▵ $LiND_2$, ◊ LiD, ‡ single crystal reflection of the sapphire sample holder; λ =186.70 pm

In situ diffraction studies at lower (15 bar, Fig. 1) and higher deuterium gas pressure (90 bar) were performed using a sapphire single crystal based gas pressure cell with an automatic gas pressure control and a 2x40W laser heating developed within LTP-5A-1 [5]. Because the colour of the starting materials (dark red-brown) and final products (light grey) of this reaction differed from those of the materials studied before with this setup, it was uncertain whether the energy takeup from the laser would be sufficient and the temperature calibration of the pyrometer was still valid. Therefore, further standard measurements were taken and analysed by Rietveld refinement. From the refined lattice parameters the temperatures were calculated and the pyrometer calibrated. While light coloured materials did not yield high temperatures as expected (e. g. colourless NaCl max. 380 K), temperature calibration functions of the pyrometer did not vary significantly, i. e. the known temperature calibration [5] could be used for all studied materials and allows for a sufficiently accurate temperature determination.

Unfortunately, *ex situ* measurements had already shown that the goniometer of the diffractometer was misaligned. A part of this problem could be reversed by action of the beamline scientist (D20 diffractometer), however, only for one position of the ω table. This still caused problems with the *in situ* experiments, where the angle ω has to be varied in order to find the ideal position for the sapphire single crystal gas pressure cell. While refinement of the sample position could correct for the Bragg peak positions, the intensities had significant systematic errors due to the effect of the radial collimator for most angles ω. Correct peak positions are sufficient for the Rietveld refinements on the NaCl structure for calibration purposes (see above). Erroneous intensities in case of the *in situ* measurements, however, impeded complete Rietveld refinements, which are the usual way to extract the maximum amount of information from *in situ* neutron powder diffraction experiments. Therefore, only qualitative phase analyses were performed and kinetics estimated by the development of the intensities of non-overlapping Bragg peaks of the individual phases.

Diffraction data with a time resolution of 3 minutes were taken on D20 at a wavelength $\lambda = 186.70$ pm using deuterium pressures up to 90 bar and temperatures up to 580 K. In the experiments both at lower (15 bar) and higher pressure (90 bar), we observed the reaction $Li_3N + 2\ D_2 \rightarrow 2\ LiD + LiND_2$ to start at approximately 473 K. Unfortunately, Rietveld refinements did not yield satisfactory results, e. g. intensity mismatch and unreasonable thermal displacement parameters, due to the above mentioned misalignment of the goniometer. Therefore, the *in situ* neutron powder diffraction data were evaluated instead for qualitative phase analysis and for the development of the intensities of individual peaks. According to this analysis the intensities of the produced phases LiD and $LiND_2$ grow according to a $t^{1/2}$ law, which is typical for a solid-gas reaction (Fig. 2).

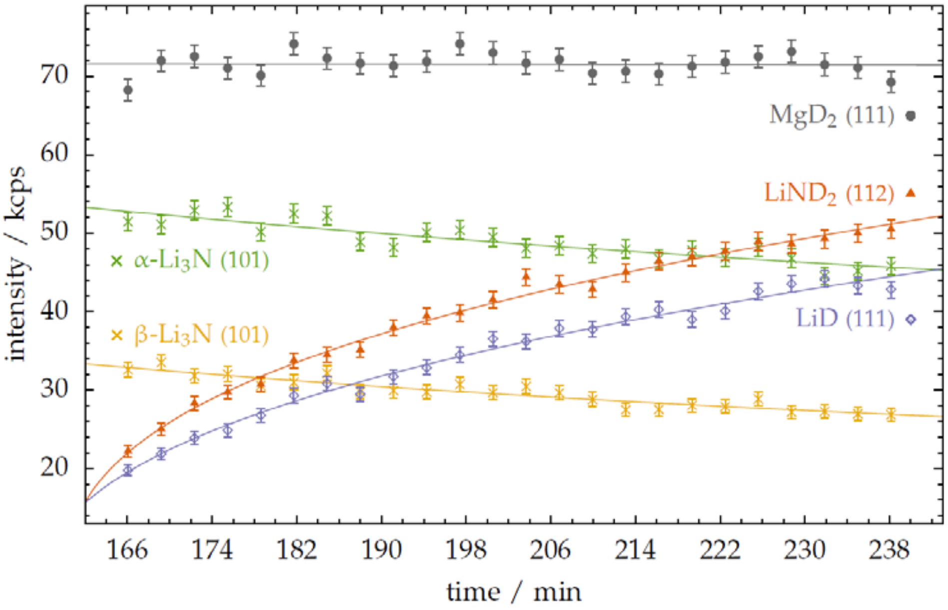

Figure 2: Development of the intensities of individual peaks during an isothermal section (494(2) K) in the *in situ* neutron powder diffraction on equimolar mixtures of Li_3N and MgD_2 under 1.5 MPa deuterium gas pressure.

This finding is in agreement with *in situ* thermal analyses and *ex situ* X-ray diffraction experiments, where the same phases were found under very similar conditions. In these experiments at higher temperatures two different reaction pathways were found. At low pressures (15 bar) an endothermic decomposition according to $LiNH_2 + MgH_2 \rightarrow LiMgN + 2\ H_2$ takes place. At higher pressures (50 bar) the hydrogen evolution is suppressed and LiMgN formed in a different way by the reaction $Li_3N + MgH_2 \rightarrow LiMgN + 2\ LiH$. Both reactions occur around 620 K, a temperature that was not reached in the *in situ* neutron diffraction experiment. Thus, these decomposition reactions could not be observed here.

The *in situ* experiment at 9.0 MPa deuterium pressure yielded very similar results with the same reaction pathway. For a more detailed study of the kinetics of the reaction $Li_3N + 2\ D_2 \rightarrow 2\ LiD + LiND_2$ the experiment would have to be repeated with correct alignment of the diffractometer. Following the second reaction to LiMgN at higher temperatures, which follows different reaction pathways for different pressures, *in situ* experiments at the diffractometer D20 would require a different heating system, because the light coloured materials would not take up enough energy from our laser heating system with a wavelength of 808 nm.

Literature

[1] H. Kohlmann, C. Reichert, P. Wenderoth, ILL experimental report 5-22-714

[2] M. Y. Song, S. N. Kwon, Y. J. Kwak, H. R. Park, *Mater. Res. Bull.* **2013**, *48*, 74-78; Y. Liu, K. Zhong, M. Gao, J. Wang, H. Pan, Q. Wang, *Chem. Mater.* **2008**, *20*, 3521-3527

[3] D. Pottmaier, F. Dolci, M. Orlova, G. Vaughan, M. Fichtner, W. Lohstroh, M. Baricco, *J. Alloys Compd.* **2011**, *509S*, S719-S723

[4] D. J. Bull, N. Sorbie, G. Baldissin, D. Moser, M. T. F. Telling, R. I. Smith, D. H. Gregory, D. K. Ross, *Faraday Discuss.* **2011**, *151*, 263-270

[5] H. Kohlmann, N. Kurtzemann, T. C. Hansen, *Powder Diffr.* **2013**, *28*, S242-S255