

STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE

Final report – In-situ SR-PXD: 01-02-962 Beamline BM01A

Initial comment

The Physics Department at Institute for Energy Technology has a strong activity on hydrogen storage materials, involving many national and international collaborators. The strong position of the group is to a high degree owing to the good access to neutrons for powder neutron diffraction (PND) using the diffractometer PUS at the Institute's research reactor JEEP II.

Synchrotron power X-ray diffraction (SR-PXD) is an invaluable supplement to PND due to the superior speed and resolution. The data acquisition times are typically 3 orders of magnitude shorter using the MAR345 image plate at BM01A compared to PUS. This allows in-situ investigations of chemical reactions that we cannot possibly follow with PND. The very high resolution offered at BM01B allows indexing and space group determination from complex structures where the problem with peak overlapping makes the task unmanageable with PND- or laboratory PXD data.

Thus, the predictable, long-term access to the beam lines at SNBL through the long-term projects 01-01-805 and 01-02-862, as well as the short projects 01-01-863 and 01-02-962, has been an invaluable supplement to our neutron diffraction facilities and the rest of our experimental activity.

This report summarizes the obtained results on project 01-02-962.

Thermal decomposition of lithium hydrazide

Lithium hydrazide (LiNHNH_2) has high hydrogen content of 8.0 mass%. LiNHNH_2 was synthesized by wet chemistry method and decomposition pathway of this compound was investigated by in situ SR-PXD at BM01A. LiNHNH_2 was heated up to 300 °C with a ramp rate of 5 °C/min under dynamic vacuum and diffraction data were collected every 2 min. As shown in Figure 1, LiNHNH_2 was decomposed into a new phase which would be $\text{Li}_2\text{N}_2\text{H}_2$. After further heating, $\text{Li}_2\text{N}_2\text{H}_2$ has disappeared and LiNH_2 and/or Li_2NH phase has formed.

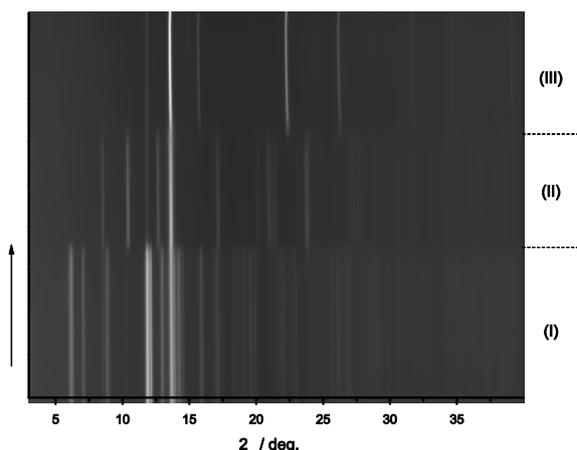


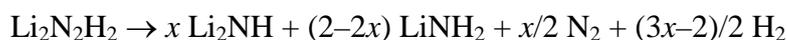
Figure 1 In-situ SR-PXD pattern of LiNHNH₂ in the temperature range of RT to 300 °C ($\lambda=0.69674\text{\AA}$). (I) LiNHNH₂, (II) Li₂N₂H₂, (III) LiNH₂/Li₂NH.

From the above results and thermogravimetry combined with thermal desorption mass spectroscopy analysis, the possible decomposition pathway of LiNHNH₂ can be deduced as follows,

1st Step: 100 – 130 °C



2nd Step: 170 – 205 °C



3rd Step: 205 – 350 °C



Structure solution of LiNHNH₂ and Li₂N₂H₂ is in progress and the results will be published.

H-sorption and Mg₂FeH₆ formation in Mg-Fe-LiBH₄ composites

The effect of LiBH₄ on the sorption properties of Mg₂FeH₆ is being investigated. Three different synthetic routes, all based on ball milling techniques, were employed to produce the LiBH₄-based composites: (i) Reactive milling of Mg, Fe, and LiBH₄ under 50 bar H₂ for 15 hours (in-situ formation of MgFeH₆); (ii) Synthesis of Mg₂FeH₆ by reactive milling under 50 bar H₂ followed by further ball milling of with LiBH₄ under 50 bar H₂ for 1 hour; (iii) Synthesis of Mg₂FeH₆ by reactive milling under 50 bar H₂ in for 15 hours followed by further ball milling with LiBH₄ under 1 bar Argon for 1 hour.

Unreacted elemental Fe is typically observed after the synthesis of Mg₂FeH₆. It was found that, after dehydrogenation-rehydrogenation cycles, the residual metallic Fe is no longer observed by lab-source PXD analysis. It was therefore important to follow the rehydrogenation process (and the “re-formation” of Mg₂FeH₆) by in-situ SR-PXD.

The measurement were planned to be carried out isothermally at 350 °C for 2 hours under about 10 bar H₂. According to DSC and H-sorption measurements such

conditions would have ensured a full re-hydrogenation of the samples under investigation. However, the re-hydrogenation reaction was not observed during in-situ SR-PXD (see Figure 2). This was likely due to the actual temperature at the sample being around 15 °C lower than the programmed temperature in the gas blower.

This group of samples are currently still under investigation in collaboration with the University of Quebec in Trois-Riviers (UQTR), Canada and will be used in a joint publication.

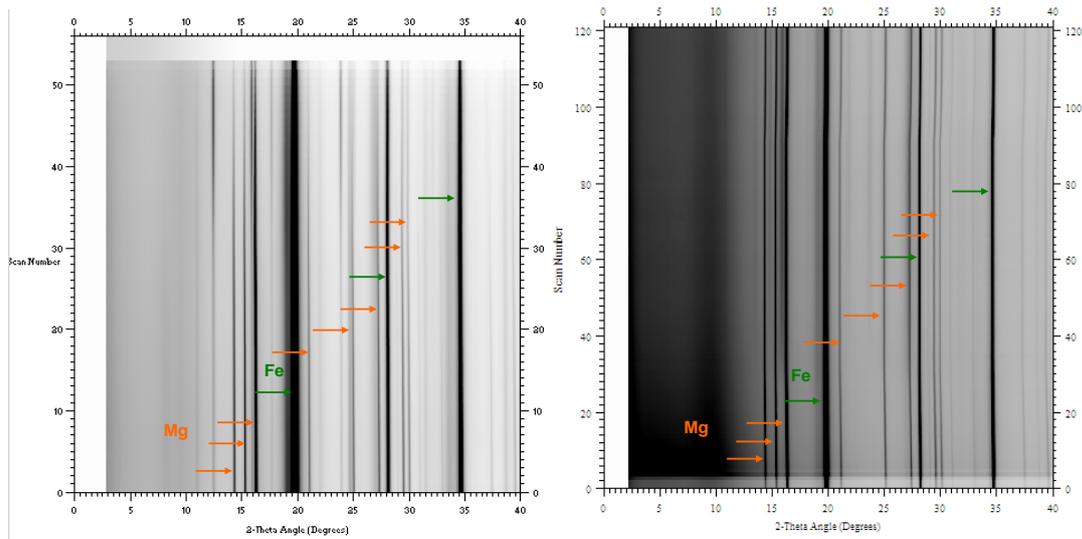


Figure 2. In situ SP-XRD for the hydrogenation of dehydrated $\text{Mg}_2\text{FeH}_6 + 5 \text{ mol.}\% \text{ LiBH}_4$ (left) and Mg_2FeH_6 (right)

Effect of alloying MgH_2 with Cr and V by high-energy ball milling technique on its sorption properties

The possible influence of elemental mixture of Cr and V on thermal decomposition of MgH_2 has been studied at BM01A. Equimolar powder mixture of $\text{Cr}_{0.7}\text{V}_{0.3}$ and MgH_2 was processed by high-energy ball mill SPEX 8000. An as-obtained powder was then heated up to study the hydrogen desorption properties.

Obtained results suggest that the starting sample consisted of three phases: BCC CrV (the main one), and two crystallographic forms of MgH_2 : tetragonal and orthorhombic.

No changes are observed in a temperature range 43⁰ C – 220⁰ C. At ~ 230⁰ C first weak peaks of Mg start to appear (Figure 3), what suggests the beginning of hydrogen desorption process. The crystallization of Mg is observed simultaneously with a decomposition of both forms of MgH_2 . However, orthorhombic phase disappears completely at 280⁰ C, while the tetragonal one only at 330⁰ C. At this temperature

desorption is completed and further heating of the powder does not cause any changes to the phase composition of the sample.

The results will be published later in a larger publication on metastable Mg-based compounds for energy storage.

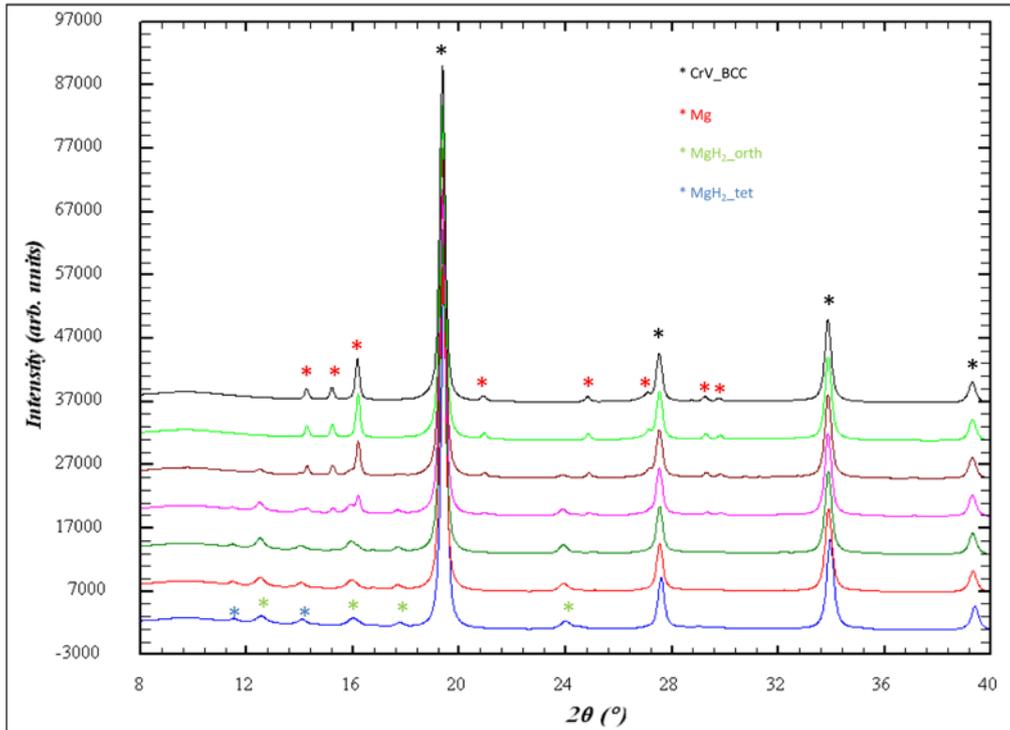


Figure 3. In situ SP-XRD for thermal decomposition of BCC Mg-Cr hydride.

Decomposition of mixed-metal borohydrides containing one light cation and one transition metal cation, $MM'(BH_4)_n$ with $M = Na$ and $M' = Mn$

The thermal stability and phase formation of the system produced by ball milling $NaBH_4$ with MnF_3 was examined by *in situ* SR-PXD (see Figure 3).

In situ PXD offers higher resolution than the laboratory source diffractometer. As a consequence, it is possible to detect NaF and MnF_2 that formed during ball milling and had not been observed so far. Similarly to $0.8NaBH_4 + 0.2TiF_3$, $0.8NaBH_4 + 0.2MnF_3$ displays an intermediate temperature zone between 250 – 400 °C in which the fraction of NaF increases whereas $NaBH_4$ and $NaMn_3F_7$ are being consumed. An unknown phase is also present. At temperatures above 400 °C, NaF is the predominant phase with a decreasing fraction of $NaBH_4$.

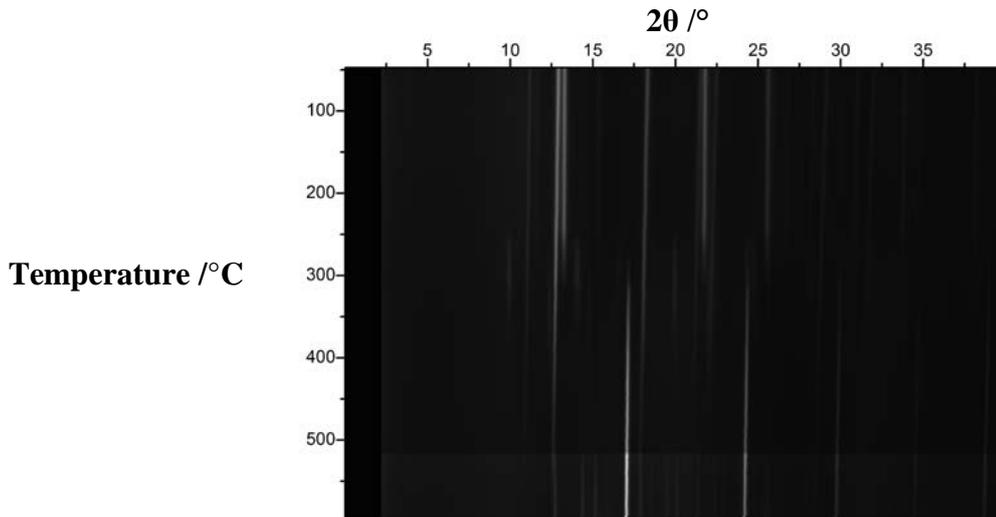


Figure 4: *In situ* PXD in the temperature region of 40 – 600 °C of the $0.8\text{NaBH}_4 + 0.2\text{MnF}_3$, as-milled.

The results have been included in the 1st year research report of the E.U project SSH2S and they are in the process to be submitted for publication. The thermal decomposition of the systems $2\text{LiNH}_2 - \text{MgH}_2 - 0.1\text{KH}$ and $2\text{LiNH}_2 - 1.1\text{MgH}_2 - 0.1\text{LiBH}_4 - 3\text{wt}\%\text{ZrCoH}_3$ has also been measured but the data are not yet analysed.

Concluding remarks

The data collected in project 01-02-962 are expected to result in at least 4 publications.