

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title: In-situ investigations of hydrogenation and dehydrogenation in borohydride-based nanocomposites for hydrogen storage.</b>	<b>Experiment number:</b> CH-3585
<b>Beamline:</b> BM01A	<b>Date of experiment:</b> from: 07/11 2012 to: 12/11 2012	<b>Date of report:</b> 26/06/2013
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dmitry Chernychov	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> Marit Riktor* <sup>1</sup> , Magnus H. Sorby* <sup>1</sup> , Christoph Frommen <sup>1</sup> , Bjørn C. Hauback <sup>1</sup> , Yaroslav Filinchuk* <sup>2</sup> <sup>1</sup> Institute for energy technology, PO Box 40, 2027 Kjeller, Norway <sup>2</sup> Univ. Catholique de Louvain, Place L. Pasteur 1, 1348 LOUVAIN-LA-NEUVE, Belgium		

## Report:

### Introduction

Complex hydrides based on boron (borohydrides) exhibit extraordinarily high gravimetric capacity for hydrogen and are therefore potential candidates as hydrogen storage materials in mobile applications. However, a major drawback is the limited reversibility. Recent work on  $\text{LiBH}_4$  + rare-earth (RE) borohydrides/hydrides (RE = Ce, Gd, Y,) composites shows good rehydrogenation properties of  $\text{LiBH}_4$  [1,2], especially when RE hydrides are formed in-situ [3]. The (de/re)-hydrogenation properties of these reactive hydride composites seem to be strongly influenced by experimental parameters such as the ratio of starting materials and the use of back pressure vs. vacuum. However, the underlying mechanisms are still not fully understood and the decomposition as well as rehydrogenation pathways remain unclear.

The aim of this experiment was to investigate in detail the reaction pathway during de- and rehydrogenation of nanocomposites of mechanically milled  $6\text{LiBH}_4 + \text{RECl}_3$  and  $6\text{LiBH}_4 + \text{RECl}_3 + \text{LiH}$  for RE = La, Sm, Gd, Er and Yb. In the latter case LiH is added to the mixture after the first milling, resulting in in-situ formation of RE hydrides during a second milling. The selected RE-elements were chosen due to expected differences in behaviour as well as different structure types for the RE borohydride.

## Experimental

All samples were heated at 5 K/min to 400 °C under vacuum and under 5 bar H<sub>2</sub> pressure. After decomposition, a hydrogen pressure of 100 bar was applied, and after a dwell time of 20 min at maximum temperature, the samples were slowly cooled down to room temperature (RT). The experiments were conducted using a new high gas-pressure setup developed by IFE in cooperation with Yaroslav Filinchuk (Univerité Catholique de Louvain, Belgium) and the SNBL for use at BM01. The gas handling system (Fig. 1) is constructed by stainless steel Swagelok tubings and fittings, VCR connections and pneumatic valves. All parts are approved for pressures > 240 bar, and preliminary tests showed no leaks when pressures up to 185 bar was used. The pneumatic valves are operated from a computer placed in the control room. This allows for fast filling and evacuation of the sample without the need to stop the experiment to enter the hutch. The sample is contained in a 1.1 mm sapphire (Al<sub>2</sub>O<sub>3</sub>) single crystal tube and connected to the sample cell using 1/16 inch Swagelok fittings sealed with ferrules made of Vespel or graphite. The sample cell is connected to the gas rig using thin PEEK tubing and constructed so that gas comes from both sides. This prevents displacement of powder during hydrogen filling.

The reaction pathways during de- and rehydrogenation were followed by *in-situ* PXD. The two-dimensional PXD data were collected at the diffractometer PILATUS@SNBL, using the software Pylatus developed at SNBL. An exposure time of 10 s was used, and the capillaries were rotated by 20° during each exposure in order to improve the powder average. The wavelength was 0.6941 Å. The two-dimensional data were calibrated with NIST LaB<sub>6</sub> standard sample and then integrated into one-dimensional powder diffraction patterns with the program Fit2D.

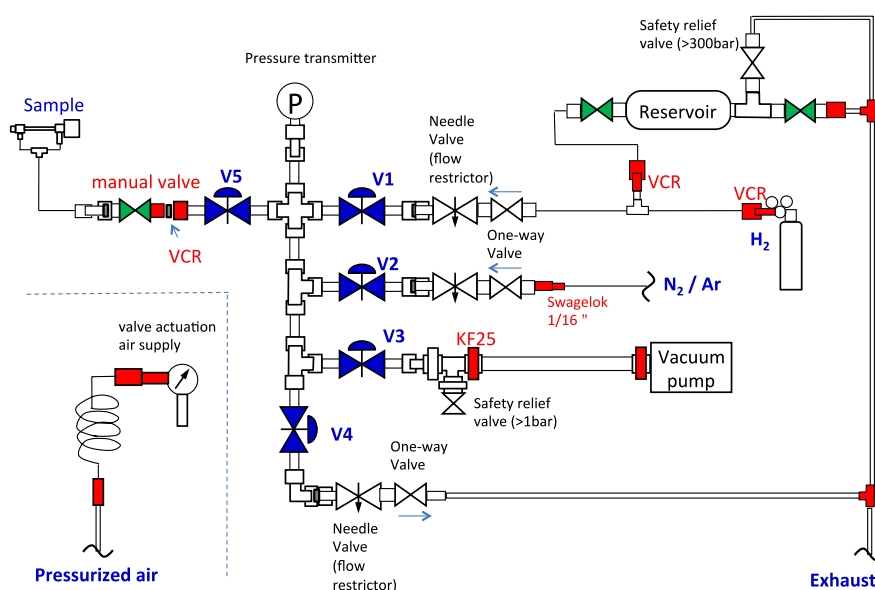


Fig. 1. Schematic of the high hydrogen-pressure rig developed at IFE for use at the SNBL (BM01)

## Results

The aim of the experiment was to compare reaction pathway and rehydrogenation properties for samples with and without LiH. Unfortunately, the experiment suffered from problems with the hot air blower which had to be moved from its position to change samples. By comparing the PXD and the DSC data it is clear that several of the samples reached lower temperatures than planned, and since  $\text{LiBH}_4$  melts before desorbing, it is not clear if  $\text{LiBH}_4$  was completely decomposed before rehydrogenation and cooling. Thus no conclusions can be drawn on rehydrogenation properties. However, very good PXD data were obtained for the thermal decomposition, revealing formation of several new intermediate phases (Fig. 2). The work on identification and structural determination of the new phases is in progress and two articles are currently in preparation. An overview article describing the differences in decomposition pathway for the different samples is also planned. The gas rig was used for the first time in this experiment. It performed very well, and is now available for users at BM01.

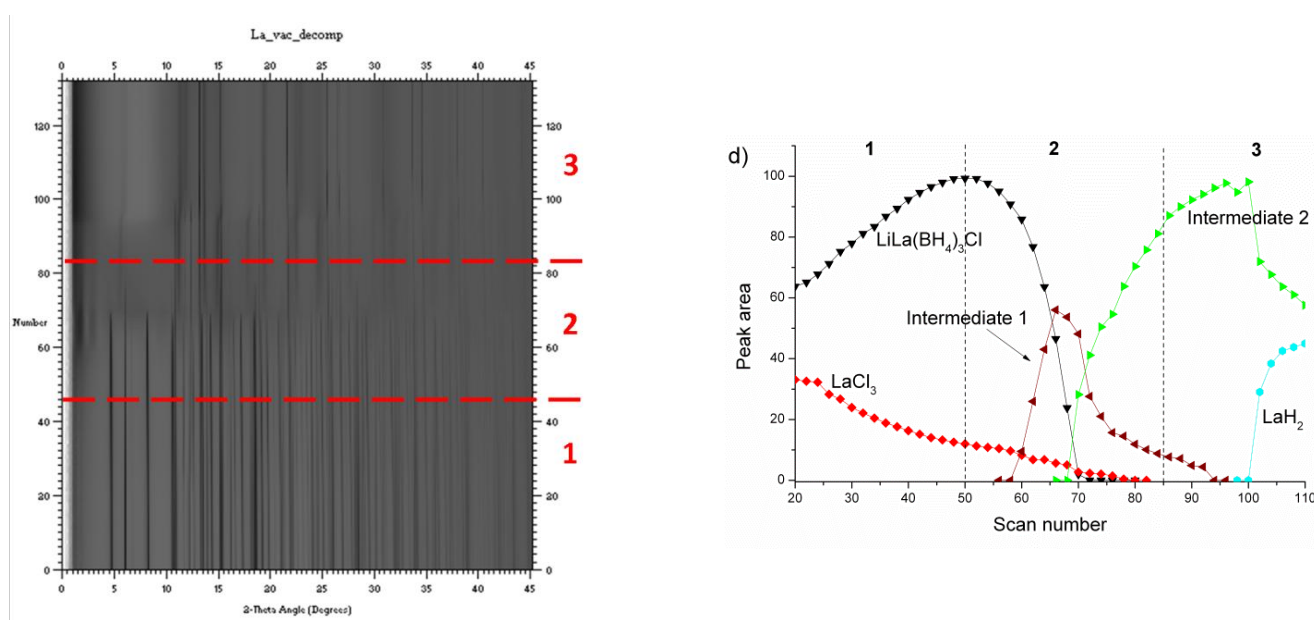


Fig. 2. In situ SR-PXD patterns during heating of the  $\text{LaCl}_3 + 6 \text{LiBH}_4$  sample. Each consecutive scan is given on the y-axis, with angles on the x-axis. The figure to the right show the peak area of selected peaks from the in situ SR-PXD patterns. The temperature regions marked by bold numbers and dashed lines are defined by DSC. Region 1: RT-150 °C, region 2: 150-230 °C and region 3: 230-300 °C.

## References

- [1] Jin, S-A., Lee, Y-S., Shim, J-H., Cho, Y-W. *J. Phys. Chem. C* **2008**, 112, 9520
- [2] Shim, J-H., Lee, Y-S., Suh, J-Y., Cho, W., Han, S-S., Cho, Y-W. *J. Alloys Comp.* **2012**, 510, L9
- [3] Gennari, F. C., Fernández Albanesi, L., Puzskiel, J. A., Arnedo Larochette, P. *Int. J. Hydrogen Energy* **2011**, 36, 563