



## 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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

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

Reports can now 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:</b> Metal borohydrides as superionic conductors.	<b>Experiment number:</b> 01-02-996
<b>Beamline:</b> BM01-A	<b>Date of experiment:</b> from: November 1 to: November 4, 2012	<b>Date of report:</b> March 2013
<b>Shifts: 9</b>	<b>Local contact(s):</b> Dr. V. Diadkin	<i>Received at ESRF:</i>

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Several bi- and tri- metallic borohydride systems were studied:

**LiBH<sub>4</sub> : KBH<sub>4</sub> (or RbBH<sub>4</sub> or CsBH<sub>4</sub>) : Y(BH<sub>4</sub>)<sub>3</sub>**

Trimetallic systems, LiBH<sub>4</sub>, KBH<sub>4</sub> (or RbBH<sub>4</sub> or CsBH<sub>4</sub>) and Y(BH<sub>4</sub>)<sub>3</sub> studied by in-situ powder diffraction led to discovery of one novel bimetallic borohydride KY(BH<sub>4</sub>)<sub>4</sub> and one trimetallic borohydride Li(Rb,Cs)<sub>2</sub>Y(BH<sub>4</sub>)<sub>6</sub>. While first one is a novel, compact polymorph of KY(BH<sub>4</sub>)<sub>4</sub> for which a complex anion [Y(BH<sub>4</sub>)<sub>4</sub>]<sup>-</sup> containing salt is known [1], the second one is a double-perovskite borohydride, potentially a good Li<sup>+</sup> conductor. Two manuscripts with the results are under preparation.

Other ball milled mixtures like LiBH<sub>4</sub>-CsBH<sub>4</sub>, CsBH<sub>4</sub>-Ca(BH<sub>4</sub>)<sub>2</sub> and RbBH<sub>4</sub>-LiNH<sub>2</sub> were studied too. The data analysis is still under progress.

**LiBH<sub>4</sub> : KBH<sub>4</sub> : Al(BH<sub>4</sub>)<sub>3</sub>**

The ball milled trimetallic mixtures allowed characterization of a bimetallic borohydride KAl(BH<sub>4</sub>)<sub>4</sub>. It crystallize in the structure type of TbSO<sub>4</sub>. Surprisingly bimetallic mixtures do not show formation of this phase, but rather broad peaks of another novel phase. The data analysis and further syntheses are currently performed.

**Ca(BH<sub>4</sub>)<sub>2</sub> : NaNH<sub>2</sub>**

This system was studied by *in situ* PXD in two different molar ratios to seek for new hydrogen containing intermediates. CaBH<sub>4</sub>NH<sub>2</sub> was expected to form after previous experiments. This compound was not observed. Instead, Ca(BH<sub>4</sub>)<sub>2</sub>.NH<sub>3</sub> was observed in small amounts, as well as Na<sub>3</sub>N. This indicates that the system decomposes releasing NH<sub>3</sub> rather than hydrogen. NH<sub>3</sub> release is also supported by the fact that the capillaries broke systematically during the experiment, due to the increased pressure. This could not happen

with hydrogen as it can diffuse through the wax used to fix the capillary on the system. Several unknown decomposition products were not yet identified. The analysis of these different unknown phases are still in progress.

### **Mg(BH<sub>4</sub>)<sub>2</sub> : NaNH<sub>2</sub>**

This system was studied in the same way as the parent Ca system. Four different mixtures from the reaction of two polymorphs of Mg(BH<sub>4</sub>)<sub>2</sub> with NaNH<sub>2</sub> were studied. The formation of Na<sub>3</sub>N was also observed, showing evidence of NH<sub>3</sub> formation rather than H<sub>2</sub>. Unfortunately, for each experiment, the capillaries broke in the same way than in the Ca system. From the data analysis, we observed the formation of NaBH<sub>4</sub> and an unidentified compound. The identification of the latter is in process.

### **Study of the amorphous $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub>**

From our last observations on the slow amorphization of  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> at room temperature in June 2012, a new study on the amorphous state obtained by compression was performed. The behavior of this freshly amorphous phase upon heating was unexpected. Indeed, a transformation from amorphous phase into crystalline  $\gamma$ -phase was observed at about 80°C then it decomposed in the same way than  $\gamma$ -phase. A paper on the amorphous  $\gamma$ -phase is in progress.

### **Reexamination of the decomposition pathway of $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> under H<sub>2</sub> back-pressure**

Previous studies on the  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> decomposition under H<sub>2</sub> back-pressure showed a straightforward amorphization after few patterns. This time a fresh  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> was measured and for the first time, transformations through crystalline polymorphs into amorphous state were observed.

### **LiBH<sub>4</sub> and Ca(BH<sub>4</sub>)<sub>2</sub> solid-state reactions with CO<sub>2</sub>**

The behavior of solid metal borohydrides with the presence of CO<sub>2</sub> is required further determination. During this experiment, we tried to observe the possible reactions between the representatives from alkali and alkali-earth borohydrides and CO<sub>2</sub>. The reaction evolution between LiBH<sub>4</sub> and CO<sub>2</sub> is not clear due to the bad quality of the starting LiBH<sub>4</sub> product. With Ca(BH<sub>4</sub>)<sub>2</sub> and CO<sub>2</sub>, we observed typical phase transitions and decomposition products for this borohydride and a new phase with low intensity was found. The systems require further investigations.

### **Study of $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> under CO<sub>2</sub> back-pressure**

The data analysis is in progress.

### **Mn(BH<sub>4</sub>)<sub>2</sub>**

Mn(BH<sub>4</sub>)<sub>2</sub> is one of the possible precursors to synthesize bi- and tri- metallic borohydride systems, but the synthesis of pure Mn(BH<sub>4</sub>)<sub>2</sub> itself is poorly characterized. We found that Mn<sub>2</sub>Li(BH<sub>4</sub>)<sub>5</sub>·Et<sub>2</sub>O is an intermediate product in the reaction MnCl<sub>2</sub> + 2LiBH<sub>4</sub> -> Mn(BH<sub>4</sub>)<sub>2</sub> + 2 LiCl (in ether). Under vacuum this compound decomposed to Mn(BH<sub>4</sub>)<sub>2</sub> and LiBH<sub>4</sub>. The data analysis is in progress.

[1] Jaron T., Grochala W. : *Dalton Trans.*, **2011**, 40, 12808