



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.



	Experiment title: New light element aluminium-nitrogen hydrogen storage materials	Experiment number: CH-4888
Beamline: BM01	Date of experiment: from: 02 Nov 2016 to: 05 Nov 2016	Date of report:
Shifts: 9	Local contact(s): Iurii Dovgaliuk (email: iurii.dovgaliuk@esrf.fr)	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Jakob Grinderslev ^{a*} , Anders Svarre Jakobsen ^{a*} , SeyedHosein Payandeh GharibDoust ^{a*} , Erika Dematteis ^{b*} , Steffen R. H. Jensen ^a , Kasper T. Møller ^a , Mark Paskevicius ^a , Torben R. Jensen ^a , Mathias Jørgensen ^a ^a Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, University of Aarhus, Denmark ^b Department of Chemistry and Inter-Departmental Center Nanostructured Interfaces and Surfaces (NIS), University of Turin, Via Pietro Giuria 7, 10125 Torino, Italy.		

Report:

We performed powder X-ray diffraction measurements on complex metal hydride materials at elevated temperatures. These measurements were designed to identify the crystal structures of new energy storage materials and understand their thermal decomposition pathways.

Several projects were followed in this experiment: 1. New light element aluminium-nitrogen hydrogen storage materials 2. Novel bimetallic sodium rare-earth borohydride as hydrogen storage materials and 3. Novel halide-free Ammine rare-earth metal borohydrides. The results of the projects are discussed briefly below.

1. New light element aluminium-nitrogen hydrogen storage materials

Materials based on boron-nitrogen bonds are promising hydrogen storage materials because of their high gravimetric hydrogen densities and in this class Al-B-N-H phases have shown excellent hydrogen storage properties. For example, $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ releases more than 10 mass% of hydrogen below 140 °C.¹ Here, a new aluminium based amidoborane, $\text{K}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$, has been synthesized. It crystallizes in a triclinic unit cell with space group symmetry $P-1$ which is isostructural to the analogue $\text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4]$.² The crystal structure consists of $[\text{K}(\text{NH}_2\text{BH}_3)_6]^{5-}$ octahedra which facilitate the bridging between K^+ in 1D chains, while also bridging K^+ to Al^{3+} to connect the 1D chains in a 3D network, see Figure 1. The SNBL data provided a useful evaluation of the synthesis method and hence the purity of the sample through data collection on

different samples and subsequent Rietveld refinement. $K[Al(NH_2BH_3)_4]$ decomposes in two steps into KBH_4 and amorphous compounds. A paper has been submitted based on this novel compound.

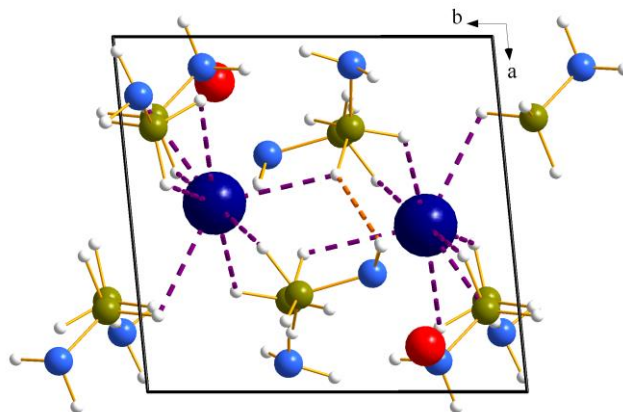


Figure 1. The crystal structure of $K[Al(NH_2BH_3)_4]$. Colour scheme: K, dark blue; Al, red; N, light blue; B, dark yellow.

2. New bimetallic sodium rareearth borohydride as hydrogen storage materials

$NaRE(BH_4)_4$ compounds have shown interesting properties, *e.g.* $NaLa(BH_4)_4$ has shown a distinct crystal structure with brucite-like layers of octahedra (*hcp* packing of anions) with half of the octahedral sites empty.³ Additionally, a Na ion conductivity of $6.92 \cdot 10^{-7} \text{ S cm}^{-1}$ has been observed for $NaY(BH_4)_4$ at *RT*.⁴ In this project we have synthesized three novel bimetallic compounds, $NaRE(BH_4)_4$, $RE = Ce, Pr, Er$ and the *in-situ* XRPD data collected at SNBL was used to solve the crystal structures. Efforts to synthesize $NaGd(BH_4)_4$ lead to an unstable, amorphous phase, which decomposes after one day at *RT*. All the new compounds crystallize in the orthorhombic crystal system and the trend in their crystal structures are investigated. The bimetallic borohydrides with larger rare-earth cations (La, Ce, Pr) crystallize in space group *Pbcn* with both cations in the octahedral coordination (Figure 2a). Bimetallic borohydrides with smaller rare-earth cations (Y, Er, Yb) crystallize in space group *Cmcm* with Na in octahedral coordination and the rare-earth cation in tetrahedral coordination (Figure 2b). The hydrogen storage properties of novel compounds were also studied by Sieverts' measurements. $NaCe(BH_4)_4$ and $NaPr(BH_4)_4$ show a reversible hydrogen storage capacity of 1.65 and 1.04 wt% after four cycles of H_2 release/uptake, respectively, whereas that of $NaEr(BH_4)_4$ continuously decreases after each cycle. The reversibility is mainly assigned to the formation of rare-earth metal hydrides and possibly sodium borohydride. Furthermore, the dehydrogenated state contains rare-earth metal borides. A paper has been submitted based on these three compounds and is currently under review.

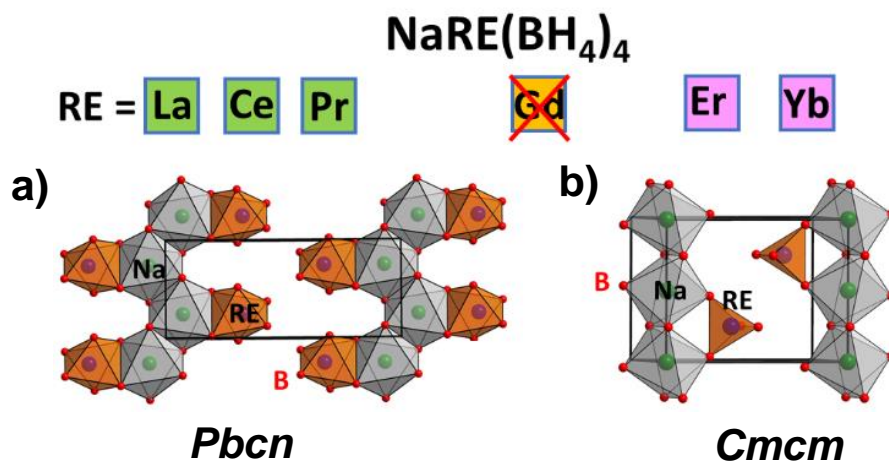


Figure 2 Crystal structures of $NaRE(BH_4)_4$ compounds with (a) *Pbcn* space group and (b) *Cmcm* space group. RE: purple, Na: green, and B: red. H atoms are removed for clarity.

3. Novel ammine metal borohydrides

Ammine metal borohydrides, $M(\text{BH}_4)_m \cdot n\text{NH}_3$ have attracted much attention due to the dihydrogen interaction between hydrogen bonded to N ($\text{H}^{\delta+}$) and hydrogen, bonded to B ($\text{H}^{\delta-}$), which may lower the hydrogen release temperature through combination of $\text{H}^{\delta+}$ and $\text{H}^{\delta-}$.⁵ In this study, novel ammine metal borohydrides, $M(\text{BH}_4)_3 \cdot x\text{NH}_3$ ($M = \text{Nd}, \text{Ho}, \text{Tb}, \text{Yb}$) were investigated by *in-situ* XRPD at SNBL, ESRF. From the high quality XRPD pattern it was possible to solve the crystal structures of 14 new ammine metal borohydrides. This was achieved by combining *in-situ* XRPD data with thermal analysis (TGA-DSC-MS). The results are illustrated in Figures 3 and 4. A discrepancy in the temperature range of the different events are observed, *e.g.* $\text{Nd}(\text{BH}_4)_3 \cdot 7\text{NH}_3$ is observed to decompose at $T \sim 76^\circ\text{C}$ by *in-situ* XRPD, however from TGA-DSC-MS it decomposes below 50°C . This is probably caused by the argon flow (40 mL/min) used for the TGA-DSC-MS, while the back pressure of NH_3 might stabilize the compounds during the *in-situ* XRPD measurement. However, the events in TGA-DSC-MS are still clearly distinguished, and were used in order to obtain the right composition of the new compounds. The trend is almost similar for $M = \text{Ho}, \text{Tb}, \text{Yb}$, however, in these cases the $M(\text{BH}_4)_3 \cdot 6\text{NH}_3$ is not observed, while only one polymorph of $M(\text{BH}_4)_3 \cdot 4\text{NH}_3$ are observed. The $M(\text{BH}_4)_3 \cdot x\text{NH}_3$ with $x > 4$ releases pure ammonia, while pure hydrogen is released at $x < 4$. A mixture of hydrogen and ammonia is observed for $M(\text{BH}_4)_3 \cdot 4\text{NH}_3$.

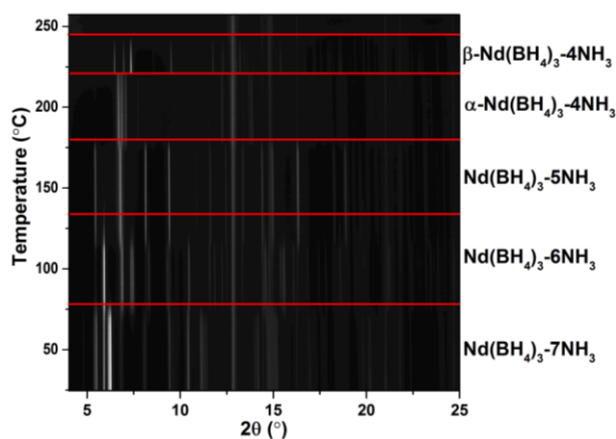


Figure 3: *In-situ* SR PXD of $\text{Nd}(\text{BH}_4)_3 \cdot x\text{NH}_3$

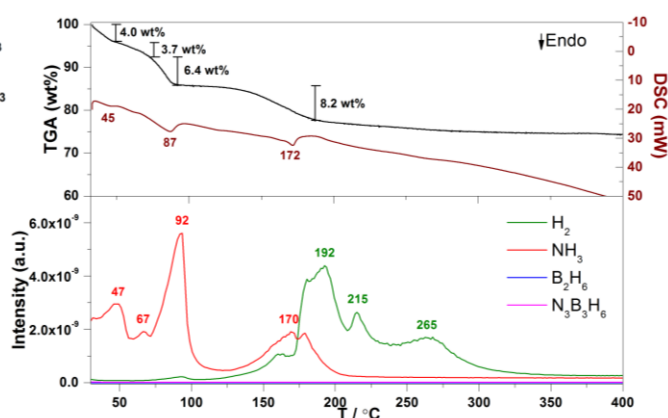


Figure 4: TGA-DSC-MS of $\text{Nd}(\text{BH}_4)_3 \cdot x\text{NH}_3$

Publications resulting from this work

We have been able to obtain a large amount of high quality data that will be included in at least three publications: two which are already submitted and one which is in preparation. Further data analysis may result in further publications or extensions to this research.

References:

- 1 L. Duchêne, R.-S. Kühnel, D. Rentsch, A. Remhof, H. Hagemann and C. Battaglia, *Chem. Commun.*, 2017, **53**, 4195–4198.
- 2 I. Dovgaliuk, L. H. Jepsen, Z. Lodziana, V. Dyadkin and T. R. Jensen, .
- 3 S. P. GharibDoust, M. Heere, M. H. Sørby, M. B. Ley, D. B. Ravnsbæk, B. C. Hauback, R. Černý and T. R. Jensen, *Dalt. Trans.*, 2016, **45**, 19002–19011.
- 4 E. Roedern, Y.-S. Lee, M. B. Ley, K. Park, Y. W. Cho, J. Skibsted and T. R. Jensen, *J. Mater. Chem. A*, 2016, **4**, 8793–8802.
- 5 L. H. Jepsen, M. B. Ley, R. Černý, Y.-S. Lee, Y. W. Cho, D. Ravnsbæk, F. Besenbacher, J. Skibsted and T. R. Jensen, *Inorg. Chem.*, 2015, **54**, 7402–14.