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ESRF

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://wwws.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.

ESRF	**Experiment title:** Spinel-like metal borohydrides-halides, fast solid state ionic conductors	**Experiment number**: 01-02-1095
Beamline:	**Date of experiment**: from: 24.02.2016 to: 27.02.2016	**Date of report**:
Shifts:	**Local contact(s)**: Dmitry Chernyshov Wouter Van beek	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Radovan Černý[a], Mark Paskevicius[b], Emilie Didelot[a], SeyedHosein Payandeh GharibDoust[b], Svend Lemming[b], Matteo Brighi[a], Pascal Schouwink[a] and Torben R. Jensen[b]

[a]Laboratory of Crystallography, Department of Quantum Matter Physics, University of Geneva, 1211 Geneva, Switzerland.
[b]Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, University of Aarhus, Denmark.

Report:

We performed powder X-ray diffraction measurements on complex metal hydride materials at non-ambient 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 materials based on rare earth (La) borohydrides and with spinel like structure as novel solid state lithium ion conduction. 2. Novel halide-free ammonium metal borohydrides and 3. New materials based on rare earth metal borohydrides (Sm) as new hydrogen storage materials and the results projects are discussed breifly bellow.

1. Synthesis, structure and Li ion conductivity of $LiLa(BH_4)_3X$, X = Cl, Br, I

Rare earth borohydride-chlorides, $LiRE(BH_4)_3Cl$, RE = La, Ce, Gd compounds with spinel like structre, have shown high lithium ion conductivity.[1–3] In this work $LiLa(BH_4)_3Cl$, is synthesized with high purity and by using a new approach based on an addition reaction between $La(BH_4)_3$ and LiCl. This method, improves the purity of the sample by preventing the formation of LiCl by-product obtained in the previous synthesis method which was based on the reaction between $LaCl_3$ and $LiBH_4$. Moreover, this approach allows to prepare new compounds, $LiLa(BH_4)_3X$, X=Br, I by reaction between $La(BH_4)_3$ and LiBr, LiI. These two new compounds are iso-structural to $LiLa(BH_4)_3Cl$ and their crystal structure were investigated by synchrotron radiation X-ray powder diffraction. The ion conduction pathway and the effect of anion substitution on the conductivity values were investigated using TOPOS program. The highest Li^+ ion conductivity was observed for $LiLa(BH_4)_3Br$, 1.8×10^{-3} S/cm^2 at 140 °C with activation energy of 0.272 eV. Thermogravimetric analysis

shows a mass loss of 4.8 and 3.6 wt% for $LiLa(BH_4)_3Cl$ and $LiLa(BH_4)_3Br$, respectively, in the temperature range of room temperature to 400 °C. Mass spectrometry shows that samples release pure hydrogen and confirms that no diborane is released. The manuscript relating to results of this project is completed and would be submitted to Journal of physical chemistry C in April 2017.

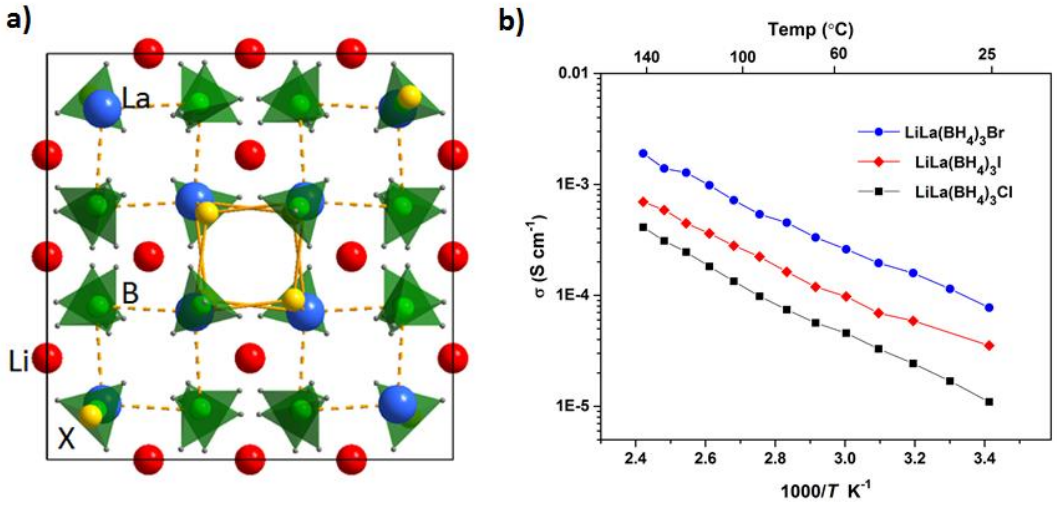

Figure 1 a) Spinel like crystal structure of the $LiLa(BH_4)_3X$, X = Cl, Br, I compounds. b) Arrhenius plots of the ionic conductivities of $LiLa(BH_4)_3X$, X = Cl, Br, I samples.

2. Novel halide-free ammonium metal borohydrides

Ammonium borohydride, NH_4BH_4, has a very high gravimetric (ρ_m = 24.5 wt% H_2) and volumetric (ρ_v = 157.3 g·H_2/L) hydrogen content and releases 18.4 wt% H_2 below 170 °C. However, NH_4BH_4 is metastable at RT and ambient pressure, with a half-life of ~6 h. The decomposition is strongly exothermic; therefore, it cannot store hydrogen reversibly. Recently, the first ammonium metal borohydride, $NH_4Ca(BH_4)_3$ was published which succcesfully stabilizes NH_4BH_4.[4] In the present work, broad range of new halide-free ammonium metal borohydrides $(NH_4)_xM_m(BH_4)_{m\cdot n+x}$, n (M = Li, Na, K, Mg, Sr, Y, Mn, La, Gd) have been formed. Mixtures of NH_4BH_4 - $NaBH_4$ do not react, while solid solutions, $K_{1-x}(NH_4)_xBH_4$, are formed for NH_4BH_4 - KBH_4. For the remaining composites, novel ammonium metal borohydrides are formed. Several of their crystal structures have been solved from high resolution powder X-ray diffraction collected in this beamtime. These ammonium metal borohydrides have high gravimetric hydrogen contents (8.59-22.1 wt% H_2), which makes them interesting as hydrogen storage materials.

The solid solution $K_{1-x}(NH_4)_xBH_4$ effectively stabilizes NH_4BH_4. On Figure 2 the unit cell volume (V) divided by the number of formula units (Z) is shown versus the temperature. As the temperature exceeds the decomposition temperature of NH_4BH_4, the solid solution gradually releases NH_4BH_4, approaching the unit cell parameters of KBH_4. The manuscript of this project is in preparation.

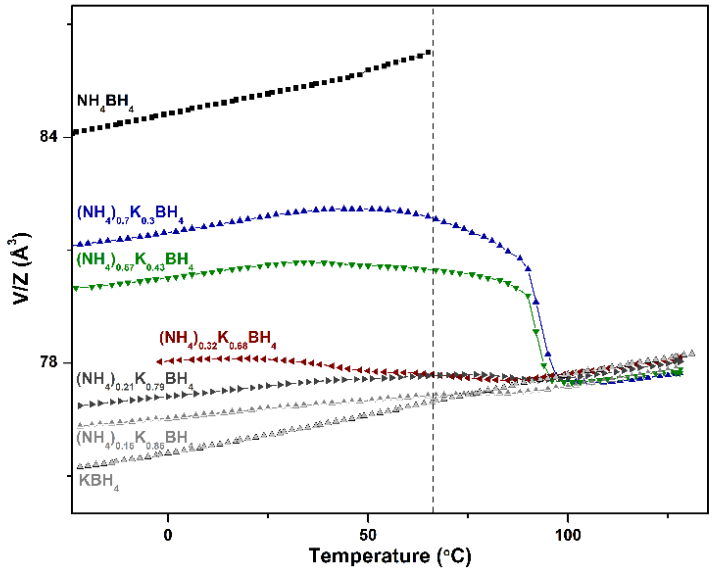

Figure 2 The unit cell volumes per formula unit *V*/*Z* for NH_4BH_4, KBH_4 and $(NH_4)_{1-n}K_nBH_4$ solid solutions extracted from the Rietveld refinement of the in situ SR-XRPD data

3. New materials based on rare earth metal borohydrides (Sm) as new hydrogen storage materials

In this project, three novel compounds $MSm(BH_4)_4$ are M = K, Rb, Cs are synthesized and their crystal structres were solved using the data collected at this beam time. The manuscrispt of this projects in in preparation and would be submitted soon.

In total, it is expected that 3 - 4 high impact papers will result from this beamtime.

References:

(1) Ley, M. B.; Boulineau, S.; Filinchuk, Y.; Jensen, T. R. New Li Ion Conductors and Solid State Hydrogen Storage Materials: LiM(BH4)3Cl, M = La, Gd. *J. Phys. Chem. C* **2012**, *116*, 21267−21276.

(2) Lee, Y.-S.; Ley, M. B.; Jensen, T. R.; Cho, Y. W. Lithium Ion Disorder and Conduction Mechanism in LiCe(BH4)3Cl. *J. Phys. Chem. C* **2016**, *120* (34), 19035–19042.

(3) Ley, M. B.; Ravnsbæk, D. B.; Filinchuk, Y.; Lee, Y.; Jensen, T. R. LiCe(BH4)3Cl, a New Lithium-Ion Conductor and Hydrogen Storage Material with Isolated Tetranuclear Anionic Clusters. *Chem. Mater.* **2012**, *24*, 1654–1663.

(4) Schouwink, P.; Ley, M. B.; Tissot, A.; Hagemann, H.; Jensen, T. R.; Smrčok, Ľ.; Černý, R. Structure and Properties of Complex Hydride Perovskite Materials. *Nat. Commun.* **2014**, *5* (May), 5706.