EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** In situ structural characterization of multifunctional hydrides	**Experiment number**: CH-4104
Beamline: BM01A	**Date of experiment**: from: 30/04-14 to: 04/05-14	**Date of report**:
Shifts: 12	**Local contact(s)**: Dr. Dmitry Chernyshov	*Received at ESRF:*

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Report:

Perovskite type metal borohydrides

Previous studies at ESRF have revealed several bimetallic borohydrides crystallizing in a perovskite-type structure, the first one being $KMn(BH_4)_3$. This led to an investigation of $Sr(BH_4)_2$ – MBH_4 (M = Na, K, Rb, Cs), which resulted in three new bimetallic compounds $MSr(BH_4)_3$ (M = K, Rb, Cs). Structural solution has been carried out for *M* = Rb and Cs, while the potassium sample is still being investigated. $KSr(BH_4)_3$ has been indexed in a orthorhombic unit cell, consistent with $RbSr(BH_4)_3$ and $CsSr(BH_4)_3$, which has also been found to crystallize in orthorhombic crystal systems. The crystal structures of the latter two possess the perovskite-type structure comparable to $KMn(BH_4)_3$. High-quality data from ESRF is important for solving the structure of $KSr(BH_4)_3$. Based on this work one manuscript is in preparation: Møller, K. T., Ley, M. B., Schouwink, P., Cerny, R., Jensen. T. R., et al., "Synthesis and Thermal Decomposition of New Perovskite Alkali Metal Strontium Borohydrides".

$LiBH_4$-KBH_4 nanoconfinement and reactive hydride composites

The eutectic melting composite of $LiBH_4$-KBH_4, which melts at *T* = 105 °C was succesfully melt infiltrated and studied by *in situ* SR-PXD, which led to the discovery of the desorption reaction pathway. Furthermore, the eutectic reactive hydride composite $LiBH_4$-KBH_4-MgH_2 in bulk and nanoconfined samples were studied. Bulk and nanoconfined samples were compared. Based on this work a manuscript is in preparation:
Hansen, B. R. S., Ley, M. B., Jensen, T. R. *Acs Nano*, 2014.

Alkali metal $M_2B_{12}H_{12}$, M = Li, Na, K, compounds

The structural decomposition of $M_2B_{12}H_{12}$ (M= Li, Na, K) was studied with *in situ* SR-PXD. Interestingly, both $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ exibit a phase transformation, whereas $K_2B_{12}H_{12}$ remain largely unaltered below 600 °C. Structural analysis and further investigations are currently performed.

Multifunctional complex hydrides

M$(BH_4)_3$, *M* = La and Ce, have recently been prepared by solvent mediated methods in our lab. Interrestingly, these two metal borhydrides are structural different from other rare earth metal borohydrides, which all crystallise in three distinct structural polymorphs usually described as low and high temperature α- and β-$Y(BH_4)_3$ and the ionic conducting polymorph $LiCe(BH_4)_3Cl$. *M*$(BH_4)_3$, *M* = La and Ce, crystallise in a new rhombohedral structure. Solvent extraction of $La(BH_4)_3$ with $(CH_3)_2S$ produces a $La(BH_4)_3 \cdot 1/2(CH_3)_2S$ solvent complex. The similar $Mg(BH_4)_2 \cdot 1/2(CH_3)_2S$ solvent complex led to the discovery of the porous γ-$Mg(BH_4)_2$. We looked at different ways of removing the solvent from $La(BH_4)_3 \cdot 1/2(CH_3)_2S$ in order to produce a porous polymorph of $La(BH_4)_3$. However, the analysed data does not point towards production of a new porous polymorph, instead a solvent complex known from $Y(BH_4)_3(CH_3)_2S$ crystallises in the samples.

Ammine metal borohydrides

A series of new ammine metal borohydrides $M(BH_4)_m \cdot nNH_3$ (M = Mg, Ca, Sr, Mn, Y, La, Ce, Gd, Dy) were structurally investigated. Several crystal structures have been solved from the powder X-ray diffraction data. $Sr(NH_3)_2(BH_4)_2$ is solved in an orthorhombic crystal system with space group $P2_122$. The structure is built up from the layers of octahedra sharing all BH_4 groups with NH_3 groups pointing between the layers acting as terminal ligands (Figure 1). The structure resembles the trigonal $Ca((BH_4)_{0.7}I_{0.3})_2$ formed by mechanochemical treatment of $Ca((BH_4)_2$-CaI_2.

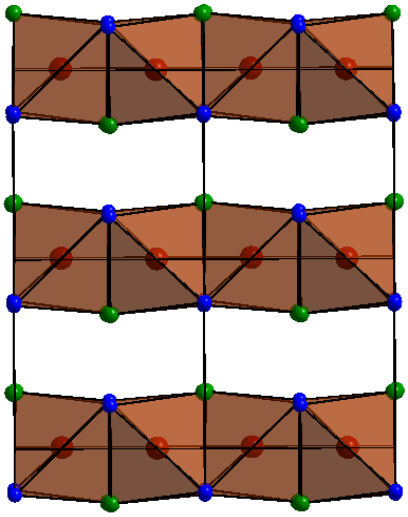

Figure 1 Crystal structure of $Sr(NH_3)_2(BH_4)_2$.

$Ca(NH_3)_4(BH_4)_2$ was solved in a monoclinic crystal system with space group $P2_1/c$. Ca is octahedrally coordinated to four BH_4 groups and two equatorial NH_3 groups (Figure 2). The structure is composed from close packed layers along [100].

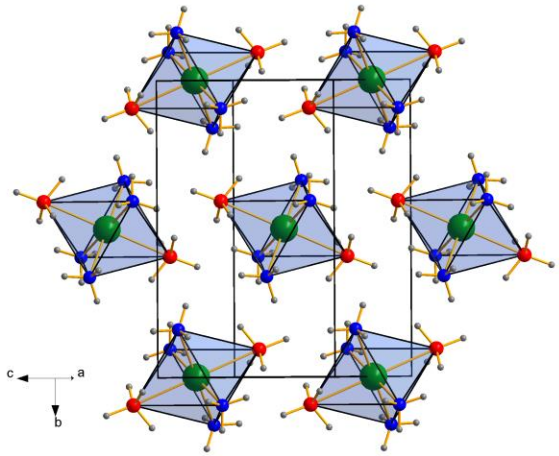

Figure 2 Crystal structure of $Ca(NH_3)_4(BH_4)_2$.

Ammine metal borohydrides $M(BH_4)_3 \cdot nNH_3$, *M* = La and Ce, n = 6 and 4, were also studied. Initially, $M(BH_4)_3 \cdot 6NH_3$ are formed for both La and Ce, which contains a new 8 fold coordination of 6 NH3 and 2 BH4 groups around the central La or Ce atom. This 8 fold coordination type is different from the previous coordination types observed in $M(BH_4)_3 \cdot 6NH_3$ (*M* = Y, Gd, Dy), which contains a octahedral coordination of 6 NH_3 groups around the central La or Ce atom. Thermolysis of $M(BH_4)_3 \cdot 6NH_3$, M = La and Ce, results in formation of a new monoclinic structure constructed of a distorded octahedral configuation of 4 NH_3 and 2 BH_4 around the central metal ion, before formation of the orthorhombic $M(BH_4)_3 \cdot 4NH_3$ polymorph known from the *M* = Y, Gd, Dy system containing a octahedral coordiantion of 4 NH_3 and 2 BH_4 groups, which ultimately leads too strong intramolecular dihydrogen bonds and hydrogen elimination. Therefore, the $M(BH_4)_3 \cdot nNH_3$ (*M* = La or Ce) system both confirm the observations from the previously studied *M* = Y, Gd, Dy systems, but also gives more information about the structural transformations leading to hydrogen release from ammine rare earth metal borohydride materials.

The high quality X-ray data obtained at SNBL has made it possible to solve a series of structures within the ammine metal borohydride material class. This makes it possible to observe trends and correlations between crystal structures and properties, e.g. strong intramolecular dihydrogen bonds are required to obtain hydrogen release.

Based on the work on ammine metal borohydrides, one paper is submitted and three are currently in preparation:
Jepsen, L.H., Ley. M. B., Filinchuk, Y., Besenbacher, F. and Jensen, T. R. "Series of ammine metal borohydrides – tailoring of properties", Submitted to Chemistry of Materials
Jepsen, L. H., Sarusie, R. S., Sørby, M. H., Hauback, B. C., Besenbacher, F., Skibsted, J., Černý, R. and Jensen, T.R., "Structures and properties of ammine alkali earth metal borohydrides, $Sr(NH_3)_2(BH_4)_2$ and $Ca(NH_3)_4(BH_4)_2$", to be submitted 2014
Jepsen L. H., Ley, M. B., Lee, Y-S., Cho, Y. W., Besenbacher, F., Skibsted, J., Černý, R. and Jensen, T.R., "Series of ammine rare-earth metal borohydrides: $M(BH_4)_3 \cdot nNH_3$ (*M* = Y, Gd and Dy; *n* = 7, 6, 5 and 4)", to be submitted 2014
Ley, M. B., Jepsen, L. H., Jensen. T. R., et al, "Ammine metal borhydrides: $M(BH4)3 \cdot nNH_3$, *M* = La and Ce, *n* = 6 and 4, in preparation, 2014