EUROPEAN SYNCHROTRON RADIATION FACILITY

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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:** Ammonium metal borohydrides	**Experiment number**: CH-4528
Beamline: BM01A	**Date of experiment**: from: 25/11-15 to: 28/11-15	**Date of report**:
Shifts: 9	**Local contact(s)**: Dr. Dmitry Chernyshov	*Received at ESRF:*

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Report:

Ammonium metal borohydrides

Ammonium borohydride, NH_4BH_4, has an extreme gravimetric (24.5 wt%) and volumetric (157.3 g H_2/L) hydrogen content, similar to solid methane and is prepared in pure form in our lab. However, it is metastable at RT and decomposes in a strongly exothermic manner; hence it cannot store hydrogen reversibly. We have synthesized a series of novel compounds with the chemical compositions $(NH_4)_xM_y(BH_4)_{x+y}$, M = Li, Na, K, Mg, Ca, Sr, Y, Gd, La that efficiently stabilize NH_4BH_4. The structures and thermal properties have been investigated. The results for M = K, Mg, Mn and Y are described below.

Solid solutions of $(NH_4)_{1-x}K_xBH_4$

Both NH_4BH_4 and KBH_4 crystallize with symmetry *Fm*-3*m*. Solid solutions with compositions $(NH_4)_{1-x}K_xBH_4$ ($0 < x < 1$) are formed during ball milling of the mixtures NH_4BH_4-KBH_4, i.e. upon applied pressure. Unit cell volumes extracted by Rietveld refinement at 250 K divided by number of formula units (Z) are plotted in Figure 1 (left). The *V*/*Z* values are all slightly lower as compared to Vegard's law, in accord with that the structures are pressure-stabilized. *V*/*Z* values as a function of temperature is plotted in Figure 1 (right). NH_4BH_4 decomposes at ~65 °C. At higher temperatures, NH_4BH_4 is released from $(NH_4)_{1-x}K_xBH_4$ and the *V*/*Z* values approaches the value for KBH_4. Clearly, $(NH_4)_{1-x}K_xBH_4$ is stabilized as compared to NH_4BH_4.

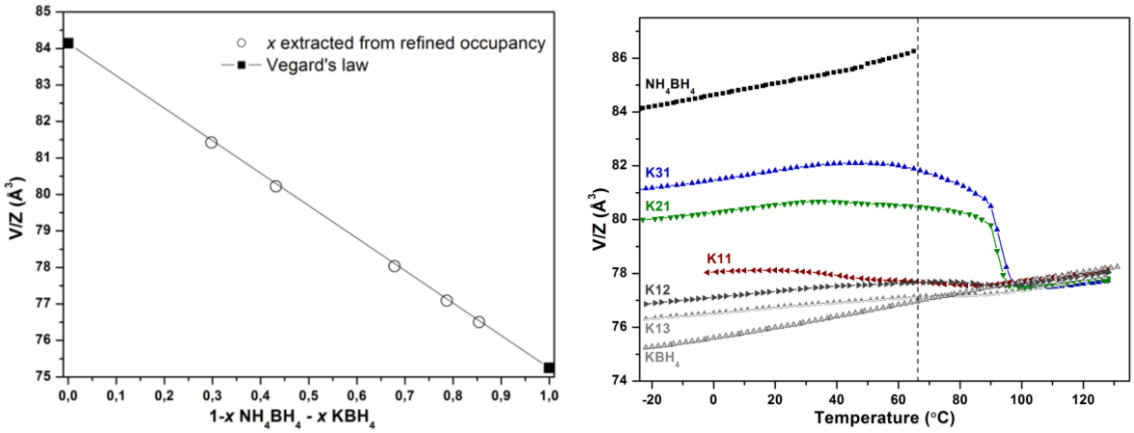

Figure 1 (Left) Unit cell volumes extracted by Rietveld refinement at 250 K divided by number of formula units (*Z*) for $(NH_4)_{1-x}K_xBH_4$. (Right) *V*/*Z* values for $(NH_4)_{1-x}K_xBH_4$ as a function of temperature.

$NH_4M(BH_4)_3$ and $(NH_4)_2M(BH_4)_4$, M = Mg, Mn

Four new compounds, $NH_4M(BH_4)_3$ and $(NH_4)_2M(BH_4)_4$, *M* = Mg, Mn, have been synthesized and the structures solved based on the SNBL PXD data. The magnesium and manganese compounds are isostructural, due to similar cation sizes. Furthermore, the structures of $NH_4M(BH_4)_3$ and $(NH_4)_2M(BH_4)_4$ are similar to K-analogues of $KM(BH_4)_3$ and $K_2M(BH_4)_4$, however, with lower symmetry due to the tetrahedral configuration of NH_4^+ as compared to the spherical configuration of K^+.

$NH_4Y(BH_4)_4$ and $(NH_4)_2Y(BH_4)_5$

Two structures of $NH_4Y(BH_4)_4$ and $(NH_4)_2Y(BH_4)_5$ have been solved in a monoclinic and an orthorhombic unit cell, respectively. The structure of $NH_4Y(BH_4)_4$ consists of complex ions $[Y(BH_4)_4]NH_4$, similar to $[Y(BH_4)_4]K$. On the other hand, compounds with the composition $(M^+)_2Y(BH_4)_5$ are not reported, and $(NH_4)_2Y(BH_4)_5$ is believed to be stabilized due to di-hydrogen contacts between $H^{\delta+}$ from NH_4^+ and $H^{\delta-}$ from BH_4^-.

The remaining structures are currently investigated. One high-impact paper is in preparation, summarizing the entire work on ammonium metal borohydrides.

Strontium borohydride ammonia borane

A new hyodrogen rich compound, $Sr(BH_4)_2(NH_3BH_3)_2$ has been synthesized in our lab. In-situ PXD data reveal two new polymorphs of the compunds, and both structures have been solved in a orthorhombic and a tetragonal unit cell, respectively. The BH_4^- ligands bridge between two Sr atoms in both structures making 2D layers of B and Sr, wheres the two NH_3BH_3 ligands coordinate to Sr as terminal ligands, pointing between the layers.

One paper is in preparation.

The high quality X-ray data obtained at SNBL has made it possible to solve a series of structures within the ammonium metal borohydride material class. This makes it possible to observe trends and correlations between crystal structures and properties.