

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.



	Experiment title: Novel materials for hydrogen storage; synthesis and characterisation	Experiment number: 01-02-851
Beamline: BM01A	Date of experiment: from: 08.04.2009 to: 14.04.2009	Date of report: 28.08.2009
Shifts: 18	Local contact(s): Yaroslav Filinchuk	<i>Received at ESRF:</i>
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Report:

Borohydride-based materials currently receive great interest as potential hydrogen storage systems due to their high gravimetric hydrogen densities. Unfortunately, many of the well known borohydrides exhibits poor thermodynamic and kinetic properties, which hamper their utilization in technological applications.^[1,2] Recently, cation substitution in known borohydrides has been realised e.g. by preparation of LiSc(BH₄)₄ and LiK(BH₄)₂.^[3,4] The latter compound possesses thermodynamic stability comparable to the average of the two compounds, LiBH₄ and KBH₄^[4]. The decomposition temperature of single cation borohydrides has been empirically related (through the enthalpy of formation) to the Pauling electronegativity of the cation^[5] suggesting that preparation of bimetallic (alkaline or alkaline earth and transition metal) borohydrides might be an interesting way of tuning the thermodynamic properties of borohydride-based hydrogen storage materials. Other attempts on the modification on metal borohydrides, using partial anion substitution was recently demonstrated by preparation of Li(BH₄)_{1-x}Cl_x.^[6]

In order to investigate and optimize the hydrogen storage properties of such novel materials, a thorough structural characterisation is of vital importance, as well as detailed studies of the decomposition pathway including indentifying the composition and structure of intermediate phases. For this variable temperature *in situ* synchrotron radiation powder X-ray diffraction (SR-PXD) is an extremely powerful tool.

The measurements were performed at beamline BM01A using a MAR345 image plate detector. Samples were mounted in sealed 0.5 mm glass capillaries. The 2D SR-PXD data were integrated into 1D powder patterns. The materials were prepared by high-energy ball milling and shipped to the ESRF. All handling and manipulation of the chemicals were performed in argon-filled gloveboxes.

So far the experiments conducted during this beamtime have resulted in three publications:

A Series of Mixed-Metal Borohydrides^[7]

A new series of borohydride-based materials, LiZn₂(BH₄)₅, NaZn₂(BH₄)₅, and NaZn(BH₄)₃ have been synthesized and detailed structural, physical, and chemical characterization have been conducted. These materials have very high hydrogen contents, low decomposition temperatures and completely novel structure types; the compound NaZn(BH₄)₃ consists of a single three dimensional network containing polymeric anions, [Zn(BH₄)₃]_nⁿ⁻, whereas LiZn₂(BH₄)₅ and NaZn₂(BH₄)₅ are build of two identical interpenetrated three

dimensional frameworks consisting of isolated complex anions, $[\text{Zn}_2(\text{BH}_4)_5]^-$. The latter type of structural topology is common for coordination polymers involving organic ligands, also known as metal–organic frameworks (MOFs), but here it is observed for the first time in metallahydrides. This similarity to MOFs suggests directionality and some covalent character of the metal– BH_4 interaction. Our findings are useful as general guidelines and inspiration for the design and synthesis of novel materials for hydrogen storage.

Structure and dynamics for LiBH_4 – LiCl solid solutions^[8]

A surprisingly high degree of structural and compositional dynamics is observed in the system LiBH_4 – LiCl as a function of temperature and time. Rietveld refinement of synchrotron radiation powder X-ray diffraction (SR-PXD) data reveals that Cl^- readily substitutes for BH_4^- in the structure of LiBH_4 . Prolonged heating a sample of LiBH_4 – LiCl (1:1 molar ratio) above the phase transition temperature and below the melting point ($110 < T < 268$ °C) can produce highly chloride substituted hexagonal lithium borohydride, $h\text{-Li}(\text{BH}_4)_{1-x}\text{Cl}_x$, e.g., $x \sim 0.42$, after heating from RT to 224 °C with 2.5 °C/min. LiCl has a higher solubility in $h\text{-LiBH}_4$ as compared to orthorhombic lithium borohydride, $o\text{-LiBH}_4$, which is illustrated by e.g. *in situ* SR-PXD from three cycles of heating and cooling of a sample with a starting composition of $\text{Li}(\text{BH}_4)_{0.91}\text{Cl}_{0.09}$. The substitution of the smaller Cl^- for the larger BH_4^- ion is clearly observed as a reduction in the unit cell volume as a function of time and temperature.

The First Mixed-anion and Mixed-cation Borohydride $\text{KZn}(\text{BH}_4)\text{Cl}_2$: Synthesis, Structure and Thermal decomposition^[9]

We present synthesis, crystal structure, MAS NMR data and an investigation of the thermal decomposition for a novel compound, $\text{KZn}(\text{BH}_4)\text{Cl}_2$ (**1**), which is the first report on a mixed-anion and mixed-cation borohydride. The decomposition temperature for $\text{KZn}(\text{BH}_4)\text{Cl}_2$ is found to be significantly lower as compared to KBH_4 , hence this study provides new inspiration for design and preparation of novel materials, which may be suitable for hydrogen storage applications. Furthermore, two other new borohydrides, **2** and **3**, are identified.

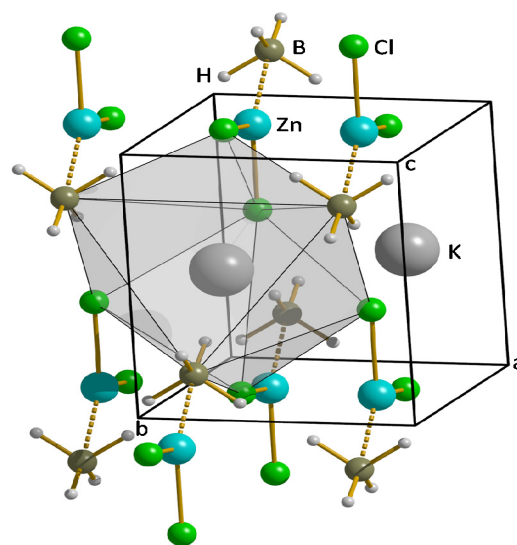


Figure 1 Structure of $\text{KZn}(\text{BH}_4)\text{Cl}_2$ determined from diffraction data measured at SNBL (BM01-A), ESRF.

References:

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