

Experiment Report Form

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The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
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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: CH-3045
Beamline: BM01A	Date of experiment: from: 31.03.2010 to: 06.04.2010		Date of report: 01.09.2010 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Yaroslav Filinchuk		
Names and affiliations of applicants (* indicates experimentalists): D. B. Ravnsbæk ^{a*} , L. H. Rude ^{a*} , L. H. Sørensen ^{a*} , T. H. Cao ^{a*} , U. Filsø ^{a*} , M. V. Andersen ^{a*} , L. H. Jepsen ^{a*} , Y. Filinchuk ^{b*} , T. R. Jensen ^a ^a Interdisciplinary Nanoscience Center (iNANO), Department of Chemistry, University of Aarhus, DK-8000 Aarhus, Denmark ^b Swiss-Norwegian Beam Lines, ESRF, FR-38043 Grenoble, France			

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 realized e.g. the novel series of alkali zinc borohydrides, $\text{LiZn}_2(\text{BH}_4)_5$, $\text{NaZn}_2(\text{BH}_4)_5$ and $\text{NaZn}(\text{BH}_4)_3$, and the first mixed-cation mixed-anion borohydride, $\text{KZn}(\text{BH}_4)\text{Cl}_2$, which were recently discovered in our laboratory. We have succeeded to solve their structures and also to study the decomposition reactions in great detail [3,4]. In addition, the structure and decomposition of $\text{NaSc}(\text{BH}_4)_4$ have been investigated [5]. Furthermore, other attempts on the modification on metal borohydrides, using partial anion substitution was recently demonstrated by preparation of $\text{Li}(\text{BH}_4)_{1-x}\text{Cl}_x$. [6,7] All these results are based on diffraction data previously measured at SNBL (BM01-A), ESRF.

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.

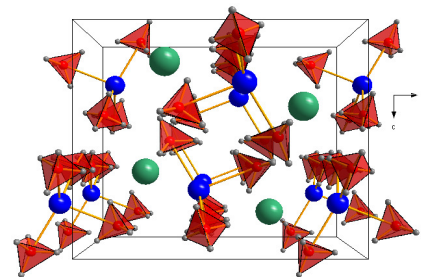
The measurements were performed at beamline BM01A using a MAR345 image plate detector. Samples were mounted in sealed 0.5 mm glass capillaries. The 2D SR-PXD data were integrated into 1D powder patterns. The materials were prepared by high-energy ball milling and shipped to the ESRF. All handling and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

So far the experiment CH3045 has resulted in a number of publications under preparation:

Structure and Characterization of $\text{KSc}(\text{BH}_4)_4$ [8]

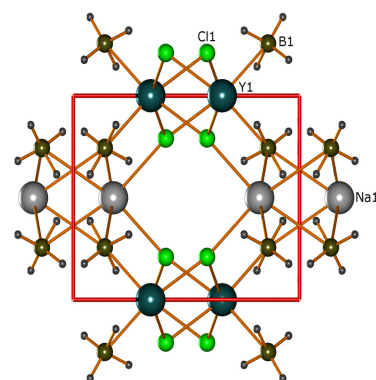
Abstract. A new potassium scandium borohydride, $\text{KSc}(\text{BH}_4)_4$, is presented and characterized by a combination of *in situ* synchrotron radiation powder X-ray diffraction, thermal analysis, vibrational and NMR spectroscopy. The title compound, $\text{KSc}(\text{BH}_4)_4$, forms at ambient conditions in ball milled mixtures of potassium borohydride and ScCl_3 together with a new ternary chloride K_3ScCl_6 , which is also structurally

characterized. This indicates that the formation of $\text{KSc}(\text{BH}_4)_4$ differs from a simple metathesis reaction, and the highest scandium borohydride yield (~31 mol%) can be obtained with a reactant ratio $\text{KBH}_4\text{:ScCl}_3$ of 2:1. $\text{KSc}(\text{BH}_4)_4$ crystallizes in the orthorhombic crystal system, $a = 11.856(5)$, $b = 7.800(3)$, $c = 10.126(6)$ Å, $V = 936.4(8)$ Å³ at RT , with the space group symmetry $Pnma$. Potassium scandium borohydride has a BaSO_4 type structure where the BH_4 tetrahedra obtain the oxygen positions. Regarding the packing of cations, K^+ , and complex anions, $[\text{Sc}(\text{BH}_4)_4]^-$, the structure of $\text{KSc}(\text{BH}_4)_4$ can be seen as a distorted variant of orthorhombic neptunium, Np , metal. Thermal expansion of $\text{KSc}(\text{BH}_4)_4$ in the temperature range RT to 405 K is anisotropic and the lattice parameter b shows strong nonlinearity upon approaching the melting temperature. The vibrational and NMR spectra are consistent with the structural model, and previous investigations of the related compounds $M\text{Sc}(\text{BH}_4)_4$ with $M = \text{Li}, \text{Na}$. $\text{KSc}(\text{BH}_4)_4$ is stable from RT up to ~405 K, where the compound melts and then releases hydrogen in two rapid steps approximately at 460 to 500 K and 510 to 590 K. The hydrogen release involves the formation of KBH_4 , which reacts with K_3ScCl_6 and form a solid solution, $\text{K}(\text{BH}_4)_{1-x}\text{Cl}_x$. The ternary potassium scandium chloride K_3ScCl_6 observed in all samples has a monoclinic structure at room temperature, $P2_1/a$, $a = 12.729(3)$, $b = 7.367(2)$, $c = 12.825(3)$ Å, $\beta = 109.22(2)^\circ$, $V = 1135.6(4)$ Å³, which is isostructural to K_3MoCl_6 . The monoclinic polymorph transforms to a cubic at 635 K, $a = 10.694$ Å (based on diffraction data measured at 769 K), which is isostructural to the high temperature phase of K_3YCl_6 .



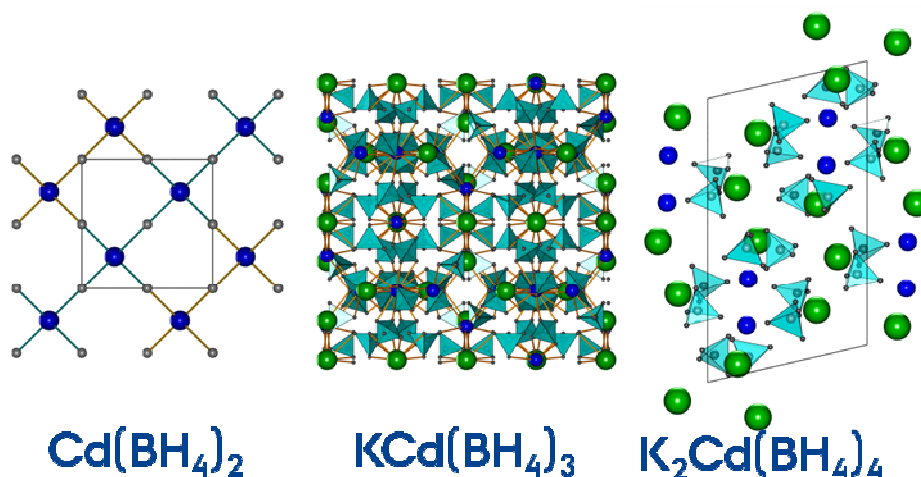
NaY(BH₄)₂Cl₂: a novel mixed-cation mixed-anion borohydride [9]

Abstract. A new sodium-yttrium borohydride-chloride, $\text{NaY}(\text{BH}_4)_2\text{Cl}_2$, is synthesized by ball milling YCl_3 and NaBH_4 , and annealed to improve the crystallinity. Its polymeric pseudo-orthorhombic crystal structure is built of edge- and corner-sharing octahedral coordination polyhedra of yttrium coordinated to 4 Cl + 2 BH_4 and sodium coordinated to 2 Cl + 4 BH_4 . The decomposition of $\text{NaY}(\text{BH}_4)_2\text{Cl}_2$ is studied by *in-situ* synchrotron powder X-ray diffraction, thermogravimetric analysis and differential scanning calorimetry. An endothermic event at ~300 °C associated with a mass loss, 2.62 wt%, somewhat smaller than the calculated hydrogen content of 3.90 wt% is observed. This is considerably lower than the decomposition temperature of NaBH_4 .



A series of novel cadmium borohydrides [10]

A series of novel cadmium borohydrides are synthesized and characterized with respect to their crystal structure and thermal decomposition pathway. All the novel compounds are formed by mechanochemical synthesis from $\text{MBH}_4\text{-CdCl}_2$ ($M = \text{Li}, \text{Na}$ or K) in a range of different composition. Both varying the used alkali cation and the ratio of the reactants are found to have a significant effect on the reactions products, i.e. several new compounds are obtained, e.g. $\text{Cd}(\text{BH}_4)_2$, $\text{KCd}(\text{BH}_4)_3$ and $\text{K}_2\text{Cd}(\text{BH}_4)_4$. These compounds exhibit fascinating structural topologies e.g. $\text{Cd}(\text{BH}_4)_2$, which is a Cu_2O -structure type and is built from two identical interpenetrated frameworks.



Investigation of the $\text{Ca}(\text{BH}_4)_2\text{-CaI}_2$ [11]

Abstract. The effects of $\text{BH}_4\text{-I}$ anion substitution in the $\text{Ca}(\text{BH}_4)_2\text{-CaI}_2$ is investigated. Heating leads to dissolution of $\text{Ca}(\text{BH}_4)_2$ into CaI_2 , resulting in formation of several solid solutions, exhibition different structural topologies. Three new compounds were identified and were structurally characterized using the Rietveld method and SR-PXD data. The structures was solved using the program FOX. Calcium borohydride dissolves in the trigonal calcium iodide structure already during ball milling forming a solid solution $\text{Ca}((\text{BH}_4)_{1-x}\text{I}_x)_2$ with an anisotropically contracted trigonal unit cell, $a = 4.311(1)$ and $c = 6.867(2)$ Å for $x \sim 0.3$ ($T = 28$ °C), space group $P\bar{3}m1$. The structure is a distorted CaI_2 -type structure. Thus, to a significant extend ($\sim 70\%$) iodide anions in CaI_2 can be replaced by the BH_4^- anions mediated by ball milling. The trigonal *tri*- $\text{Ca}((\text{BH}_4)_{0.70}\text{I}_{0.30})_2$ transforms at ~ 180 °C to an orthorhombic phase of the same composition, *ort*- $\text{Ca}((\text{BH}_4)_{0.70}\text{I}_{0.30})_2$, with a CaCl_2 -type structure with cell parameters $a = 7.271(2)$, $b = 7.042(1)$ and $c = 4.4601(7)$ Å ($T = 322$ °C), space group $Pnmm$. The structure of *ort*- $\text{Ca}((\text{BH}_4)_{0.70}\text{I}_{0.30})_2$ is similar to the structure of (distorted) $\beta\text{-Ca}(\text{BH}_4)_2$. Further heating of this CaCl_2 -type compound to ~ 330 °C leads to a transition to a tetragonal phase with cell parameters $a = 4.1062(2)$ and $c = 24.822(2)$ Å ($T = 340$ °C, $x \sim 0.62$), space group $I4mm$. This iodide-rich compound *tet*- $\text{Ca}((\text{BH}_4)_{0.38}\text{I}_{0.62})_2$, has a new structure type. The tetragonal phase finally decomposes to CaHI and CaB_6 at $T > 345$ °C. The presence of CaB_6 at elevated temperatures was determined by MAS NMR. All three novel compounds found in the $\text{Ca}(\text{BH}_4)_2\text{-CaI}_2$ system are stable down to RT . The preparation method has a significant influence on the reaction pathway and preparation of a similar sample by hand mixing instead of ball milling reveals that substitution upon heating needs temperatures of 360 °C to succeed, forming *tet*- $\text{Ca}((\text{BH}_4)_{1-x}\text{I}_x)_2$. Increasing the iodide content in the sample gives an indication of the limit of substitution in the trigonal and tetragonal- $\text{Ca}((\text{BH}_4)_{1-x}\text{I}_x)_2$ which is reached at $x \sim 0.30$ and 0.82 , respectively. The trigonal phase seems to be more stable upon the higher degree of excess CaI_2 content in the sample and no orthorhombic phase is observed.

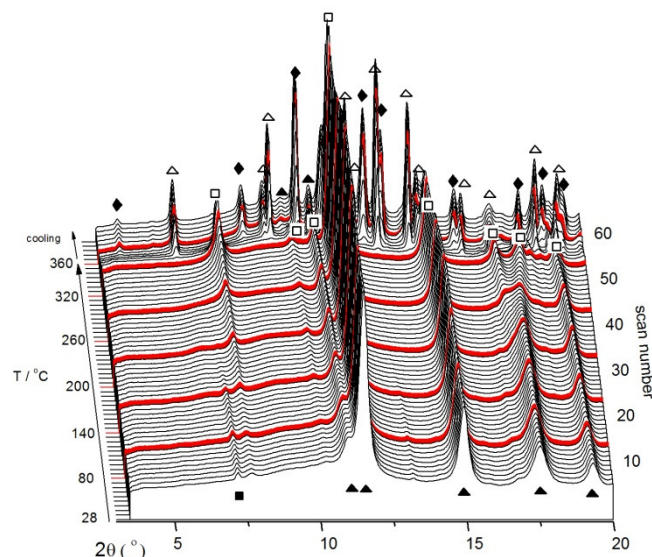


Figure 5 *In situ* SR-PXD data measured for $\text{Ca}(\text{BH}_4)_2\text{-CaI}_2$ (0.71 : 0.29) heated from RT to 360 °C (heating rate 3 °C/min, $\lambda = 0.6548$ Å). Symbols: ■ $\alpha\text{-Ca}(\text{BH}_4)_2$, ▲ *tri*- $\text{Ca}((\text{BH}_4)_{1-x}\text{I}_x)_2$, □ *ort*- $\text{Ca}((\text{BH}_4)_{1-x}\text{I}_x)_2$, △ *tet*- $\text{Ca}((\text{BH}_4)_{1-x}\text{I}_x)_2$, and ◆ CaHI .

Furthermore, have the experiment allowed us to obtain data on the following systems: $\text{KBH}_4\text{-YCl}_3$, $\text{MBH}_4\text{-SrCl}_2$ ($M = \text{Li, Na, K}$), $\text{MBH}_4\text{-BaCl}_2$ ($M = \text{Li, Na, K}$), $\text{LiBH}_4\text{-LiBr}$, $\text{LiBH}_4\text{-LiBF}_4$, $\text{NaBH}_4\text{-NaBF}_4$ and $\text{Mg}(\text{BH}_4)_2\text{-ZnCl}_2$ ect. These results are now been analysed carefully and seems to be very promising. Many of the projects will most likely result in publication in high impact journals.

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