

# STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE

**Report - High Resolution SR-PXD measurement: 01-01-745 (September 2007)**  
**Beamline BM01B**

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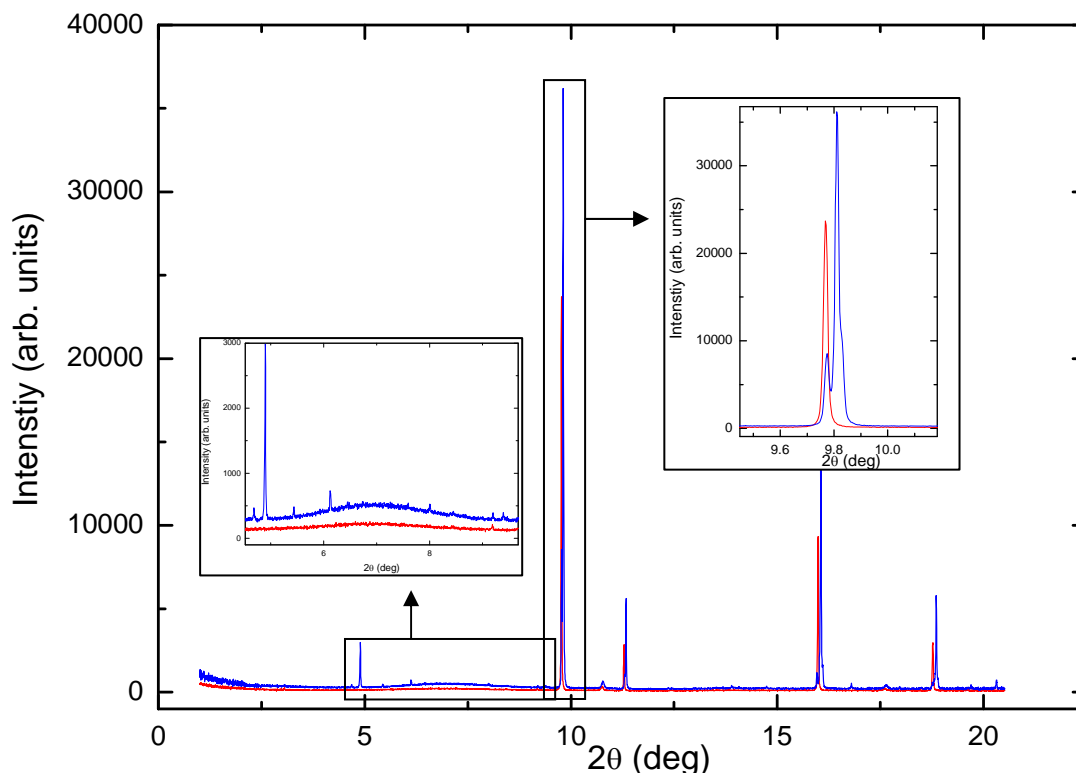
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## Li<sub>2</sub>ND

Li<sub>2</sub>NH (lithium imide) is an intermediate product in several reactions considered for hydrogen storage. Its crystal structure is not unambiguously determined. The most thorough investigation was performed by Balogh *et al* [M.P. Balogh *et al.*, J. Alloys Compd. 420 (3006) 326] by SR-PXD and PND on a deuterated sample, Li<sub>2</sub>ND. They found 3 structure models, one disordered cubic ( $a \sim 10 \text{ \AA}$ ) and two ordered orthorhombic (pseudo-cubic), which described the experimental data equally well. Above ca. 90°C, the phase took a (more) disordered face-centered cubic structure ( $a \sim 5 \text{ \AA}$ ).

A double isotope substituted lithium imide sample, <sup>7</sup>Li<sub>2</sub>ND, was prepared to clarify the room-temperature structure. <sup>7</sup>Li was used due to its far smaller absorption cross section for neutrons than natural Li. PND (PUS, JEEP II) show several weak peaks that are inconsistent with cubic symmetry.

SR-PXD measurements at BM01B were collected at room temperature and 100°C. The 100°C pattern could be indexed according the cubic unit cell suggested by Balogh *et al*. The RT pattern is noticeably different in two aspects: 1) there are additional peaks and 2) the cubic peaks are split into multiplets. The first point indicates an enlargement of the unit cell and the second point indicates lattice deformation. None of the unit cells suggested previously are consistent with the present data. Structure determination is in progress.

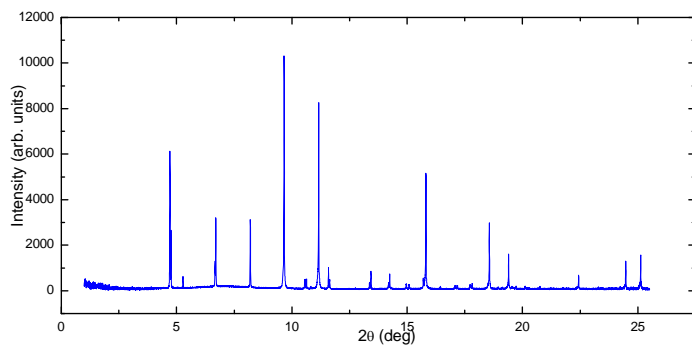


SR-PXD data for  ${}^7\text{Li}_2\text{ND}$  at RT (blue) and  $100^\circ\text{C}$  (red). Insets show ordering reflections (left) and peak splitting (right) at RT.

### **$\text{LiSc}(\text{BH}_4)_3$**

Borohydrides,  $\text{M}^{n+}(\text{BH}_4^-)_n$ , are of great interest for hydrogen storage due to their very high gravimetric and volumetric hydrogen density. However, all borohydrides investigated in the literature suffer from impractically high temperature for hydrogen desorption.

A new borohydride,  $\text{LiSc}(\text{BH}_4)_3$  was synthesized at Hawaii University and measured at BM01B. The data reveals a highly crystalline product with no resemblance to any phases in the PDF-4 database. The pattern was successfully indexed with a pseudo-cubic tetragonal unit cell. The crystal structure was solved and refined in space group  $P-42c$ . A manuscript on the crystal structure is submitted to *The Journal of Physical Chemistry*.

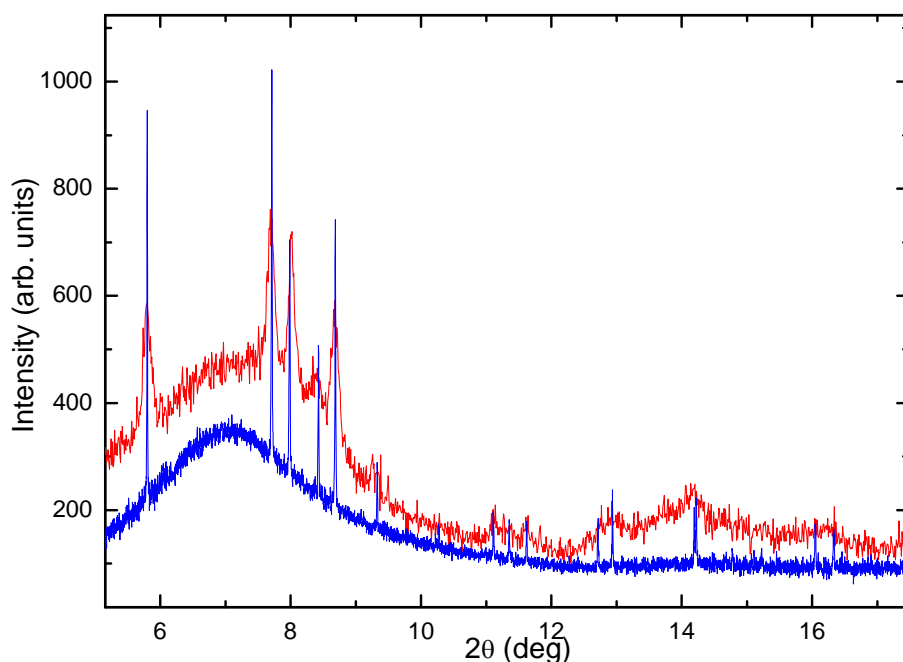


*SR-PXD data for  $\text{LiSc}(\text{BH}_4)_2$*

### **$\text{LiBH}_4$ in carbon aerogel**

Preparation of  $\text{LiBH}_4$  as nanoscopic particles is a possible route to lower the hydrogen desorption temperature [J. Vajo *et al.*, Scripta Mat. 56 (2007) 829].

$\text{LiBH}_4$  embedded in a carbon aerogel with a nominal pore size of 25 Å was measured at BM01B. The Bragg peaks were severely broadened compared to bulk  $\text{LiBH}_4$ . The particle size was estimated to 20.3(7) nm using Rietveld refinement the Scherrer formula. It was assume to be no peak broadening from strain.

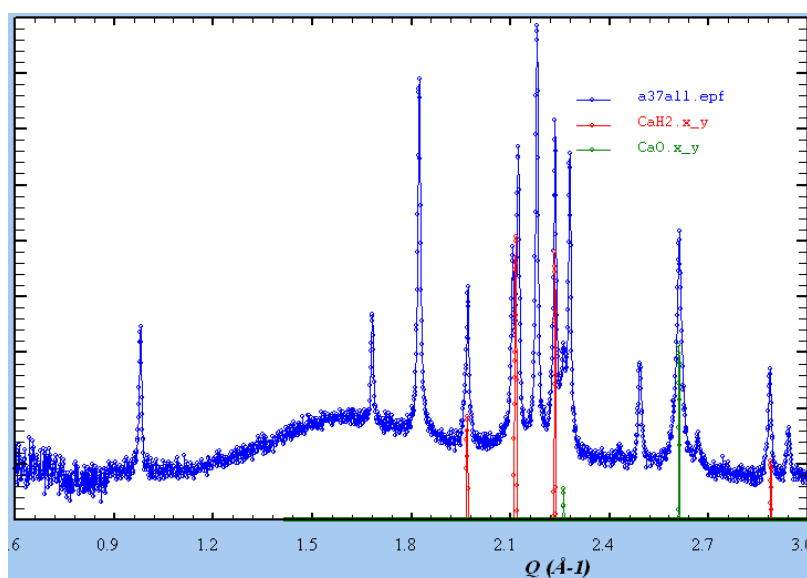


*Bulk  $\text{LiBH}_4$  (blue) and  $\text{LiBH}_4$  embedded in a carbon aerogel (red)*

### **$\text{Ca}(\text{BH}_4)_2$ and decomposition product phases**

$\text{Ca}(\text{BH}_4)_2$  is considered as an attractive hydrogen storage material due to high gravimetric capacity and expected thermodynamic properties suitable for mobile hydrogen storage applications. However, the decomposition route of this compound is unclear, and previous investigations show formation of unknown intermediate phases. For this SR-PXD investigation, samples of  $\text{Ca}(\text{BH}_4)_2$  were pre-heated to selected

temperatures under dynamical vacuum and measured at room temperature. Bragg peaks from a well-crystalline unknown intermediate Ca-B-H phase as well as from  $\text{CaH}_2$  (product phase) and  $\text{CaO}$  (contamination) was observed for the sample pre-heated to  $368^\circ\text{C}$ . The peaks from the unknown phase could be indexed according to an orthorhombic cell with extinction rules consistent with space group  $Pnma$ . The phase is believed to be an Ca-B-H containing phase, and from Rietveld refinement a structure model for the Ca-B sublattice is proposed. A manuscript for publication is in preparation.



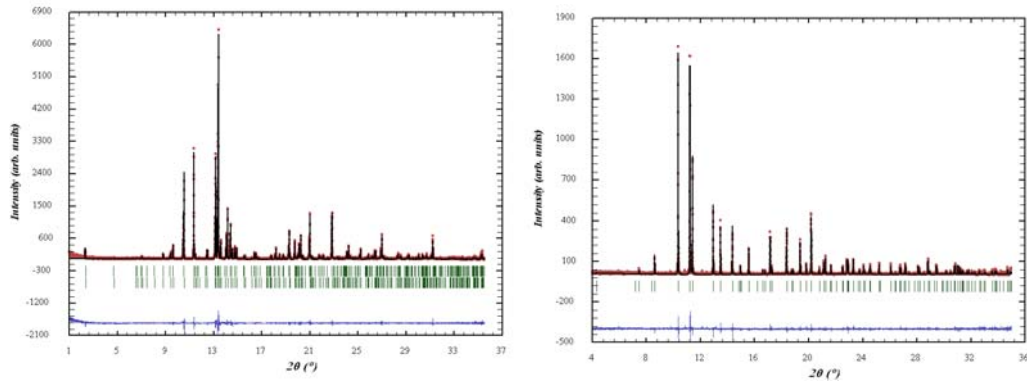
*SR-PXD data for  $\text{Ca}(\text{BH}_4)_2$  pre-heated to  $368^\circ\text{C}$  and measured at room temperature. The red and green reflections are calculated data for  $\text{CaH}_2$  and  $\text{CaO}$ , respectively, and the green reflections are calculated data for  $\text{CaO}$ .*

### **$\text{La}_x\text{Mg}_{2-x}\text{Ni}_{3.5}\text{D}_y$ and ABC-type intermetallics**

Certain types of intermetallic hydrides, especially ABC- and  $\text{A}_2\text{B}_7$ -based hydrides are suggested to have H-H separations far shorter than the usually observed limit of  $2 \text{ \AA}$ . The aim for this investigation is to examine transition metal – hydrogen systems likely to display short H-H and/or H-p-metal contacts to better understand the hydrogen capacity and thermostability of hydrogen storage materials.

Series of ABC-type alloys ( $\text{LaPdIn}$ ,  $\text{NdPdIn}$ ,  $\text{LaPt}_{0.75}\text{Ni}_{0.25}\text{In}$ ,  $\text{LaPt}_{0.90}\text{Ni}_{0.10}\text{In}$ ) prepared by arc-melting and annealing. SR-PXD data were collected at BM01B station at room temperature. Based on recorded data, impurity phases were identified and structure refinements were performed. The alloys will be deuterated and characterized by PND.

Synchrotron powder diffraction pattern was collected for a deuteride sample of  $\text{A}_2\text{B}_7$  alloy (La – Mg – Ni system). The data were used to perform the phase analysis as well as the Rietveld structure refinements of the metal sublattice. The phase will be further investigated by PND.



*Observed, calculated and differential synchrotron powder diffraction patterns of  $\text{La}_{1.64}\text{Mg}_{0.38}\text{Ni}_{3.5}\text{D}_x$  (left) and  $\text{NdPdIn}$  (right).*