SNBL	**Experiment title:** Borohydrides MM'$(BH_4)_4$: alloying of alkaline metal and alkaline earth borohydrides with transition metal borohydrides.	**Experiment number:** 01-02-834
Beamline: BM01A	**Date of experiment:** from: 3-Dec-08 to: 6-Dec-08	**Date of report:** 26-Feb-09
Shifts: 6	**Local contact(s):** Yaroslav FILINCHUK	*Received:*

Names and affiliations of applicants (* indicates experimentalists):

*Radovan Černý[1]
*Yaroslav Filinchuk[2]
Hans Hagemann[3]

[1]Laboratory of Crystallography, University of Geneva
[2]SNBL, ESRF Grenoble
[3]Physical Chemistry, University of Geneva

Following samples were studied by in-situ powder diffraction :

$ScCl_3 + 4NaBH_4$
Sample from C.M.Jensen, Hawaii, prepared by ball milling, temperature ramp 100-500 K.
The data did not allowed the structure solution of expected $NaSc(BH_4)_4$. New samples were asked.

$ZnCl_2 + 3LiBH_4$
Sample from Geneva, prepared by ball milling, temperature ramp 100-500 K.
The measurement has completed the data measured in July 2008 within the project no. 01-02-805. Two new compounds are structurally characterized: $LiZn(BH_4)_3$ and $NaZn(BH_4)_3$. The results are being prepared for publication.

$xZnCl_2 + yKBH_4$, x:y = 1:2 and 3:8
Sample from Geneva, prepared by ball milling, temperature ramp 100-500 K.
The data are being processed for the structure solution of expected $Zn(BH_4)_2$ and $K_2Zn_3(BH_4)_8$.

$xMnCl_2 + yLiBH_4$, x:y = 1:2 and 1:3
$MnCl_2 + 3KBH_4$
Sample from Geneva, prepared by ball milling, temperature ramp 100-500 K. The sample with $LiBH_4$ has allowed the structural characterization of the first transition metal borohydride $Mn(BH_4)_2$. The data measured on the sample with KBH_4 shows powder patterns of another new phase and are currently being treated.

$Mn(BH_4)_2$

Solvent-free homoleptic manganese borohydride $Mn(BH_4)_2$ forms at ambient conditions in ball-milled mixtures of alkali metal borohydrides and $MnCl_2$. It crystallizes in the trigonal crystal system with the space group symmetry $P3_112$ and is stable from 90 up to 450 K, where the compound melts. The structure of $Mn(BH_4)_2$ shows interesting similarity to α-$Mg(BH_4)_2$: the two structures are made of similar layers L with the composition $M_4(BH_4)_{10}$ per cell (see Figure 1). The layers are stacked along the *c*-axis, and rotated by 120° by the 3_1 axis in $Mn(BH_4)_2$ and by 60° by the 6_1 axis in α-$Mg(BH_4)_2$. Three identical layers are stacked along one unit cell vector *c* in $Mn(BH_4)_2$, six layers are stacked in α-$Mg(BH_4)_2$. In $Mn(BH_4)_2$ the layers L are connected directly, and share atoms. In α-$Mg(BH_4)_2$ the layers L are intercalated by a thin layer L' which contains one Mg atom per layer per cell. The layer L is chiral, and both borohydrides crystallize in chiral space groups. Similar to α-$Mg(BH_4)_2$, the structure of $Mn(BH_4)_2$ is not densely packed and contains isolated voids with the estimated volume of 21 $Å^3$ each, which occupy in total 6% of the space. The resemblance between $Mn(BH_4)_2$ and α-$Mg(BH_4)_2$ is also reflected in their Raman and infrared spectra.

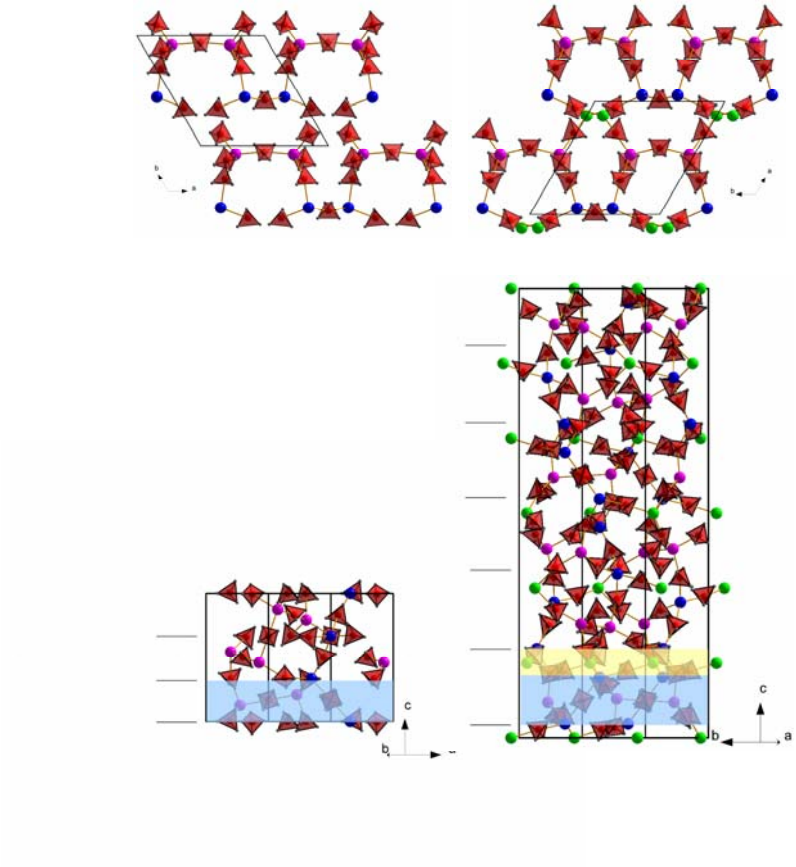

Figure 1. Crystal structure of $Mn(BH_4)_2$ (left) and α-$Mg(BH_4)_2$ (right) made from the similar layers L (top). The layers contain two independent *M* atoms (blue and violet). The layer of $Mn(BH_4)_2$ is shown here as a mirror image of the layer of α-$Mg(BH_4)_2$. The layers are stacked along the *c*-axis (bottom), and rotated by 120° by the 3_1 axis in $Mn(BH_4)_2$ and by 60° by the 6_1 axis in α-$Mg(BH_4)_2$. In $Mn(BH_4)_2$, the layers L (light blue) are overlapping, sharing atoms. In α-$Mg(BH_4)_2$, the layers L (light blue) are intercalated by a thin layer L' (yellow) containing the third independent Mg atom (green).

The results are submitted for publication [1].

[1] Černý R., Penin N., Hagemann H., Filinchuk Ya. *J. Phys. Chem. C*, submitted