SNBL	**Experiment title:** Borohydrides $MM'(BH_4)_4$: alloying of alkaline metal and alkaline earth borohydrides with transition metal borohydrides.	**Experiment number**: 01-02-864
Beamline: BM01A	**Date of experiment**: from: 4-Mars-10 to: 6-Mars-10	**Date of report**: 20-Sept-10
Shifts: 6	**Local contact(s)**: Yaroslav FILINCHUK	*Received:*

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Following ball-milled mixtures were studied by in-situ powder diffraction :

$AlCl_3$ + $NaBH_4$ and $AlCl_3$ + $2NaBH_4$

Samples from Inge Lindemann, IFW Dresden, prepared by ball milling. The temperature ramp 100-500 K has been measured for the mixture 1:1. The data allowed to identify and solve the structure of a novel alkaline aluminium borohydride/chloride $NaAl(BH_4,Cl)_4$ shown in the Figure 1. The results of in-situ powder diffraction are currently completed by DSC and TG decomposition studies performed at the IFW Dresden, and will be published soon.

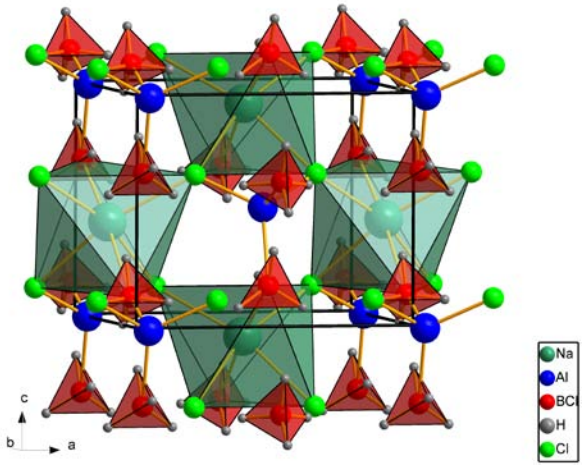

Figure 1. Crystal structure of $NaAl(BH_4,Cl)_4$.

$TiF_3 + 3LiBH_4$, $CoF_2 + 2LiBH_4$ and $NiF_2 + 2LiBH_4$

Samples have been prepared by ball milling in Bordeaux. Using the fluorides instead of chlorides for the synthesis of transition metal and/or double cation borohydrides we expected lower kinetics of metathesis reaction and consequently possibility of capture the unstable transition metal borohydrides during in situ powder diffraction experiment. The temperature ramps 100-500 K have been measured for all three mixtures.
Unfortunately the titanium and cobalt samples have shown the formation of the LiF as a result of the metathesis reaction between the fluoride and borohydride. However, no crystalline phases which could be attributed to the formation of transition metal or double cation borohydrides were observed. The nickel sample shows also the formation of LiF and of unknown crystalline phase still stable at 500 K. Its crystal structure is currently being analyzed.

$LiBH_4 + Mg(BH_4)_2$

A recent study [1] reported the formation of a double cation compound in the $LiBH_4$: $Mg(BH_4)_2$ system. We have therefore decided to study ball-milled mixture in the ratio 1:1. In the Figure 2 the evolution observed with increasing temperature from 293 to 500 K is shown. At 385 K, the LT-HT phase transition of $LiBH_4$ is observed (seen very clearly for 2 = 12.2). At 456 K, the lines of $Mg(BH_4)_2$ disappear, while HT $LiBH_4$ is still seen. This behavior is probably related to an eutectic transition. No other compound than $LiBH_4$ and $Mg(BH_4)_2$ was found after cooling (red pattern). The DSC experiment in [1] on the $LiBH_4/Mg(BH_4)_2$ mixture shows signals at 116 and 183 °C (389 and 456 K), in good agreement with the changes seen in the Figure 2.

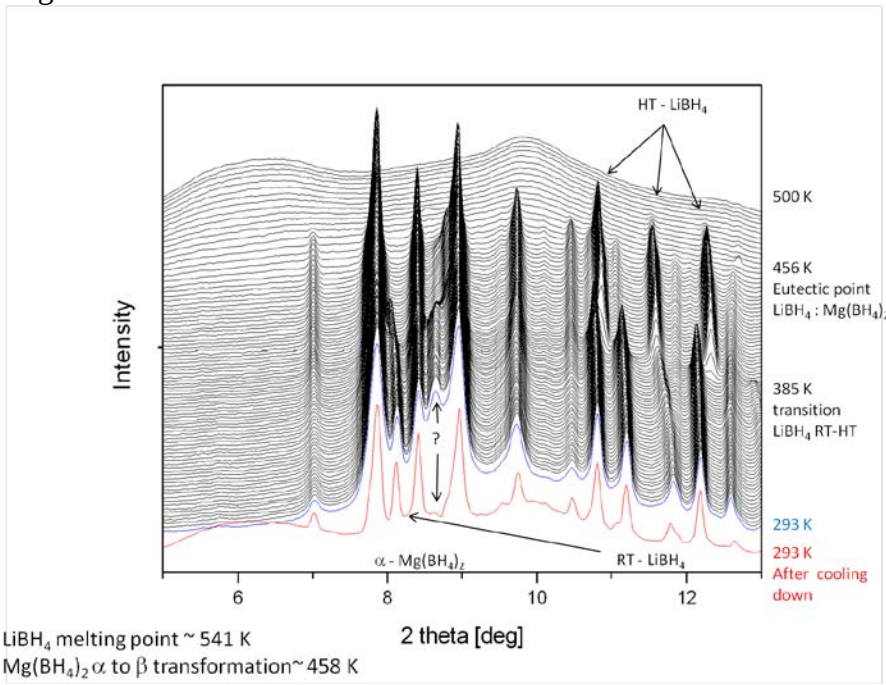

Figure 2. In situ X-ray diffraction from room temperature (blue) to 500 K (top) of $Mg(BH_4)_2$: $LiBH_4$ mixture. The lowest trace (in red) corresponds to the sample cooled back to 293 K.

The results are submitted for publication [2].

[1] Z.Z. Fang, X.D. Kang, P. Wang, H.W. Li and S. Orimo, *J. Alloys Comp*. **491** (2010) L1-L4.
[2] H.Hagemann, V. D'Anna, J.P. Rapin, R. Černý, Y. Filinchuk, K. Kim, D. Sholl and S.F. Parker, *J. Alloys Comp*., Proceedings of MH2010, Moscow.