SNBL	**Experiment title:** Hydrolysis of chemical hydrides and formation of intermediate phases: in-situ and ex-situ diffraction studies	**Experiment number**: 01-02-798
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The project is dedicated to the *in-situ* and *ex-situ* powder diffraction study of hydrolysis reactions of light metal hydrides which are considered as possible hydrogen carriers for future mobile applications. Their reaction with water is one of the ways to liberate hydrogen [1]. *In-situ* diffraction experiments allowed us to follow the evolution of the crystalline phases during hydrolysis and thus shed some light on the reaction mechanisms in hydride-H_2O systems.

In-situ and *ex-situ* synchrotron powder diffraction study of the hydrolysis of $NaBH_4$, $Mg(BH_4)_2$, $LiAlH_4$, $NaAlH_4$, α-AlH_3, $NaMgH_3$, $Ca_4Mg_3H_{14}$ was done and the possibility of the ammonia-borane (NH_3BH_3) hydrate and KBH_4 hydrates formation was investigated. For this purpose MAR345 area detector was used to collect X-ray synchrotron powder patterns each 2 minutes during the reactions. To influence the kinetics, the reaction volume was cooled or heated by the Oxford Cryostream 700+ system. To provide suitable pressures of water vapour an in-house system was constructed at SNBL. For investigation of the hydrolysis reactions three different setups were used, where hydrides were allowed to react with 1) air humidity; 2) water vapour brought by a stream of wet nitrogen gas; 3) a droplet of water placed in a direct contact with the sample or in a close proximity to it. To study the possibility of the KBH_4 and NH_3BH_3 hydrate formation water solution of these compounds with different concentrations were prepared.

$NaBH_4$

The synchrotron powder patterns were collected during the reactions of the sample with humid air, water and water vapour, with catalyst $CeNi_3$ and without it in the temperature interval 20 – 120^0 C.

$NaBH_4$ is the most stable with respect to hydrolysis: in the reaction with water or water vapour below 40^0 C it yields only the hydrate $NaBH_4 \cdot 2H_2O$ [2], while at higher practical temperatures (<120^0 C) the H_2 release is very slow.

α-AlH_3

The initial sample contained four different polymorphs of alane: α-, β-, γ- and α'-AlH_3 phases: α-AlH_3 (94.1 wt%); β-AlH_3 (3.1 wt%); γ-AlH_3 (1.4 wt%); α '-AlH_3 (1.4 wt%).

The synchrotron powder patterns were collected during the reactions of the sample with water and water vapour at room temperature. The compound reacts without formation of intermediate phases, yielding $Al(OH)_3$.

$Mg(BH_4)_2$

The synchrotron powder patterns were collected during the reactions of the sample with humid air, water and water vapour in the temperature interval -30 – +60^0 C. The compound reacts without formation of intermediate phases, yielding an amorphous phase as a final product of the hydrolysis reaction.

$LiAlH_4$

The synchrotron powder patterns were collected during the reactions of the sample with humid air, water and water vapour in the temperature interval -30 – +40^0 C. The final product of the reaction with water or water vapour is $LiAl_2(OH)_7 \cdot 2H_2O$ and the amorphous phase forms as an intermediate product of the hydrolysis reaction. $LiOH \cdot H_2O$ forms as an intermediate in the reaction of $LiAlH_4$ with water at lower temperatures (3°C). $LiAlH_4$ is very reactive and on contact with air it reacts with atmospheric CO_2 forming the carbonate Li_2CO_3.

$NaAlH_4$

The synchrotron powder patterns were collected during the reactions of the sample with humid air, water and water vapour in the temperature interval -20 – +25^0 C. The final product of the reaction with water or water vapour is $Al(OH)_3$ and the amorphous phase forms as an intermediate product of the hydrolysis reaction. $NaAlH_4$ is very reactive and on contact with air it reacts with atmospheric CO_2 with carbonate Na_2CO_3 and carbonate hydrate $Na_2CO_3 \cdot H_2O$ formation.

$NaMgH_3$

The initial sample was prepared using standard solid-state method at the Laboratoire de Cristallographie, Université de Genève and contains $NaMgH_3$ (86.90 wt%); NaH (7.56 wt%); MgO (5.54 wt%).
The synchrotron powder patterns were collected during the reactions of the sample with humid air and water vapour at room temperature. The final product of the reaction is $Mg(OH)_2$ and the amorphous phase forms as an intermediate product of the hydrolysis reaction. $NaMgH_3$ is very reactive and on contact with air it reacts with atmospheric CO_2 with carbonate Na_2CO_3 and carbonate hydrate $Na_2CO_3 \cdot H_2O$ formation.

$Ca_4Mg_3H_{14}$

The initial sample contains $Ca_4Mg_3H_{14}$ (53.74 wt%); CaH_2 (27.02 wt%); Mg (19.24 wt%).
The synchrotron powder patterns were collected during the reactions of the sample with humid air, water and water vapour at room temperature. The final product of the reaction is $Ca(OH)_2$ and the amorphous phase forms as an intermediate product of the hydrolysis reaction.

KBH_4

According to the paper [3] a few solid hydrates of potassium borohydride occur at temperatures below 0^0 C. For this purpose four solutions were prepared 1) 0.2 g KOH – 1.2 g KBH_4 – 11 ml H_2O; 2) 0.98 g KOH – 0.99 g KBH_4 – 10 ml H_2O; 3)1.33 g KOH – 1.0 g KBH_4 – 10 ml H_2O; 4) KBH_4 – H_2O saturated in the borohydride. The synchrotron powder patterns were collected during the reactions of the sample in the temperature interval -110 – +25^0 C and revealed the formation of KBH_4 cubic crystals only.

NH_3BH_3

Ammonia-borane is rather stable with respect to the hydrolysis at room temperature. It was interesting to obtain a hypothetical hydrate of ammonia-borane and to study its crystal structure. For this purpose the saturated water solution was prepared and cooled down to -33^0 C at a rate of 40^{0}C/h. To promote hydrolysis the solution was heated up to 150^0 C at a rate 20^{0}C/h. The synchrotron powder patterns were collected simultaneously. Ammonia-borane was observed as the only crystalline phase.

The results were presented at the Swiss Society for Crystallography meeting in Zurich, on 8-9 Sept. 2008.

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