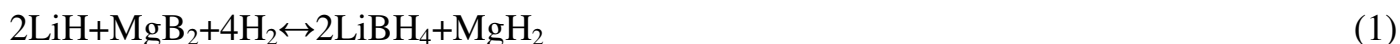




	Experiment title: Investigations of sorption reactions in Reactive Hydride Composites (RHC) with combined in-situ XRD and Raman spectroscopy	Experiment number: CH 2618
Beamline: BM01B	Date of experiment: from: 19.03.2008 to: 26.03.2008	Date of report: 17.02.2009
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Report:

Metal hydrides are considered as one of the most reliable and safe storage methods for hydrogen because of the chemical stability of the metal-hydrogen bonds. Essential for a highly efficient storage system for mobile applications is the combination of high gravimetric hydrogen capacities above 6 wt% with a desorption pressure of several bars in the temperature range of 80-120°C, because then the waste heat of an advanced Proton Exchange Membrane (PEM) fuel cell can be used to release the hydrogen from the hydride. To master these challenges, the so called Reactive Hydride Composites (RHC) have been developed [1,2]. These systems show a reduced total reaction enthalpy due to the formation of a new compound in the desorbed state but also remaining high gravimetric storage capacities. One of these RHC systems is for example the system of:



It has a theoretical storage capacity of 11.4wt% hydrogen and theoretically an equilibrium temperature at 1bar hydrogen of 170°C. The exothermic formation of MgB₂ lowers the overall reaction enthalpy. Experiments have shown, that the uptake of hydrogen, especially the formation of LiBH₄, is much facilitated from these compounds in comparison to the formation from the elements.

However, at present the composite materials show relatively poor kinetics even at elevated temperatures. To tackle these drawbacks, a deeper understanding of the reaction mechanism

in dependence of pressure and temperature is necessary. For this, in-situ synchrotron radiation X-ray powder diffraction in combination with Raman spectroscopy and tracking of pressure changes is an extremely powerful tool. Raman spectroscopy is especially important because of the liquid and/or amorphous nature of some B-H containing compounds at the reaction temperatures.

The measurements were performed in a specially designed sample cell made of single crystal sapphire at beamline SNBL-BM01 station B, ESRF. The composite materials were prepared by high-energy ball milling and shipped to the ESRF. All handling and preparation was performed under continuously purified argon atmosphere in a glove box.

In figure 1 an example an in-situ XRD measurement of a hydrogen desorption reaction of $\text{LiBH}_4\text{-MgH}_2$ composites is shown. For this experiment the sample was kept under approximately 5 bar hydrogen and is heated to 400°C and then kept isothermal. With the available laser wavelength strong fluorescence was measured for this material.

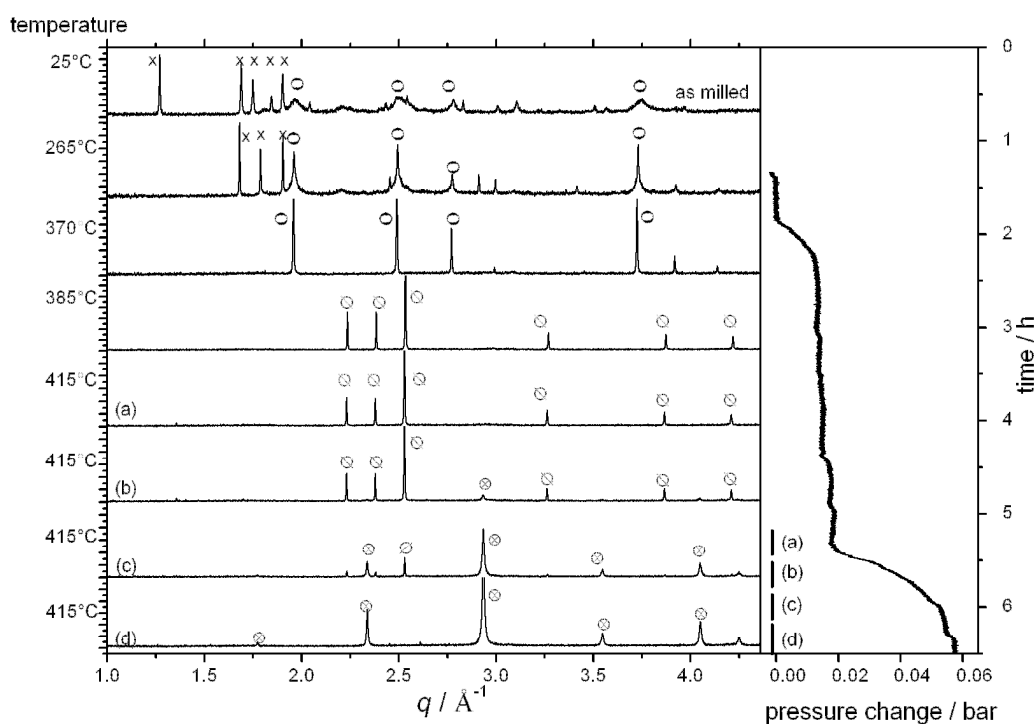


Figure 1: In-situ XRD and pressure record of the first desorption of pre $\text{LiBH}_4\text{-MgH}_2$ composites performed at the ESRF BM01B under approximately 5bar hydrogen, heating to 415°C and keeping isothermal. Symbols: x- LiBH_4 , O- MgH_2 , ∅-Mg and ⊗- MgB_2 .

In the first scan, the nanocrystalline starting materials LiBH_4 and MgH_2 are identified. Upon heating, the phase transformation of LiBH_4 into its hexagonal polymorph takes place. Coarsening and relaxation of the MgH_2 phase can be observed. At temperatures above 270°C the LiBH_4 melts and cannot be observed further with X-ray diffraction. Upon further heating the MgH_2 releases its hydrogen. Simultaneously to the formation of metallic Mg, a rise in pressure in the right diagram can be observed. The material is heated further to 400°C . Similar to the volumetric measurements in a Sievert's apparatus [3], a lengthy incubation period without further reaction is observed. However, after approximately 3 hours, the formation of MgB_2 can be observed simultaneously to a significant rise in pressure. The desorption of LiBH_4 and the formation of MgB_2 take place simultaneously. The reaction enthalpy is effectively lowered, because desorption of LiBH_4 takes place below its thermodynamic equilibrium temperature for 5 bar hydrogen. In a different experiment at lower pressures and higher temperatures, the desorption of LiBH_4 was observed to occur

independently from the formation of MgB_2 . The formation of MgB_2 is a key issue for reversibility for these materials. The desorption pathway was observed to be strongly dependent on the present pressure, temperature and heating rates [4].

For the composite system of $2\text{NaBH}_4 + \text{MgH}_2 \leftrightarrow 2\text{NaH} + \text{MgB}_2$ much less is known about the individual compounds, which is why we additionally investigated the behavior of pure NaBH_4 during heating in vacuum. The evolution of the Raman signal with temperature is shown in figure 2.

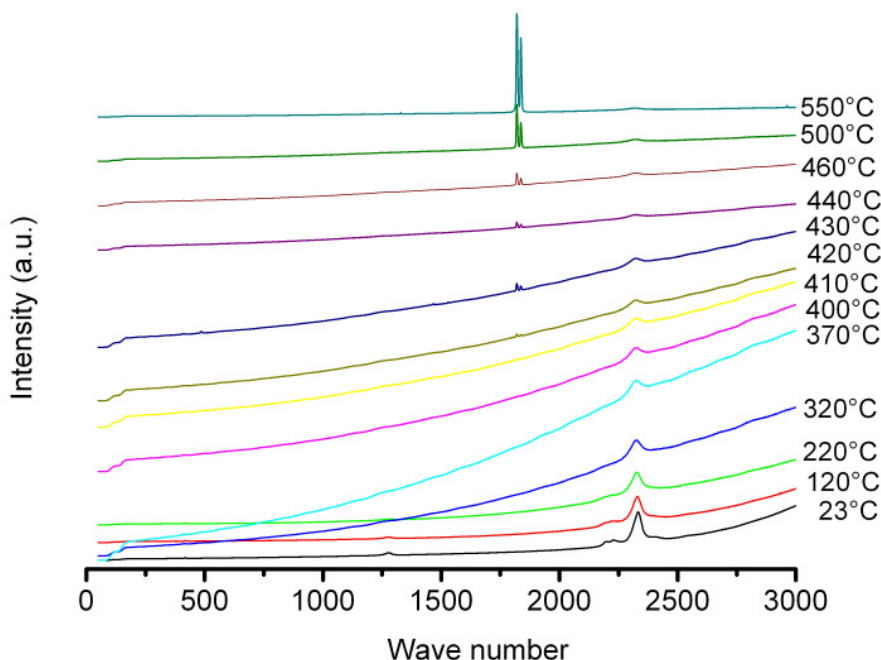


Figure 2: Raman spectra of NaBH_4 heated from RT to 550°C ($5^\circ\text{C}/\text{min}$ heating rate).

In the sample at room temperature both B-H bending and stretching modes around 1300 and 2300 cm^{-1} are clearly visible. With rising temperature a small shift of the both Raman modes towards lower wavenumbers coupled with increased broadening of both signals is observed. At a temperature of approximately 400°C two new peaks start to appear at 1820 and 1837 cm^{-1} . With increasing temperature the intensity of these two peaks increases whereas the peaks associated with NaBH_4 modes become broader and have almost disappeared at 550°C . The phase corresponding to these new modes could not be identified, yet. The change occurs simultaneously to the formation of an unknown crystalline phase that was observed by in-situ X-ray diffraction.

Another example of a RHC system is $\text{LiBH}_4\text{-Al}$, which has been estimated by thermodynamic calculations to release hydrogen at much lower temperatures than single-phase LiBH_4 [5]. The system has previously been studied by PCT, TPD, *ex situ* PXD, etc. [6, 7]. However, a deeper insight into the reaction pathways during release and uptake of hydrogen is still needed.

In situ synchrotron radiation X-ray powder diffraction data and pressure record for the desorption of hydrogen of a $\text{LiBH}_4\text{-Al}$ composite powder is shown in Figure 3. During the experiment the sample was kept under approximately 0.1 bar helium and heated with $5^\circ\text{C}/\text{min}$ and then kept isothermal at selected temperatures.

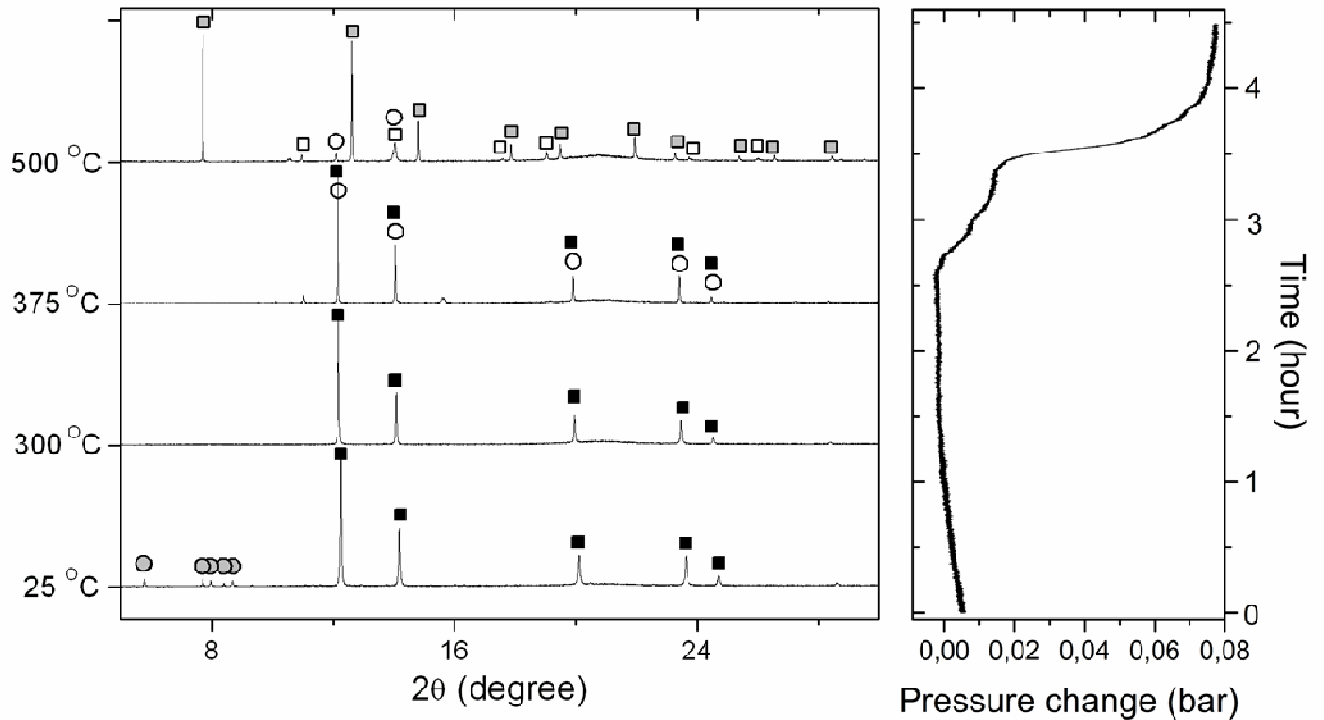


Figure 3: *In situ* SR-PXD for the hydrogen desorption of a LiBH₄-Al composite (left) performed at the ESRF SNBM01B. The pressure change Δp in the sample holder is recorded (right) measured relative to the initial pressure $p(\text{He}) \sim 0.1$ bar. The sample was heated to selected temperatures and kept isothermal, heating rate: 5 °C/min. Symbols: \circ LiBH₄, \blacksquare Al, \circ LiH, \square AlB₂, \blacksquare LiAl ($\lambda = 0.500$ Å).

Upon heating of the LiBH₄-Al sample to 300 °C LiBH₄ melts and only diffraction from Al is observed. No change in pressure is observed, i.e. LiBH₄ has not desorbed hydrogen at this stage. At 375 °C, Al, LiH and an unidentified phase is observed. This reaction step is accompanied by an increase in pressure. By heating the sample to 500 °C LiAl and AlB₂ is formed while a further increase in pressure is observed. This suggests that the overall reaction for desorption of hydrogen takes place according to eq. 2., which is also suggested by the thermodynamical calculation [5].



After desorption the sample was cooled to room temperature, $p(\text{H}_2) \sim 20$ bar was applied and the sample was heated to 400 °C and kept isothermal for 2 hours. An intermediate measurement was done at 200 °C in order to study the rehydrogenation pathway, which was observed to be similar to the dehydrogenation. At 200 °C reformation of Al was observed and upon cooling from 400 °C LiBH₄ recrystallized, i.e. the RHC system is reversible.

This study indicates that in the LiBH₄-Al composite, all 18.4 wt% in LiBH₄ is available as opposed to the 13.9 wt%, which can normally be obtained under these relatively benign conditions. To further investigate the reaction pathway the high resolution of the obtained SR PXD data will be utilized to solve the structure of the unidentified phase in the first desorption step, since this might play a crucial role for the optimization of the kinetic and thermodynamic properties of this RHC system [8].

Besides the RHC, $\text{Mg}(\text{BH}_4)_2$ is a very promising compound for hydrogen storage because of its low reaction enthalpy and therefore suitable reaction temperatures at a high gravimetric capacity of 14.9 wt%. Llamas et al. [9] have shown, that the ball milling of LiBH_4 and MgCl_2 leads to the formation of nanocrystalline $\text{Mg}(\text{BH}_4)_2$ and LiCl only under very specific conditions. The decomposition of these materials is complex and suggests the presence of a variety of $\text{Mg}(\text{BH}_4)_2$ and Li-Mg-Cl phases that transform their structure upon heating. To complement ex-situ measurements, temperature dependent in-situ powder diffraction and simultaneous Raman spectroscopy studies at 20 bar H_2 were performed at the beamline SNBL-BM01 station B, ESRF. The results confirmed the phase transformation of the milling products with temperature observed by Llamas et al. [10], but showed small variations of the decomposition path when comparing with ex-situ measurements. The detailed analysis of the data is ongoing.

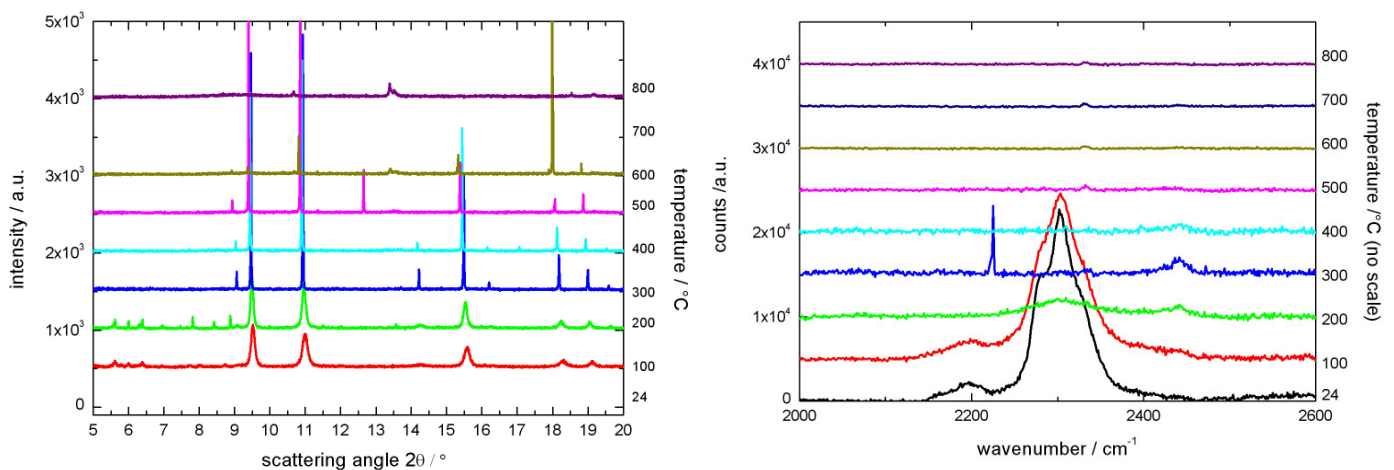


Figure 4(a) In-situ diffraction patterns of a sample synthesised by ball milling under 1 bar Ar and simultaneous Raman spectroscopy (b). The measurements were carried out under 20 bar H_2 in sapphire capillaries. A heating, rate of 10°C per minute was used from RT to 800°C. The plot shows the spectral range between 2000 and 2600 cm^{-1} , with the typical B-H stretching vibrations centered at 2300 cm^{-1} .

In general, in-situ XRD especially in combination with Raman spectroscopy is an extremely powerful tool to characterize light-metal hydrides for hydrogen storage applications. The observations of the reaction pathways and their dependence on pressure and temperature contribute to the understanding of the ongoing reactions and will thus allow for further improvement.

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