

# STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE

## **Preliminary report – In situ SR-PXD measurement: 01-02-772 (October 2008) Beamline BM01A**

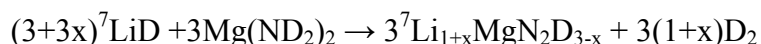
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### **Thermal decomposition of $\text{Li}_{1+x}\text{MgN}_2\text{D}_{3-x}$ with $x=0$ and $2$**

In 2002 Chen *et al.*<sup>[1]</sup> reported that a mixture of lithium amide and lithium hydride could store up to 6.5wt% of hydrogen. Unfortunately the working temperature ( $>250^\circ\text{C}$ ) is impractically high for hydrogen storage applications. However Luo *et al.*<sup>[2]</sup> have shown that a mixture of  $\text{LiNH}_2$  and  $\text{MgH}_2$  requires a lower working temperature and suggested the formation of  $\text{Li}_2\text{Mg}(\text{NH})_2$  during decomposition.

We have studied the thermal decomposition of  ${}^7\text{Li}_{1+x}\text{MgN}_2\text{D}_{3-x}$  with  $x=0$  and  $2.66$  by the mean of in situ SR-PXD. Simultaneous Raman spectroscopy have been performed during the desorption process of  ${}^7\text{Li}_{1+x}\text{MgN}_2\text{D}_{3-x}$ . Samples were prepared by the following solid state reaction at  $200^\circ\text{C}$ :



The samples were prepared with  ${}^7\text{Li}$  and  $\text{D}$  in order to study the material with neutron diffraction combined with the synchrotron X-rays. The materials were inserted in a quartz capillary and place in dynamical primary vacuum. The samples were heated with a ramping rate of  $2\text{C}/\text{min}$  and diffraction patterns where collected every second over a range of  $40^\circ$  in  $2\theta$  with  $\lambda = 0.70007\text{\AA}$ . Data from SR-PXD and the similar Raman spectroscopy measurements of  ${}^7\text{Li}_{1+x}\text{MgN}_2\text{D}_{3-x}$  with  $x=0$  and  $2$  are shown in Fig. 1 and Fig. 3, respectively.

Under dynamical vacuum the samples exhibit a characteristic transition temperature of about  $260^\circ\text{C}$  both observed in the diffraction patterns and Raman shift (Fig.3). Analyses of the collected data are still in progress.

[1] P. Chen *et al.*, Nature **420**, 302 (2002).

[2] W. Luo *et al.*, J. Alloys Compd **381**, 284 (2004).

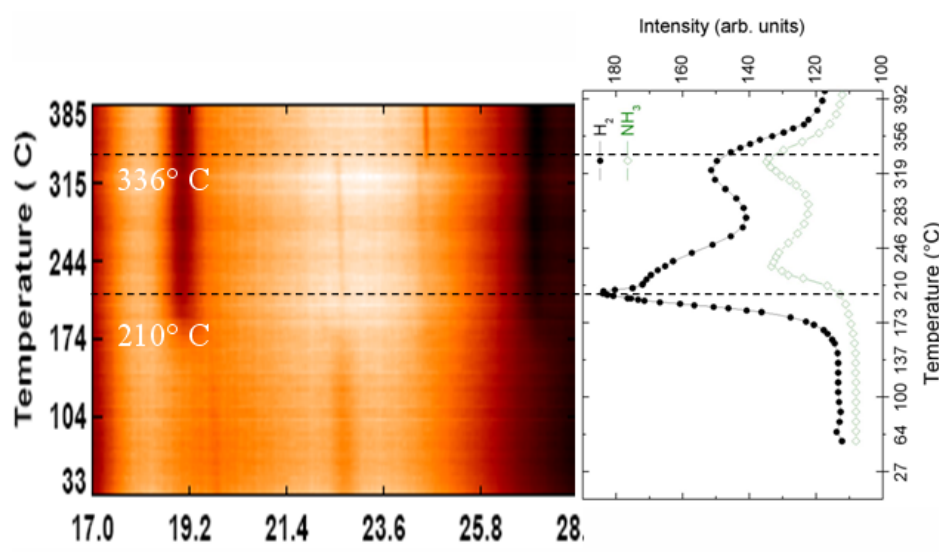


Fig. 1. Colour plot representing the evolution of  $\text{Li}_1\text{MgN}_2\text{D}_3$  diffraction pattern versus temperature (left panel) (x-axis represent the  $2\theta$ (degree), the y-axis the temperature and the colour the intensity). The right panel is the TPD coupled with mass spectrometry analysis of the desorbed gas.

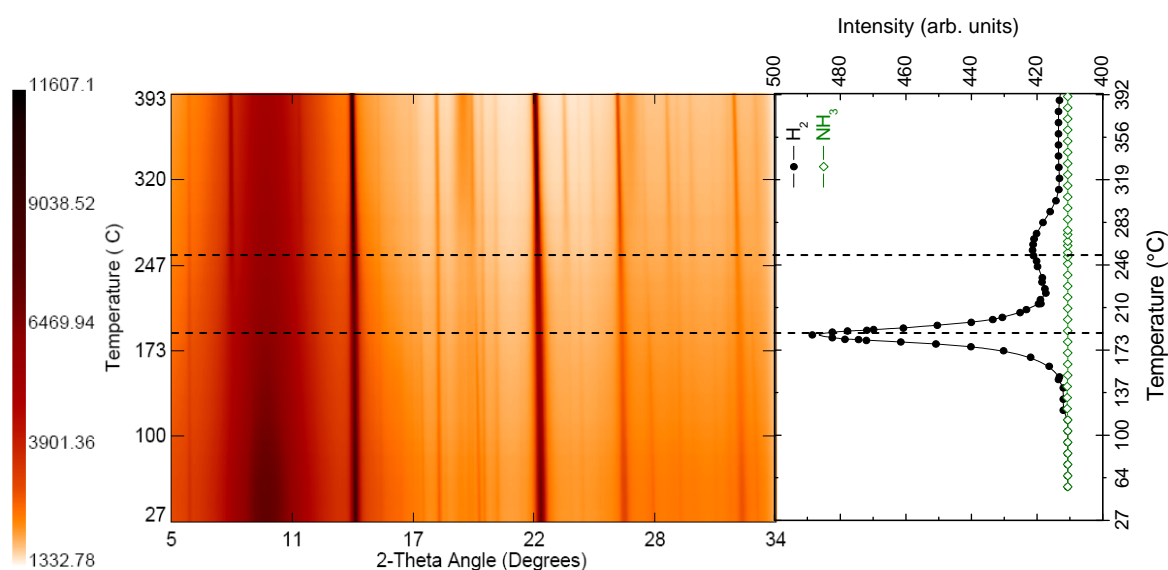


Fig. 2. Colour plot representing the evolution of  $\text{Li}_3\text{MgN}_2\text{D}_1$  diffraction pattern versus temperature (left panel) (x-axis represent the  $2\theta$ (degree), the y-axis the temperature and the colour the intensity). The right panel is the TPD coupled with mass spectrometry analysis of the desorbed gas

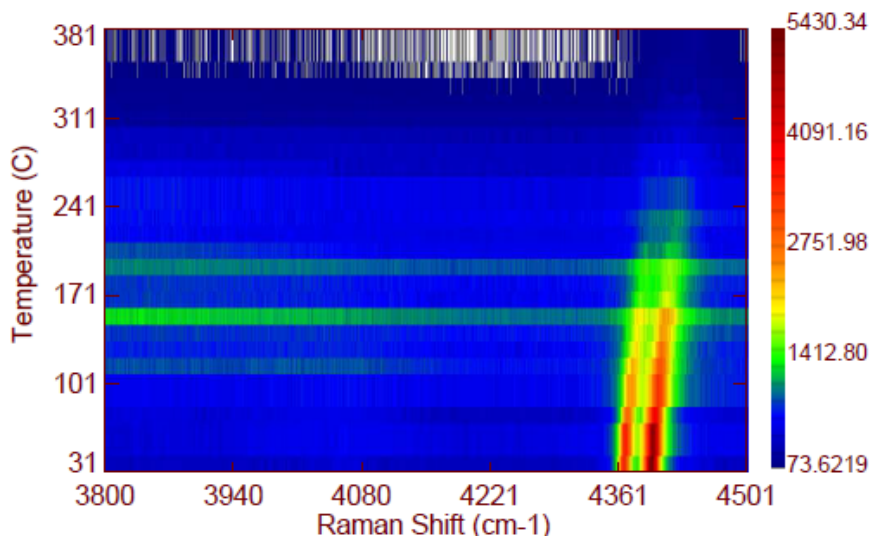


Fig. 3. Colour plot representing the evolution of Raman spectra of  $\text{Li}_1\text{MgN}_2\text{D}_3$  versus temperature (x-axis represent the Raman shift, the y-axis the temperature).

### Phase transformations in $\text{Ca}(\text{BH}_4)_2$

$\text{Ca}(\text{BH}_4)_2$  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 is still unclear. In this experiment *in-situ* measurements on powders prepared by different synthesize methods were performed.

#### $\gamma/\beta\text{-Ca}(\text{BH}_4)_2$ and decomposition product phases

Based on data from a previous measurement on BM01B a structure model for a hitherto unknown intermediate Ca-B-H containing phase has been proposed. The formation of this phase seems to depend heavily on experimental conditions, and in this MAR-measurement the decomposition behavior of  $\text{Ca}(\text{BH}_4)_2$  was studied by using different conditions such as different heating rates, additives in the powder and effect of cooling after heating to selected temperatures. The earlier observed Ca-B-H containing intermediate phase prepared at IFE could not be observed in any of these measurements.

#### Phase transformations of $\alpha\text{-Ca}(\text{BH}_4)_2$

Previous results from *in-situ* measurements on  $\alpha\text{-Ca}(\text{BH}_4)_2$  show several polymorphous phase transformations prior to desorption of hydrogen. In addition to the first-order phase transformation from  $\alpha\text{-Ca}(\text{BH}_4)_2$  to  $\beta\text{-Ca}(\text{BH}_4)_2$ , what is believed to be a second order phase transformation is observed prior to the formation of the so far undetermined modification called  $\delta\text{-Ca}(\text{BH}_4)_2$ . In the present MAR-measurement the powder was heated using a different heating rate than earlier. By comparing these two data sets we hope to be able to describe in more detail the phase transformation behavior of this material and to use this knowledge to find the right conditions for synthesize of the uncharacterized  $\delta\text{-Ca}(\text{BH}_4)_2$ .

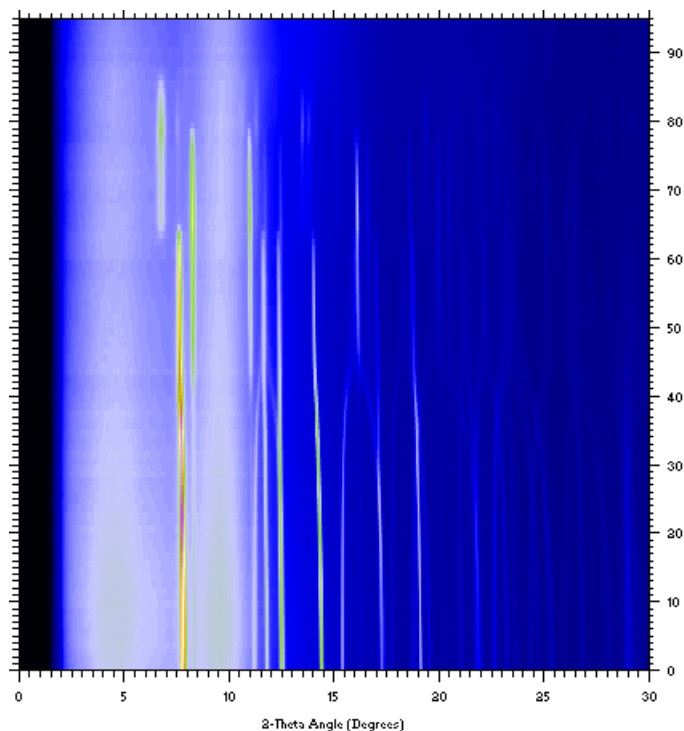
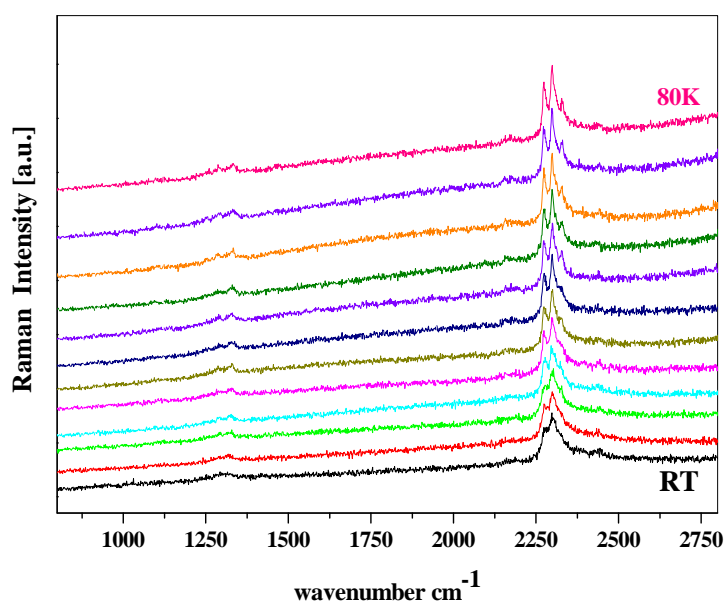


Fig. 4. Phase transformation and thermal decomposition of  $\alpha$ -Ca(BH<sub>4</sub>)<sub>2</sub>

### New polymorph of Ca(BH<sub>4</sub>)<sub>2</sub>

A new polymorph modification of Ca(BH<sub>4</sub>)<sub>2</sub> was produced by ball milling LiBH<sub>4</sub> and CaCl<sub>2</sub> at room temperature. LiCl is formed as a side product. The work on the structure identification of the Ca(BH<sub>4</sub>)<sub>2</sub> phase using high-resolution data collected at BM01B is progressing but has proven to be difficult. In this experiment, in situ Raman spectroscopy at low temperature was performed as an additional technique. Due to dynamical disorder at room temperature it is suitable to perform Raman spectroscopy at low temperature in order to identify clearly Raman modes. The experiment was carried out while cooling from room temperature to 80K. Fig. 5 shows changes of the Raman spectra with cooling. Raman modes at 80K are clearly resolved compare to those observed at room temperature. The bands in the range 2200 – 2500 cm<sup>-1</sup>, correspond to the stretching modes of -BH<sub>4</sub> group and those between 1250 and 1350cm<sup>-1</sup>



belong to the bending region. Further work supported by DFT calculation will be performed using the Raman spectra after solving the structure of the unknown Ca(BH<sub>4</sub>)<sub>2</sub>. SR-PXD patterns were collected simultaneously with Raman spectra during cooling. There are no phase transitions detected at low temperature. Only shrinking of the crystal lattice is observed (Fig. 6). The experiment confirms that the unknown phase is indeed a borohydrides.

Fig. 5. Raman spectra vs temperature of unknown (CaBH<sub>4</sub>)<sub>2</sub> + LiCl

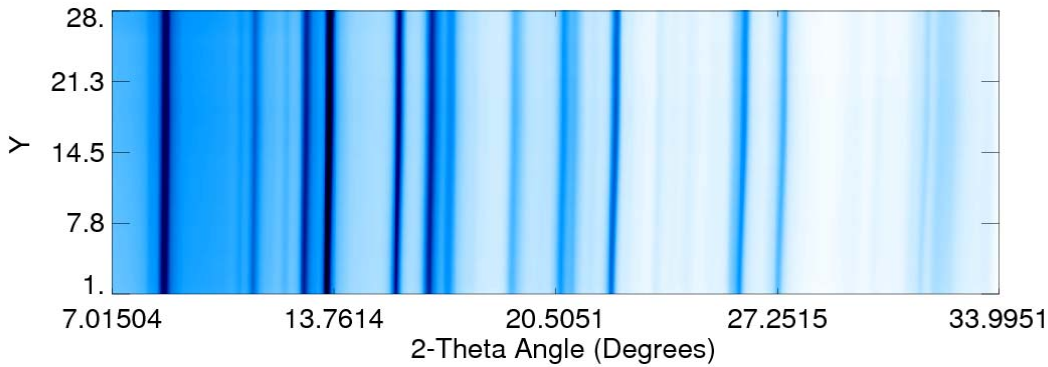


Fig.6. 2D plot of SR-PXD pattern of  $\text{Ca}(\text{BH}_4)_2 + \text{LiCl}$  during cooling to 80K

### Hydride formation in Mg-based ternary systems

Further investigations have been carried out on the hydride formation in mechanically activated –i.e. ball milled – Mg-based ternary systems.

In the  $(\text{Mg}_{0.8}\text{Ti}_{0.2})_2\text{Fe}$  system two samples were investigated: One was produced by reactive milling in a  $\text{H}_2$  atmosphere (50 bar). For the second powders ball milled in Ar were annealed in  $\text{H}_2$  at 325 °C and 30 bar.

*In-situ* SR-PXD showed (Fig. 7) that the reactively milled sample consisted of  $\text{Mg}_2\text{FeH}_6$ ,  $\text{TiH}_2$  and a Fe-rich Fe-Ti solid solution. The broad diffraction peaks observed for all the phases indicate the nanocrystalline nature of the composite powder. Upon heating (2 K/min),  $\text{Mg}_2\text{FeH}_6$  decomposes into Mg and Fe, whereas  $\text{TiH}_2$  remains stable up to 400 °C. A more

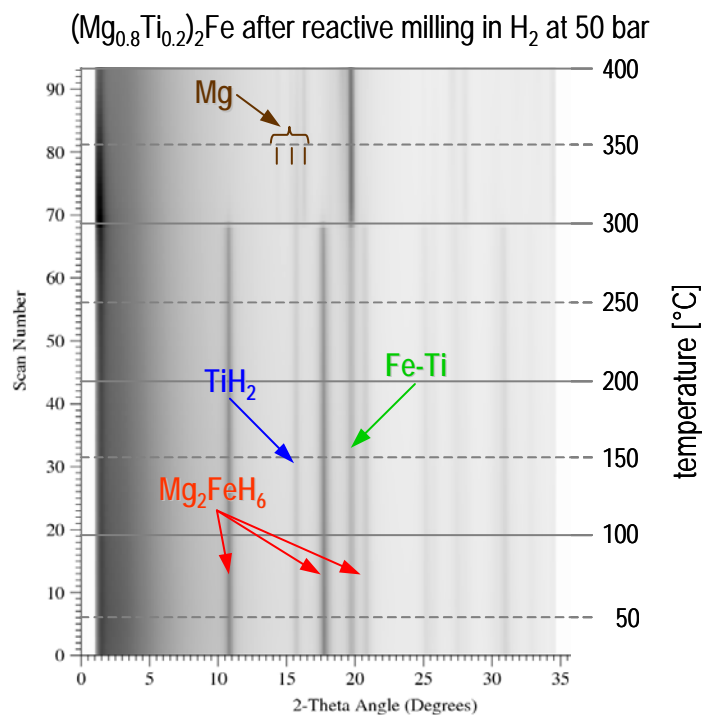


Fig. 7. *In-situ* PXD analysis of the desorption for  $(\text{Mg}_{0.8}\text{Ti}_{0.2})_2\text{Fe}$  reactively milled in 50 bar  $\text{H}_2$ .

detailed analysis of data (quantitative analysis of the constituent phases, determination of structural parameter) is planned to investigate the role of the Fe-Ti solid solution in the hydrogen desorption reaction.

The data shown above were compared with the hydrogenated sample obtained by ball milling in Ar and annealing in H<sub>2</sub> at 325 °C and 30 bar (Fig. 8). In this case, the as-hydrogenated powder consists mainly of MgH<sub>2</sub> and amorphous Fe-Ti, the latter being formed after ball milling in Ar. Diffraction peaks of Mg<sub>2</sub>FeH<sub>6</sub> can also be observed. Upon heating (2 K/min), nucleation and growth of Mg is detected at 300 °C, indicating the beginning of hydrogen desorption. The desorption reaction is completed at 375 °C, as the diffraction peaks for MgH<sub>2</sub> and Mg<sub>2</sub>FeH<sub>6</sub> are no longer observed. The comparison with the data for the reactively milled powder points out the benefits of using high-pressure reactive milling to obtain destabilized hydride phases.

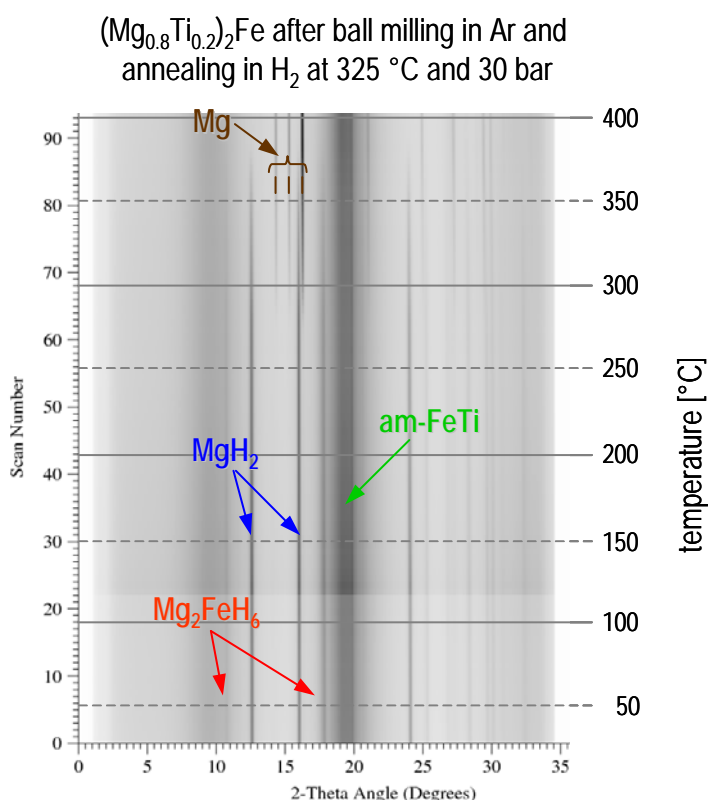


Fig. 8. *In-situ* PXD analysis of the desorption for (Mg<sub>0.8</sub>Ti<sub>0.2</sub>)<sub>2</sub>Fe ball milled in Ar and annealed in H<sub>2</sub> at 325 °C and 30 bar.

Finally, investigations were carried out on a Mg<sub>2</sub>Fe<sub>0.5</sub>Co<sub>0.5</sub> powder sample which was first ball milled in Ar and subsequently annealed in H<sub>2</sub> at 325 °C and 30 bar (Fig. 9). The as-hydrogenated sample consists of a cubic K<sub>2</sub>PtCl<sub>6</sub>-type phase which likely corresponds to the mixed transition metal complex hydride Mg<sub>2</sub>(FeH<sub>6</sub>)<sub>0.5</sub>(CoH<sub>5</sub>)<sub>0.5</sub>. Neutron powder diffraction analysis on the deuterated compound is necessary to confirm the presence of the quaternary hydride. MgH<sub>2</sub> and FeCo are also detected in the as-hydrogenated powder, together with

traces of orthogonal  $\text{Mg}_6\text{Co}_2\text{H}_{11}$ . The phase composition for this sample is significantly different from the  $\text{Mg}_2\text{Fe}_{0.5}\text{Co}_{0.5}$  sample processed by reactive milling in 50 bar  $\text{H}_2$  (see May 2008 report). The reactively milled sample consists of only two phases:  $\text{Mg}_2(\text{FeH}_6)_{0.5}(\text{CoH}_5)_{0.5}$  and  $\text{FeCo}$ . Upon heating at 2 K/min (see Fig. 9), nucleation and growth of  $\text{Mg}$  is observed at 250 °C, suggesting the beginning of the hydrogen desorption reaction. At 300 °C,  $\text{MgH}_2$  and  $\text{Mg}_6\text{Co}_2\text{H}_{11}$  are no longer detected and the intensities of the diffraction peaks from  $\text{Mg}_2(\text{FeH}_6)_{0.5}(\text{CoH}_5)_{0.5}$  have decreased significantly. At the same time, the peaks for  $\text{Mg}$  and  $\text{FeCo}$  have grown. Above 300 °C, the desorption reaction proceeds slowly and at 400 °C  $\text{Mg}_2(\text{FeH}_6)_{0.5}(\text{CoH}_5)_{0.5}$  is still detected. It is worth mentioning that the desorption reaction for the reactively milled sample is completed at about 325 °C. This point out an increased stability of the quaternary hydride obtained by annealing in  $\text{H}_2$  the powders ball milled in Ar.

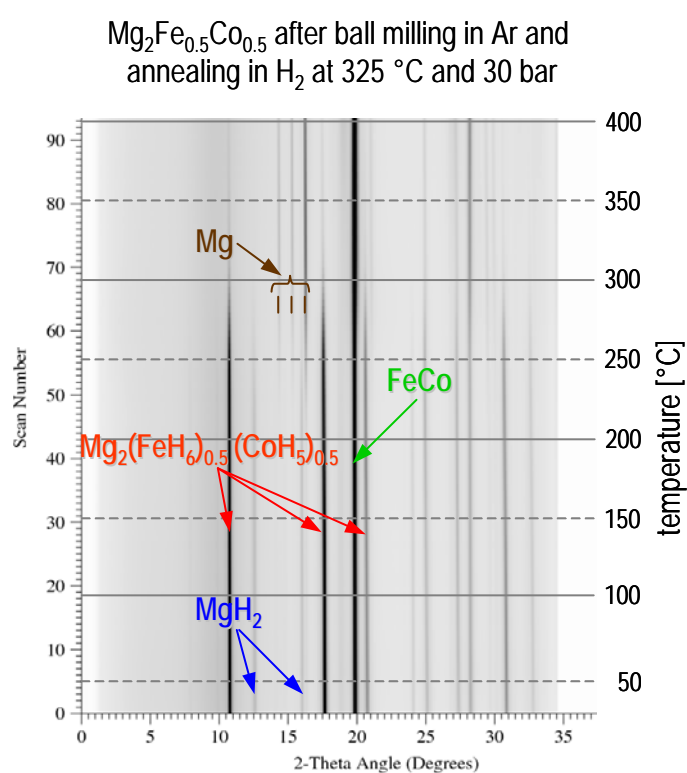


Fig. 9. *In-situ* PXD analysis of the desorption for  $\text{Mg}_2\text{Fe}_{0.5}\text{Co}_{0.5}$  ball milled in Ar and annealed in  $\text{H}_2$  at 325 °C and 30 bar