

STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE

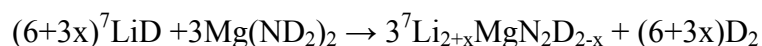
Preliminary report – In-situ SR-PXD measurement: 01-02-772 (April 2008) Beamline BM01A

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${}^7\text{Li}_{1+x}\text{MgN}_2\text{D}_{3-x}$

Chen *et al.* (Nature **420** (2002) 302) reported in 2002 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.* (J. Alloys Compd. **381** (2004) 284) have shown that a mixture of LiNH_2 and MgH_2 requires a lower working temperature and suggested the formation of $\text{Li}_2\text{Mg}(\text{NH})_2$. Several related *non-stoichiometric* phases, ${}^7\text{Li}_{2+x}\text{MgN}_2\text{D}_{2-x}$, with $x = -1, 0, 0.66$ and 1 , were synthesised with the direct reaction.



The isotope ${}^7\text{Li}$ was used to reduce neutron absorption in the sample.

The thermal decomposition of ${}^7\text{Li}_{2+x}\text{MgN}_2\text{D}_{2-x}$ with $x=0$ and 0.66 were investigated by the in-situ SR-PXD. Simultaneous Raman spectroscopy was been performed during the desorption process. The materials were inserted in a sapphire capillary and place in dynamical primary vacuum. The sample was heated with a ramping rate of $2\text{C}^\circ/\text{min}$ and diffraction patterns where collected every 2 minutes.

Under dynamical vacuum the samples exhibits a characteristic transition temperature of about 260°C both observed in the diffraction patterns and Raman shift. Preliminary high resolution SR-PXD data suggest that the unit cell parameter for $x = 0.66$ is bigger than the one previously reported.

PND data were recorded at PUS for the four different compositions.

The analysis of the collected SR-PXD and PND data are still in progress.

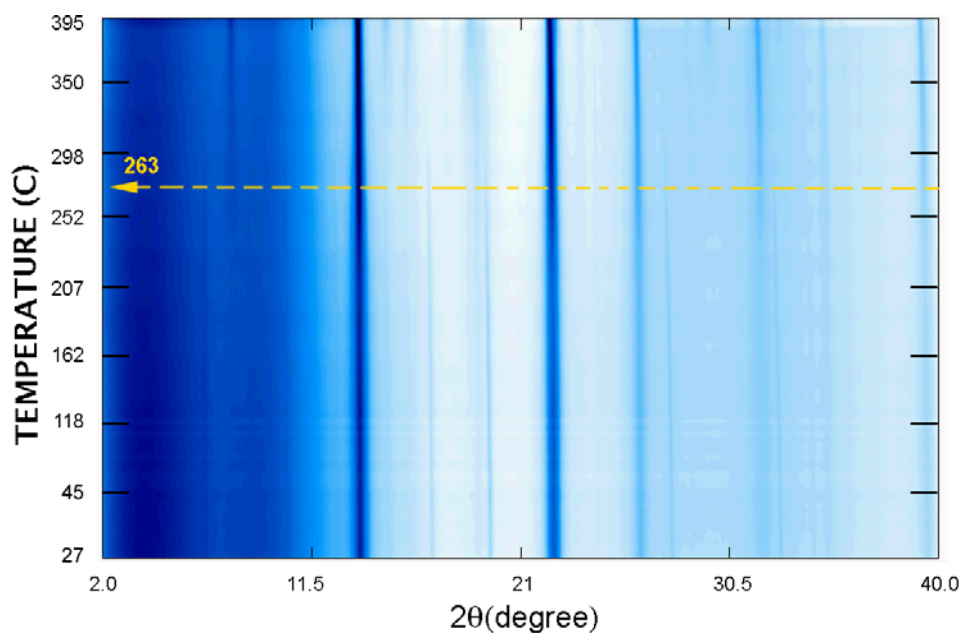


Fig. 1. Color plot representing the evolution of $\text{Li}_2\text{MgN}_2\text{D}_2$ diffraction pattern versus temperature (x-axis represent the 2θ the y-axis the temperature and the colour the intensity).

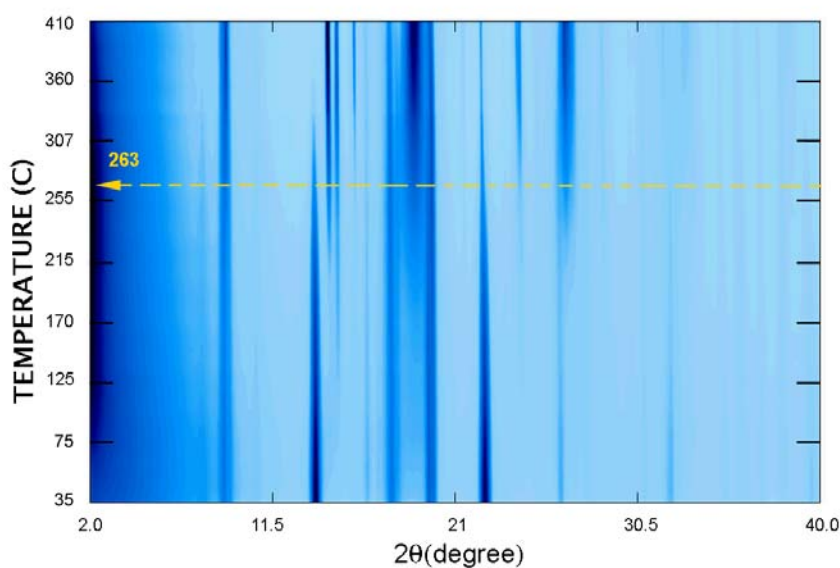


Fig 2: Color plot representing the evolution of $\text{Li}_{2.66}\text{MgN}_2\text{D}_{1.66}$ diffraction pattern versus temperature (x-axis represent the 2θ (degree), the y-axis the temperature and the color the intensity).

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

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

LiAl(NH₂)₄

The amides LiAl(NH₂)_x and NaAl(NH₂)_y were synthesized by a mechanochemical reaction between liquid ammonia (NH₃) and the alanates LiAlH₄ and NaAlH₄, respectively. The milling conditions were optimized to achieve the highest possible amide content (x and y). It is clear that y was 4, which is the highest known amide content in this group of materials. x was somewhat lower, probably close to 2. The materials were characterized by a combination in-situ synchrotron SR-PXD and Raman scattering.

The material was inserted in a sapphire capillary and placed under dynamical primary vacuum. The sample was heated with a ramping rate of 2°C/min and diffraction patterns were collected every 2 minutes over a range of 40° in theta. The temperature evolution of NaAl(NH₂)₄ is illustrated in Fig. 3. The sample exhibits two characteristic transitions at 110°C and 238°C; observed both in the diffraction patterns and Raman shift (see Fig. 3 and 4). Up to 110°C NaAl(NH₂)₄ remains crystalline and its structure is described in *P*2₁/*c* space group (Fig. 5). The transition temperatures are in agreement with TDS measurements. They correspond to the two consecutive discharges of 0.5 NH₂ and 1.5 NH₂ mole per formula units in NaAl(NH₂)₄. Above 110°C the sample presents short-range ordering characterized by broad diffuse scattering around 4.2 and 1.2 Å. Raman data indicated that [Al(NH₂)₄]⁻ remains up to the second transition at 238°C and are not anymore observed at 300°C (Fig. 4).

The analysis of the collected data are still in progress.

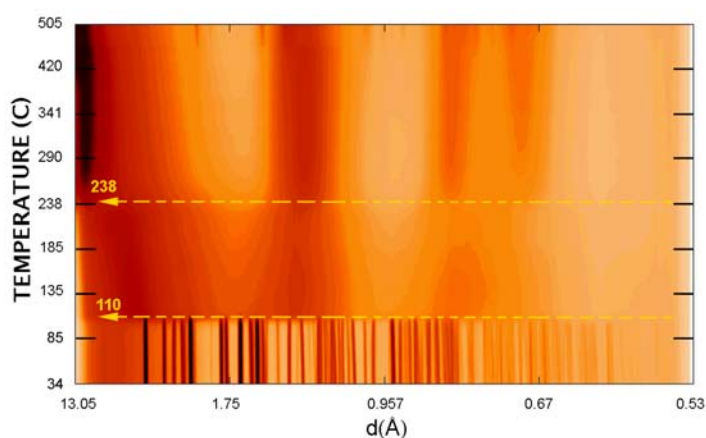


Fig. 3. Color plot representing the evolution of NaAl(NH₂)₄ diffraction pattern versus temperature (x-axis represent the d-space, the y-axis the temperature and the color the intensity).

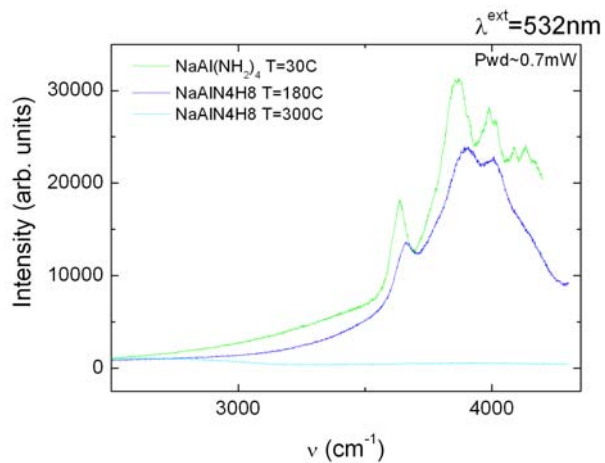


Fig 4: Evolution of the Raman spectra of $\text{NaAl}(\text{NH}_2)_4$ taken at 3 characteristic temperatures (30, 180, 300°C) with $\lambda^{\text{ext}}=532\text{nm}$. The Raman shift is focused in the region of 2000-4300 cm^{-1} . The incident power is of about 0.7mW.

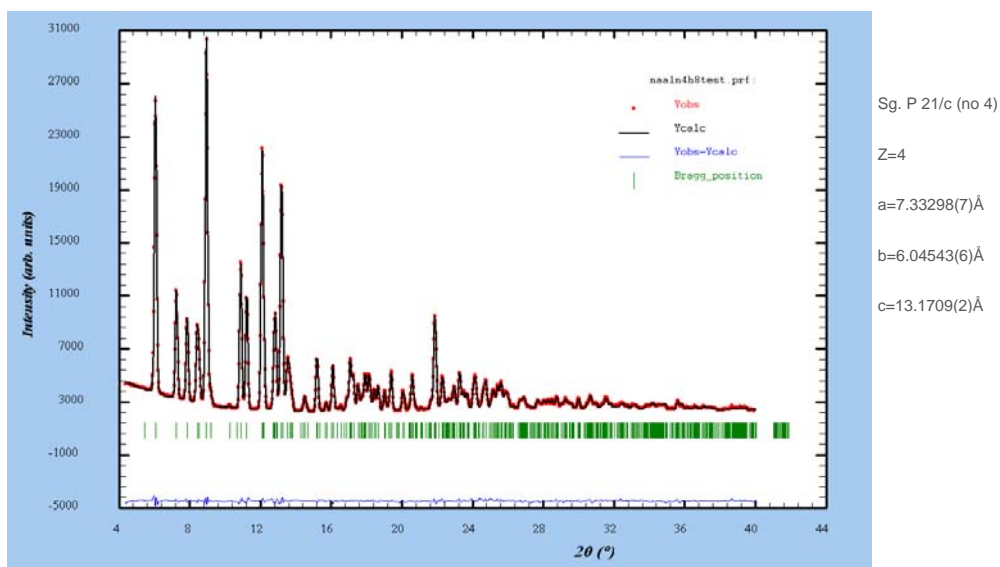


Fig. 5: Rietveld refinement result at room temperature of $\text{NaAl}(\text{NH}_2)_4$.

Mg(BH₄)₂

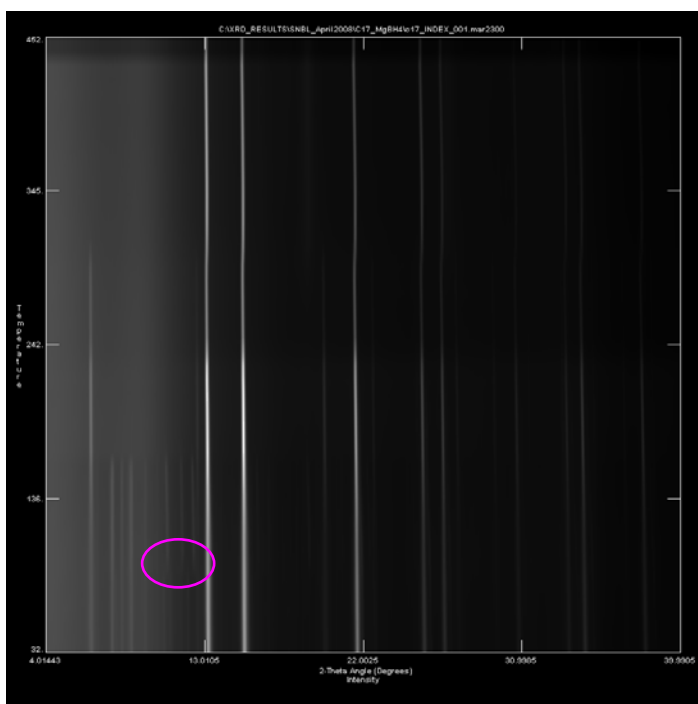
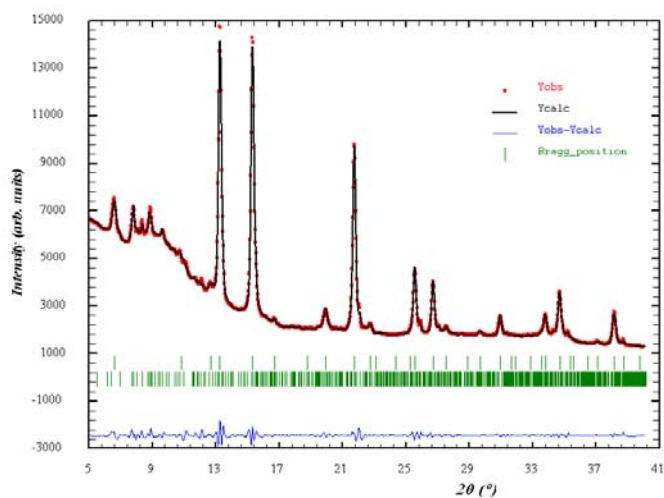


Fig. 6 (top) Diffraction profile of cryomilled Mg(BH₄)₂ and Li₂MgCl₄; (bottom) 2D plot of decomposition of LT Mg(BH₄)₂

Mg(BH₄)₂ was produced by cryomilling LiBH₄ and MgCl₂. Thermal desorption spectroscopy (TDS) carried out on the product with 5°C/min shows 5 stages of desorption. The sample was studied at SNBL (MAR) with the same heating rate.

In the beginning of the reaction we can see the diffraction peaks of low temperature phase of Mg(BH₄)₂ (second simulated phase in the Fig. 6 (top)) and Li₂MgCl₄. Upon heating the diffraction peaks of LT phase disappear at about 170°C. At about 100°C a phase transition for the LT Mg(BH₄)₂ phase is observed before the desorption started. This phase transition was not detected before with TDS. In the later stage of the desorption reaction at 180°C some of the peaks of Mg(BH₄)₂ disappear and transformation to amorphous state is clearly observed. Raman spectroscopy was carried out in order to understand those structural changes during desorption. Data analysis is still in progress.

Ca(BH₄)₂ and decomposition product phases

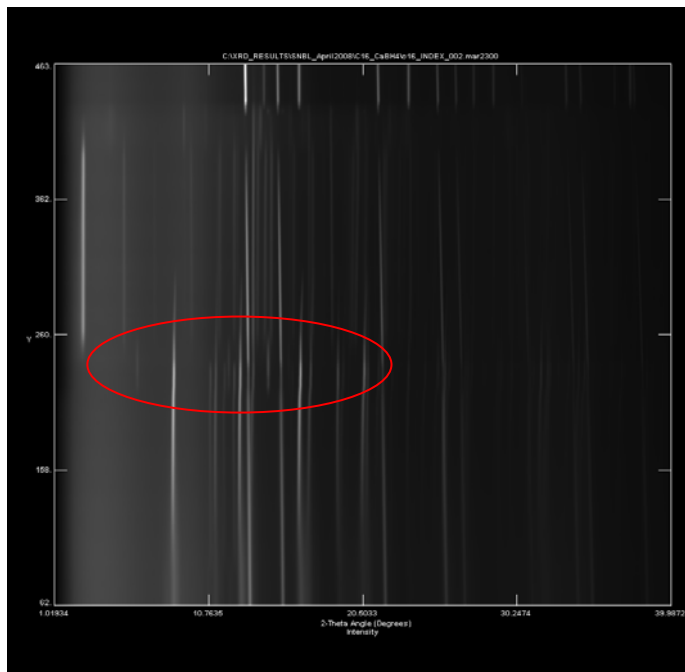
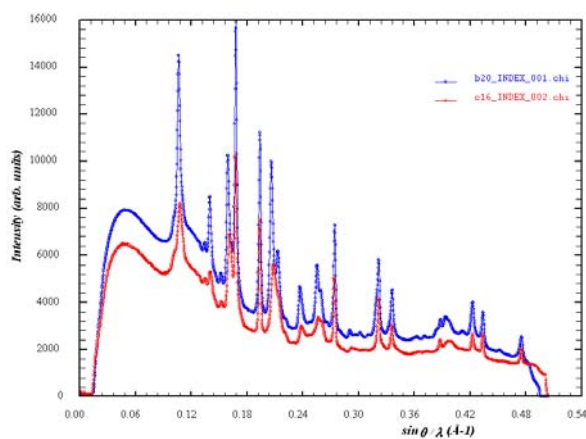
Ca(BH₄)₂ is considered as an attractive hydrogen storage material due to high gravimetric capacity and expected thermodynamic properties suitable for mobile hydrogen storage applications. However, the decomposition route is still unclear.

A challenge in the investigation of the decomposition route for this material is the formation of X-ray amorphous decomposition product phases and high sensitivity to experimental conditions. In this investigation, the thermal decomposition of α -Ca(BH₄)₂ preheated to 350°C was studied using quartz capillary and a heating rate of 2°C/min. Bragg peaks from the so-called “ δ ”-phase mentioned in previous reports are observed, as are peaks from the unknown phase observed in the measurement using glass capillary and γ/β -Ca(BH₄)₂ as starting material. This unknown phase was however **not** observed in our previous measurement (december 2007) using quartz capillaries.

By combining the results from the 3 different experiments at BM01 on this material, good information on possible elemental composition for the different observed unknown phases can hopefully be obtained.

Ca(BH₄)₂ from ball milling

An unknown modification of Ca(BH₄)₂ was produced by cryomilling LiBH₄ and CaCl₂ and thermal decomposition was studied at MAR. LiCl was formed as a side product, Fig. 7 shows MAR data for starting material of ball milled and cryomilled powder. The peaks for the cryomilled material are more broad than the peaks for ball milled material. 2D plot of cryomilled unknown phase of Ca(BH₄)₂ shows clearly the phase transition, which was detected before with TPD at about 250°C. It also interacts with LiCl at certain stage of the decomposition reaction. Raman measurements were also performed on that sample. Data analysis is in progress.



Figur 7 – (left) comparison between MAR-data for ball milled (blue) and cryomilled (red) Ca(BH₄)₂; (right) 2D plot for thermal decomposition of cryomilled Ca(BH₄)₂

Hydride formation in Mg-based ternary systems

Hydride formation in mechanically activated (i.e. ball-milled) Mg-based ternary systems (Mg-Ti-Ni, Mg-Ti-Al, Mg-Ti-Fe, and Mg-Fe-Co) was investigated. $(\text{Mg}_{0.8}\text{Ti}_{0.2})_2\text{Ni}$ and $(\text{Mg}_{0.8}\text{Ti}_{0.2})_2\text{Fe}$ powders ball-milled in Ar were analysed at BM01B in May 2008. Such powders are precursors that will be hydrogenated in a conventional Sievert apparatus. In April 2008 $\text{Mg}_2(\text{Fe}_{0.5}\text{Co}_{0.5})$ powders which were ball milled in a H_2 (D_2) atmosphere at 50 bar were analysed at BM01A. Reactive milling results in the formation of a novel cubic quaternary hydride, which upon heating ($2^\circ\text{C}/\text{min}$) in vacuum decomposes at about 320°C (Fig. 8). Neutron diffraction analysis is currently carried out at IFE to confirm the structure of the Mg-Fe-Co hydride. The above results will be presented at international conferences this coming summer.

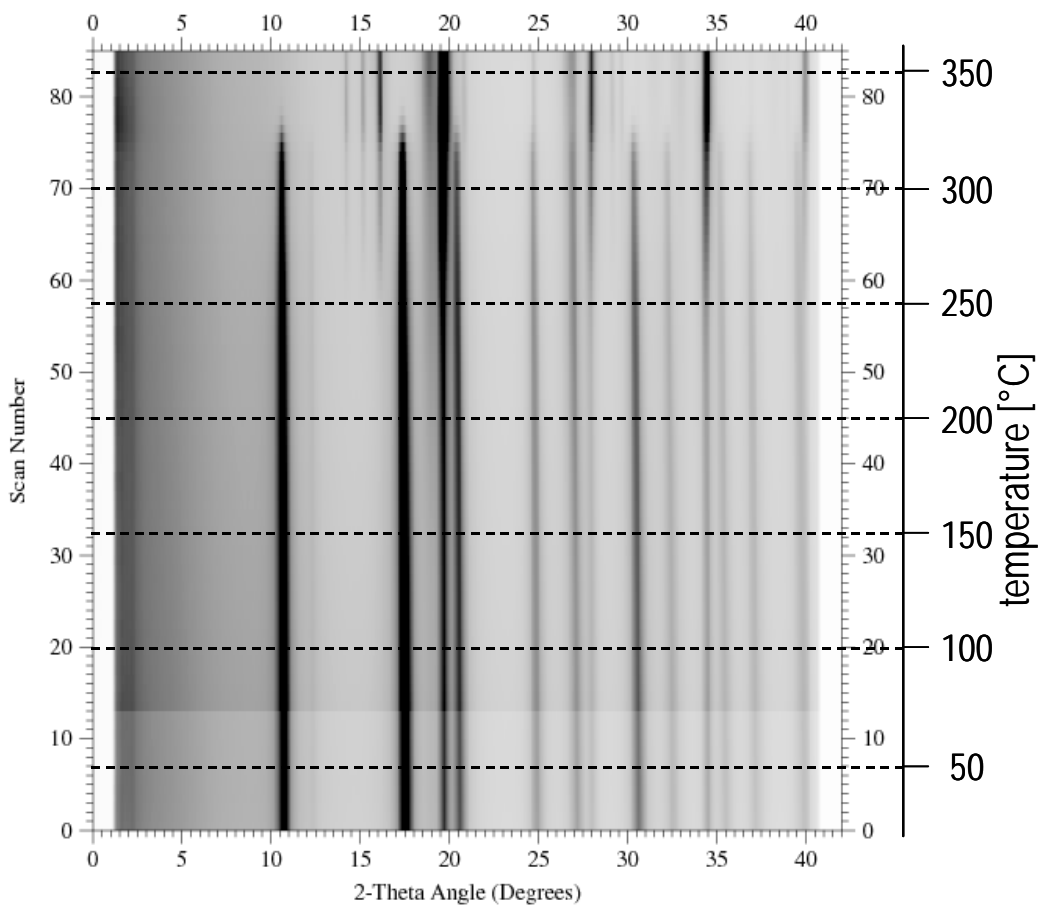


Fig. 8 In-situ formation of novel quaternary Mg-Fe-Co-H phase.

LiCl + 10vol% MgH₂ and LiCl + 5vol% MgH₂

Highly dispersed MgH₂ in a LiCl matrix was synthesised by ball milling LiH and MgCl₂. Laboratory PXD was used to investigate the phase content of the mixture, but the signal from MgH₂ was too weak to be distinguished from the background and the strong peaks from the LiCl matrix. With the data from the SR-PXD measurements it was possible to see different Mg-compounds together with Fe contaminant from the milling balls.

The samples were heated from 40 °C to 350 °C with a constant rate of 4 °C/min.

Decomposition of MgH₂ happened from 280 °C. Unwanted formation of MgO started at around 140 °C.

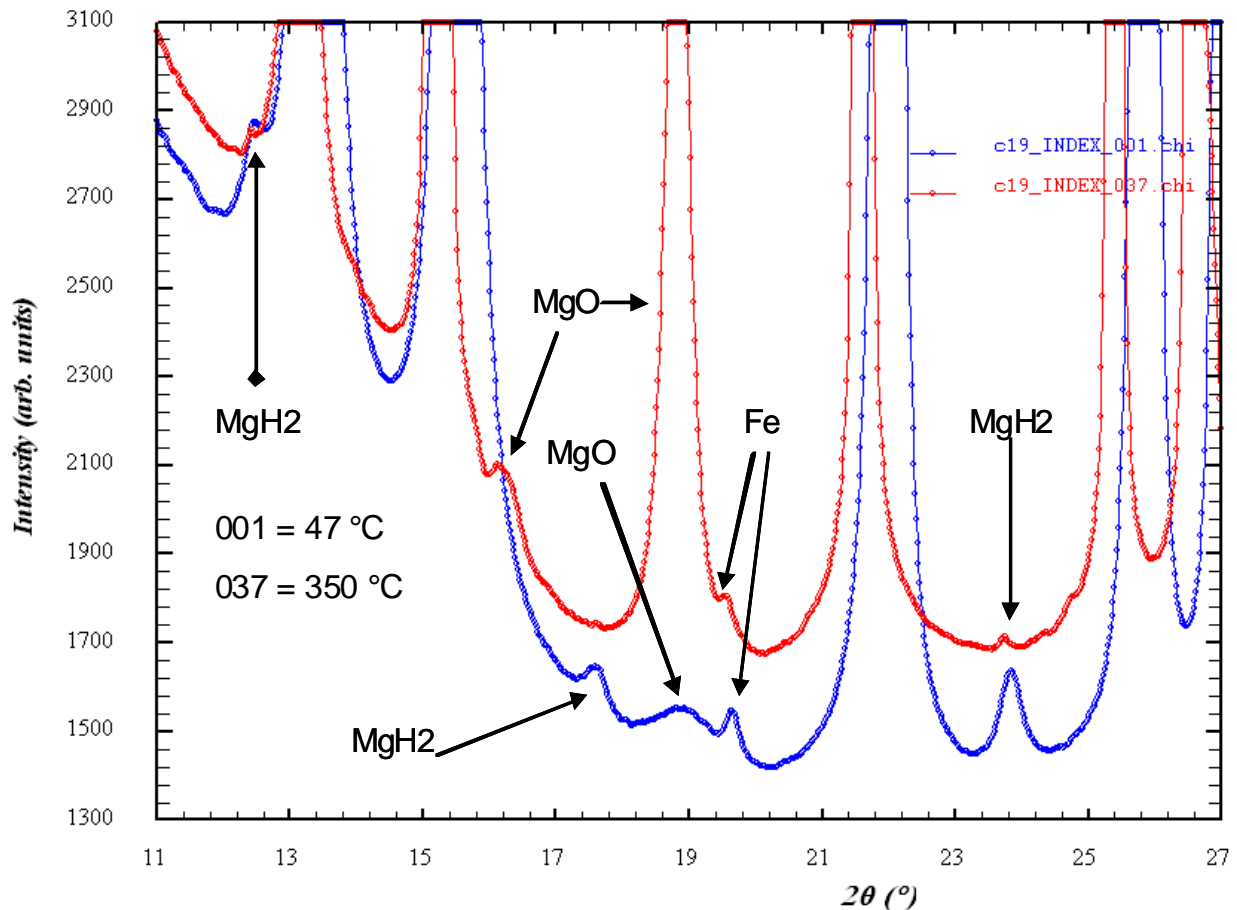


Fig. 9: XRD patterns from the sample with 10 vol% MgH₂ at 47°C and 350°C.