

1. *Publishable Summary*

1.1. *Summary description of the project context and the main objectives*

At present there is **no hydrogen storage system available fulfilling all requirements for use especially in mobile applications**: 1. high storage density, 2. temperatures and heats of operation compatible with PEM fuel cells, 3. high hydrogen loading and unloading rates in the range of a few minutes and 4. low system costs. FLYHY focused especially on the first three points by

- (i) exploiting findings on tailoring of materials thermodynamics by anion substitution in alane, borohydrides and Reactive Hydride Composites, in order **to achieve a breakthrough in the thermodynamic hydrogen sorption properties of these materials exhibiting the highest hydrogen capacities known at present**,
- (ii) obtaining an **in depth scientific understanding of the sorption properties** of the substituted compounds by extended structural and thermodynamical characterisation and modelling, to optimise the investigated materials,
- (iii) determining **tank relevant materials properties** like e.g. compaction behaviour and thermal conductivity of selected compounds,
- (iv) **scaling-up materials production** and doing first tests in a **prototype tank** together with a HT PEM fuel cell.

Tailoring of physical properties such as thermodynamics, i.e. working temperatures, and reaction kinetics, was achieved **by adding halogens to the storage materials** and employing **novel paths of materials synthesis**.

Substitution of an element, i.e. hydrogen, with a more electronegative element in a functional group or a complex, changes the bond strength of the remaining elements and thereby may facilitate release and possibly uptake of hydrogen. We have chosen the most electronegative element, fluorine, as the focus of this research project and also its group members in the periodic table, chlorine, bromine and iodine. By partially substituting halogens for hydrogen or functional groups like $(\text{BH}_4)^-$, the enthalpy of reaction of too stable and too unstable high capacity hydrogen storage materials was to be changed to the desired range of -30 to -40 kJ/(mol H_2), while retaining as much hydrogen storage capacity as possible.

In the 2nd period of FLYHY, work focused on:

Borohydrides, which exhibit some of the highest theoretical gravimetric hydrogen contents (e.g. LiBH_4 18.5 wt%), but for practical use are much too stable or too unstable, respectively, and

Reactive Hydride Composites (RHC) (with a reversible capacity up to 11 wt% ($\text{LiBH}_4 + \text{MgH}_2$)), having the unique advantage - compared to all other methods for modifying hydrogen storage materials - that upon reaction of two or several hydrides in the composite, an average hydrogen storage capacity together with a substantially reduced reaction enthalpy is achieved.

The objectives of the FLYHY project in the 2nd period were to obtain more fundamental knowledge on

- (i) **novel routes for reproducible and safe materials synthesis**, (ii) the **influence of the modified materials structures on hydrogen sorption properties**, (iii) **assessment of the different storage materials** with regard to raw materials and production cost and necessary expense for storage tank construction with regard to tank capacity, heat management and tank safety, (iv) hydrogen sorption and other properties of larger amounts of powders, and long term stability, (v) (if promising materials are available at milestone in month 30) **upscaled production processes as well as materials behaviour in a laboratory prototype test tank**, giving input for future improvements in the time following this project.

1.2. Description of the work performed since the beginning of the project and the main results achieved so far

New route for synthesis of halogen free α -Ca(BH₄)₂

A new method for synthesis of Ca(BH₄)₂ with very high elemental- and phase purity was developed by Aarhus University, and is currently being patented. Powder X-ray diffractograms of the synthesis products (Fig 1.) demonstrate the viability of the method. Besides the advantage of synthesis of very pure material (e.g. for fundamental scientific investigations) the method offers a significant cost advantage compared to commercially available borohydrides.

Solid state synthesis of Al(BH₄)₃ and Zr(BH₄)₄

The unstable borohydride systems Al(BH₄)₃ and Zr(BH₄)₄ could be synthesized from AlCl₃ or ZrCl₄ mixed with stable borohydrides LiBH₄, NaBH₄, Ca(BH₄)₂ or Mg(BH₄)₂ via a metathesis reaction.

The initial characterization generally showed lower decomposition temperatures compared to the pure metal borohydride material. A very large weight loss was often observed, indicating that other gases than H₂ were released (Fig. 2). Complex two- and three-step decomposition pathways were observed.

Also single crystals of Zr(BH₄)₄ could be synthesized by the metathesis reaction of LiBH₄-ZrCl₄ using high energy ball milling followed by vapour deposition. Their structure could be solved being a cubic unit cell of space group *P*-43*m* and unit cell parameter *a* = 4.8387(4) Å (at *T* = 100 K). Furthermore, an *in situ* SR-PXD study verifies the melting point of Zr(BH₄)₄ at 29 °C. The structure was also calculated by *ab initio* modelling.

Reaction pathway of fluorinated Ca-based RHC's

Reaction enthalpy and activation energy of the dehydrogenation reaction in the system CaF₂+3CaH₂+4MgB₂ were determined from DSC experiments. The reaction enthalpy was estimated at ca. 49 kJ/(mol H₂) and later confirmed by preliminary PCI measurements. This has to be compared with that of pure Ca(BH₄)₂ of 69 kJ/(mol H₂) as determined by PCI measurements in FLYHY. It was found, that F addition changes the reaction path compared to the pure CaH₂ + MgB₂ significantly and new phases like Ca₄Mg₃H₁₄ are formed, whereas continuous formation of amorphous boron and Ca₂B₁₂H₁₂ during cycling is observed to a much lesser degree than in the pure system (Fig. 3). In the long term, i.e. after the first cycle, reversible hydrogen loading and unloading seem to take place between a CaH₂-CaF₂ solid solution plus Mg, partially MgB₂ (dehydrogenated state) and Ca₄Mg₃H₁₄ plus CaF₂ (hydrogenated state).

Fluorine substitution observed by *in situ*-SR-PXD

LiBH₄-LiBF₄ mixtures were examined using *in situ*-SR-PXD techniques and analysed by Rietveld refinement. Refinements indicate that F substitutes directly for H in the BH₄ unit, however, this effect is observed only for the hexagonal LiBH₄ polymorph, thus suggesting that substitution occurs gradually as heating and decomposition progresses (Fig. 4). Decomposition of the substituted material occurs immediately as it forms. More detailed investigations are underway in order to firmly establish the occurrence of fluorine substitution.

Modelling of crystal structures and thermodynamic data

Enthalpies of mixing of a broad range of simple and borohydrides have been calculated by *ab initio* and CALPHAD methods. For selected borohydrides also chlorine and bromine substitutions have been investigated theoretically. (Fig. 5)

It is confirmed that a change in the halide substitution (i.e. Cl or Br instead of F) reduces significantly the positive enthalpy of mixing, likely because of steric effects. These conclusions are in good agreement with the experimental results obtained in FLYHY.

1.3. Expected final results and their potential impacts and use (including socio-economic impact and the wider societal implications of the project so far)

The investigations made in FLYHY point towards that fluorine incorporation is affecting the stability of the materials significantly, i.e. the decomposition temperatures have been decreased drastically, e.g. by mixing metal tetrafluoroborates with metal borohydrides, or by adding simple fluorides in the synthesis of Reactive Hydride Composites. On the other hand, the larger halides appear to mainly affect the hydrogenation properties to the extent that some improvements in reversibility have been observed. Overall, this could be interpreted as a result of two types of substitution, BH_4^- units for large halides (Cl, Br, I) and individual hydrogens for fluorine.

Still, a mixture such as $\text{NaBH}_4\text{-NaBF}_4$ exhibits the best of both worlds; strongly destabilised borohydride material, improved rehydrogenation properties and release of large amounts of hydrogen. In accordance with the different types of metal borohydrides and tetrafluoroborates available, the potential of combining different metals in these mixtures should be tested, e.g. mixing LiBF_4 with any other available metal borohydride, in order to screen optimal mixture compositions.

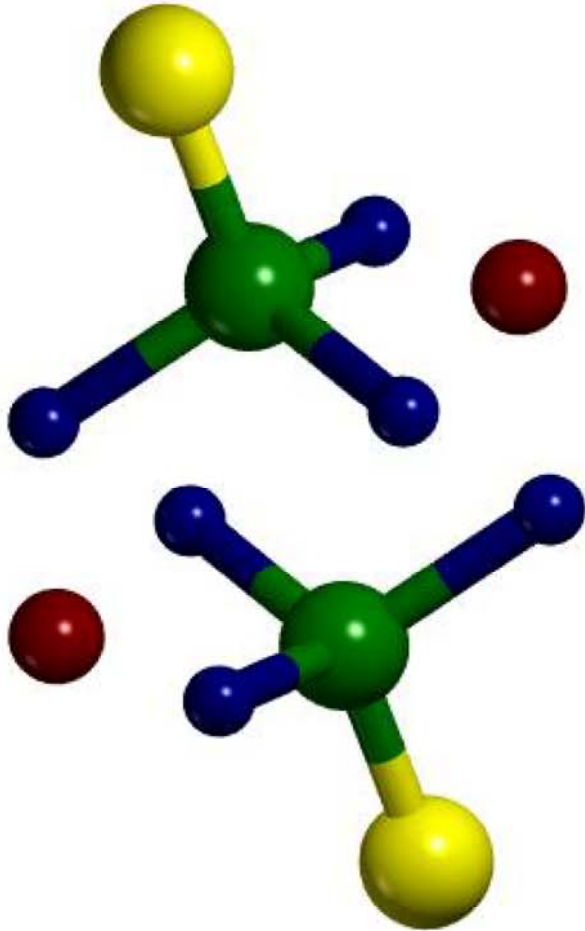
Also the findings in Reactive Hydride Composites implicate, that F not only strongly influences reaction kinetics and thermodynamics, but also can change completely the reaction pathway. Therefore more detailed investigations of the dependence of the reaction pathways on hydrogenation temperature and pressure are necessary, to fully exploit the positive effects of Fluorine addition.

The experience gathered and the synthetic method development (AU-patent) allows for easier and cheaper access to stable borohydride materials in the future. The prospect of applying the method for larger scale production is attractive and is kept in mind for the patent. The vapour deposition technique employed for the synthesis of $\text{Zr}(\text{BH}_4)_4$ could also be exploited for attempting to synthesize related unstable (less stable) metal borohydrides in the future.

In summary, FLYHY lead to a significant increase in fundamental knowledge on the positive effects of halogen substitution in high capacity storage materials, and opened up routes to follow in future optimisation of the materials. Especially interesting are also the results on stabilisation of the high temperature phases of borohydrides down to room temperature by substitution with halogens like Cl, Br or I. As found by AU and other groups worldwide, these substituted borohydrides might also find applications as room temperature solid state ion conductors in batteries of the future due to their exceptional high ion conductivity.

Whereas the developed routes for materials synthesis now can be optimised, and – provided interest from industry – scaled-up and transferred to industrial production, there is still need for more fundamental investigations on the materials themselves, finding proper additives for enhancing reaction kinetics and producing the materials from cheaper raw materials, to finally deliver a competitive hydrogen storage technology based on the materials investigated in FLYHY. The developed routes for synthesis are very suitable for industrial use by SME's.

The simple storage tank technology, employed in FLYHY, is also very suitable for manufacturing by SME's like partner TROPICAL, which is in strong contrast to the complicated manufacturing technology of composite high pressure storage tanks. Especially in stationary applications where weight is only relevant in the second line, this opens up a new market for companies being experienced in construction of e.g. pressurised steel containers and heat exchangers.



FLYHY

**Fluorine Substituted High Capacity Hydrides
for Hydrogen Storage
at Low Working Temperatures**

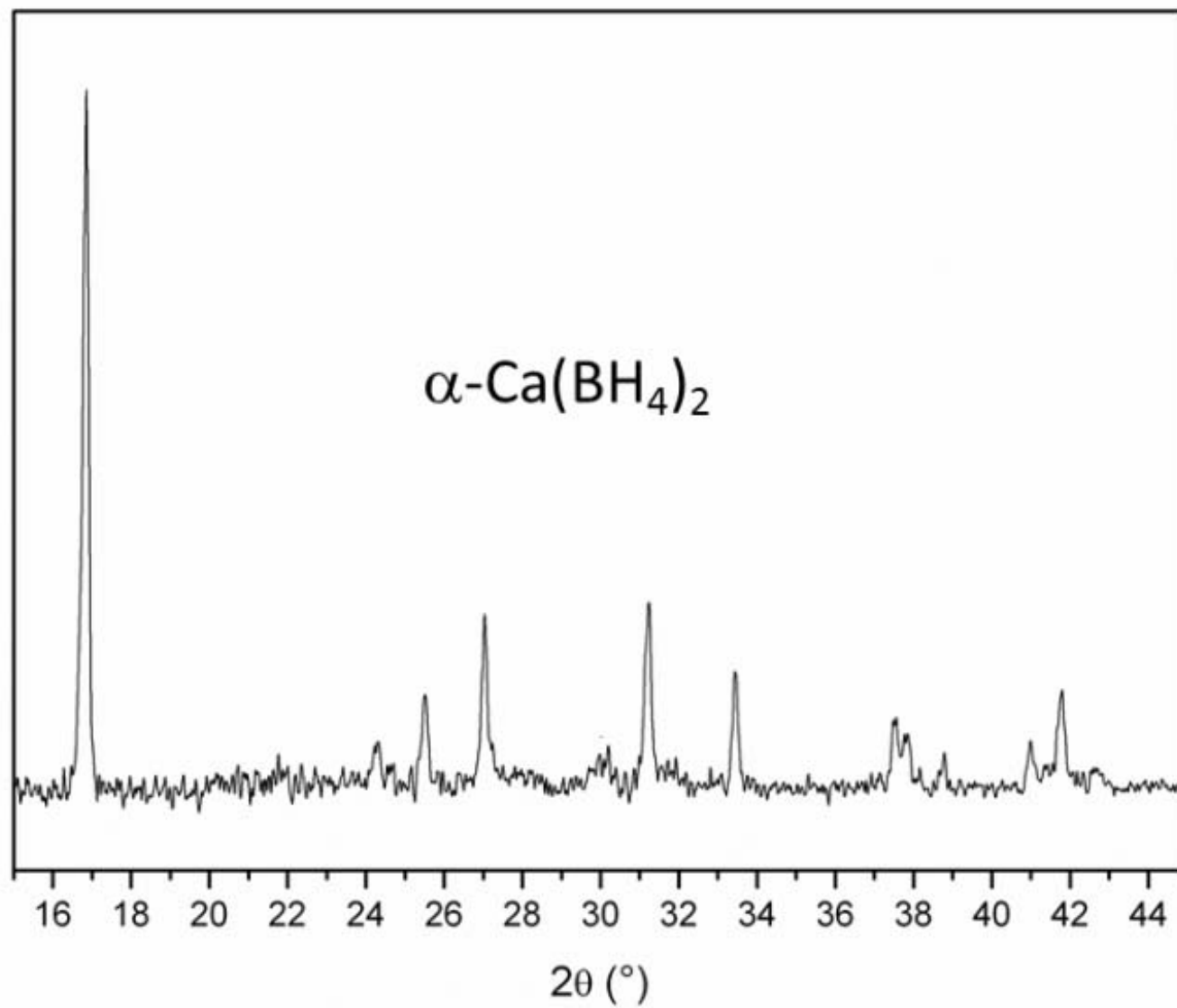


Fig. 1: Powder X-ray diffraction for as-synthesized $\alpha\text{-Ca(BH}_4)_2$, using a novel synthesis route.

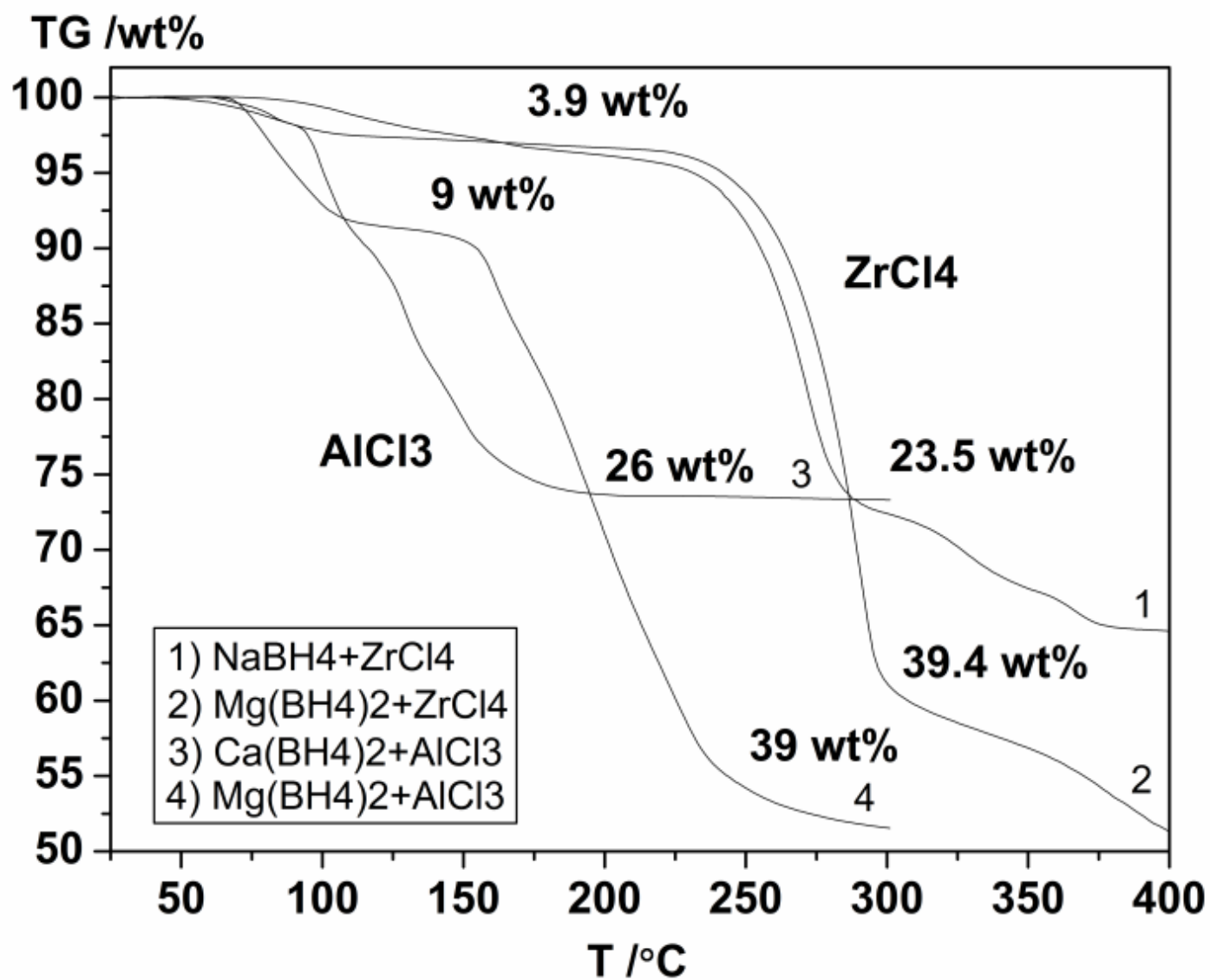


Fig. 2: TGA for a number of samples of the unstable borohydride systems heated from RT to 300, 350 or 400 °C using a heating rate of 10 °C/min

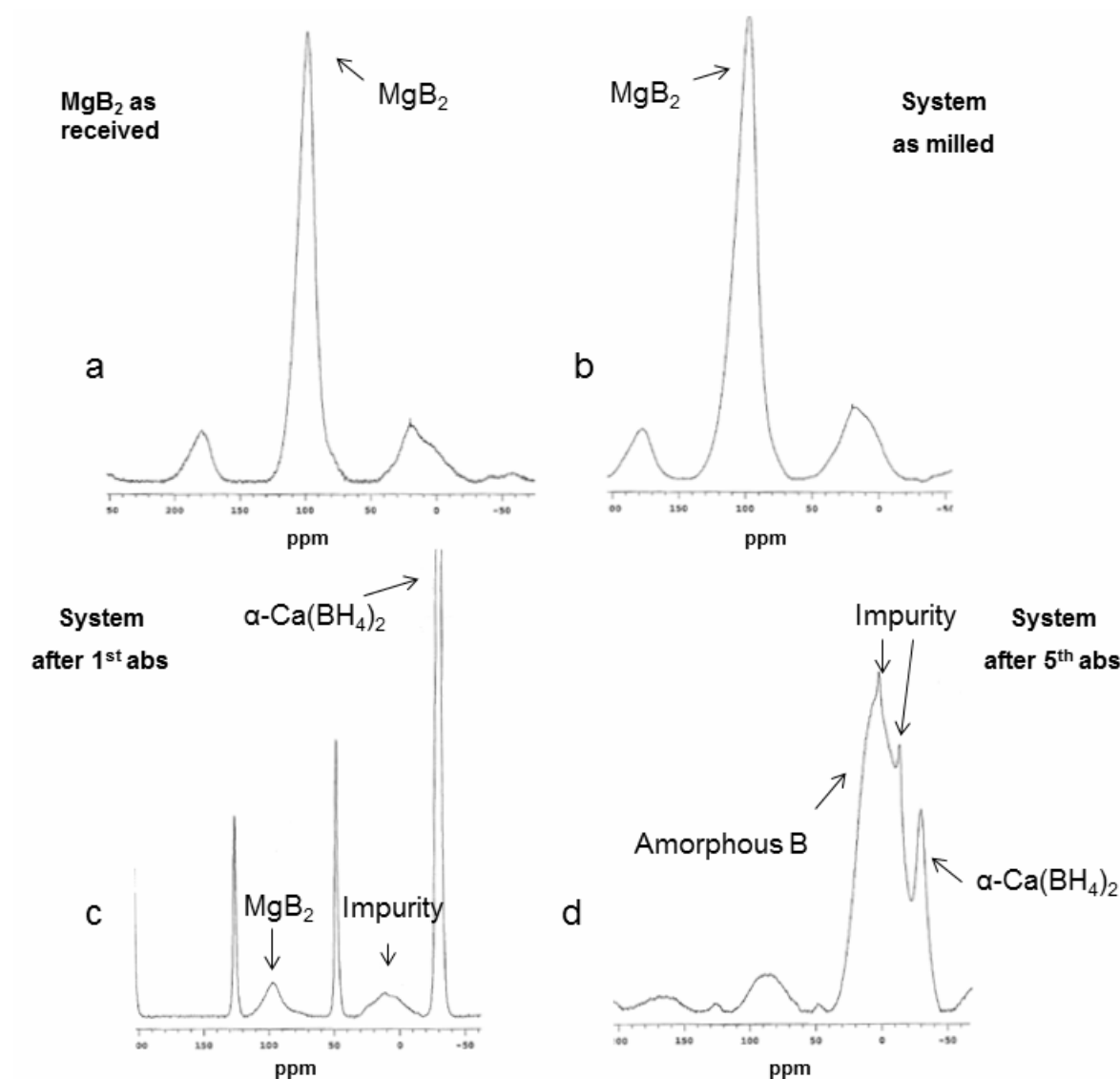


Fig. 3: ^{11}B MAS NMR analysis of the $\text{CaF}_2 + 3\text{CaH}_2 + 4\text{MgB}_2$ system: a) material as received, b) material as milled, c) material after first absorption, d) material after fifth absorption.

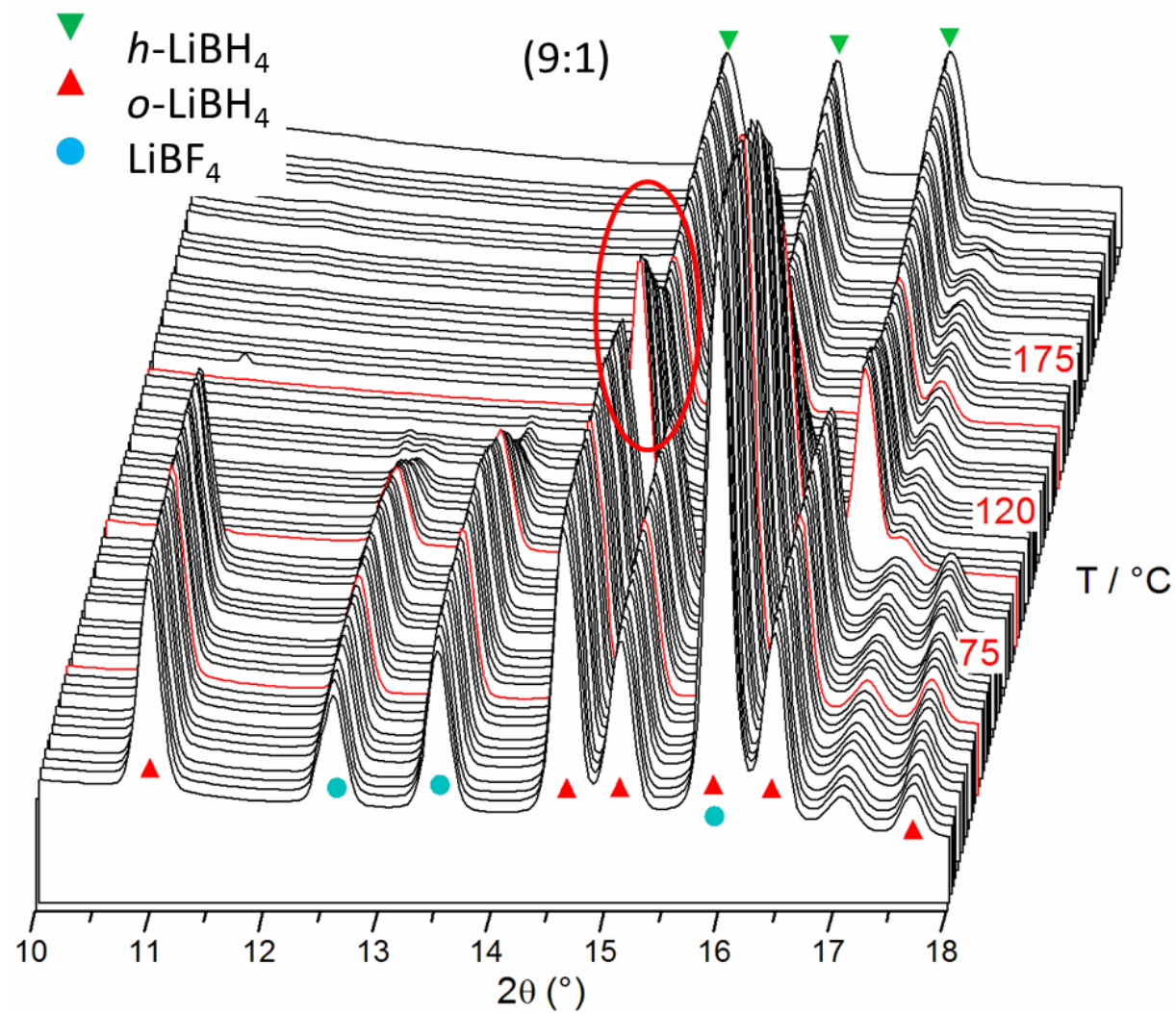


Fig. 4: *In situ-SR-PXD data for $\text{LiBH}_4\text{-LiBF}_4$ (9:1) The red circle indicates the most clear intensity anomaly (left).*

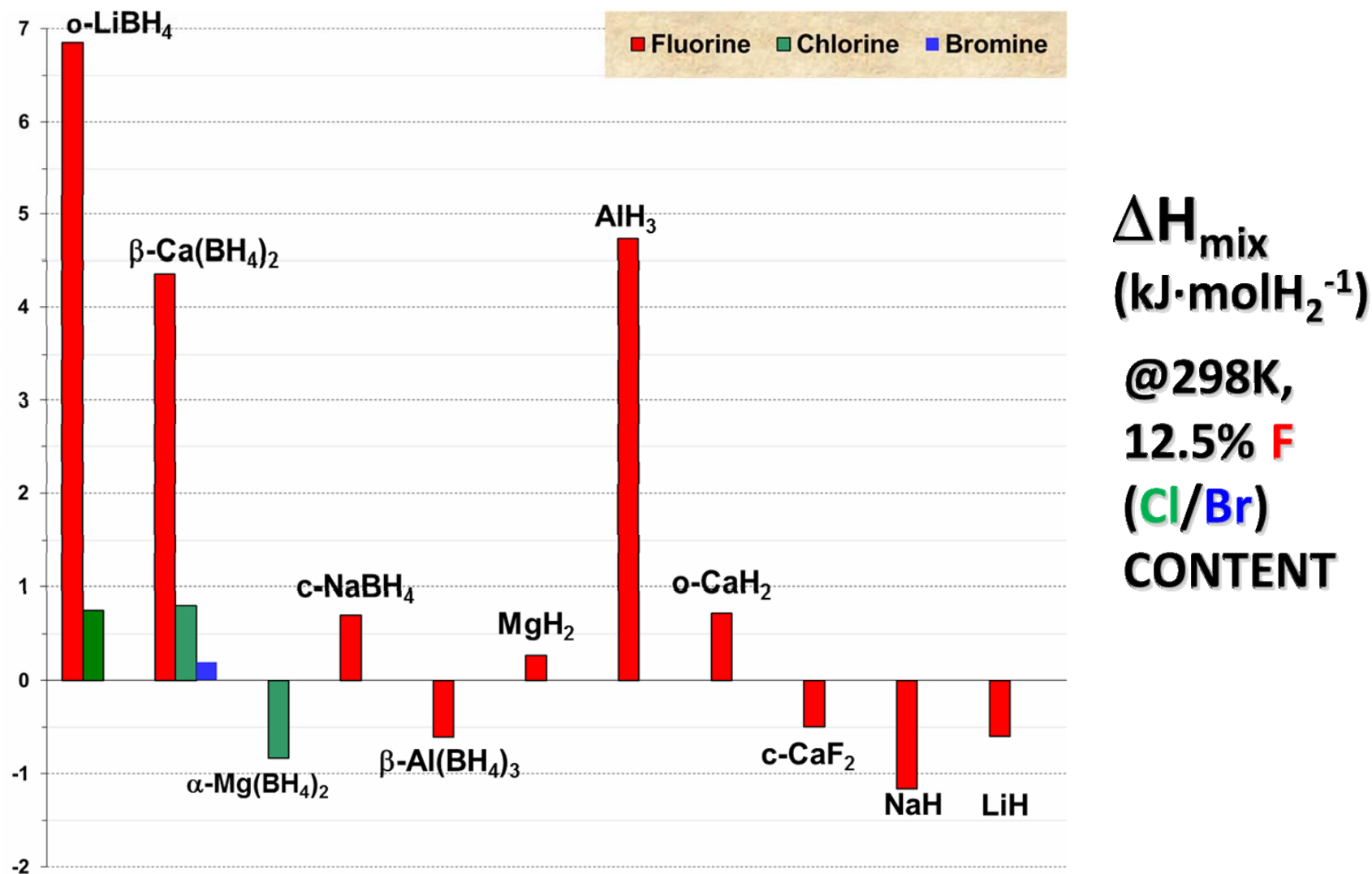


Fig. 5: Enthalpies of mixing at 12.5% fluorine content, in kJ/molH₂. In case of CaF₂, the same content of hydrogen was considered. Results for chlorine and bromine substitutions are shown for comparison.