



Preparation and characterization of borohydrides-based reactive hydride composites (RHCs)

C. Milanese¹, A. Girella¹, S. Garroni², G. Mulas², R. Campesi³, B. Schiavo⁴, E. Pellicer⁵, M.D. Baro⁵, A. Marini¹

¹Pavia H₂ Lab, CSGI & Physical Chemistry Section, Chemistry Department, University of Pavia, Italy

²Chemistry Department, University of Sassari, Italy

³European Commission - Joint Research Centre - Institute for Energy (IE), Petten, The Netherlands

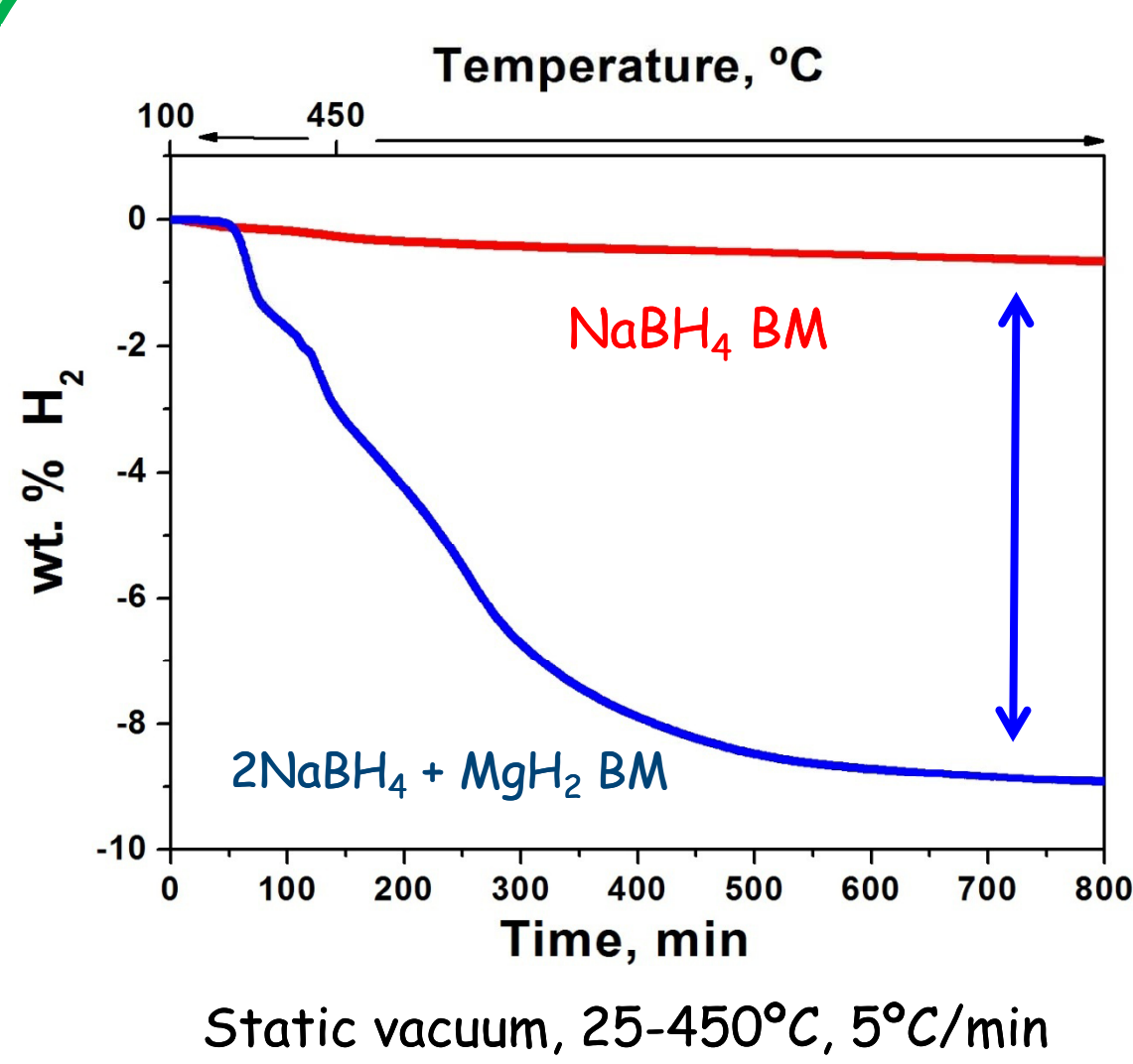
⁴Department of Physics, University of Palermo & Institute for Advanced Technology, Trapani - Italy

⁵Department of Physics, Universitat Autònoma de Barcelona, Spain

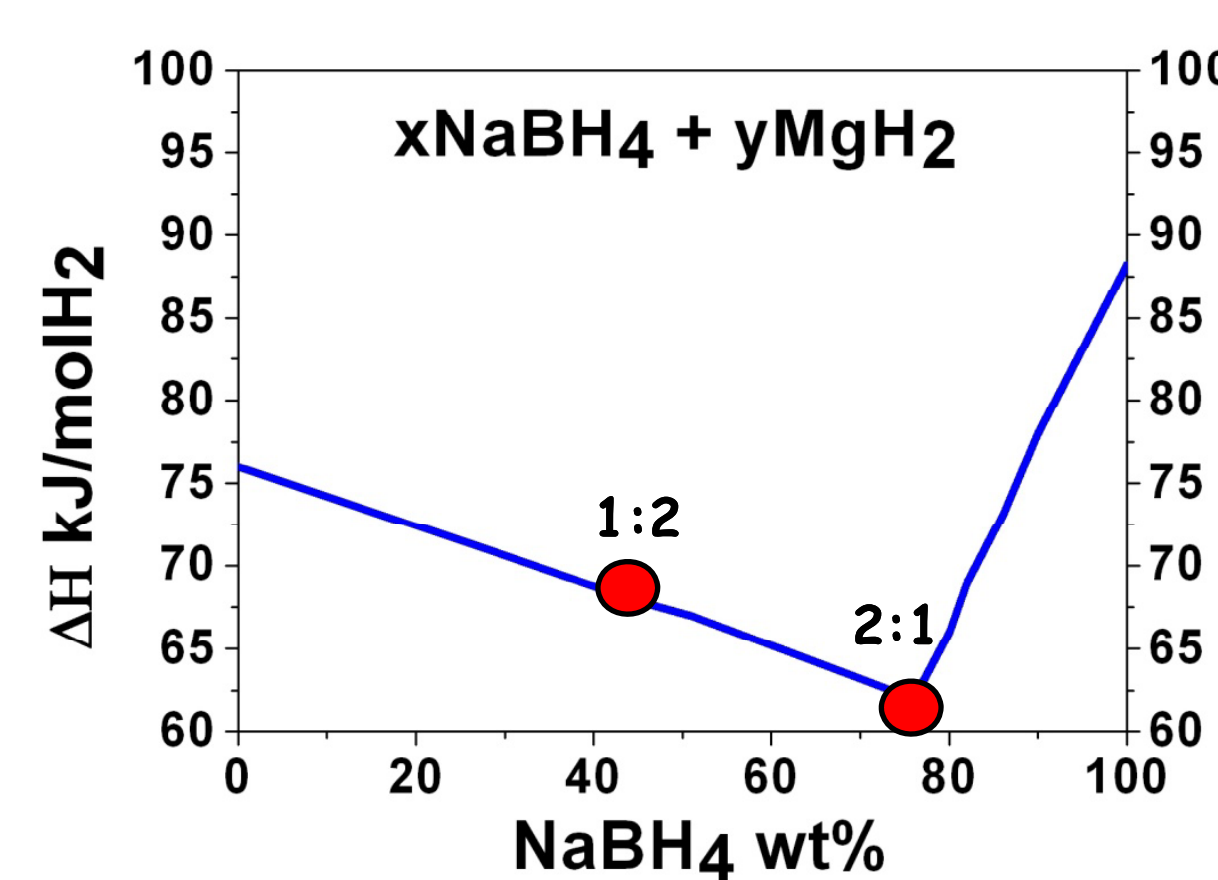


NaBH₄ - MgH₂ system

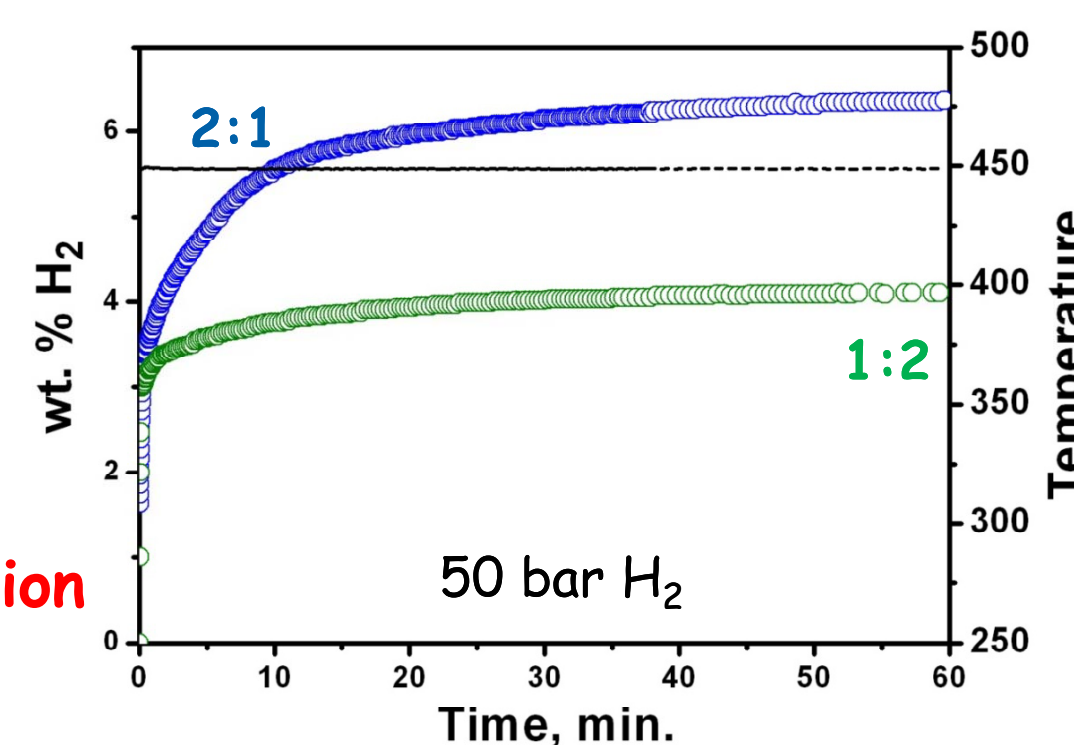
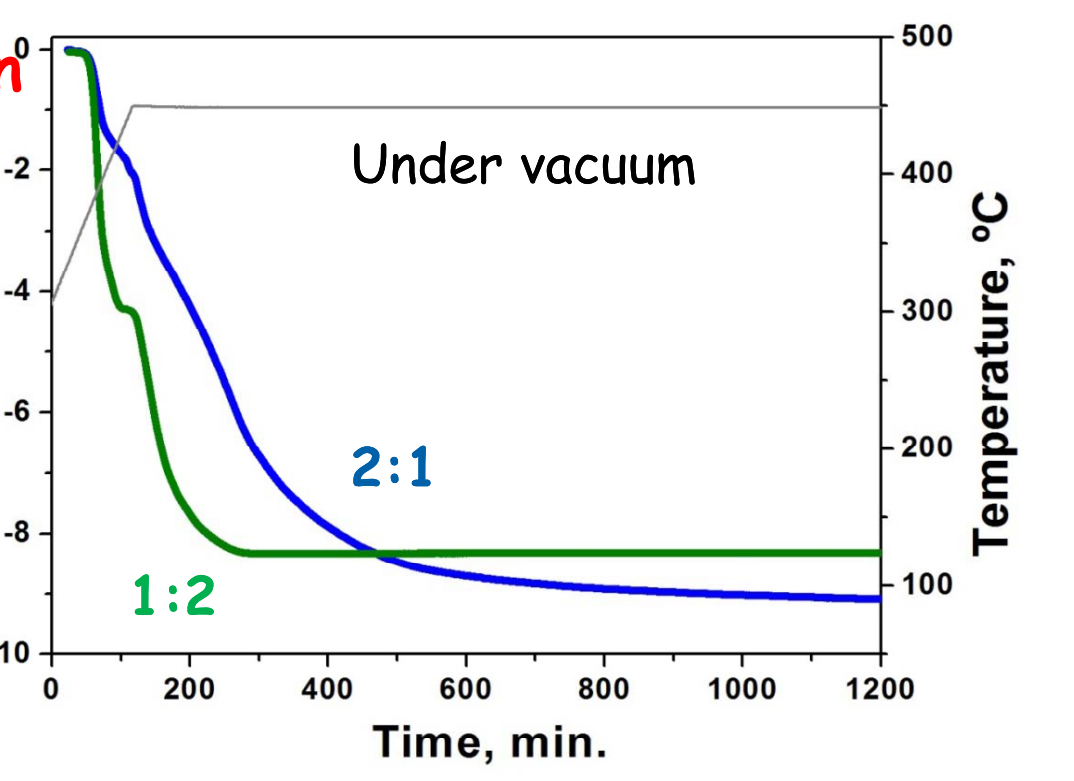
The RHC effect



Which stoichiometry?



Samples milled for 20 h under Ar



Desorption

Re-Absorption

XRPD after re-absorption test

□ Fast kinetics was achieved for the absorption process

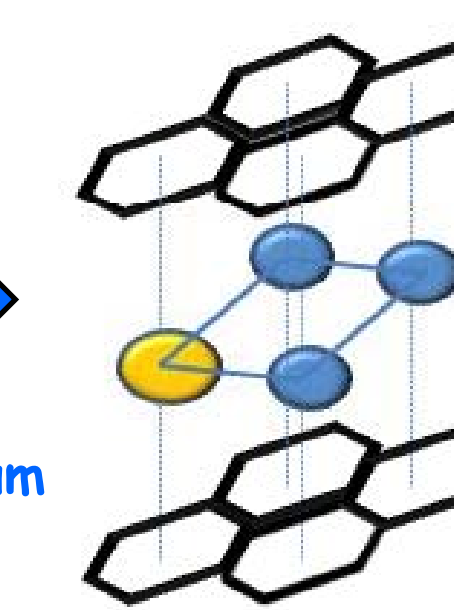
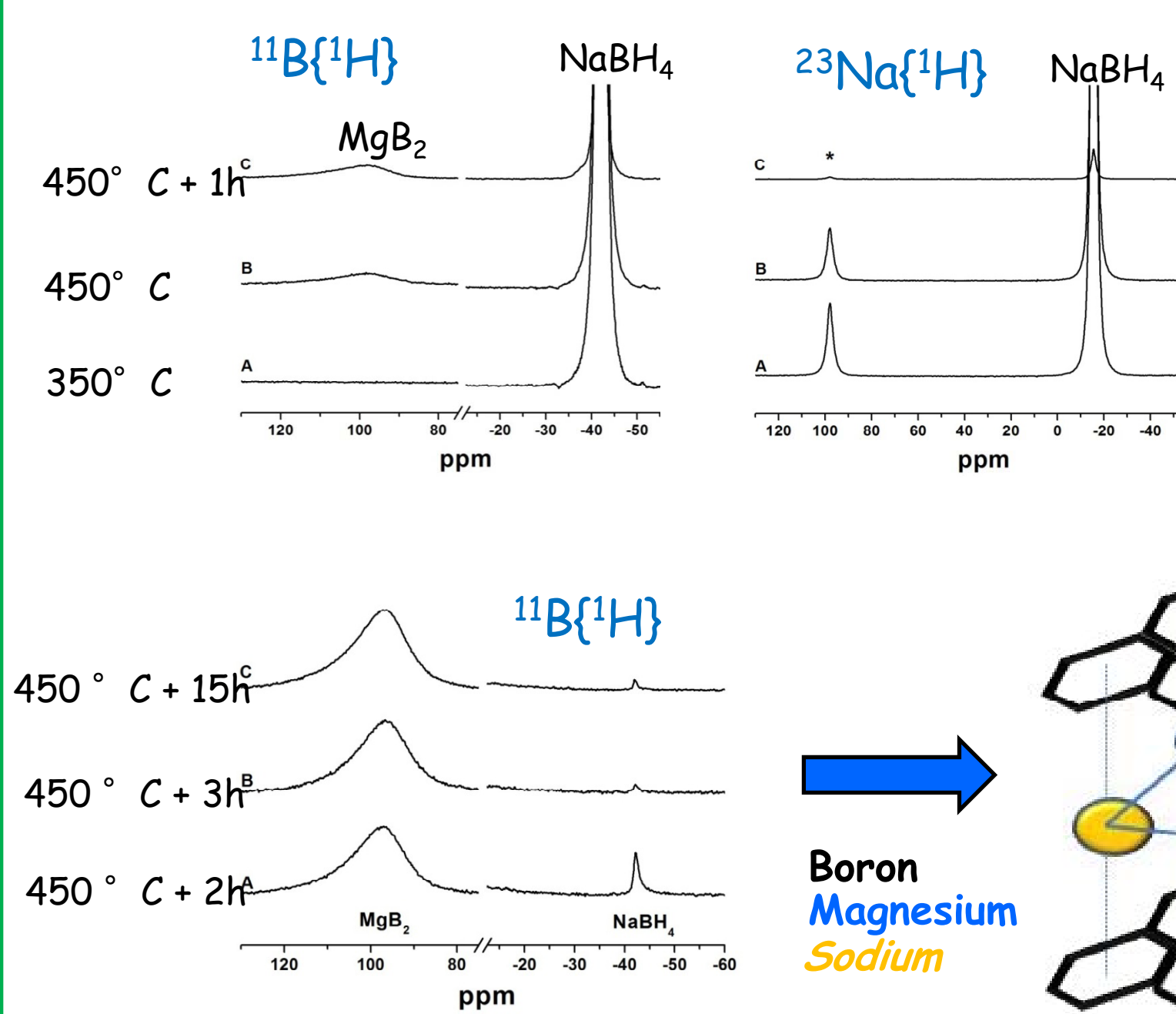
□ NaMgH₃ phase is detected: work is in progress to avoid its formation

□ Fast re-absorption up to 3% is attributed to NaH formation.

wt %	2:1	1:2
NaBH ₄	54,1	25,9
MgH ₂	13,1	28,9
Mg	9,7	24,5
NaMgH ₃	11,4	17,8
MgB ₂	11,7	2,9

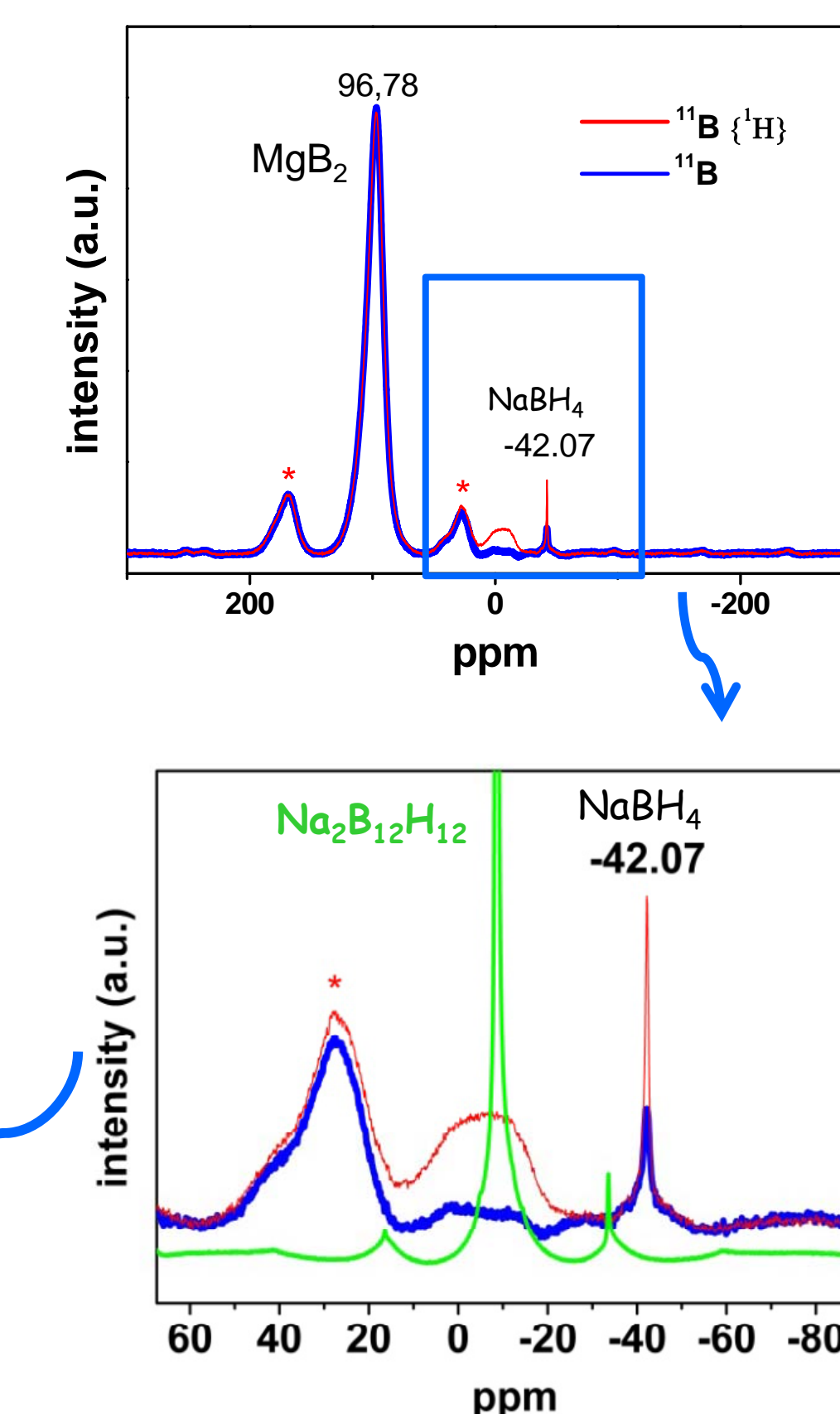
¹¹B and ²³Na solid state MAS NMR

¹¹B solid state MAS NMR of the fully desorbed 2NaBH₄ + MgH₂ mixture

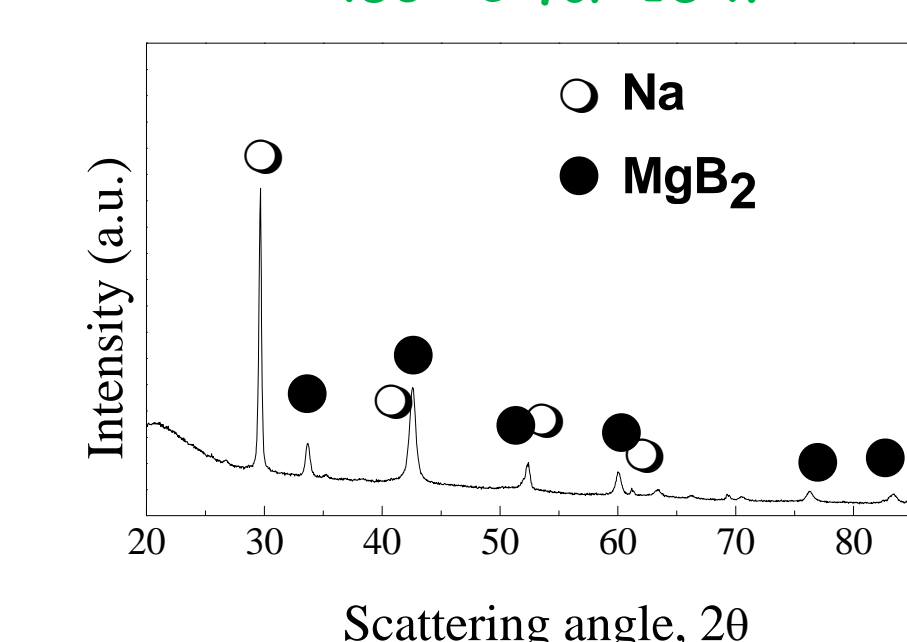
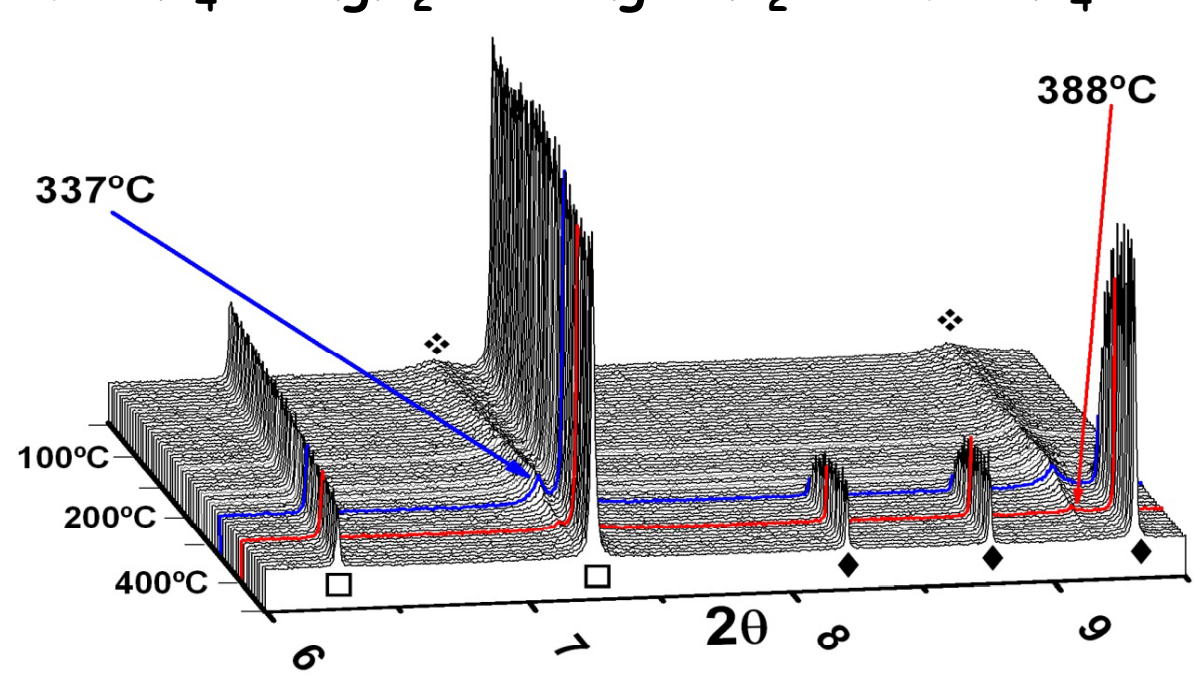
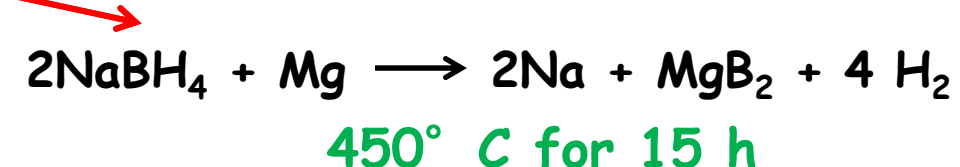
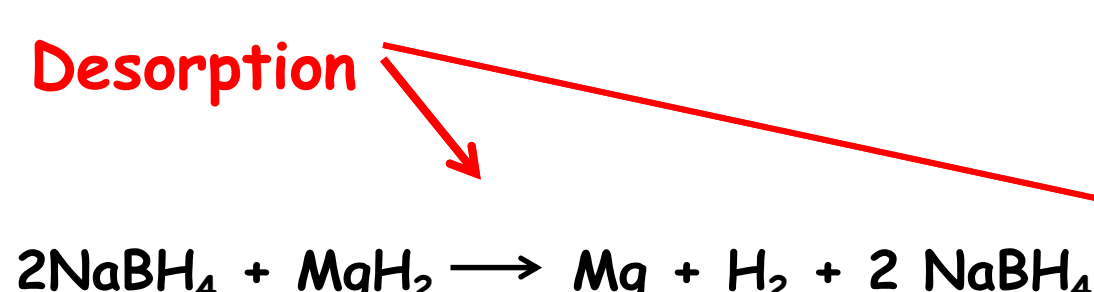


□ Amorphous Na₂B₁₂H₁₂ is detected as one of the final products of the dehydrogenation reaction

□ During the MgB₂ formation, a significant number of magnesium sites are exchanged with atoms of sodium



Sorption mechanism

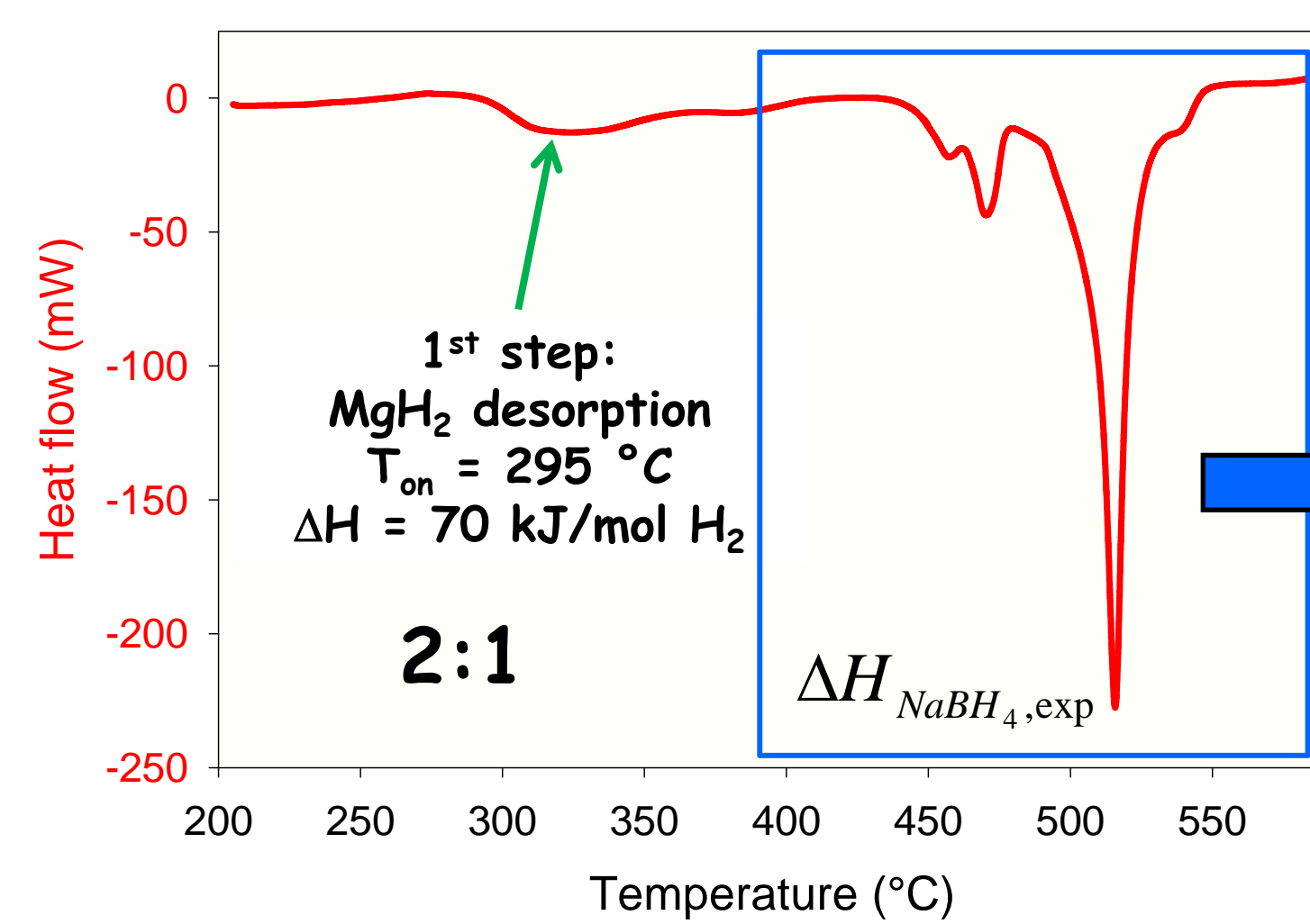


1

2

Thermodynamic studies: the 2:1 case

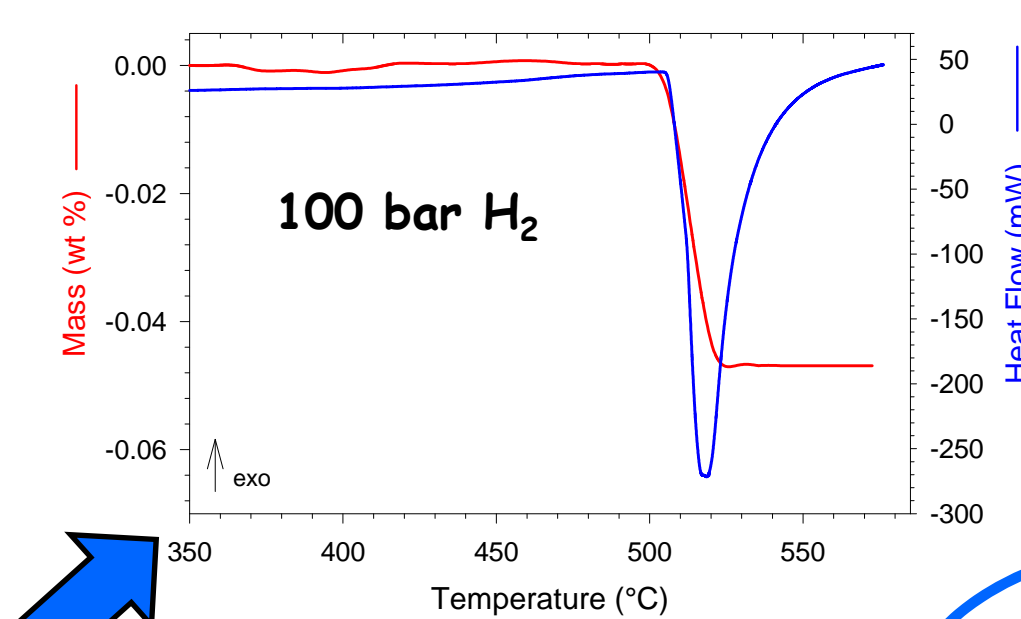
Calorimetric analysis [1]



Up to 580° C - 0.1 bar H₂

Evaluation of the melting enthalpy of NaBH₄

ΔH_m = 8.5 kJ/mol H₂



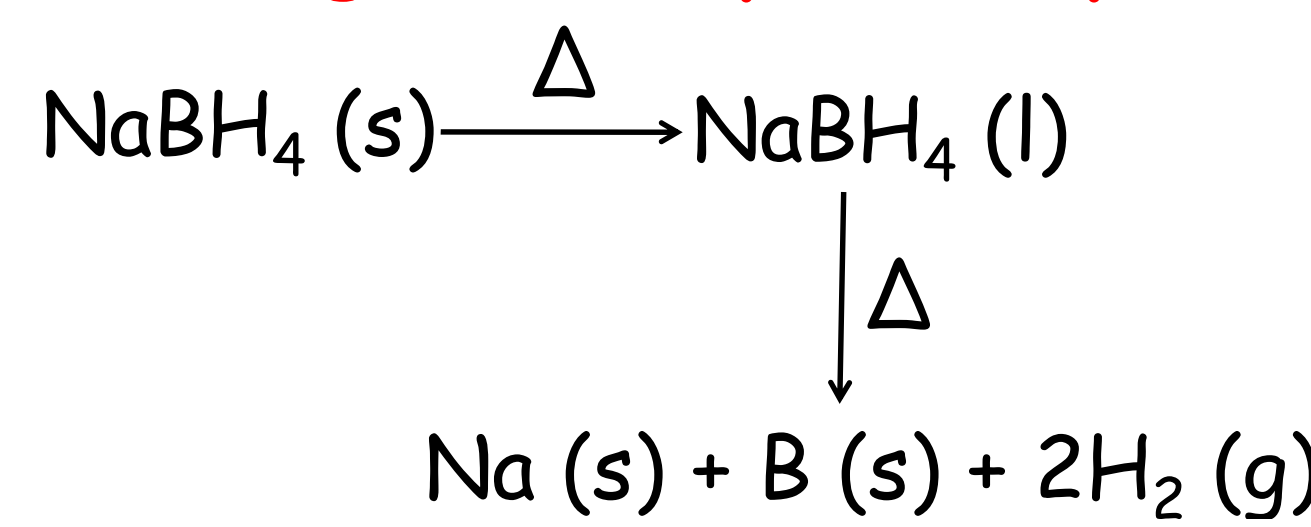
□ Decomposition of NaBH₄ ?

□ Exothermic formation of MgB₂ (-91.96 kJ/mol H₂)

□ Melting of NaBH₄ (496° C - 505° C; ΔH_m = ?)

$$\Delta H_{NaBH_4,exp} = \Delta H_{dec,NaBH_4} + \Delta H_{melt,NaBH_4} + \Delta H_{form,MgB_2}$$

Melting - decomposition process

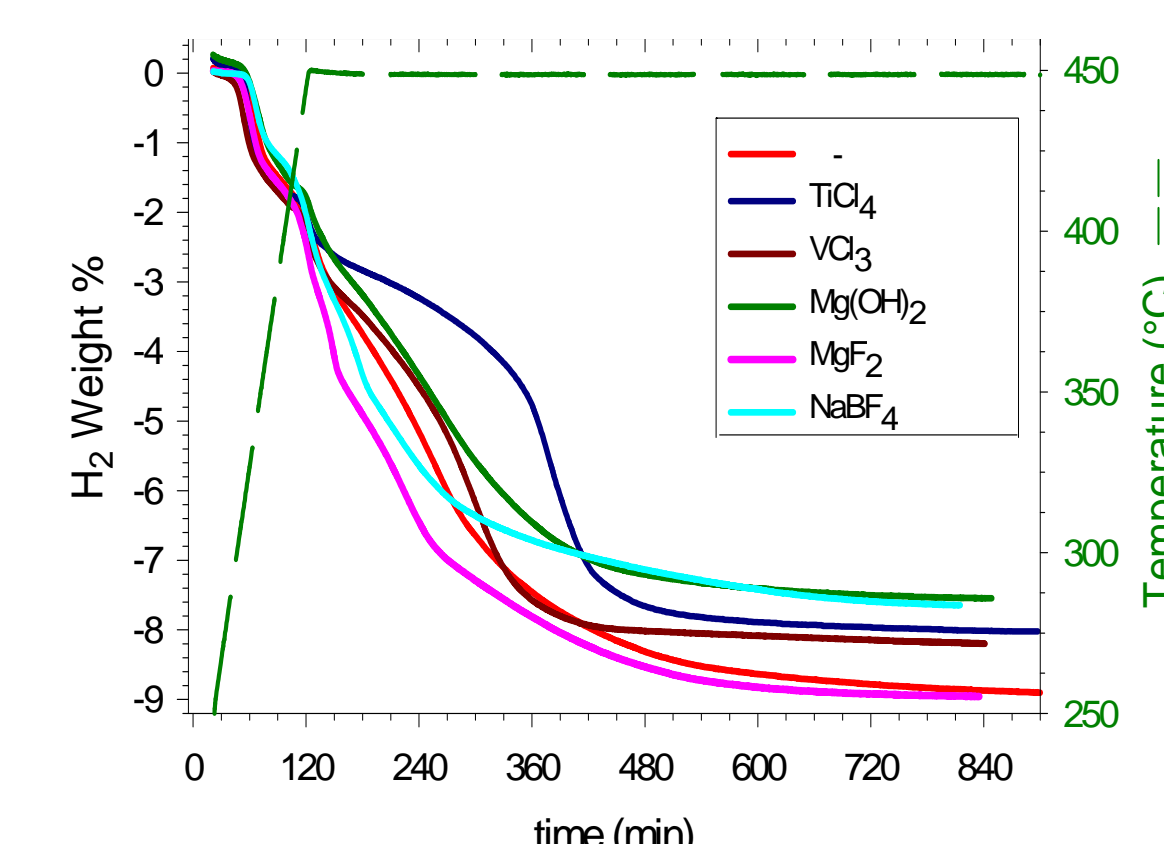


$$\Delta H_{dec,NaBH_4} = 90.9 \text{ kJ/mol H}_2$$

Literature values for the pure compound: 106.8 - 108 kJ/mol H₂ [2]

[1] C. Milanese et al., J. Phys. Chem. C., 115 (2011) 3151-3162.
[2] IEA/DOE/SNL Hydrides Databases available at Hydride Information Centre, Sandia National Laboratories home page: <http://hypark.ca.sandia.gov/>

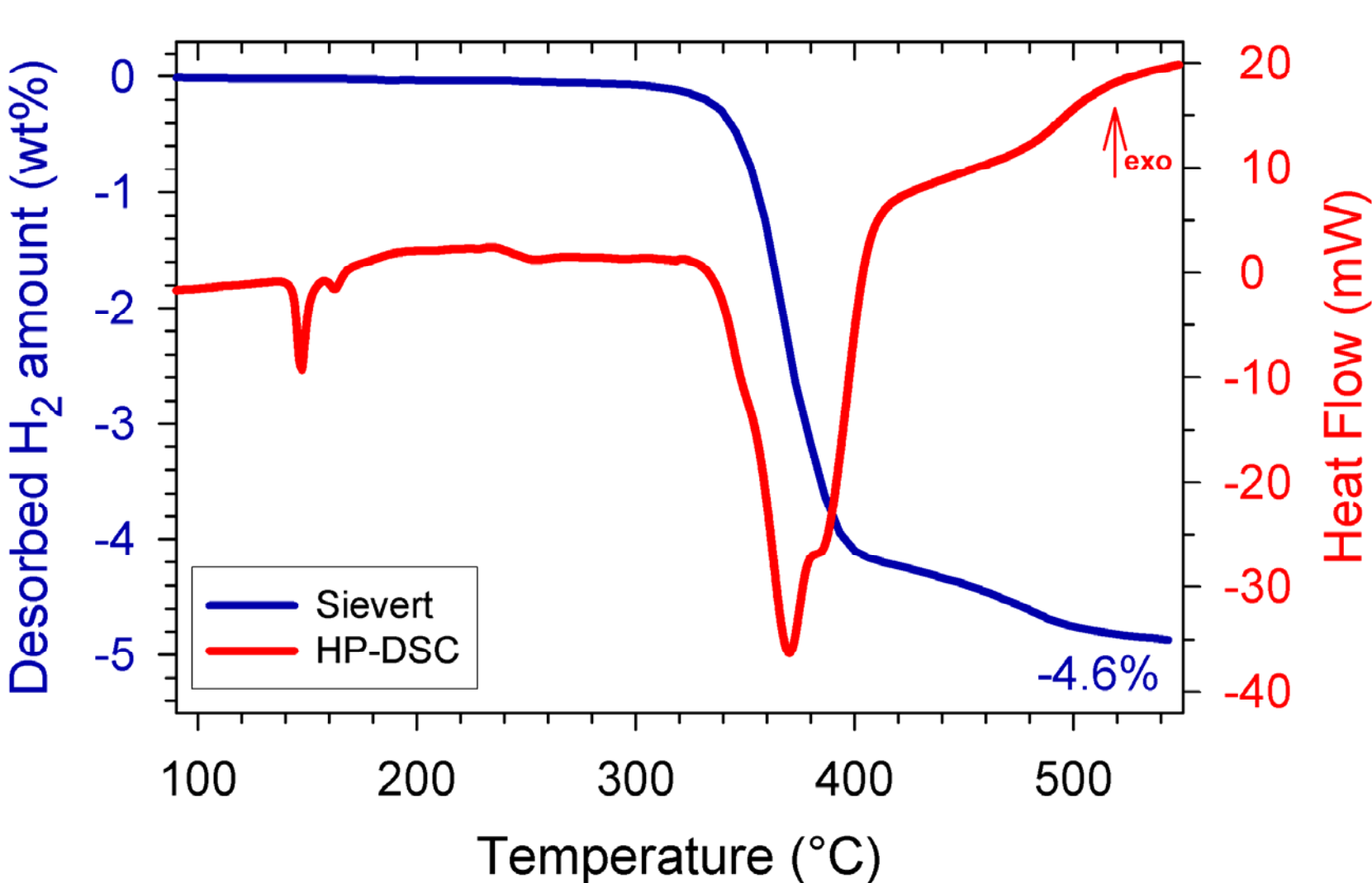
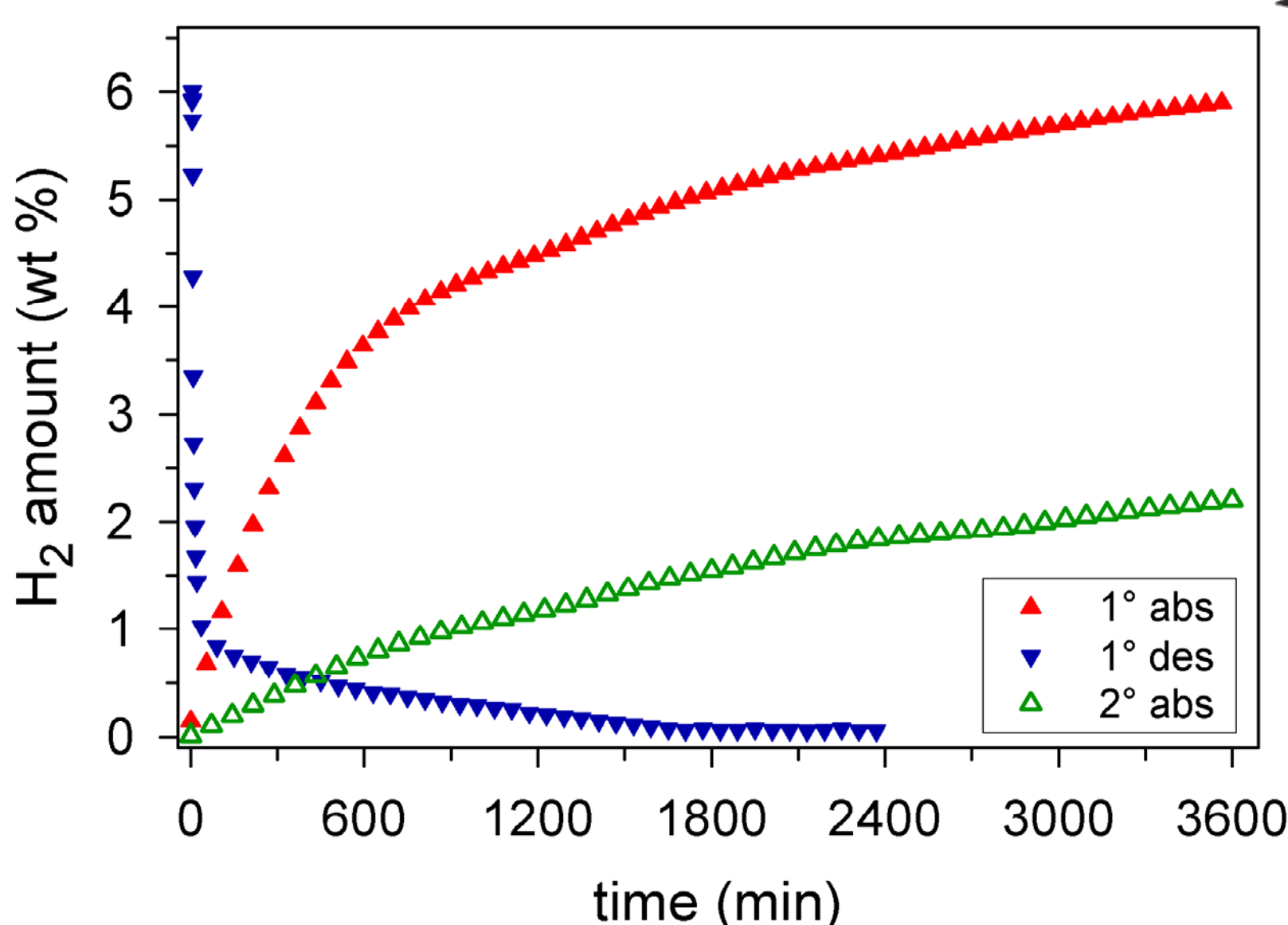
Influence of the additives (2:1 mixture)



Considering that the desorption process of the 2NaBH₄ + MgH₂ mixture follows a multi step reaction, we introduced a new parameter (%ΔT_{RHC-gap}) in order to quantify the influence of a single additive on decreasing the gap between the onset desorption temperatures of MgH₂ and NaBH₄.

Best results (even if small improvements): MgF₂

Sample 1: Abs: 360° C - 120 bar
Des: 390° C; vacuum



Sample 1: Coupled manometric - calorimetric measurement up to 500° C; 0.1 bar hydrogen; 2° C/min.

CaH₂ - MgB₂ - AlB₂ system

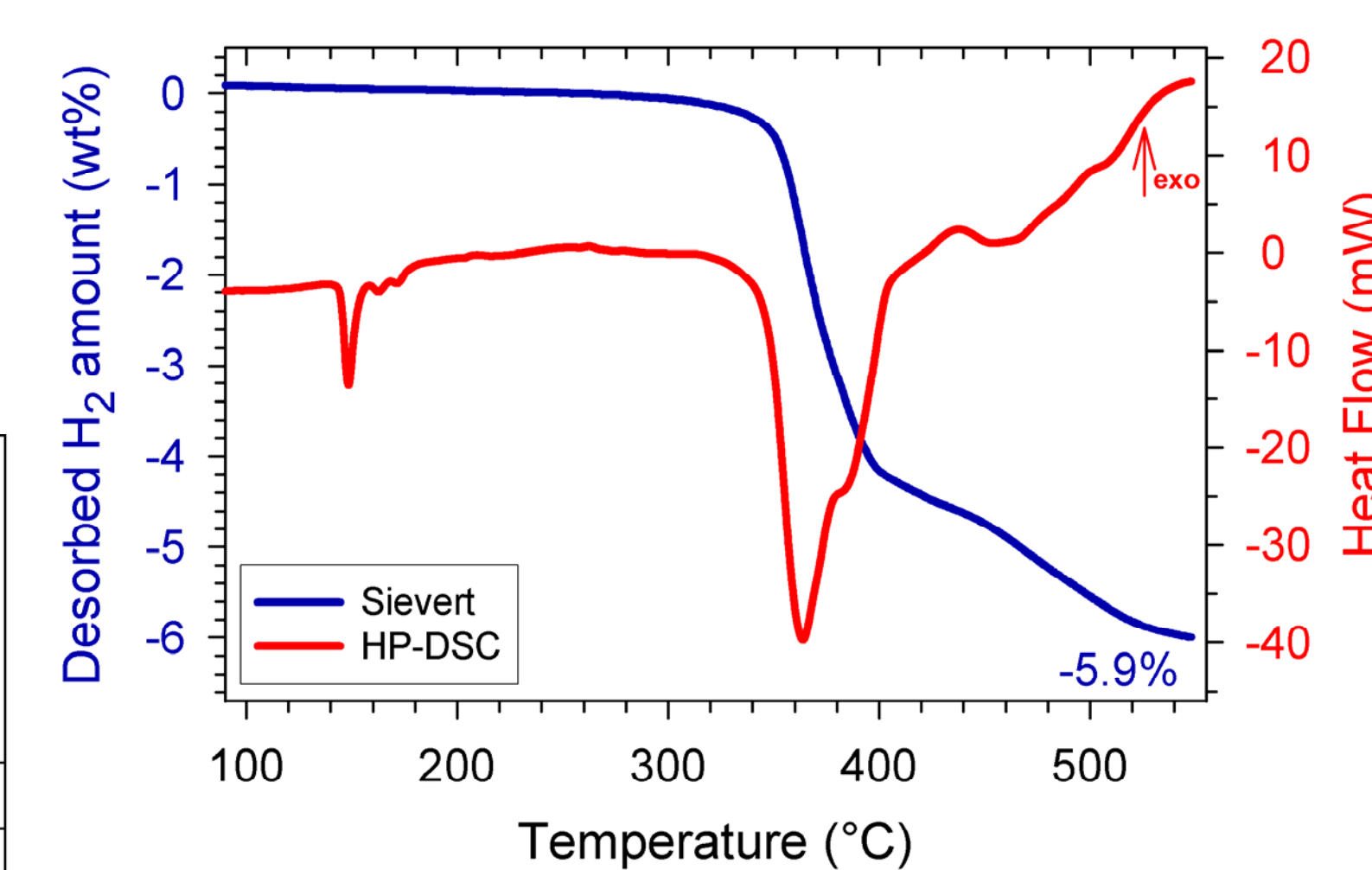
We started from the "classical" composed system CaH₂ + MgB₂ (sample 1) to form the hydrogenated compounds Ca(BH₄)₂ + MgH₂ [1]. High energy ball milling of the two initial compounds has been performed under Ar (900 min). By hydrogenation at 360° C and 120 bar the system reached the 72% of the full theoretical capacity. All the absorbed hydrogen amount has been released with desorption at 390° C under static vacuum, in almost 1/3 of the time needed for the final absorption. The ex-situ synchrotron radiation powder diffraction (SR-PXD) measurements of the absorbed samples revealed the presence of significant amount of Ca₄Mg₃H₁₄, which is an intermediate hydrogenated phase. The presence of this species, together with some amount of unreacted initial compounds indicates that the hydrogenation reaction was incomplete. The second absorption run under the same conditions revealed the partial reversibility of the system.

The system in which MgB₂ was totally substituted with AlB₂ (sample 3) showed improved hydrogen sorption performances [1]. The same amount of 6 wt% was reached even though the theoretical capacity of this system is lower compared to that of the MgB₂-based one. On the contrary the system with both the borides (MgB₂:AlB₂ = 1/2 : 1/2, theoretical capacity = 7,32 wt% - sample 2) did not show any improvement.

Sample	theoretical H ₂ capacity [wt%]	% H ₂ released after hydrogenation for 3000 min [wt%]	H ₂ released amount vs theoretical capacity	H ₂ release onset T [°C]	ΔH double-peak [kJ/molH ₂]	H ₂ re-absorbed amount vs theoretical capacity
1	8.34	5.8	70 %	343	51.4	16 %
2	7.32	4.1	56 %	346	58.0	18 %
3	6.25	5.9	94 %	341	45.3	21 %

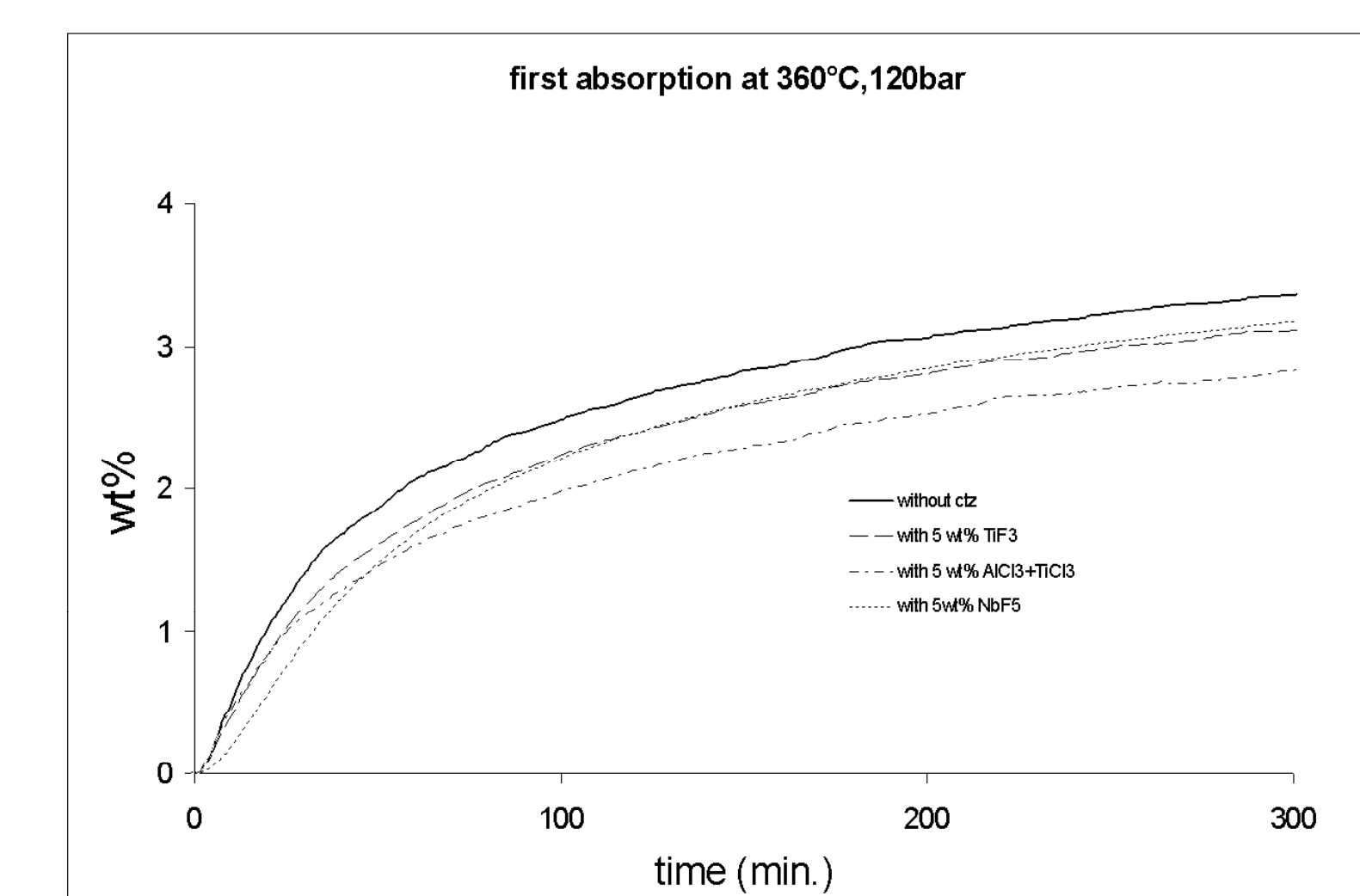
Sample 3: In-situ SR-PXD measurements have been performed in order to follow the dehydrogenation process of the absorbed sample. As expected, under 200° C the low temperature α-phase changes to the β- and γ- phases, stable at high temperature. Above 350° C the borohydride releases hydrogen and CaH₂ forms back. On the other side, Al did not turn back to AlB₂, as the total amount of Aluminum seems not react from the system in the absorbed state (Ca(BH₄)₂ + Al) and no AlB₂ peaks were detected. This is in line with the still poor reversibility of the system (21%) obtained with the second absorption run.

AlB₂ based system (sample 3)



Coupled manometric - calorimetric measurement up to 500° C; 0.1 bar hydrogen; 2° C/min.

Tests with additives (ctzs) on sample 3



Tests with substances with possible catalytic effect are in progress. Up to now, we tested chlorides and fluorides, that unfortunately are not working well ☹.

[1] B. Schiavo, A. Girella, F. Agresti, G. Capurso, C. Milanese, Ball-milling and AlB₂ addition effects on the hydrogen sorption properties of the CaH₂ + MgB₂ system, J. Alloys Compd (in press).