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METAL HYDRIDE CENTER OF EXCELLENCE

Lightweight Intermetallics for Hydrogen Storage

DOE Award #: DE-FC3605GO15062

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GE Global Research

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– A Member of the DOE Metal Hydride Center of Excellence –

This presentation does not contain any proprietary or confidential information

Project ID: ST16

Program Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- Percent complete: 40%

Barriers

- Right heat of formation
- Absorption / desorption kinetics
- Reversibility for borohydrides

Budget

- Total Project Funding: *$3.47M*
  - DOE Share: $2.78M
  - GE Share: $0.69M
- Funding Received for FY06
  $450K (DOE), $112K (GE)
- Funding Received for FY07
  $375K (DOE), $100K (GE)

Partners/Collaborations

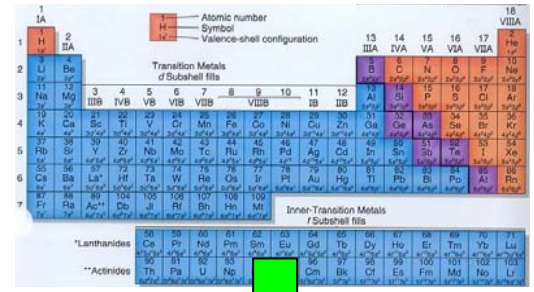
- Member of DOE MHCoE
- Collaborations with ORNL, JPL, Caltech, UIUC, CMU, U. Pitt, SNL, Univ. Nevada

Objectives

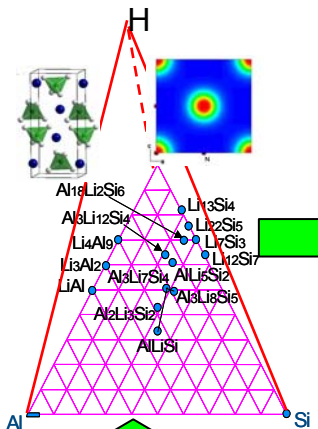
Overall	Discover and develop a high capacity (> 6 wt.%) lightweight hydride capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.
FY05	• Develop a combinatorial synthesis and high-throughput screening methodology for metal hydride discovery • Identify hydrides from combinatorial samples and validate them through gram-quantity sample tests
FY06	• Identify the crystal structures of $Mg(BH_4)_2$ using XRD, neutron diffraction and computer modeling • Perform combinatorial and computational screening of catalysts and dopants for $Mg(BH_4)_2$
FY07	• Perform combinatorial and computational screening of catalysts, dopants and complexes for $Mg(BH_4)_2$ • Explore ways to make the materials reversible

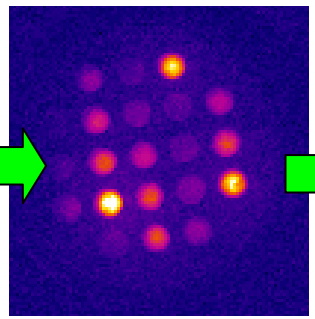
Approach

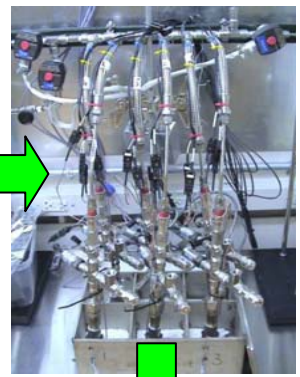
High-throughput screening (HTS) & mechanistic understanding are important parts of GE's methodology

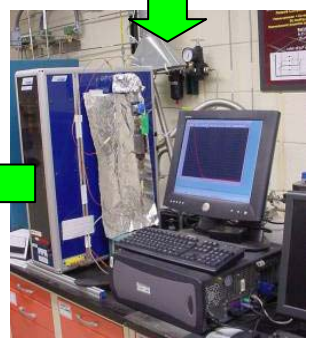


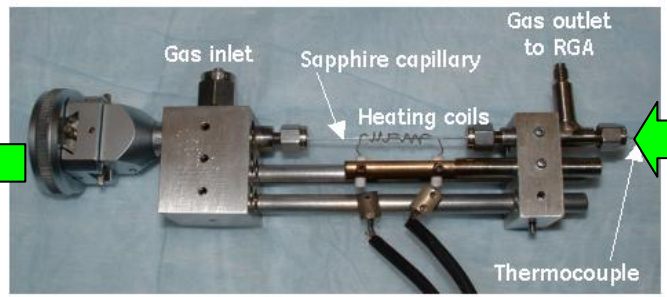
System requirements
Phase diagrams
Thermodynamics
Compounds
Availability
Toxicity
Cost

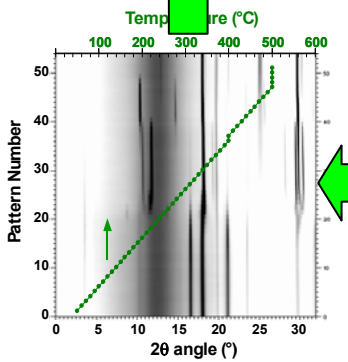








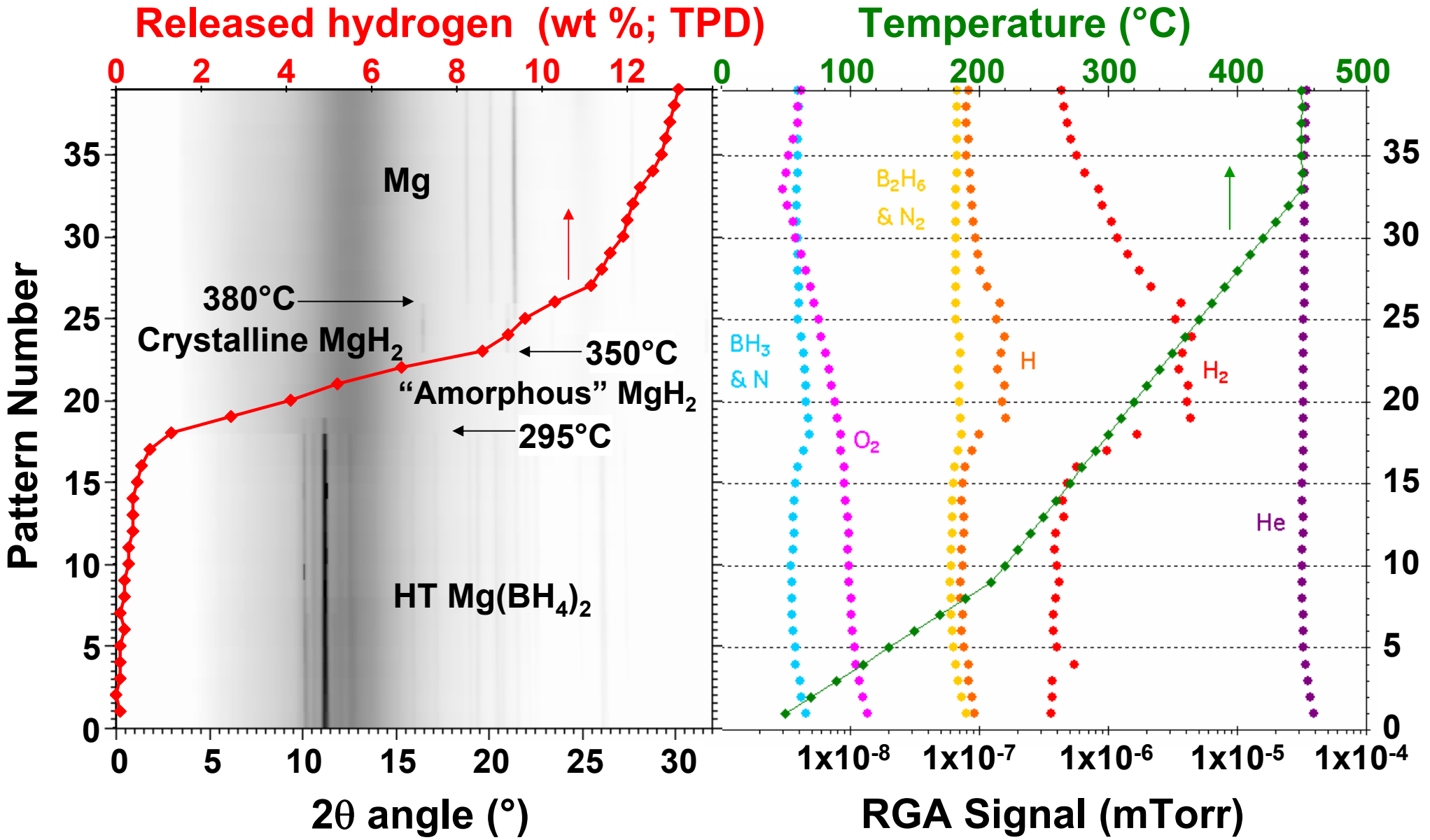




GE downselected $Mg(BH_4)_2$ family borohydrides for further exploration

$Mg(BH_4)_2$ Desorption

$Mg(BH_4)_2$
(14.8 wt.% H theoretical)



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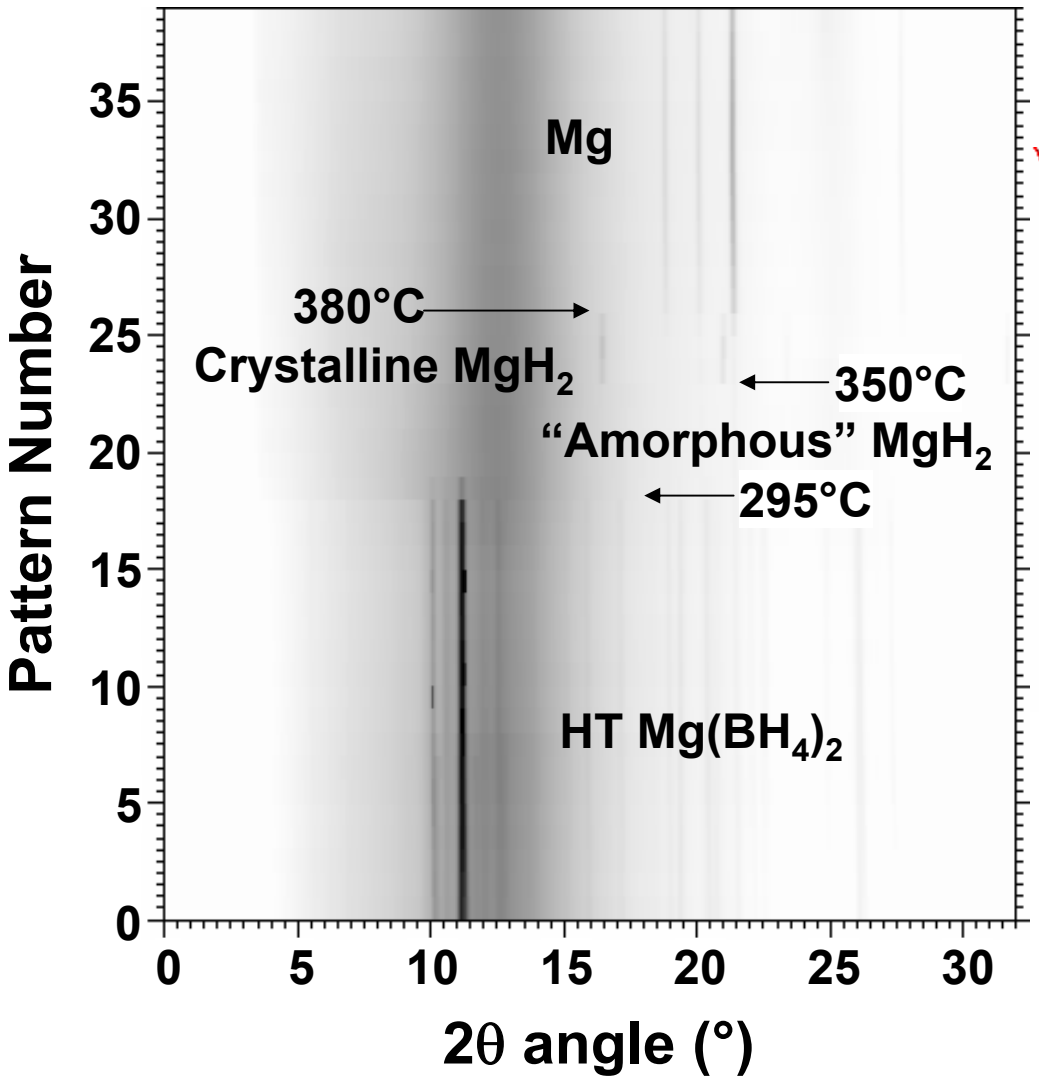
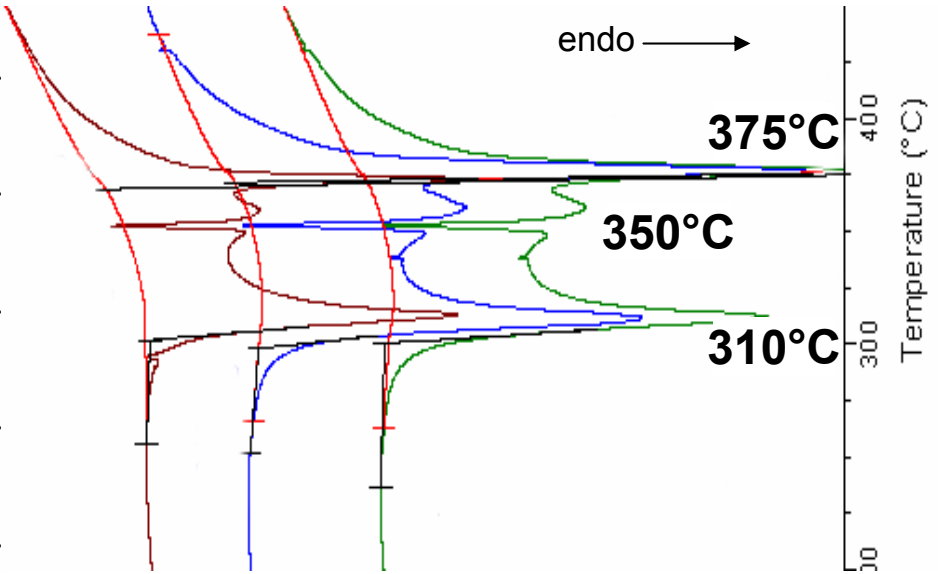
$Mg(BH_4)_2$ Desorption



DSC

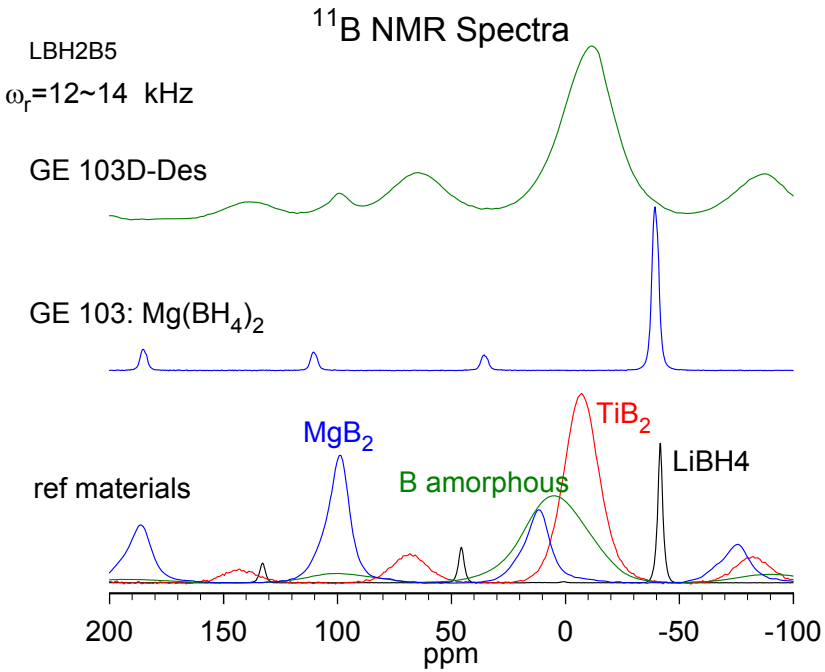


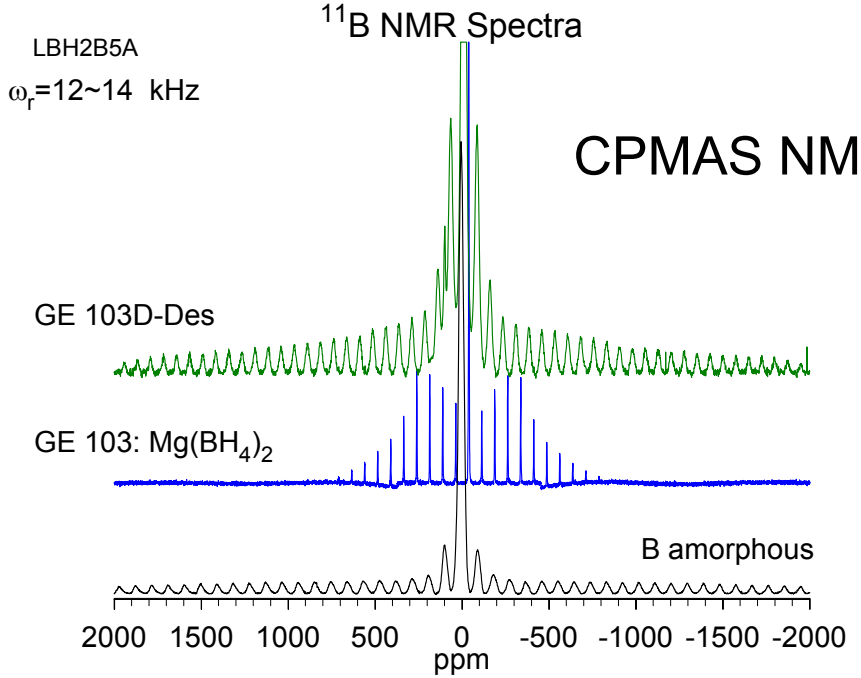
$Mg(BH_4)_2$
→ "amorphous MgH_2" + "amorphous boron" + H_2
→ crystalline MgH_2 + "amorphous boron"
→ Mg + "amorphous boron" + H_2

Complimentary data from 4 types of experiments

$Mg(BH_4)_2$: Initial NMR Measurements

Samples: GE-103: $Mg(BH_4)_2$ GE103D: desorbed $Mg(BH_4)_2$





- Certainly remarkable structural change around boron elements is observed via ^{11}B MAS NMR
- The ^{11}B peak for $Mg(BH_4)_2$ is very close to that for $LiBH_4$ (i.e., with similar BH_4^- ion environments).
- The desorbed sample shows the formation of "amorphous" boron & some MgB_2 (peak at ~100 ppm).
- The quantity of MgB_2 is minor in GE-103D & seems to be absent in GE-103, which is only $Mg(BH_4)_2$.
- ^{11}B CPMAS NMR with protons on GE-103D indicated that the main peak at ~ 0 ppm is protonated, suggesting formation of amorphous boron with some H attachment. More study underway.
- The full widths of the ^{11}B for GE-103 and GE-103D are very different & also different from reference amorphous boron. This reflects significant differences in the quadrupolar interactions for this nucleus - giving us another tool to extract information on the local structure and bonding parameters.

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Measurements performed by
Sonjong Hwang and Bob Bowman

CALIFORNIA INSTITUTE OF TECHNOLOGY 1891

JPL

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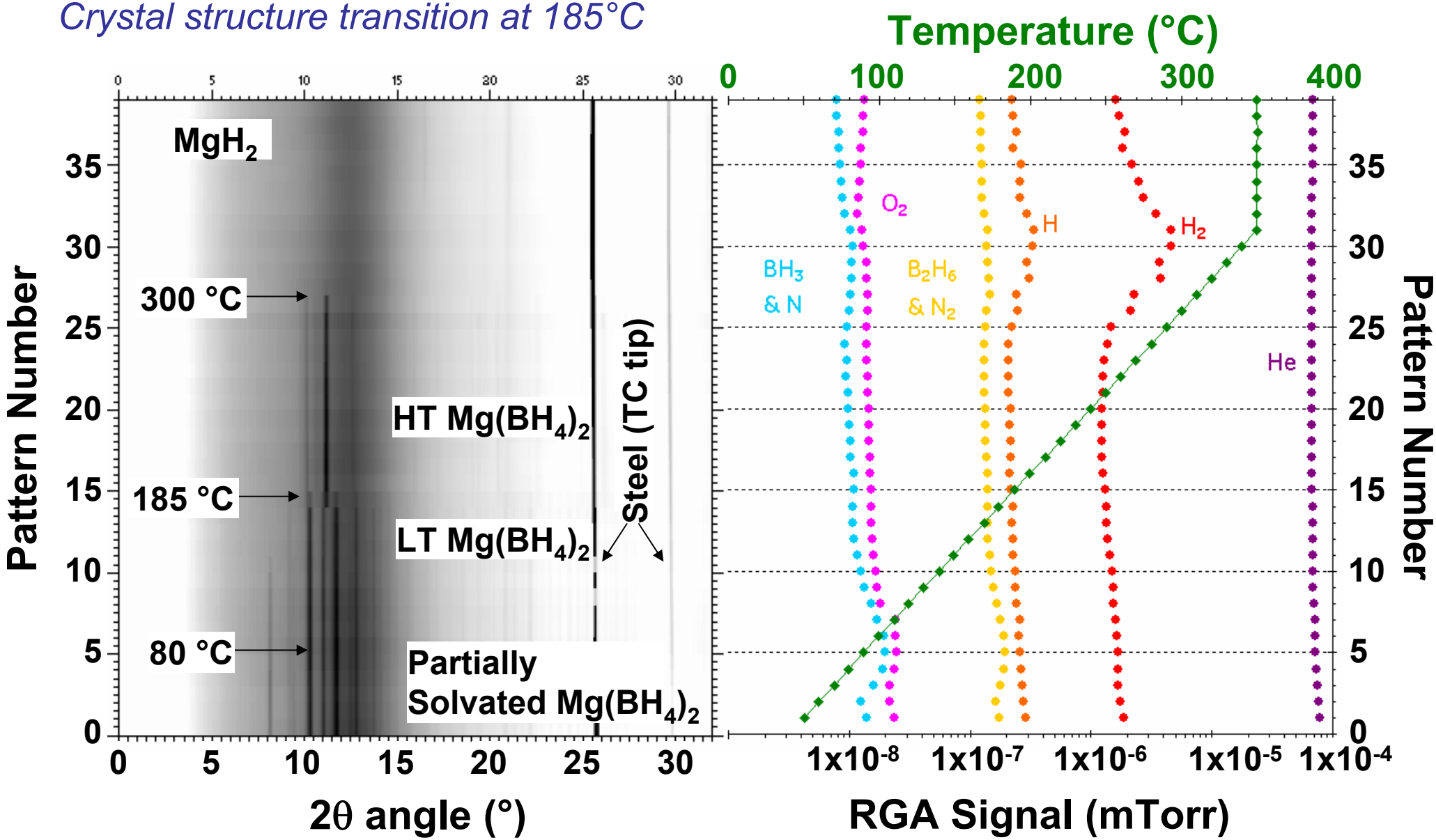
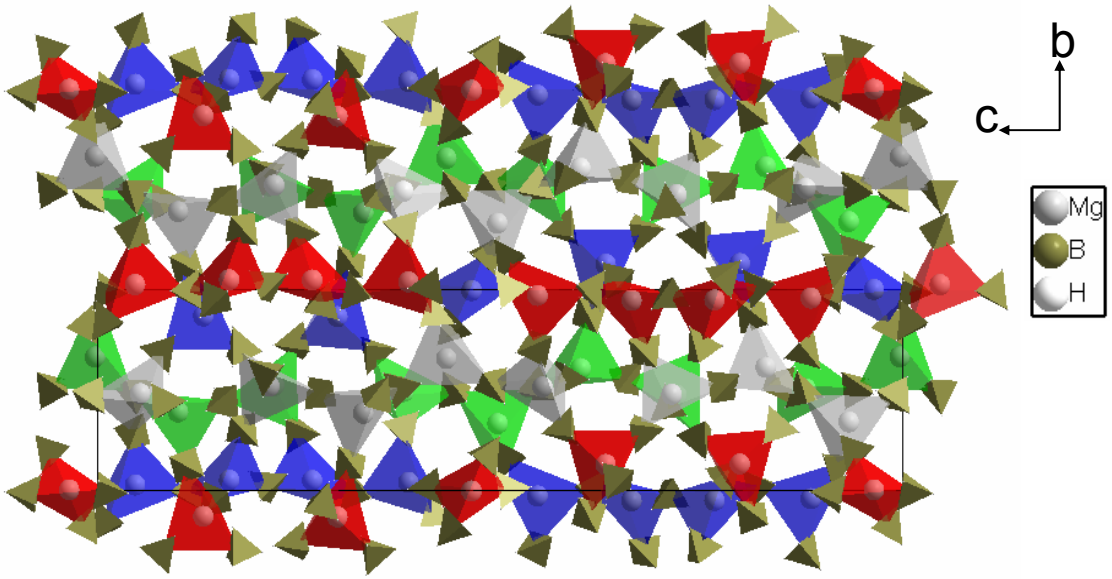
$Mg(BH_4)_2$: Crystal Structures & Decomposition

Crystal structure transition at 185°C



$Mg(BH_4)_2$ LT structure



LT-phase, viewed along the hexagonal a-axis. Color schemes represent the MgB_4 tetrahedron at different projection on the a-axis.

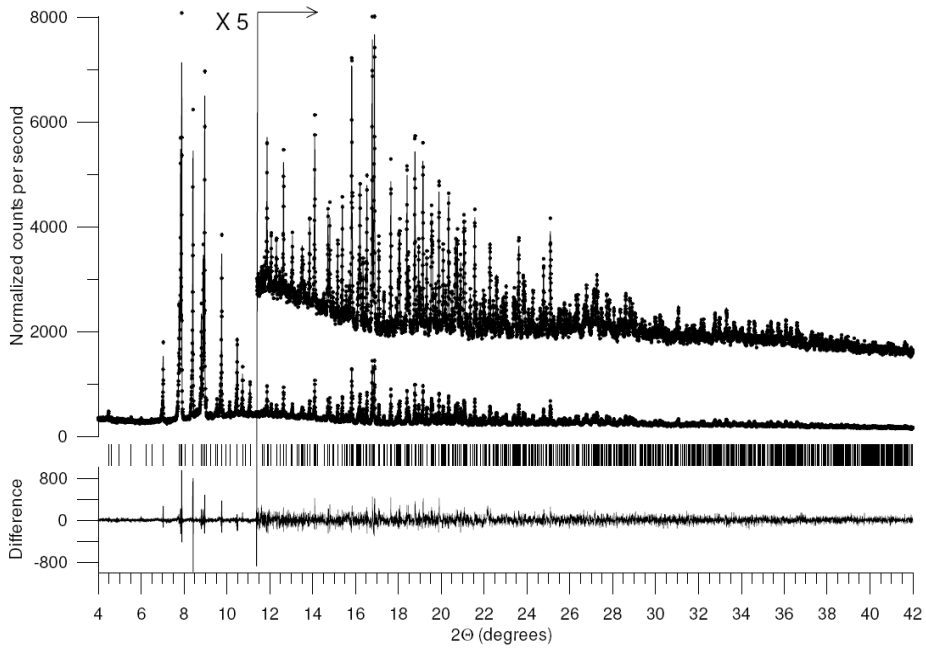
Hexagonal, corner-shared $Mg(BH_4)_4$ tetrahedrons (Mg: center, BH_4: vertex). Tetrahedral BH_4 (B: center, H: vertex). B-H bond length: 1.12 Å. Mg-B bond lengths: 2.34 -2.47 Å. Mg is bonded to 8 H.

Crystal structure ID is essential for computational screening of dopants

LT $Mg(BH_4)_2$

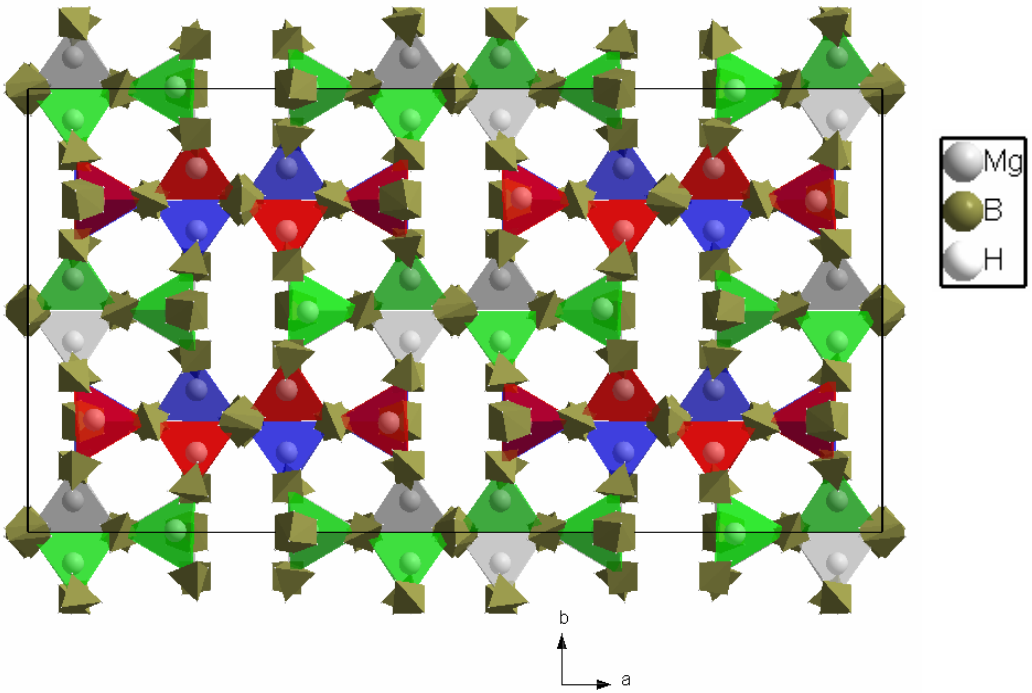
- Hexagonal – $P6_1$
- a = 10 Å, b = 10 Å, c = 37 Å
- V = 3435 Å^3; Z = 30
- Density = 0.785 calc

The fit of experimental and calculated powder diffraction data by Rietveld refinement for the LT $Mg(BH_4)_2$ phase. The high-angle data are enlarged 5x for clarity.



In collaboration with J.H. Her and P. Stephens at SUNY Stony Brook

$Mg(BH_4)_2$ HT structure



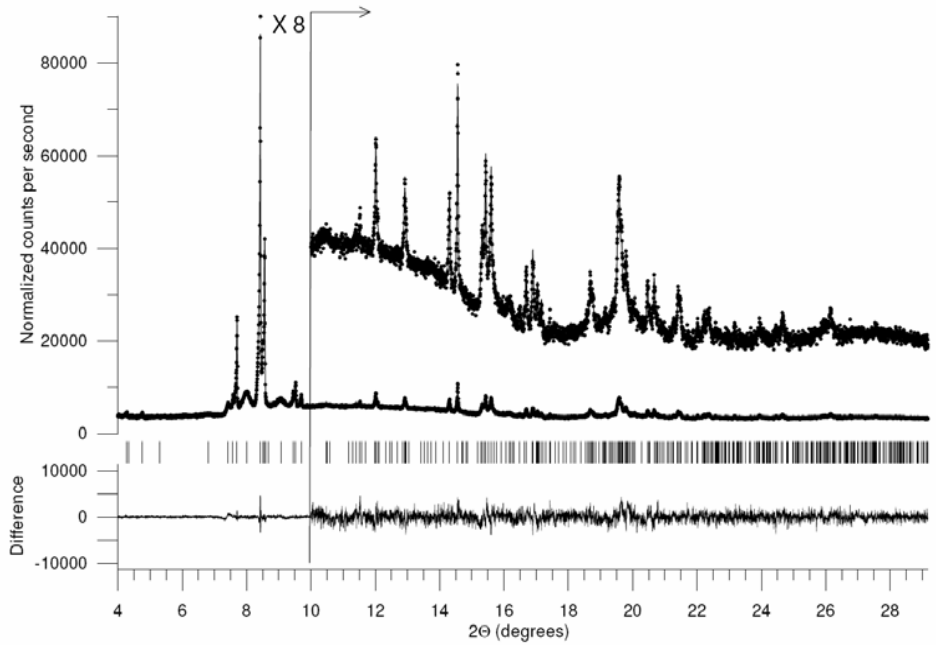
HT phase, viewed along the orthorhombic c-axis.

Orthorhombic, corner-shared $Mg(BH_4)_4$ tetrahedrons (Mg: center, BH_4: vertex). The BH_4 unit is also tetrahedral (B: center, H: vertex). B-H bond length: 1.14 Å. Mg-B bond lengths: 2.34 - 2.47 Å.
Mg is bonded to 8-12 H.

HT $Mg(BH_4)_2$

- Orthorhombic – *Fddd*
- a = 37 Å, b = 18.5 Å, c = 11 Å
- V = 7550 Å^3; Z = 64
- Density = 0.7 meas.; 0.76 calc

The fit of experimental and calculated powder diffraction data by Rietveld refinement for the HT $Mg(BH_4)_2$ phase. The high-angle data are enlarged 8x for clarity.



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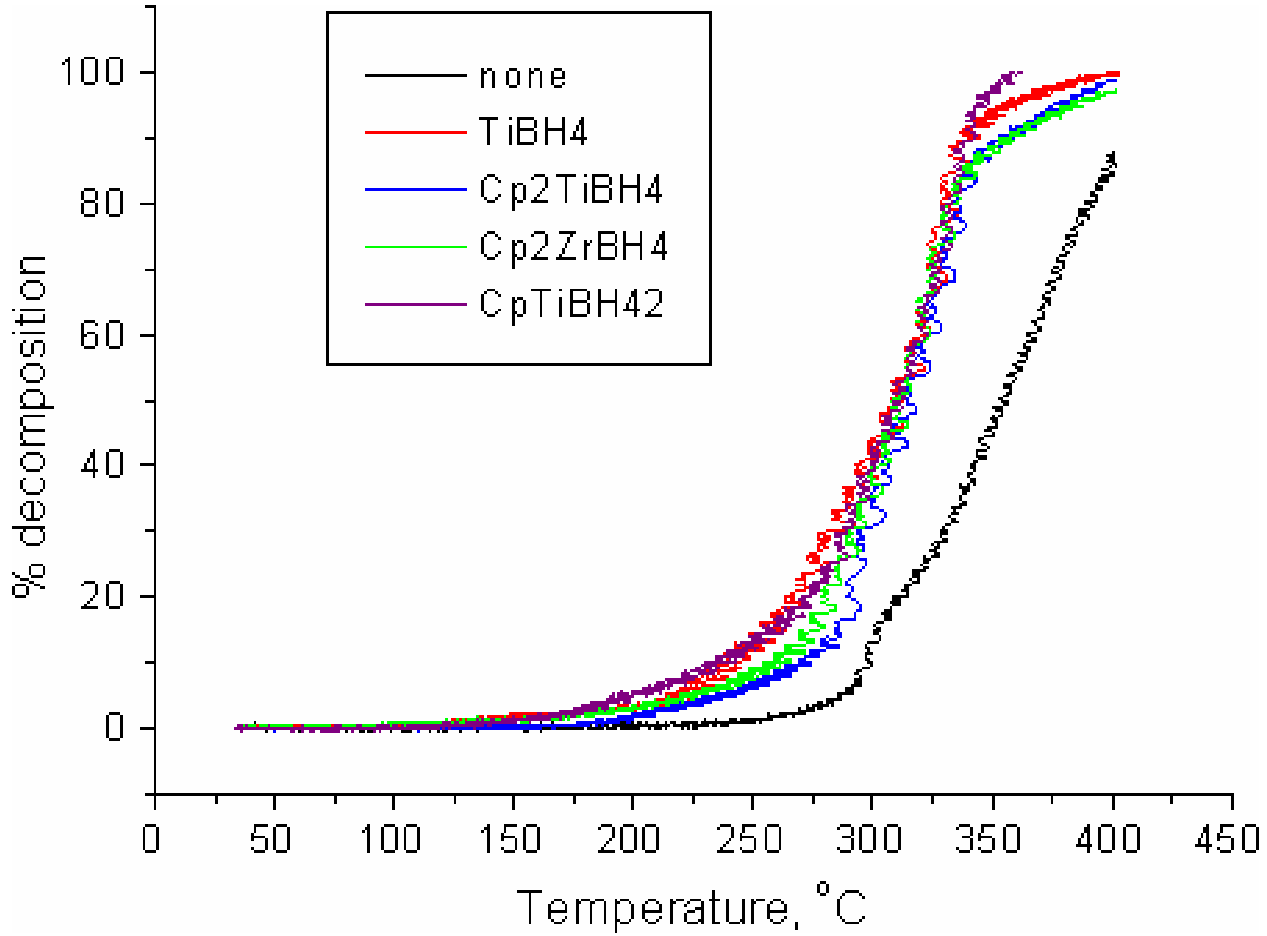
$Mg(BH_4)_2$: Catalyst Screening Results

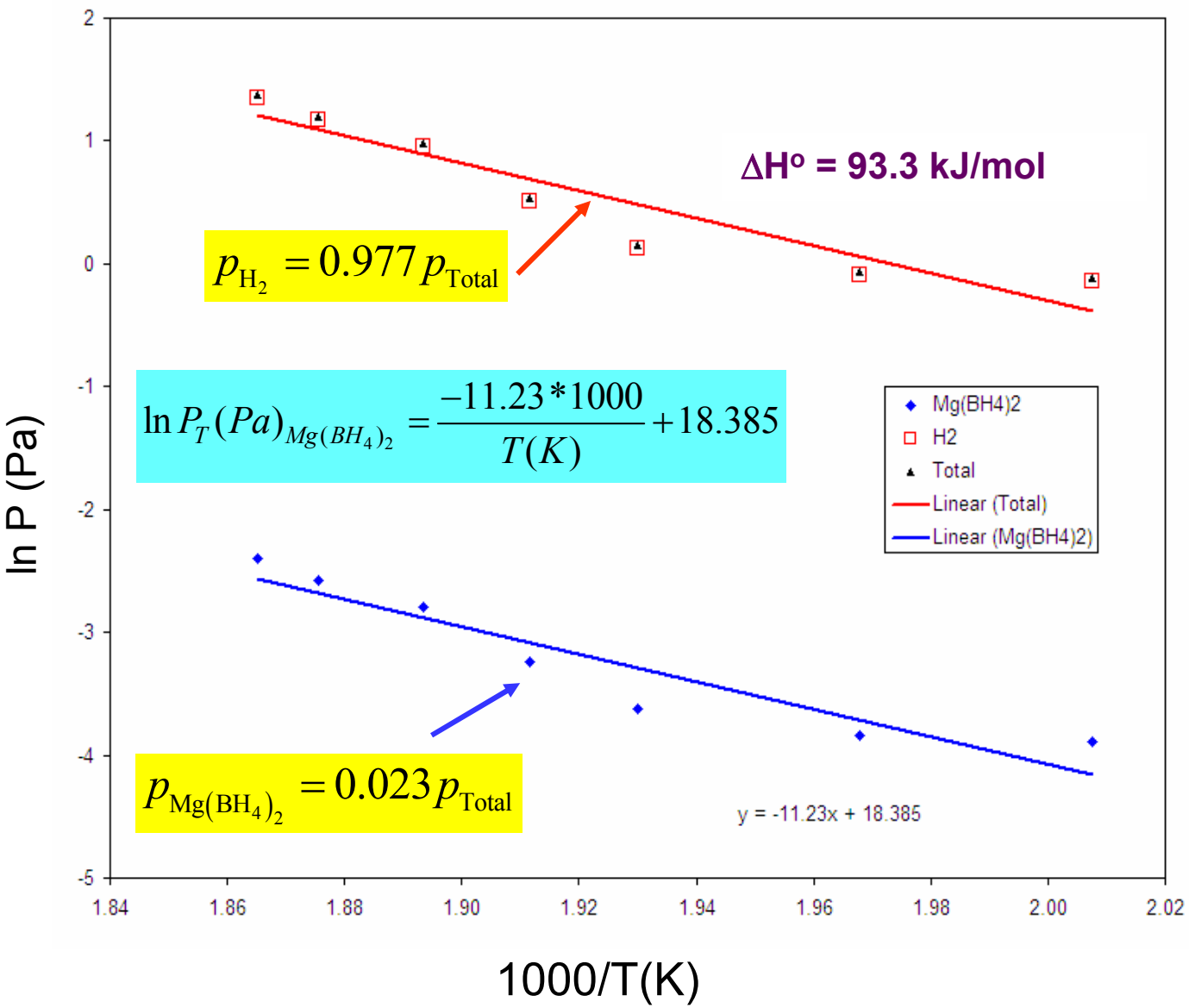


- Catalyst screening performed for many compositions
- The catalyst precursors $Ti(BH_4)_3$, $CpTi(BH_4)_2$, Cp_2TiBH_4 and Cp_2ZrBH_4 reduce $Mg(BH_4)_2$ decomposition temperature by up to 50 °C
- No catalyst found yet to enable $MgH_2 + 2B + 4H_2 \rightarrow Mg(BH_4)_2$ reaction

$Mg(BH_4)_2$: Vapor Pressure

Measurement performed by Dhanesh Chandra

$$Mg(BH_4)_2(s) \rightarrow Mg(BH_4)_2(g) + H_2$$



Summary

- No detrimental *cations* effusing out – stable
- Low Vapor pressures observed up to ~250ºC
- ~98% of Pressure is due hydrogen evolution
- $P_{H2(225°C)}$ = 8.8×10^{-6} atm (8.8×10^{-1} Pa)
- $P_{Mg(BH4)2}$ = 2.03×10^{-7} atm (225ºC) (2×10^{-2} Pa)
- Measured Average MW: 2.42 g/mol of effusing gas between 25°C and 250°C

Cleanest borohydride tested for vapor pressure

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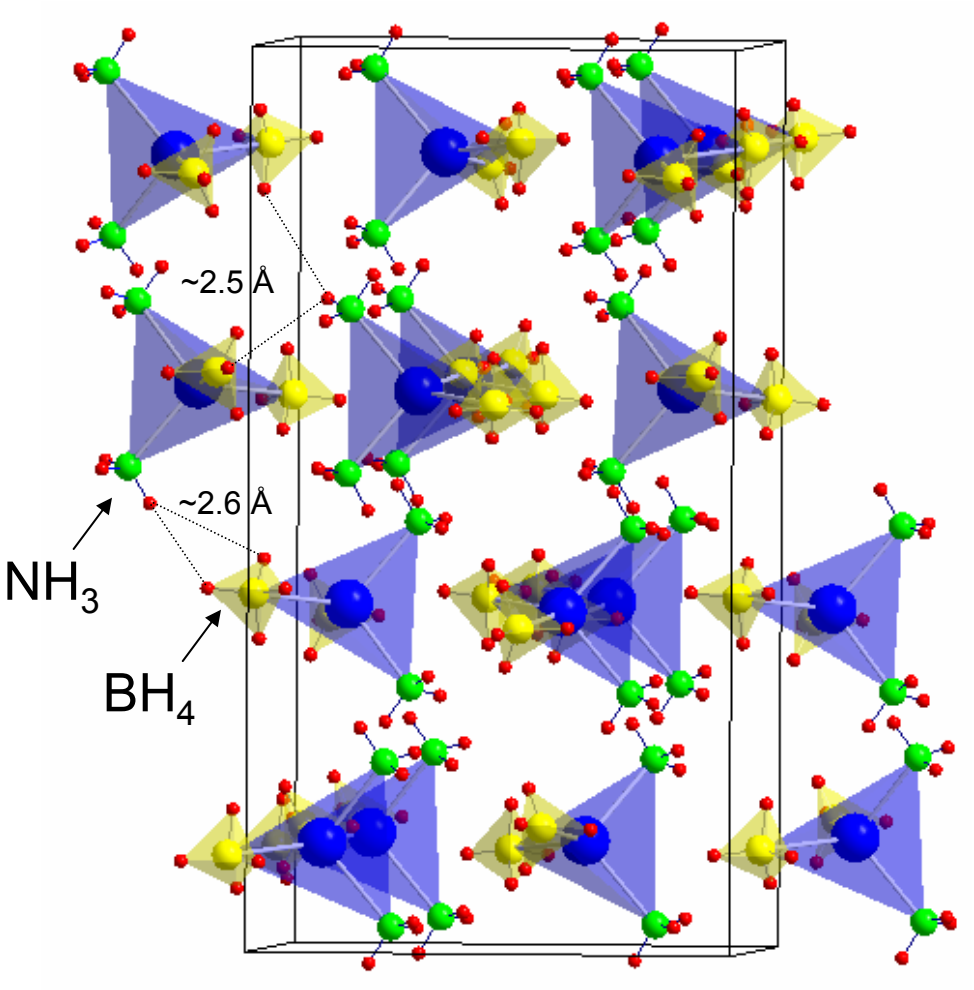
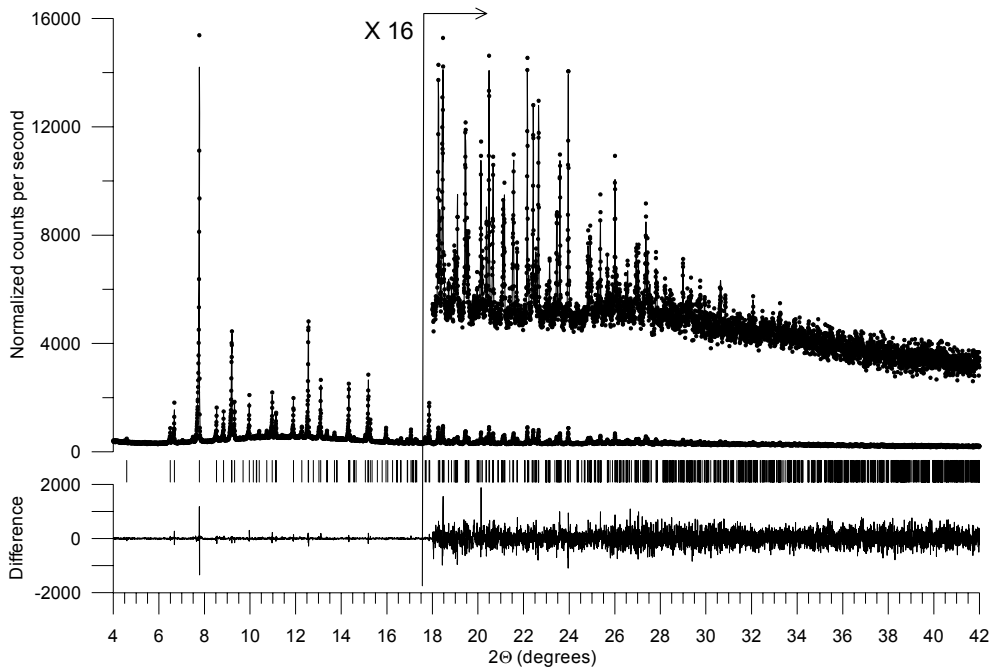
$Mg(BH_4)_2(NH_3)_2$ Structure

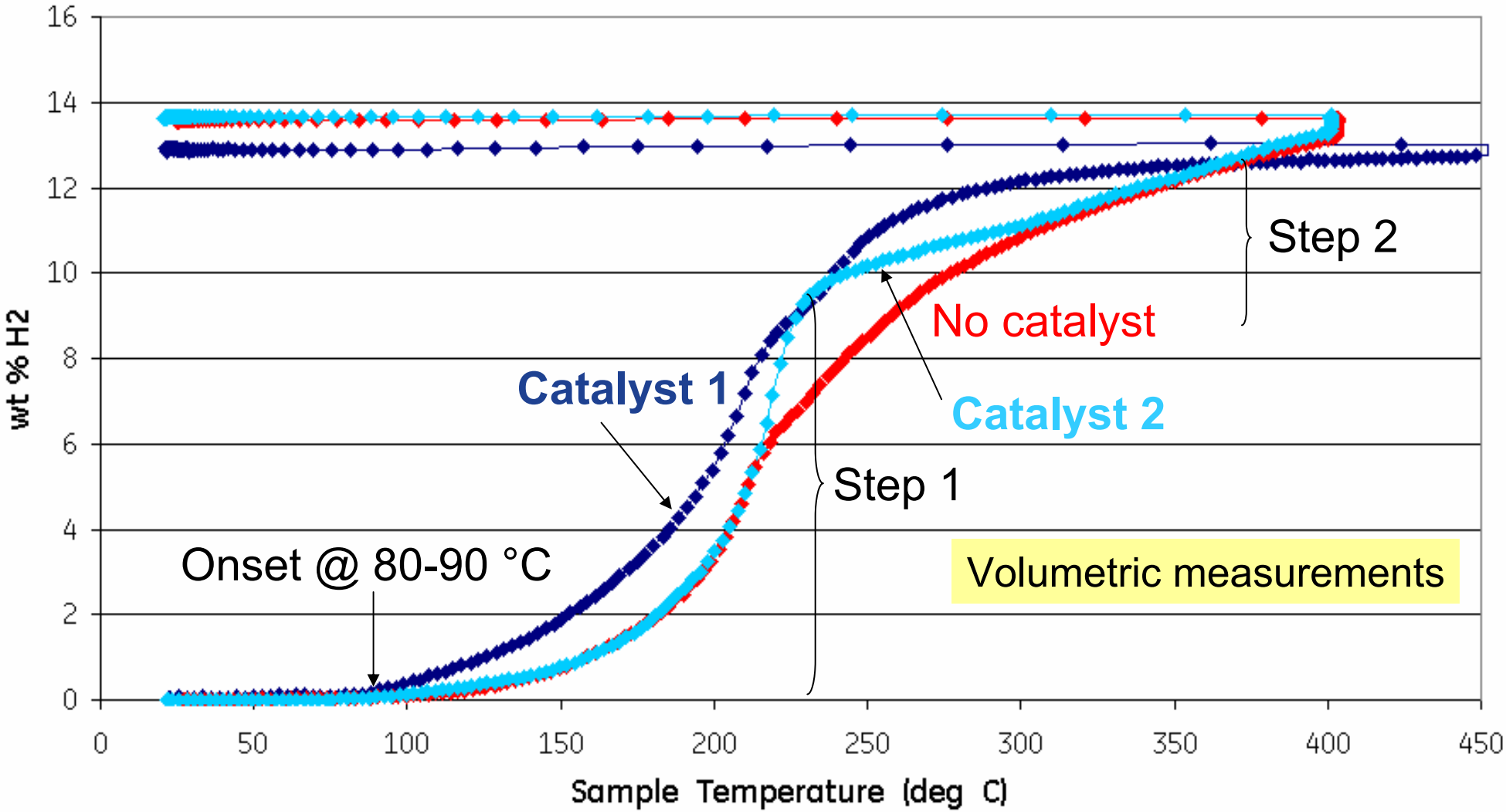


- 16 wt% H theoretical
- Complexes to reduce the T_{des}



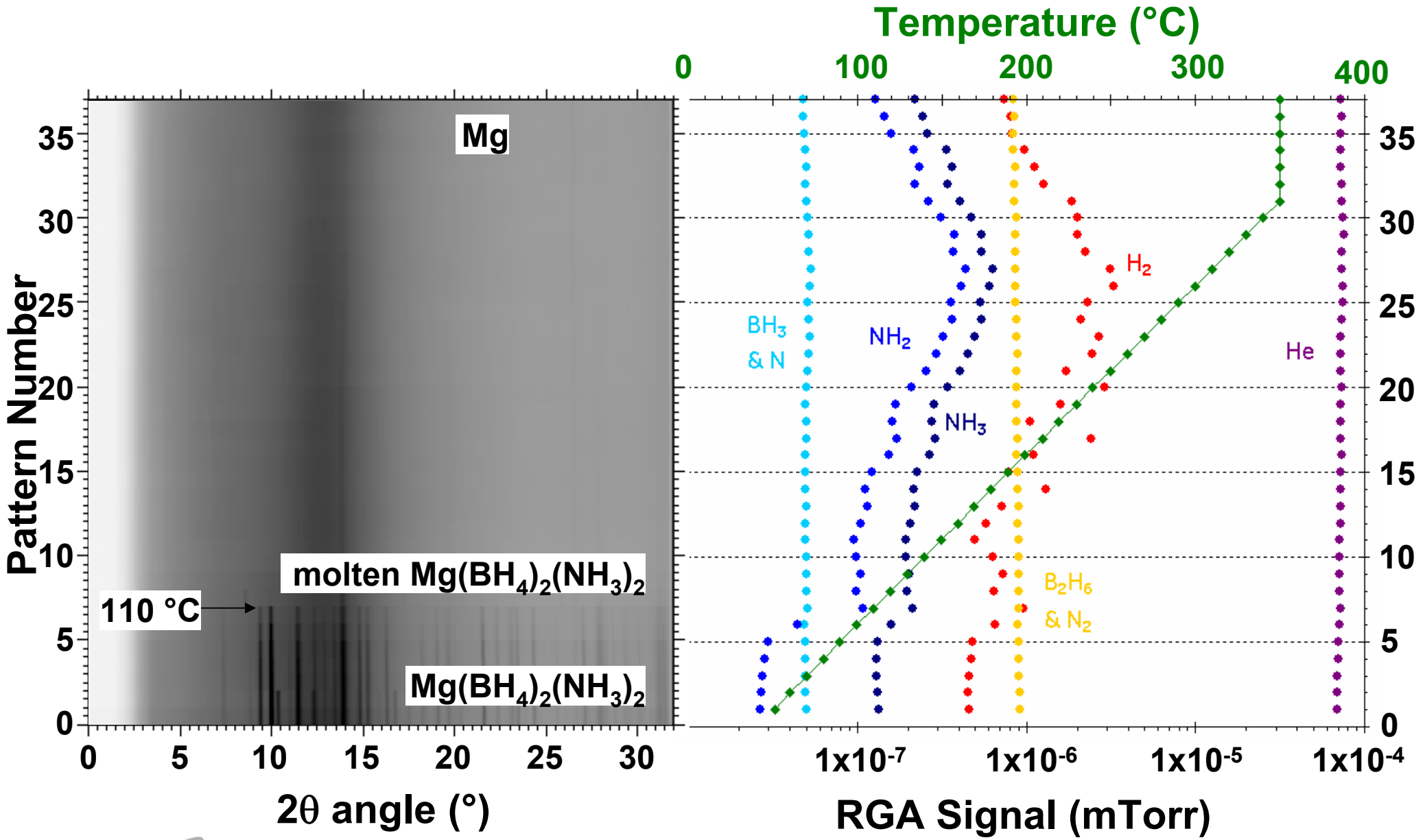
$Mg(BH_4)_2(NH_3)_2$: orthorhombic (*Pcab*; *a* = 17.487Å, *b* = 9.413Å, c = 8.732Å.
It consists of isolated tetrahedra of $Mg(BH_4)_2(NH_3)_2$. The tetrahedra are weakly connected via B-H---H-N "hydrogen" bonds to form three-dimensional network.

$Mg(BH_4)_2(NH_3)_2$ Desorption



- 10 wt.% H released by 225°C, 13 wt.% total, 16 wt.% theoretical
- Assumes H_2 is only gas released
- Only partially reversible – see slide 16

$Mg(BH_4)_2(NH_3)_2$ Desorption



- Significant NH_3 observed with some BH_3 / B_2H_6
- Decomposition product liquid → amorphous → Mg

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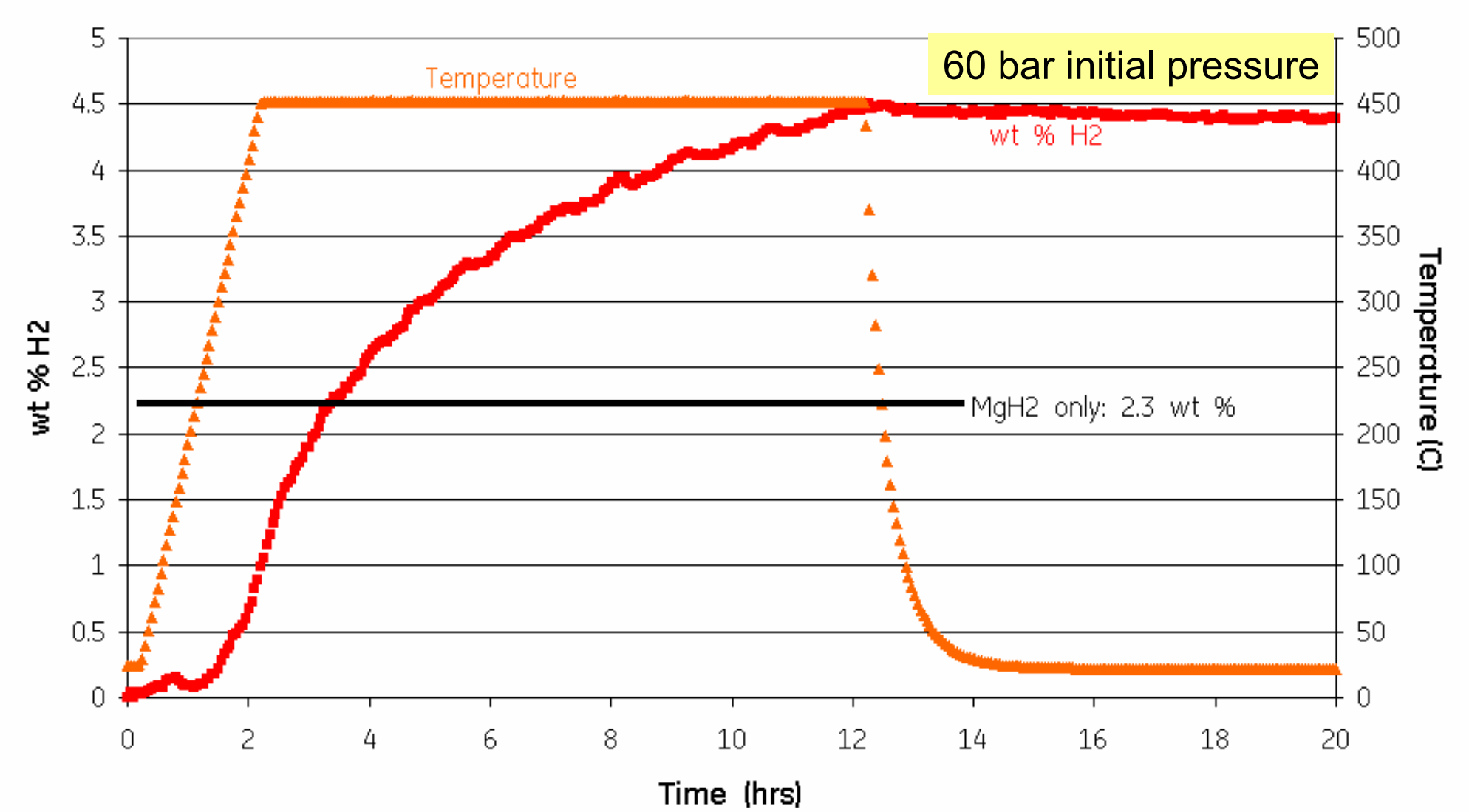
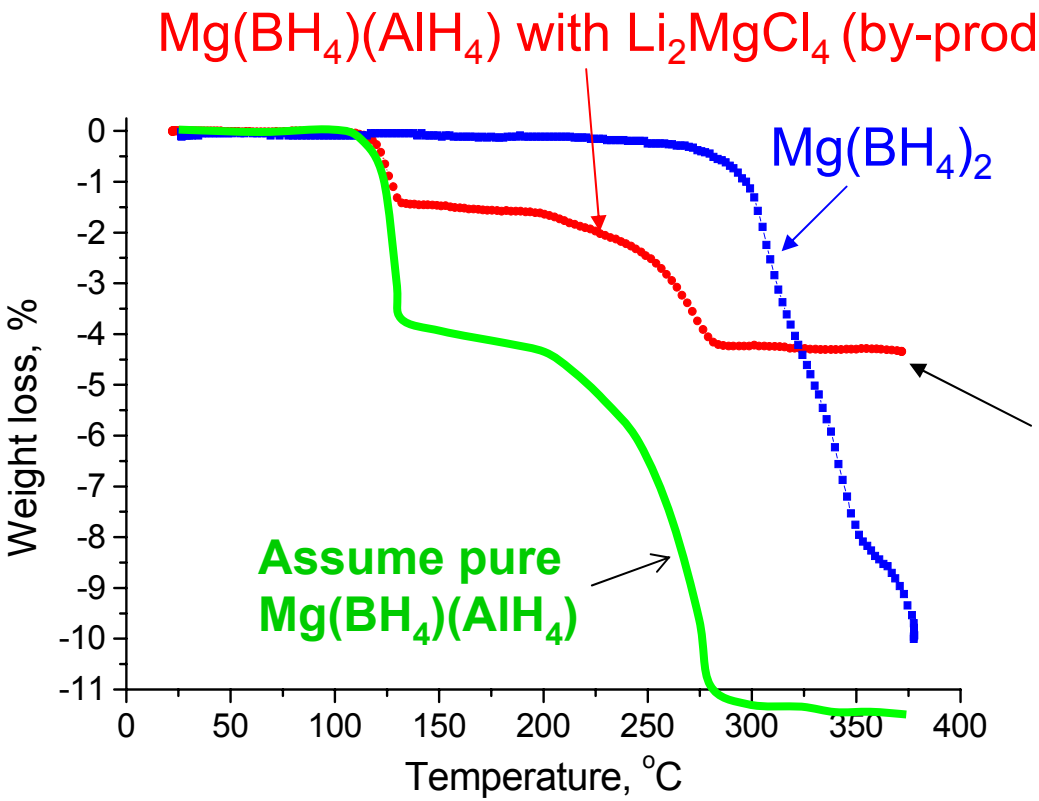
$Mg(BH_4)_2(NH_3)_2$: partial recharging?



- No change seen in XRD – most phases amorphous
- Recharging beyond Mg to MgH_2, but not fully reversible

$Mg(BH_4)(AlH_4)$: Synthesis & Decomposition

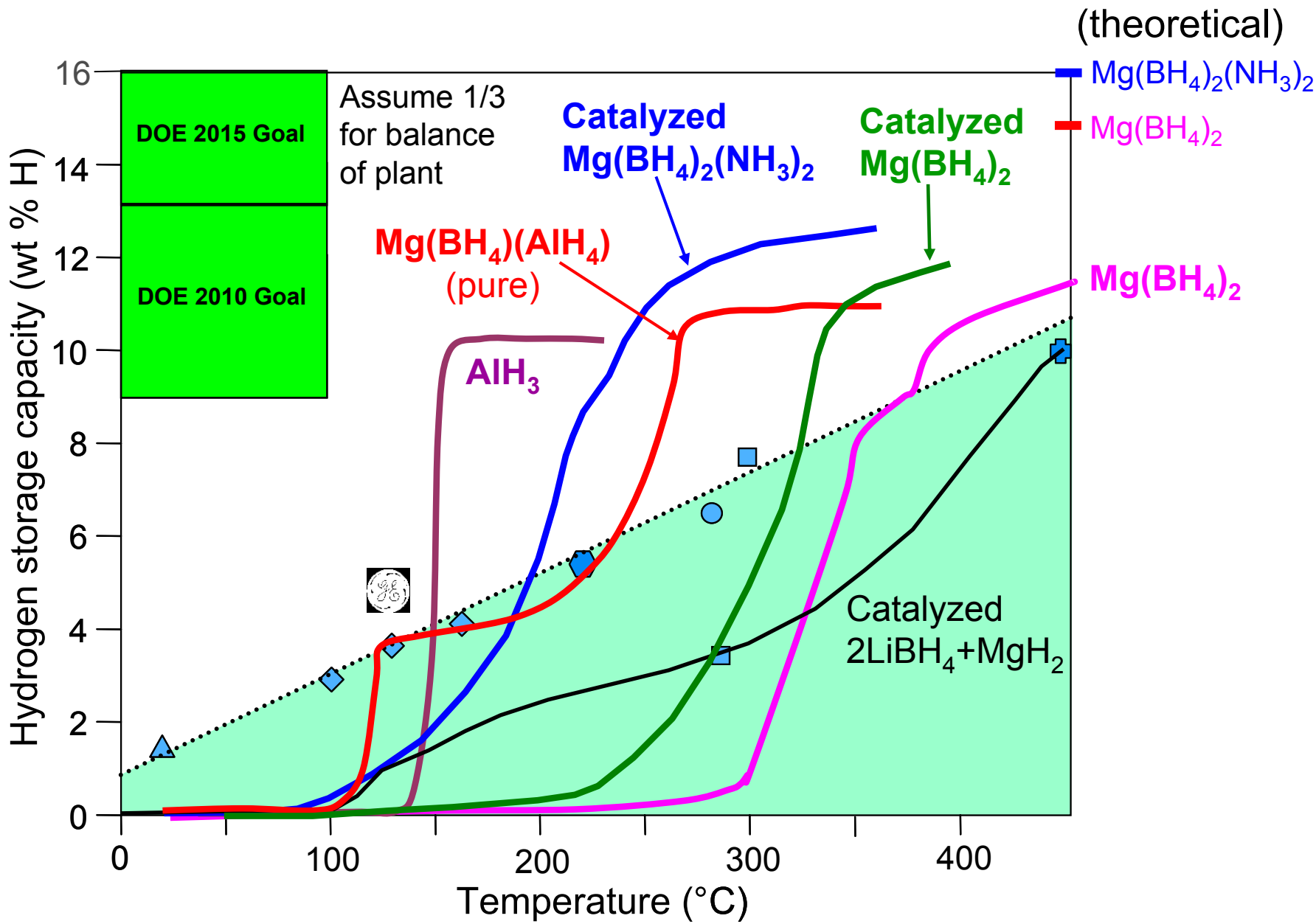
$$2\ MgCl_2 + LiAlH_4 + LiBH_4 \xrightarrow{Et_2O} Mg(BH_4)(AlH_4) + Li_2MgCl_4$$



- Substantial decrease in T_{des} comparing to $Mg(BH_4)_2$
- Low wt. % hydrogen due to the presence of Li_2MgCl_4

Attractive desorption temperature & capacity (**11.4 wt.% H** theoretical)

Summary: Status vs DOE Targets



Summary

- $Mg(BH_4)_2$ crystal structure identification accomplished – enable more realistic theoretical predictions of dopants & energistics
- Combinatorial screening found effective catalyst precursors that reduce the T_{des} of $Mg(BH_4)_2$ by 50°C.
- $Mg(BH_4)_2(NH_3)_2$ synthesized & crystal structure identified
- Catalyzed $Mg(BH_4)_2(NH_3)_2$ desorption starts at 80-90°C & can complete at <300°C, giving 13 wt% H (16 wt%H theoretical)
- $Mg(BH_4)(AlH_4)$ desorption starts at ~100°C & completes at 250°C (11.2 wt%H, theoretical)
- Collaborations ongoing with MHCoE partners to explore mechanisms and ways to reversibility

Future Work

FY07

- Combinatorial screening of dopants and catalysts for $Mg(BH_4)_2(NH_3)_2$, $Mg(BH_4)(AlH_4)$, & $Mg(BH_4)_2$
- Computational predictions of dopants for these hydrides
- Borane & high P reversibility experiments
- Mechanistic understanding for reversibility clues
- Go/No-Go for $Mg(BH_4)_2$

FY08

- Continue on catalyst and doping study of $Mg(BH_4)_2(NH_3)_2$, $Mg(BH_4)(AlH_4)$, & $Mg(BH_4)_2$ to improve reversibility & kinetics
- Perform system-level evaluation of properties such as cycling stability/degradation, thermal conductivity
- Go/No-Go for $Mg(BH_4)_2(NH_3)_2$ & $Mg(BH_4)(AlH_4)$ reversibility: < 400°C & < 200 bar

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