DOE Hydrogen Program

Lightweight Intermetallics for Hydrogen Storage

DOE Award #: DE-FC3605GO15062

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METAL HYDRIDE CENTER OF EXCELLENCE

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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: STP22

Program Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- Percent complete: 60%

Barriers

- Right heat of formation (J)
- Absorption / desorption kinetics (E)
- Reversibility for borohydrides (D, P)

Budget

- Total Project Funding: *$3.47M*
  - DOE Share: $2.78M
  - GE & OSU Share: $0.69M
- Funding Received for FY07

  $430K (DOE), $115K (GE)

Partners/Collaborations

- Member of DOE MHCoE
- Collaborations with ORNL, JPL, Caltech, U. Pitt, SNL, Univ. Nevada, U. Utah, and Brookhaven.

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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
FY08	• Study the desorption mechanism and explore ways to make the $Mg(BH_4)_2$ reversible • Explore new hydride materials

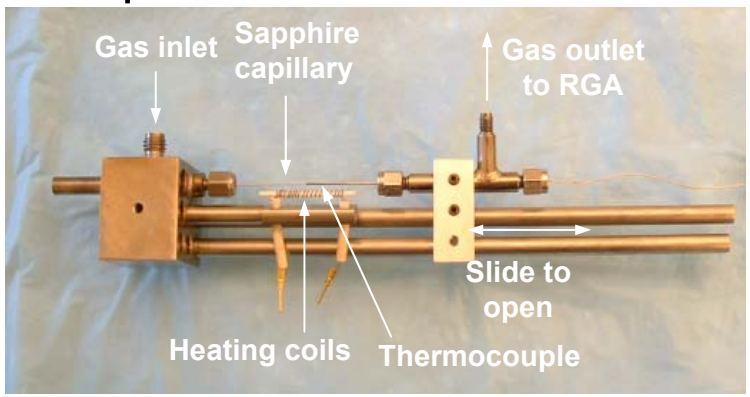
Approach

- Study the crystal structures and the decomposition mechanisms using multiple techniques such as in-situ XRD, interrupted PCT tests, boron NMR, IR, DSC, and residual gas analysis;
- Develop reversibility strategy from detailed mechanistic understanding of the complex desorption processes;
- Synthesize new hydrides and complexes.

Mechanistic Understanding:

Combined In-situ XRD and gas analysis

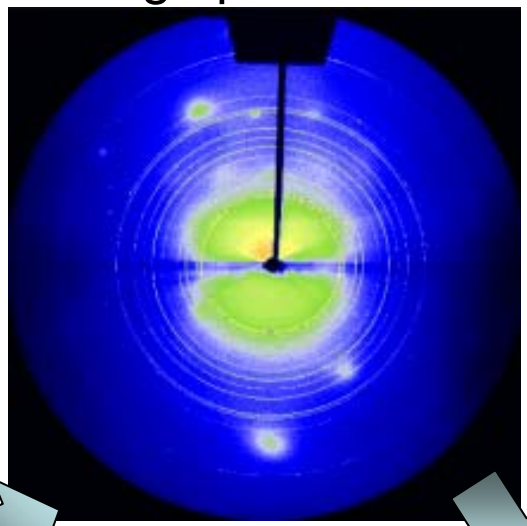
Sample holder



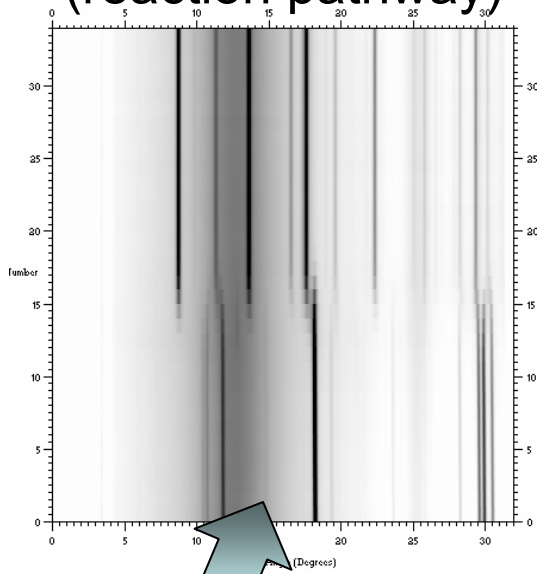
max T: 450 °C

max P: 2000 psi

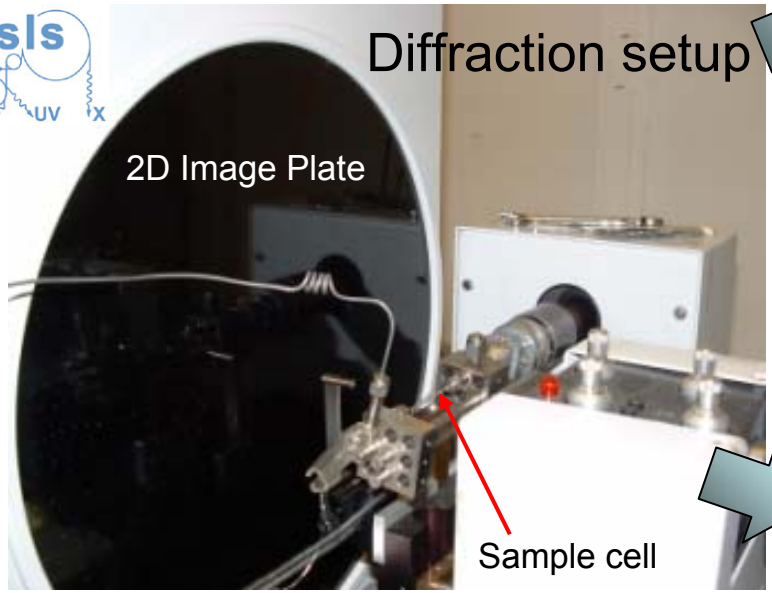
Image plate readout



Time resolved patterns (reaction pathway)

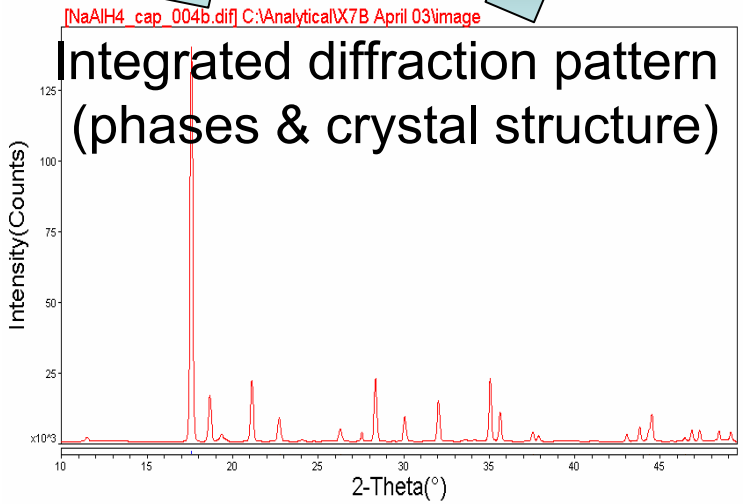


Diffraction setup



RGA (gas analysis)

Integrated diffraction pattern (phases & crystal structure)



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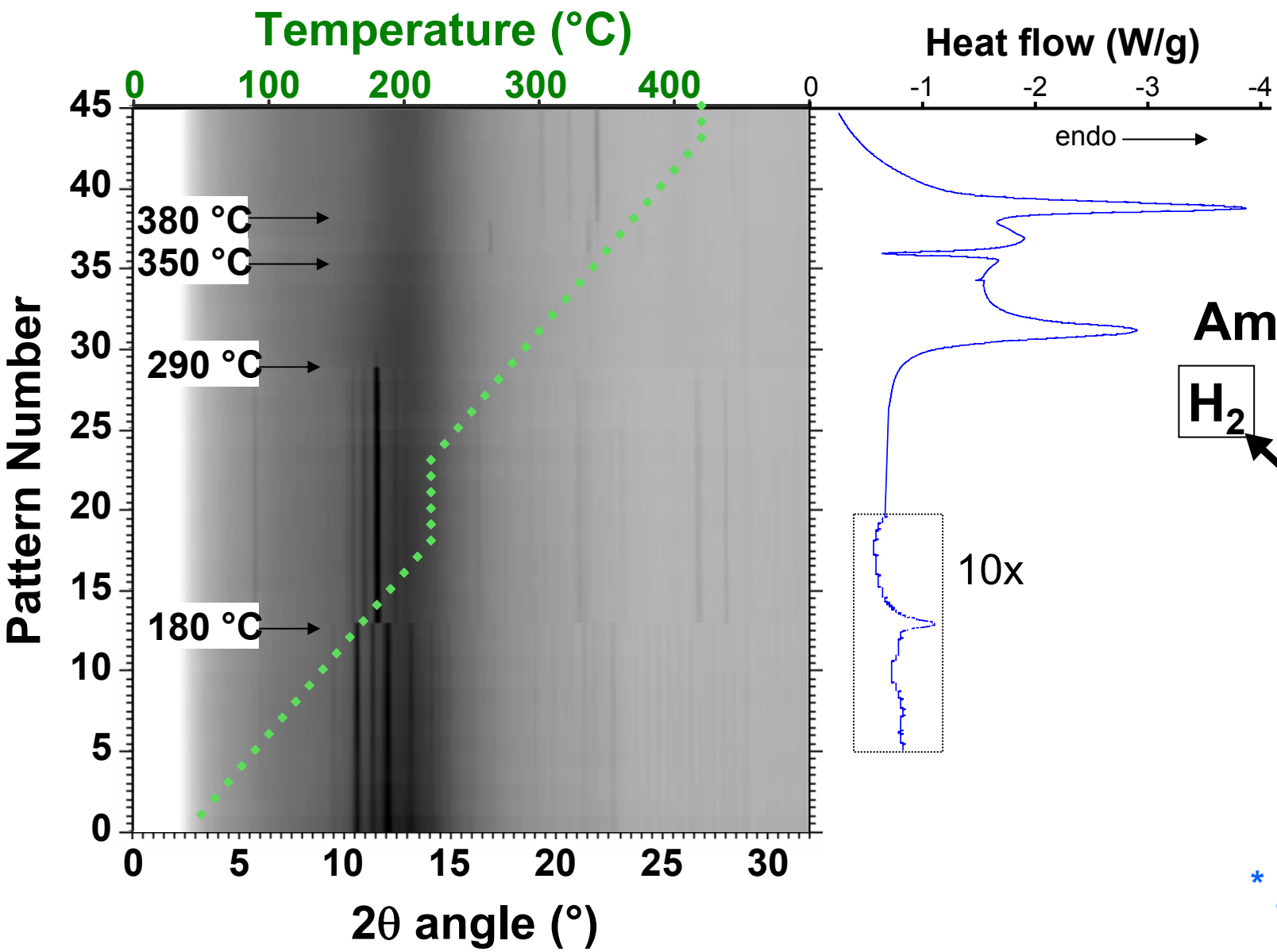
$Mg(BH_4)_2$ – Hydrogen Desorption (XRD)



$Mg + B^*$ H_2

$MgH_2 + B^*$

$Amorphous^* + B^*$

H_2

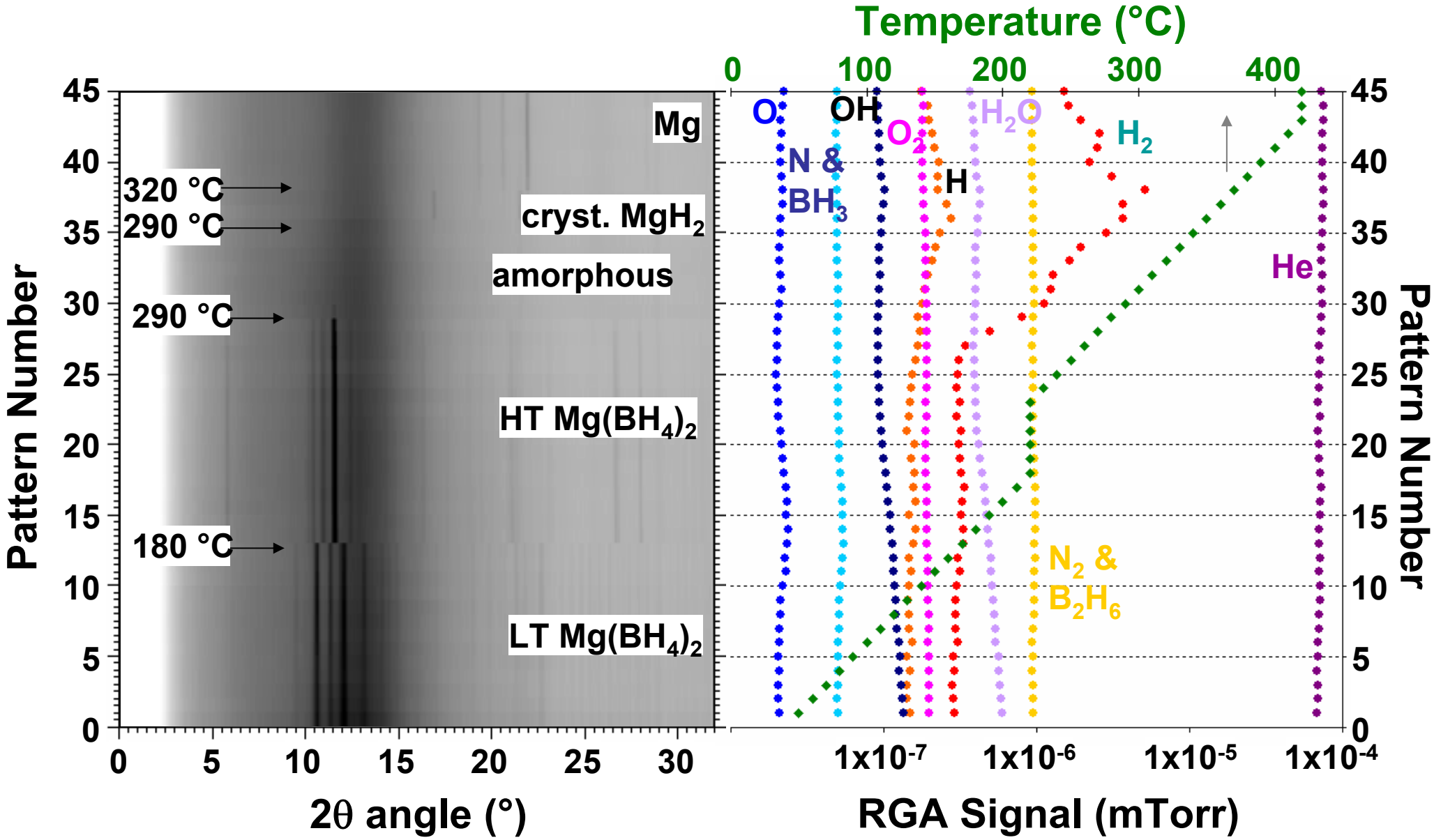
$HT\ Mg(BH_4)_2$

$LT\ Mg(BH_4)_2$

* amorphous

Complex hydrogen desorption pathway

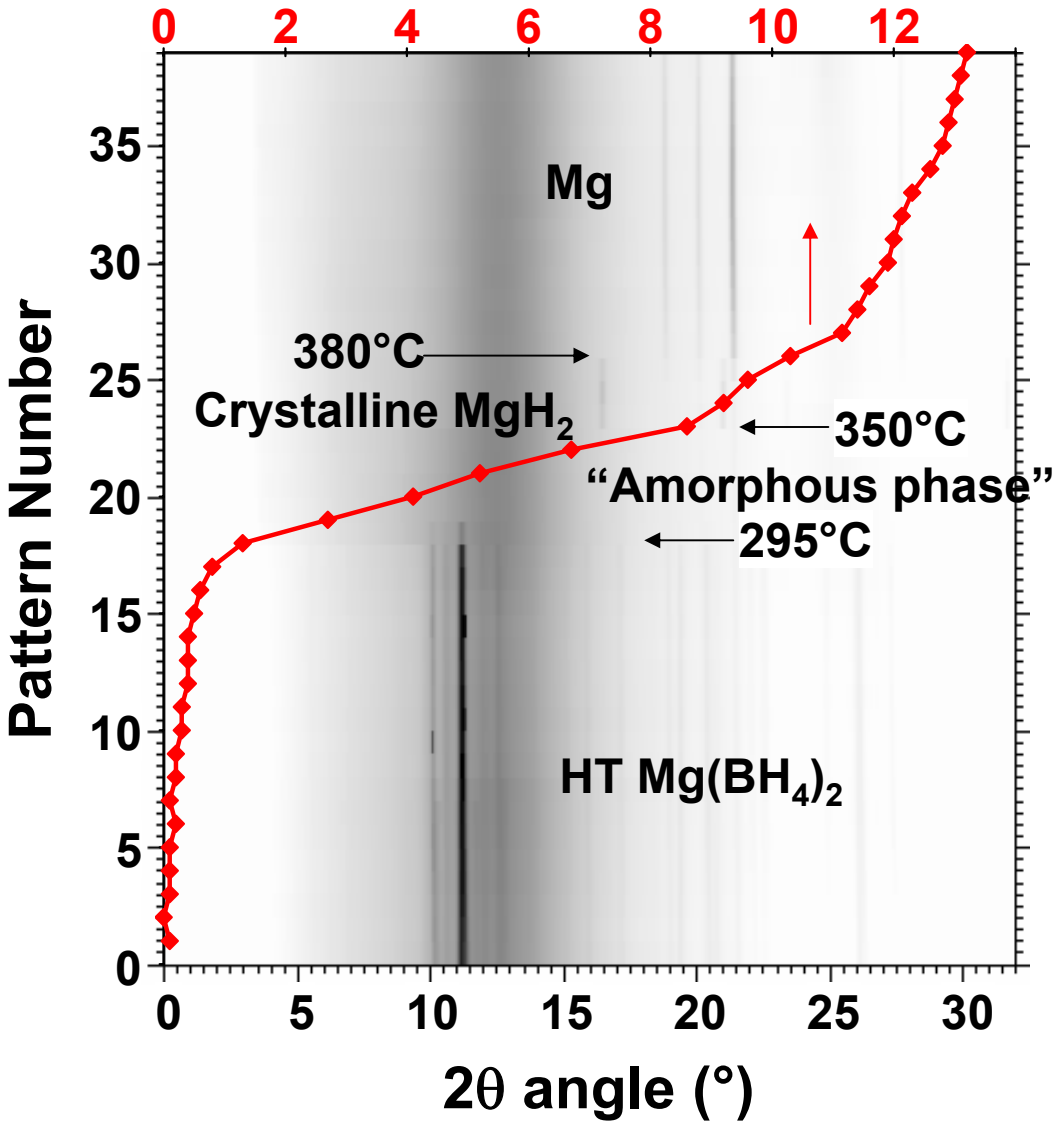
$Mg(BH_4)_2$ – Hydrogen Desorption (MS)



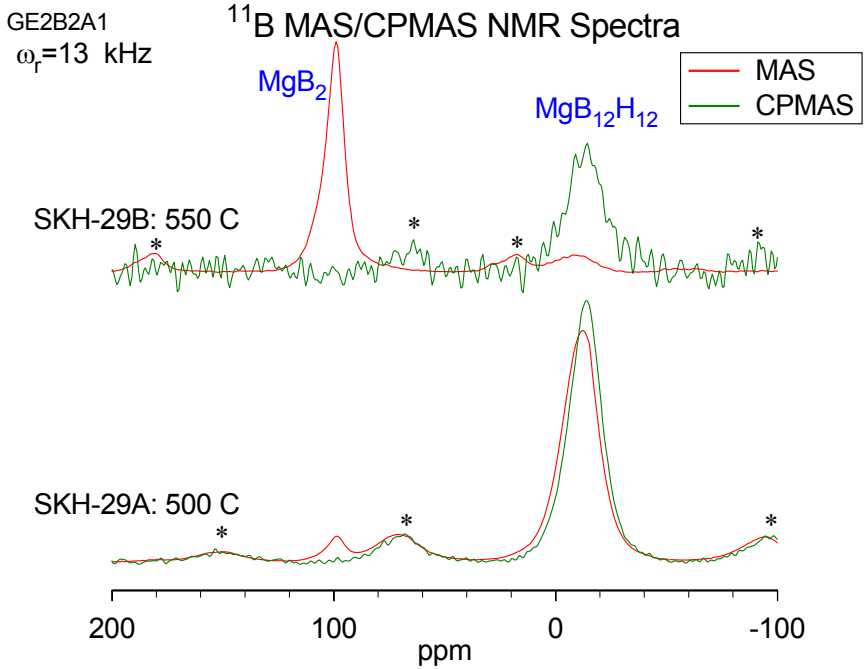
$Mg(BH_4)_2$ Desorption (NMR)

$Mg(BH_4)_2 \rightarrow$ Intermediate $\rightarrow MgH_2 + 2B + 3H_2$

Released hydrogen (wt %; TPD)



$MgH_2 \leftrightarrow Mg + H_2$



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

S.-J. Hwang, R.C. Bowman, Jr., J.W. Reiter, J. Rijssenbeek, G.L. Soloveichik, J.-C. Zhao, H. Kabbour, and C.C. Ahn. **J. Phys. Chem. C**., 2008; **112**; 3164-3168.

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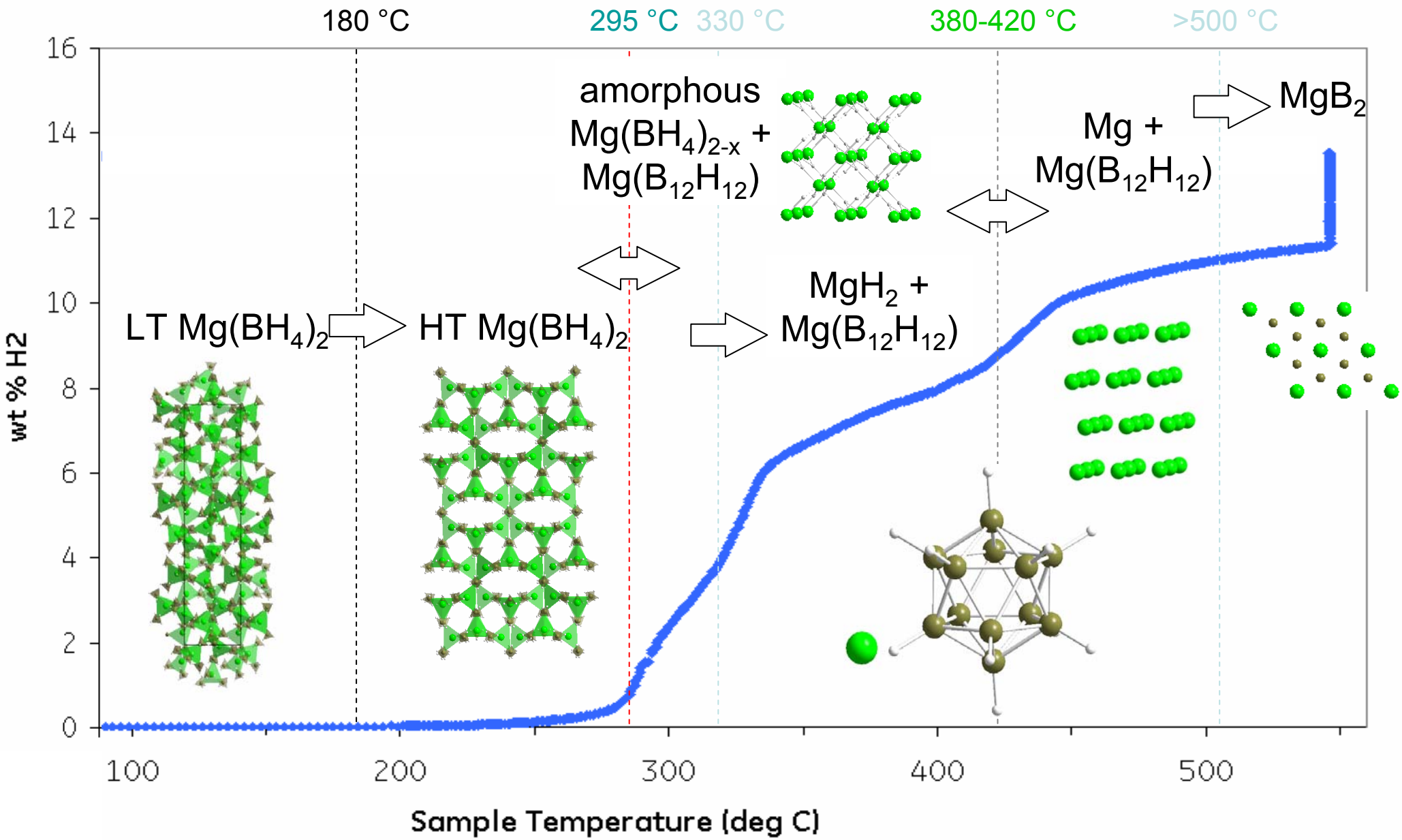
$Mg(BH_4)_2$ Desorption



Much clearer understanding of the complex desorption process achieved.

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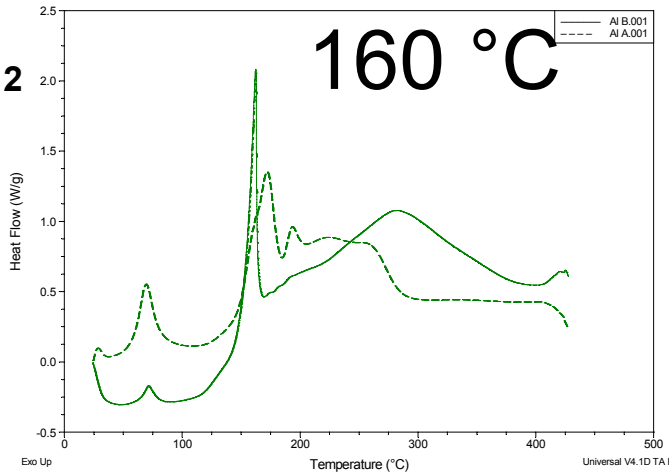
NH_3 Complexes of Metal Borohydrides

$$MCl_n + 2{+}n\ LiBH_4 \xrightarrow[3\ hrs]{Et_2O} Li_2Mg(BH_4)_2 \xrightarrow[-30\ ^oC]{NH_3} M(BH_4)_n{\cdot}6NH_3 + 2\ LiBH_4$$

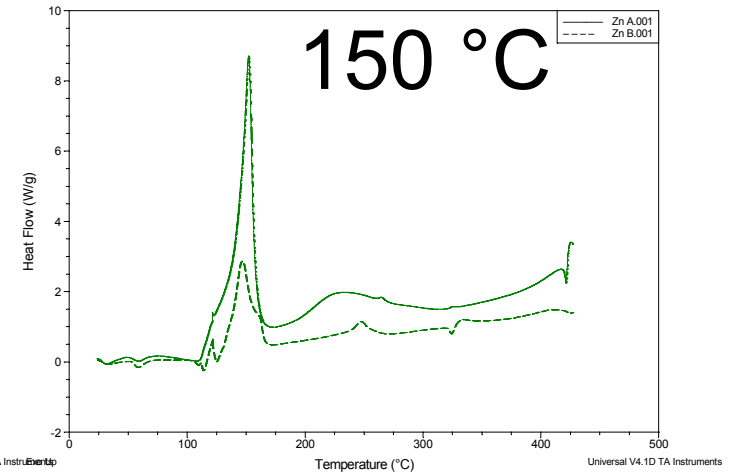
$2\ LiCl$

$M(BH_4)_n{\cdot}6NH_3 \rightarrow \mathbf{M(BH_4)_n{\cdot}2NH_3}$

$M(BH_4)_n{\cdot}2NH_3$	wt % H_2
$Mg(BH_4)_2{\cdot}2NH_3$	16.0
$Zn(BH_4)_2{\cdot}2NH_3$	10.9
$Al(BH_4)_3{\cdot}2NH_3$	17.1
$Ti(BH_4)_3{\cdot}2NH_3$	14.3



$Al(BH_4)_3{\cdot}2NH_3$



$Zn(BH_4)_2{\cdot}2NH_3$

- NH_3 complexes of several metal borohydrides synthesized.
- Aluminum and zinc borohydrides have low H_2 desorption T.
- Reversibility unexplored yet.

NH_3 Complexes of Metal Borohydrides

- NH_3 complexes may be a very effective way to fine-tune the thermodynamics of borohydrides:
  - Reduction of desorption temperature (T_{des}) when the borohydride T_{des} is high, e.g. reduce the T_{des} of $Mg(BH_4)_2$ from 290ºC to ~ 100ºC in $Mg(BH_4)_2(NH_3)_2$.
  - Increase T_{des} of several borohydrides when their T_{des} is low (too unstable), e.g. increase the T_{des} of $Al(BH_4)_3$ and $Zn(BH_4)_2$ to ~ 150-160ºC
- Need to understand the mechanism to take full advantage of this tunability.
- Ammonia formation may be a concern.
- Need more work to explore reversibility of such complexes.

Summary

- Gained significant better understanding of the desorption process of $Mg(BH_4)_2$ in collaboration with JPL/Caltech using five independent techniques.
- Discovered the formation of an amorphous $MgB_{12}H_{12}$ intermediate phase.
- Discovered reversible behavior at about 300˚C and 100 bar H_2 pressure from $Mg(BH_4)_2$ to $Mg(BH_4)_{2-x}$ during the initial decomposition process of $Mg(BH_4)_2$.
- Synthesized NH_3 complexes of several borohydrides and found favorable tunability of their desorption temperatures,
- Recommend to explore reversible hydrogen storage via $(Li,Na,Mg,K,Ca)_XB_{12}H_{12} \leftrightarrow (Li,Na,Mg,K,Ca)(BH_4)_X$.

Future Work

FY08

- Borane & high P reversibility experiments
- Synthesis of single-phase $MB_{12}H_{12}$ phase for mechanism and structure study (M = Li, Mg, and Ca)
- Synthesize other complexes of $(Mg,Ca)(BH_4)_2$

FY09

- Synthesize $Mg(BH_4)(AlH_4)$ & other $Mg(BH_4)_2$ complexes to improve desorption temperature, reversibility & kinetics
- Explore new classes of materials in collaboration with ORNL, Sandia, U. Utah, and JPL/Caltech
- Continue mechanistic work for improving reversibility