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 –

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Project ID #14

Program Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- Percent complete: *30%*

Barriers

Right heat of formation

Absorption / desorption kinetics

Budget

- Total Project Funding: *$3.47M*
  - DOE Share: $2.78M
  - GE Share: $0.69M
- Funding Received for FY05

  $450K (DOE), $112K (GE)
- Funding Received for FY06

  $450K (DOE), $112K (GE)

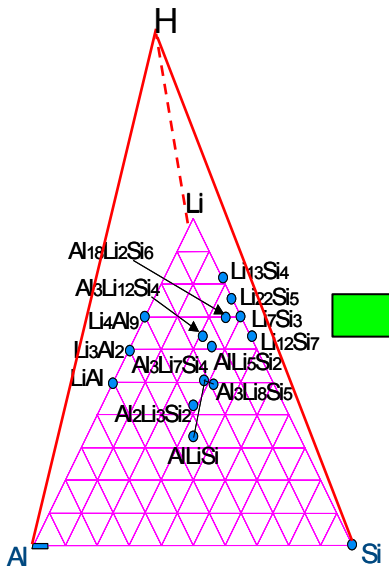
Partners/Collaborations

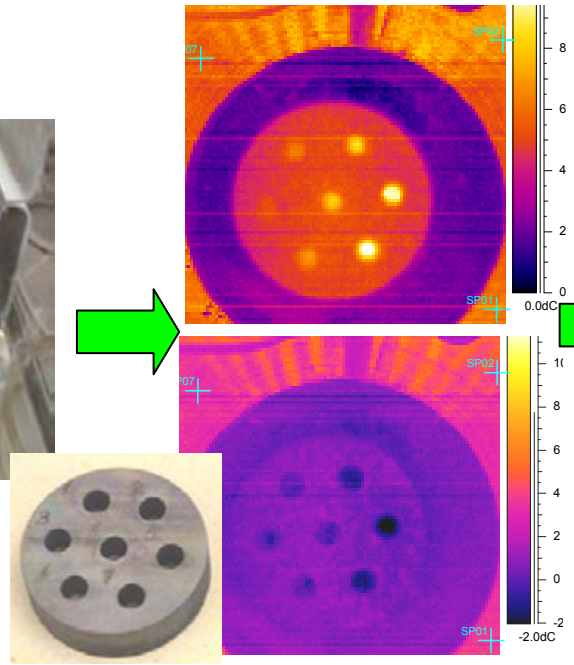
- Member of DOE MHCoE
- Collaborations with BNL, NIST, UIUC, CMU, U. Pitt, SNL, Univ. Nevada

Objective

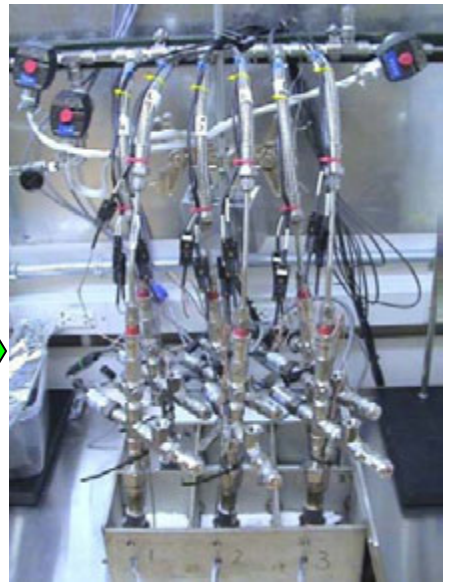
Overall	Discover and develop a high capacity (> 6 wt.%) lightweight hydride capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.
FY05	• Develop a high-efficiency combinatorial synthesis and high-throughput screening methodology for metal hydride discovery • Identify hydrides from combinatorial 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 $Mg(BH_4)_2$

Approach

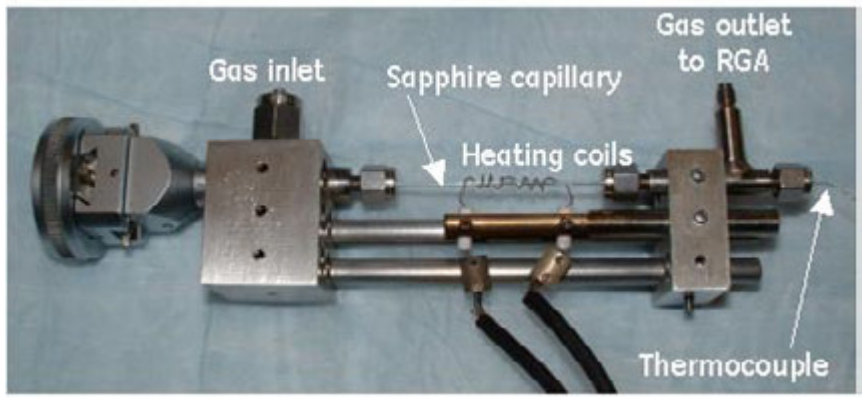




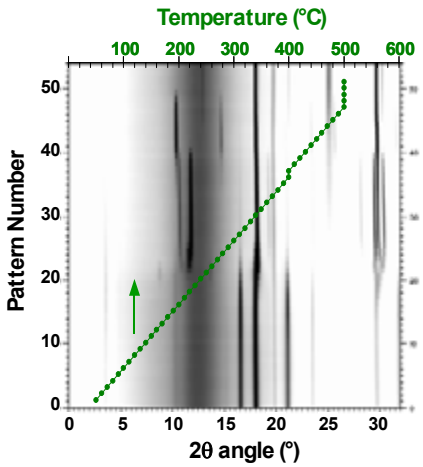
T: <400 °C P: <70 bar



T: <400 °C P: <140 bar



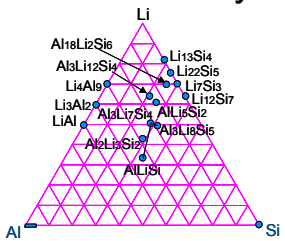
max T: 550 °C max P: 140 bar



Robust combinatorial/high-throughput methodology developed & validated by confirming the observations with bulk PCT tests

Combi findings in aluminides & silicides

$(AlLi + Si)\ Al_xLi_ySi_z + H_2 \rightarrow AlLiSiH_{0.9} + Li_7Si_3\ (Li_{12}Si_7) + AlLi + Al$



H_2

$AlLi + Li_{12}Si_7 + Al$

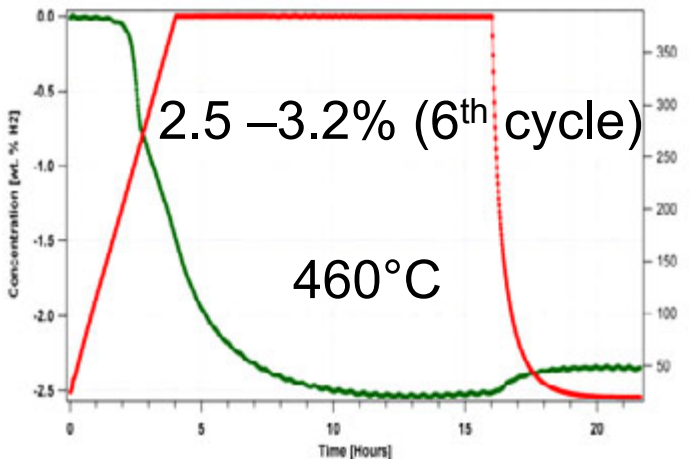
- All compositions goes to AlLiSiH
- 300-380°C, ~1 wt.%
- Found using diffusion multiple

$MgH_2 \leftrightarrow Mg + H_2$ 7.0 wt % 300°C

$MgH_2 + 0.71\ Al \leftrightarrow MgAl_{0.71} + H_2$ 4.4 wt % 230°C

- Reduced T & wt.%
- Faster kinetics
- Found using shaker
- Known in literature

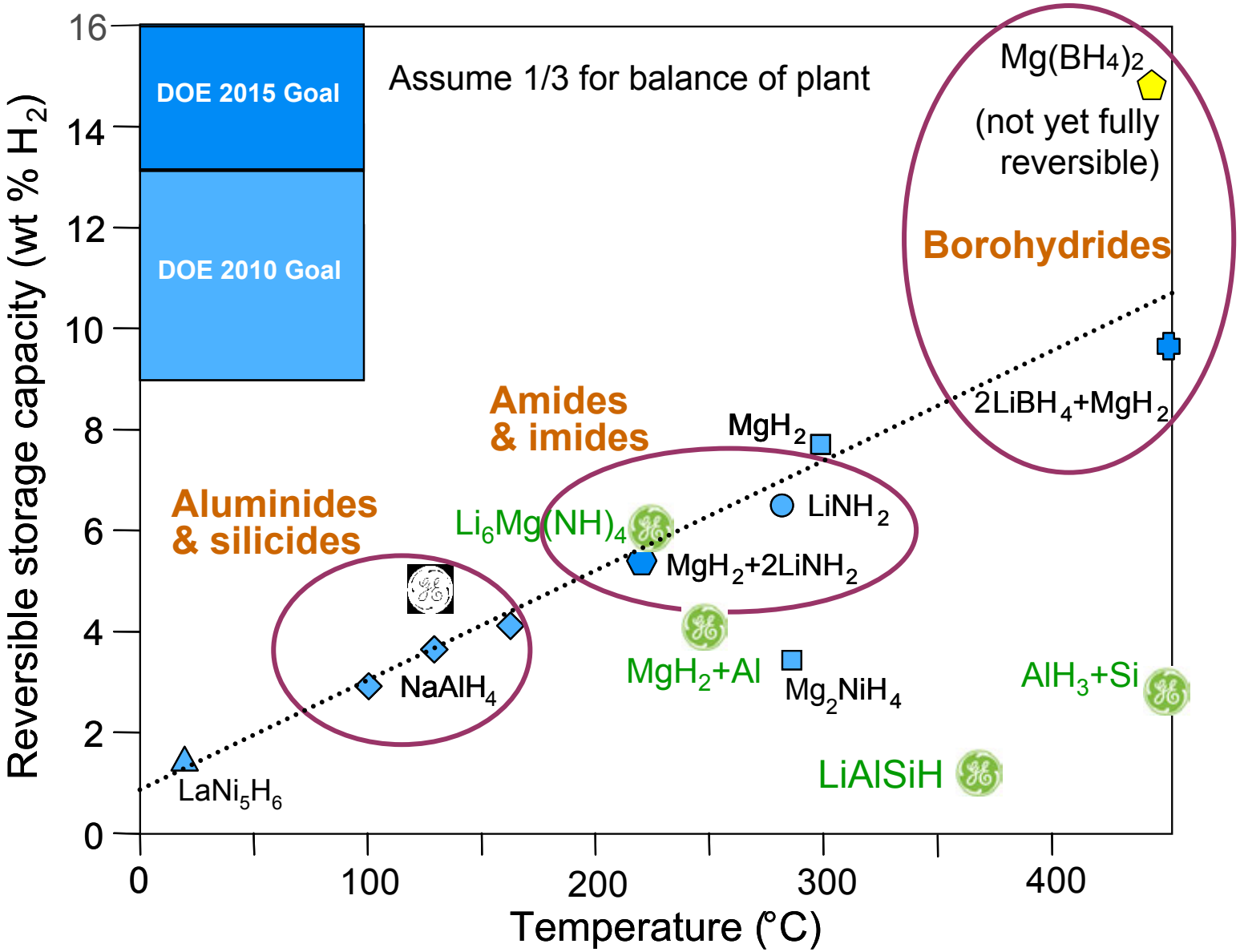
AlH_3 + Si:



- 400-460°C, ~3 wt.%
- Found using multi-well shaker
- Surprising finding
- Don't understand what's going on yet
- Shows the power of Combi/HTS

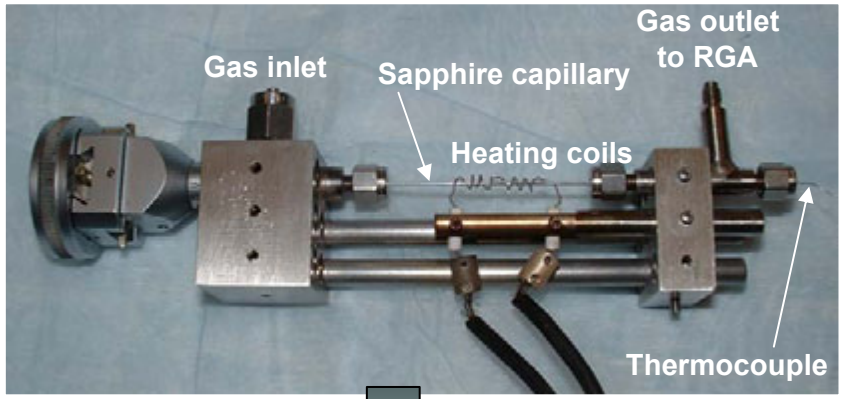
- Screened > 10 ternary systems (Al-Li-Si, Al-Mg-Ti, Al-Si-Ti, Al-Li-Mn, Li-Na-Si, etc.)
- No promising hydrides found, suspending efforts in this area

Metal hydrides against DOE targets



Combined *In-situ* XRD and gas analysis

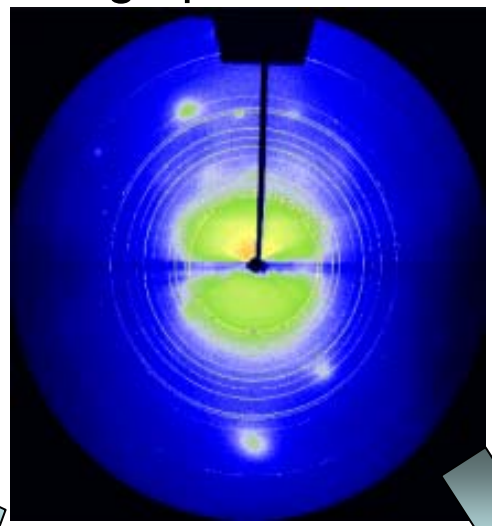
Sample holder



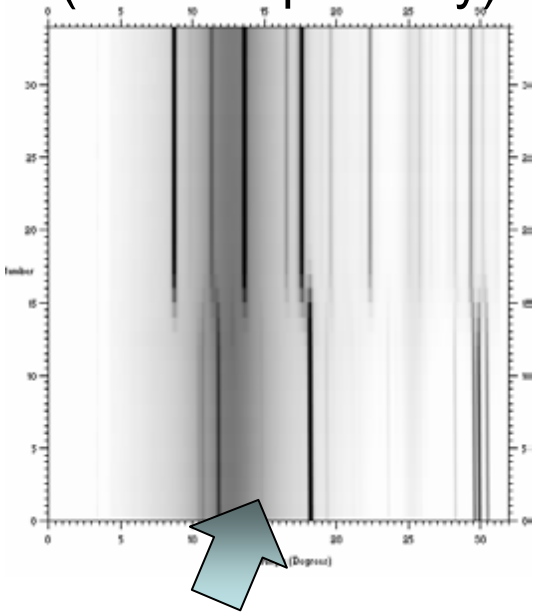
max T: 550 °C

max P: 140 bar

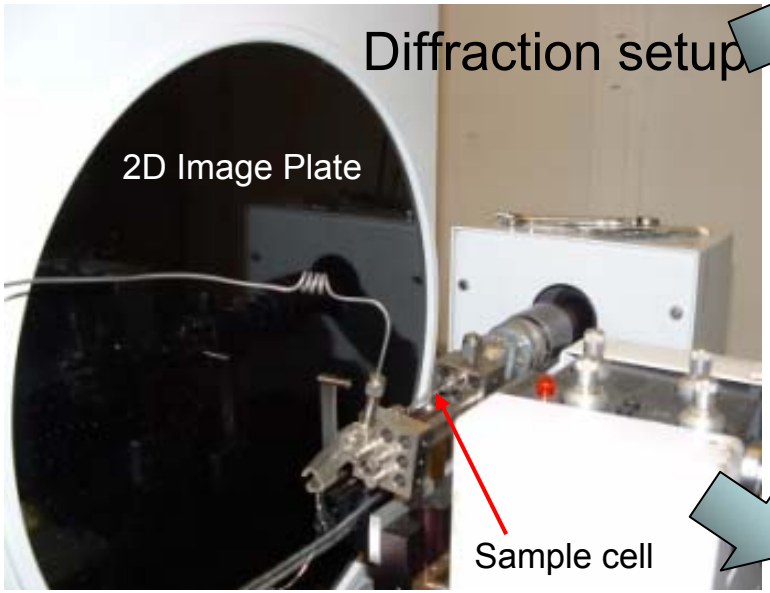
Image plate readout



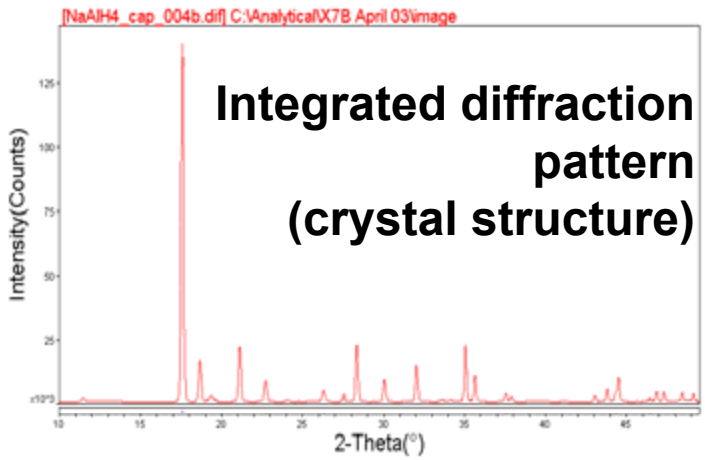
Time resolved patterns (reaction pathway)



Diffraction setup



Provides unmatched information about reaction pathways / mechanism

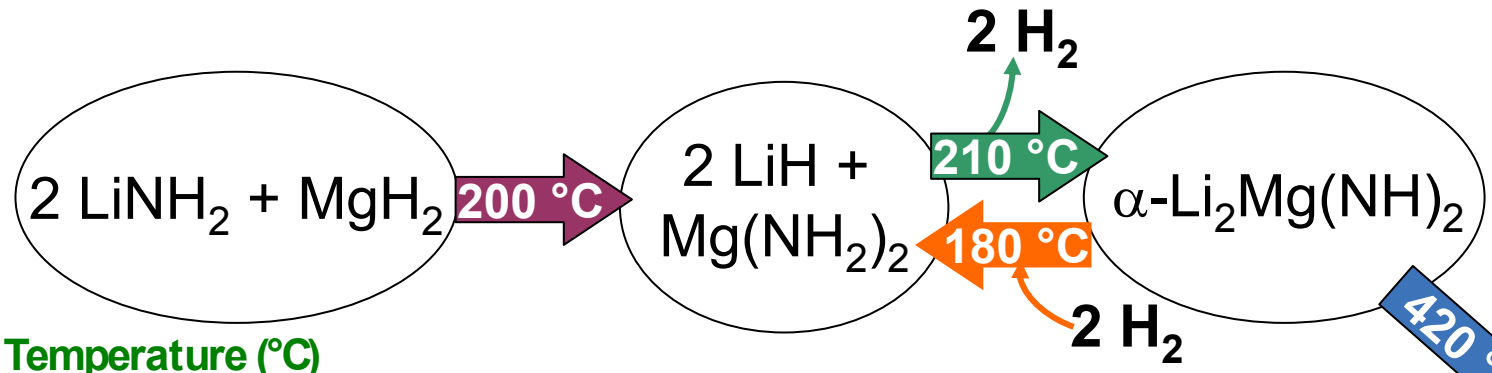


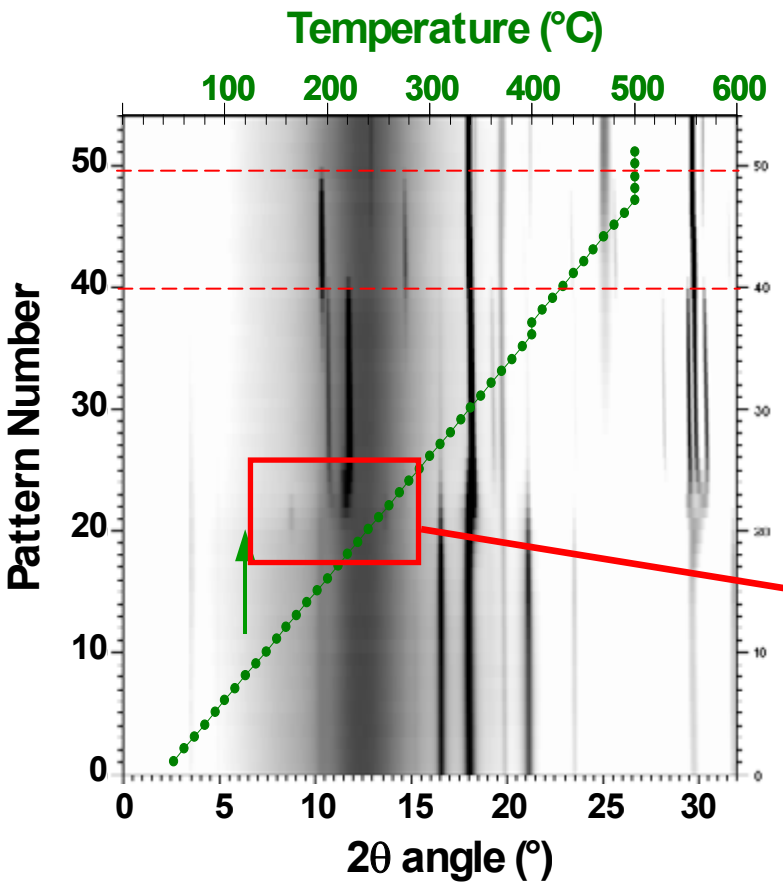
Integrated diffraction pattern (crystal structure)

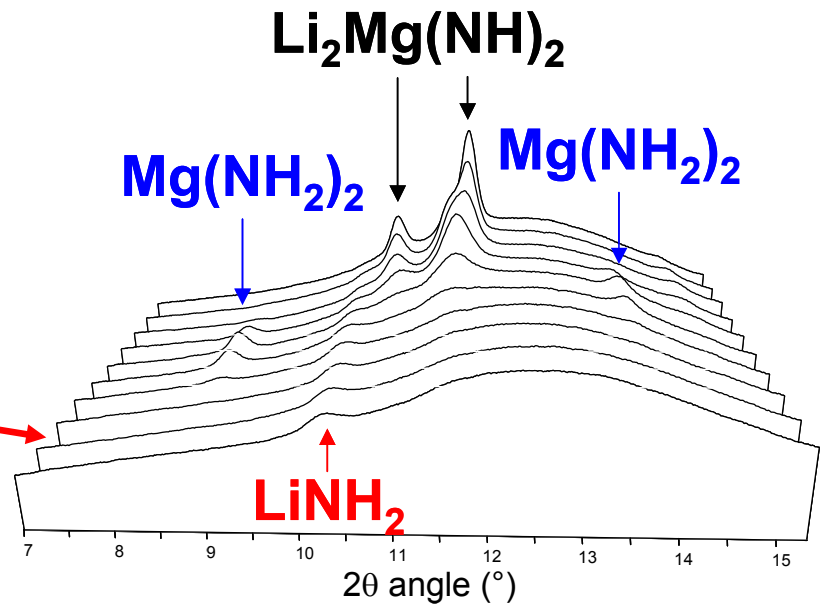
RGA (gas analysis)

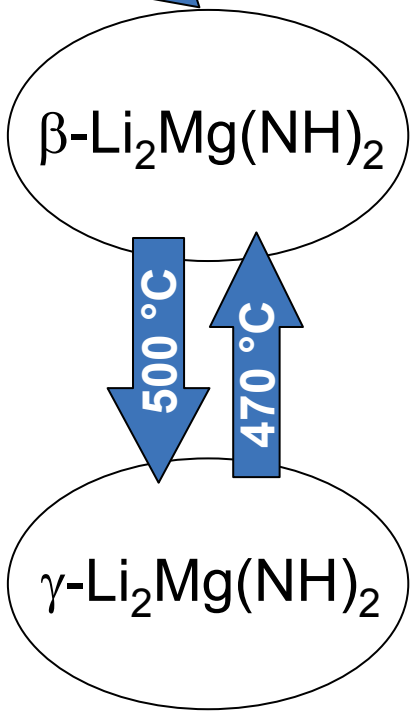
Looking inside amide-hydride reactions

$2\ LiNH_2 + MgH_2 \rightarrow$ "$Li_2Mg(NH_2)_2$" $\leftrightarrow 2\ LiH + Mg(NH_2)_2$ 5.6 wt % H_2 @ ~200 °C (Luo et al., Sandia)









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Entire reaction pathway from one experiment

imagination at work

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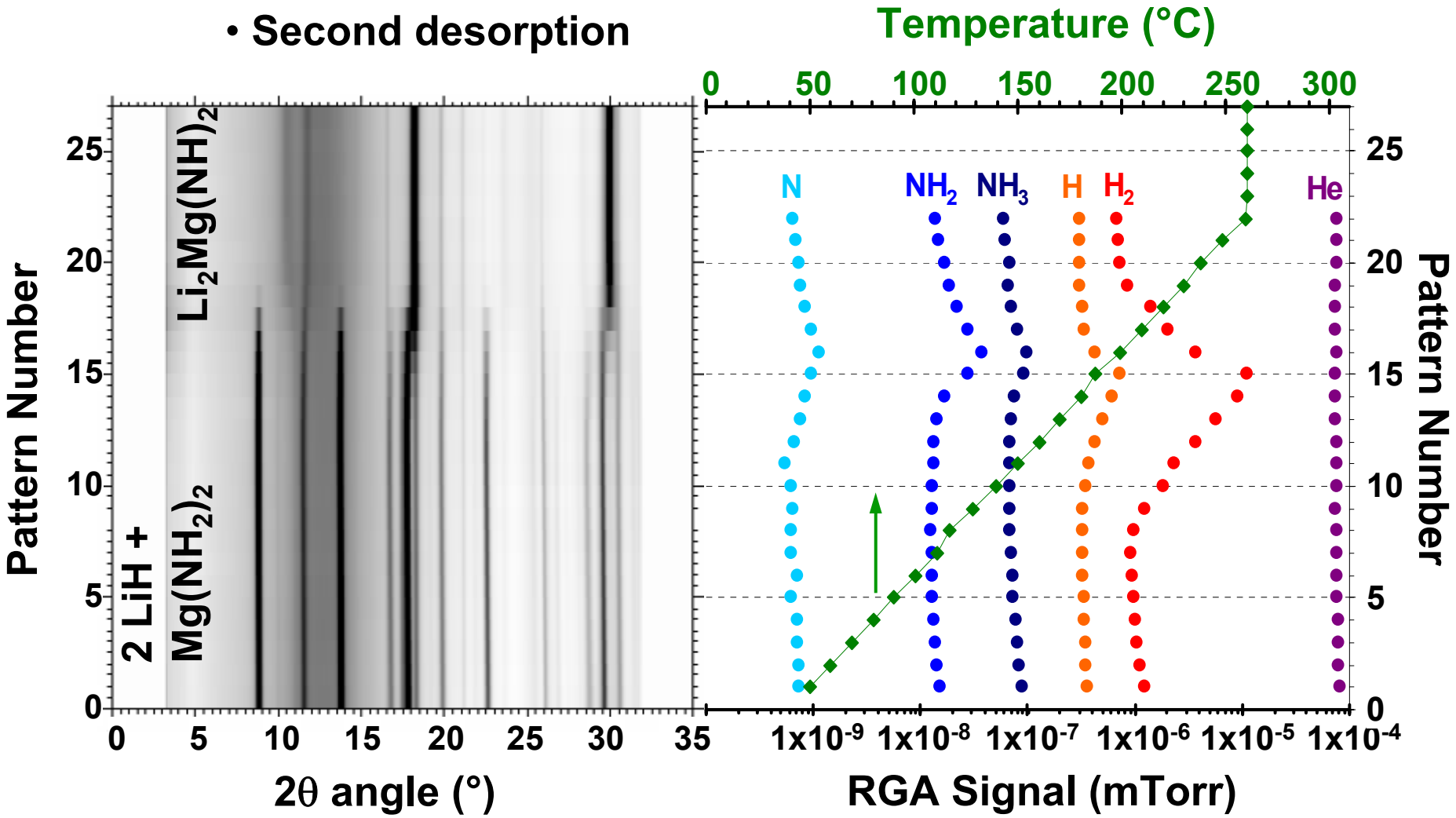
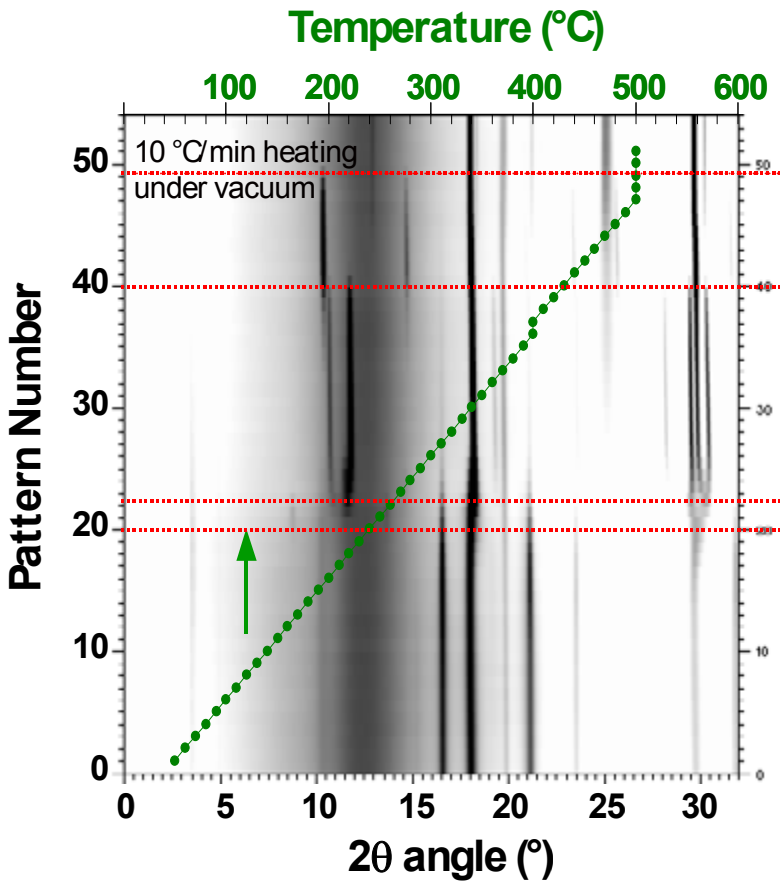
Gas analysis during H_2 release reaction



- Combined RGA & in-situ XRD provide unmatched information about reaction pathways
- Studied NH_3 formation in the hydride-imide systems
- NH_3 still there at low level at 2nd and subsequent desorption

Vacancy ordering determines structure



γ-$Li_2Mg(NH)_2$

500 °C

β-$Li_2Mg(NH)_2$

400 °C

α-$Li_2Mg(NH)_2$

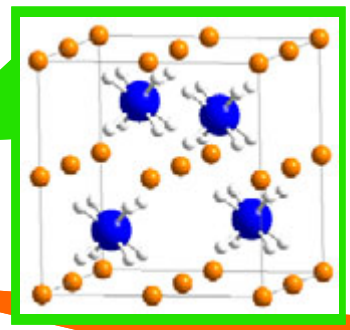
240 °C

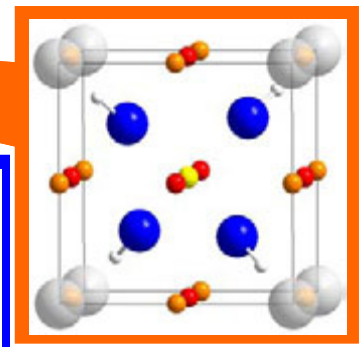
2 LiH
+ $Mg(NH_2)_2$

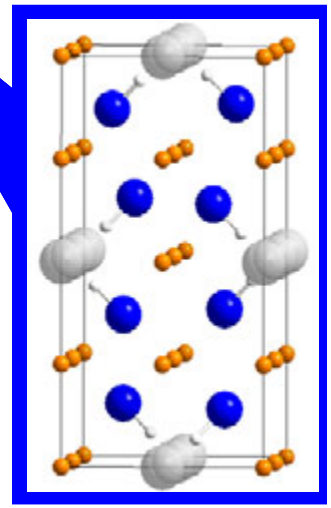
220 °C

$2\ LiNH_2 + MgH_2$

Space group: $Fm\bar{3}m$ 1 disordered site for Li/Mg/□
a = 5.056 Å







1 site for Li
2 sites for Li/Mg
1 site for vacancy
Space group: P-43m
a = 5.094 Å

2 sites for Li/Mg
1 site for vacancy
Space group: *Iba*2
a = 9.788 Å, b = 4.993 Å, c = 5.202 Å

- Determined 3 new imide crystal structures using high-resolution X-ray & neutron diffraction
- Identified a new family of imides with formula $Li_{4-2x}Mg_x(NH)_2$ (up to 6 wt % H_2 @ ~220 °C)

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imagination at work

BROOKHAVEN NATIONAL LABORATORY

NIST

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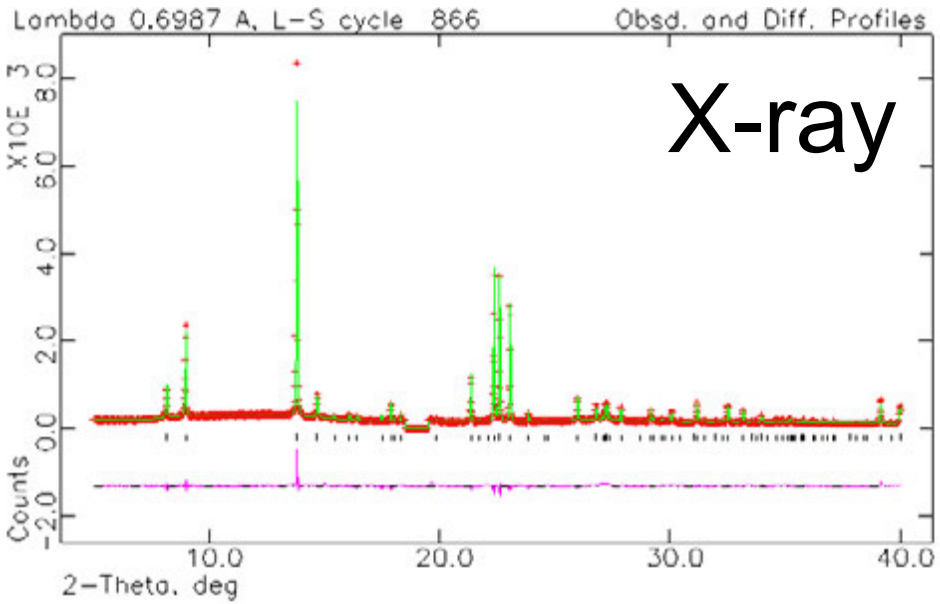
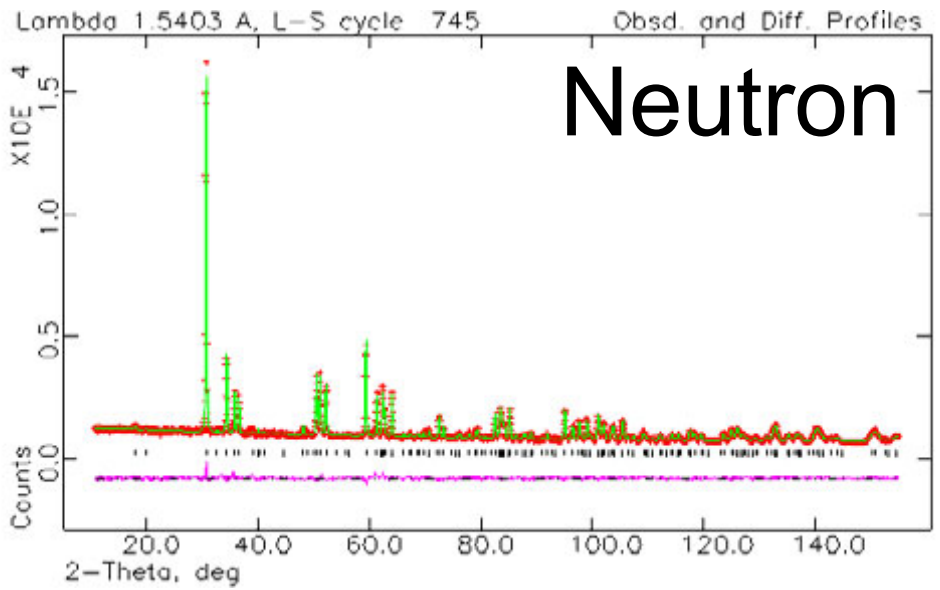
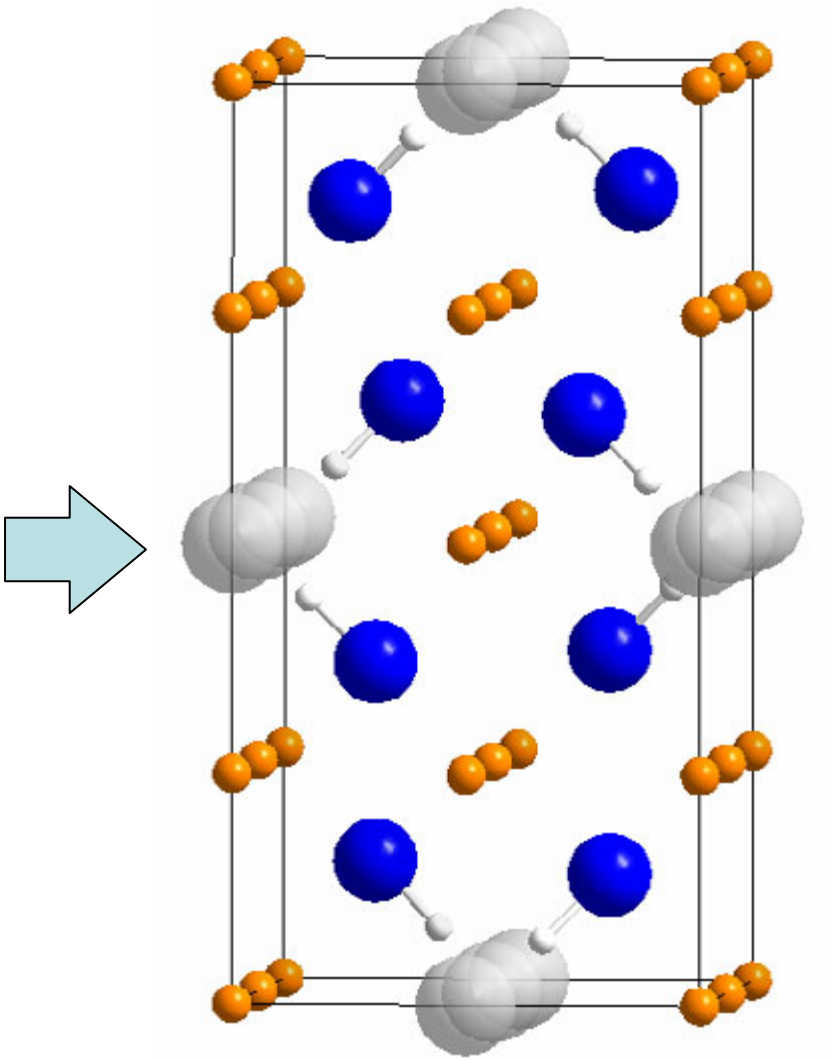
Crystal structure of α-$Li_2Mg(NH)_2$



X-ray



Neutron



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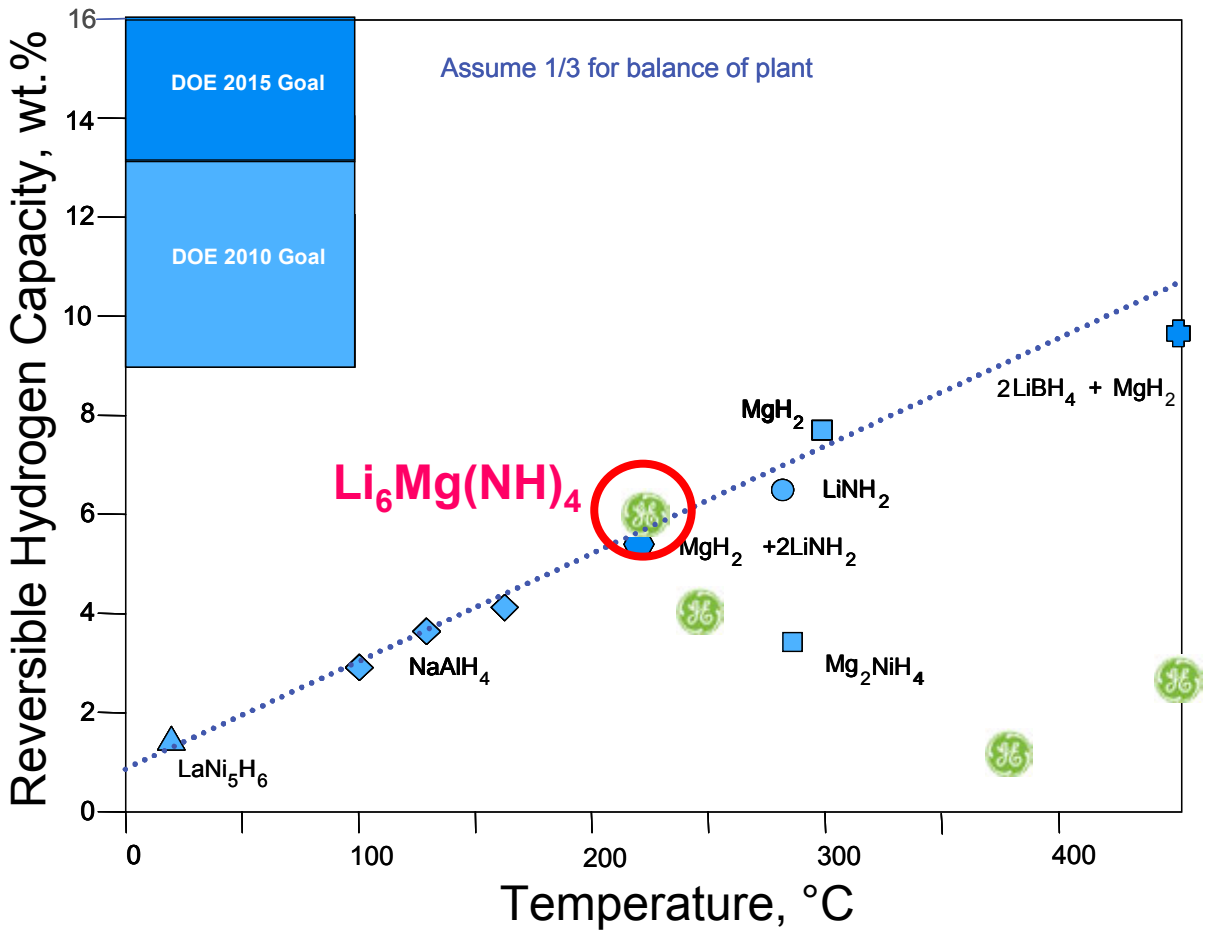
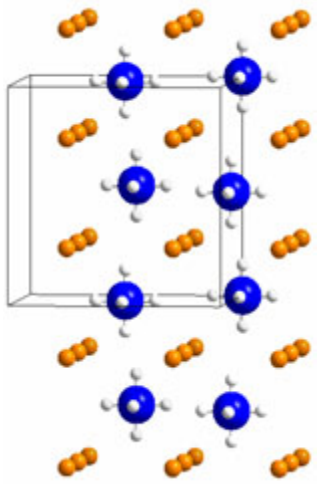
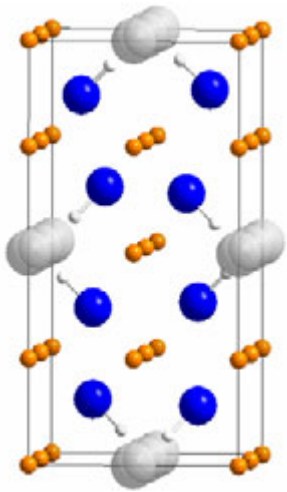
Imide-amide systems





c-Li_2NH

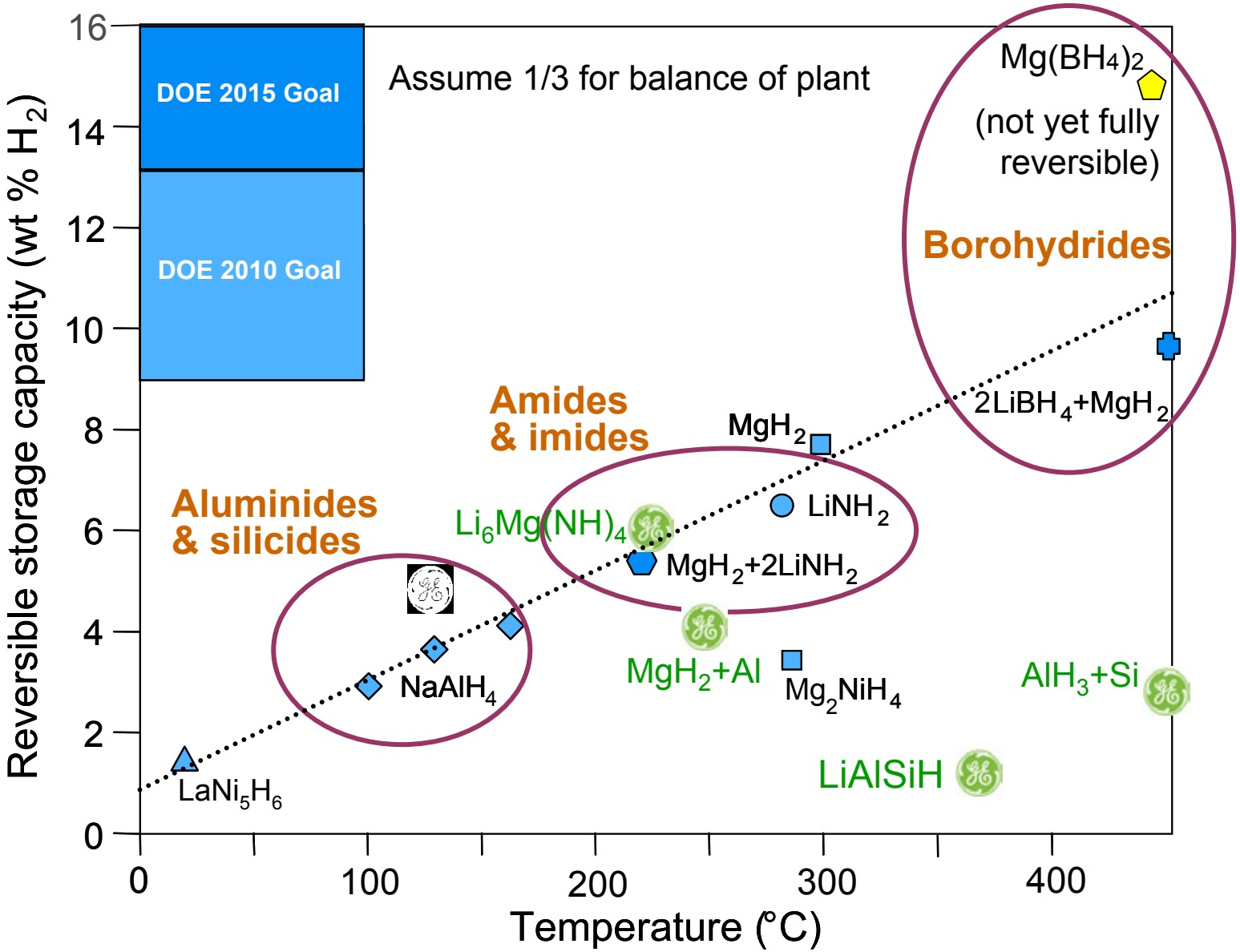
$Li_{4-2x}Mg_x\square_x(NH)_2$



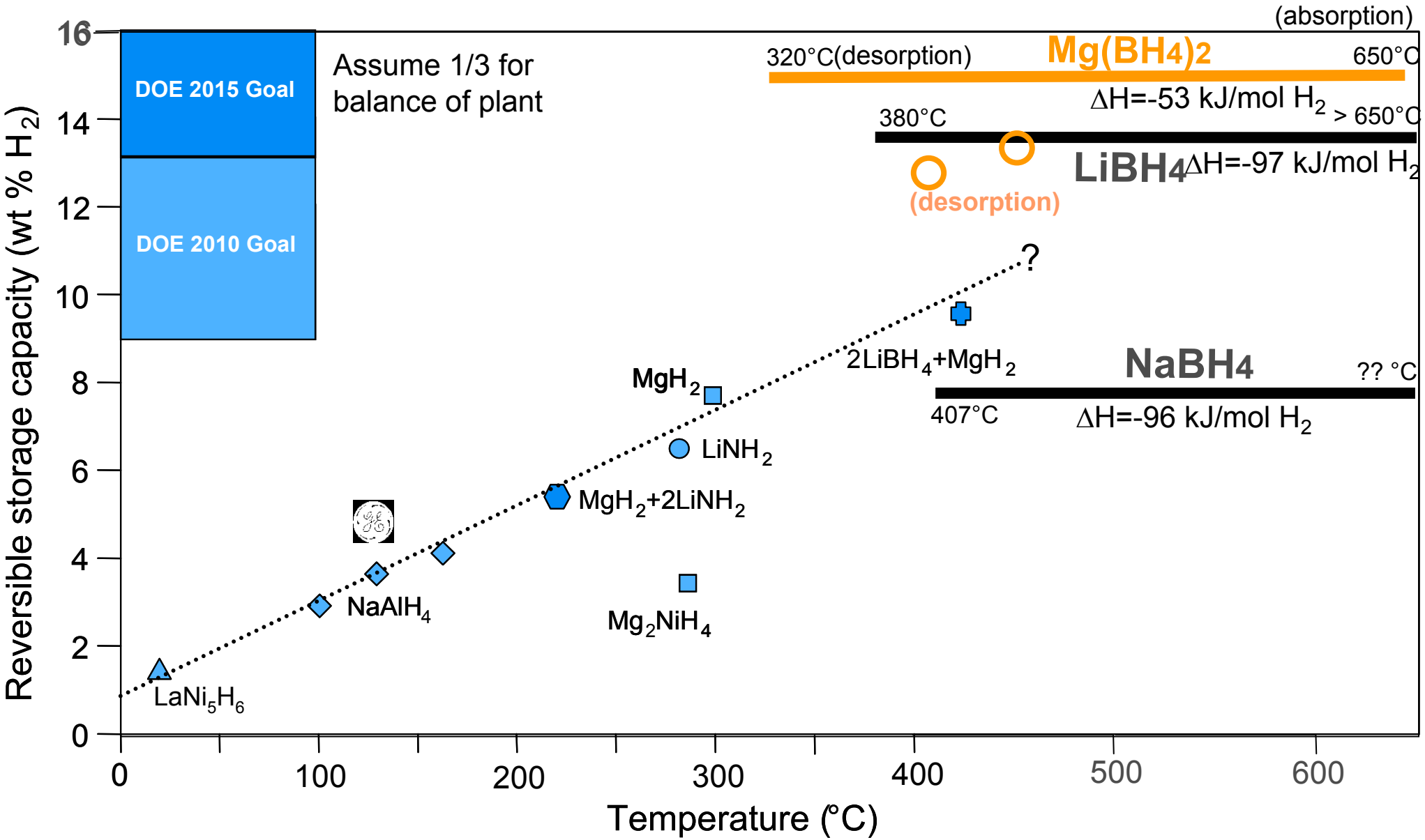
α-$Li_2Mg\square(NH)_2$

- Crystal structure understanding led to **$Li_6Mg(NH)_4$**: 6 wt.% @ ~220°C
- No effective catalysts found from combinatorial screening work
- Higher (6.9) wt.% (i.e., $8LiH + 3Mg(NH_2)_2 \rightarrow 4Li_2NH + Mg_3N_2 + 8H_2$) only at >~340°C
- Suspended effort at GE – available to help the amide-imide group in MHCoE

Metal hydrides against DOE targets

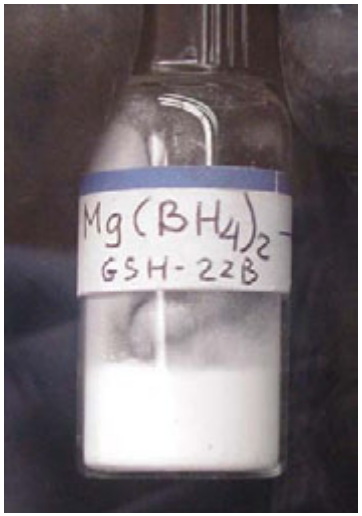


$Mg(BH_4)_2$

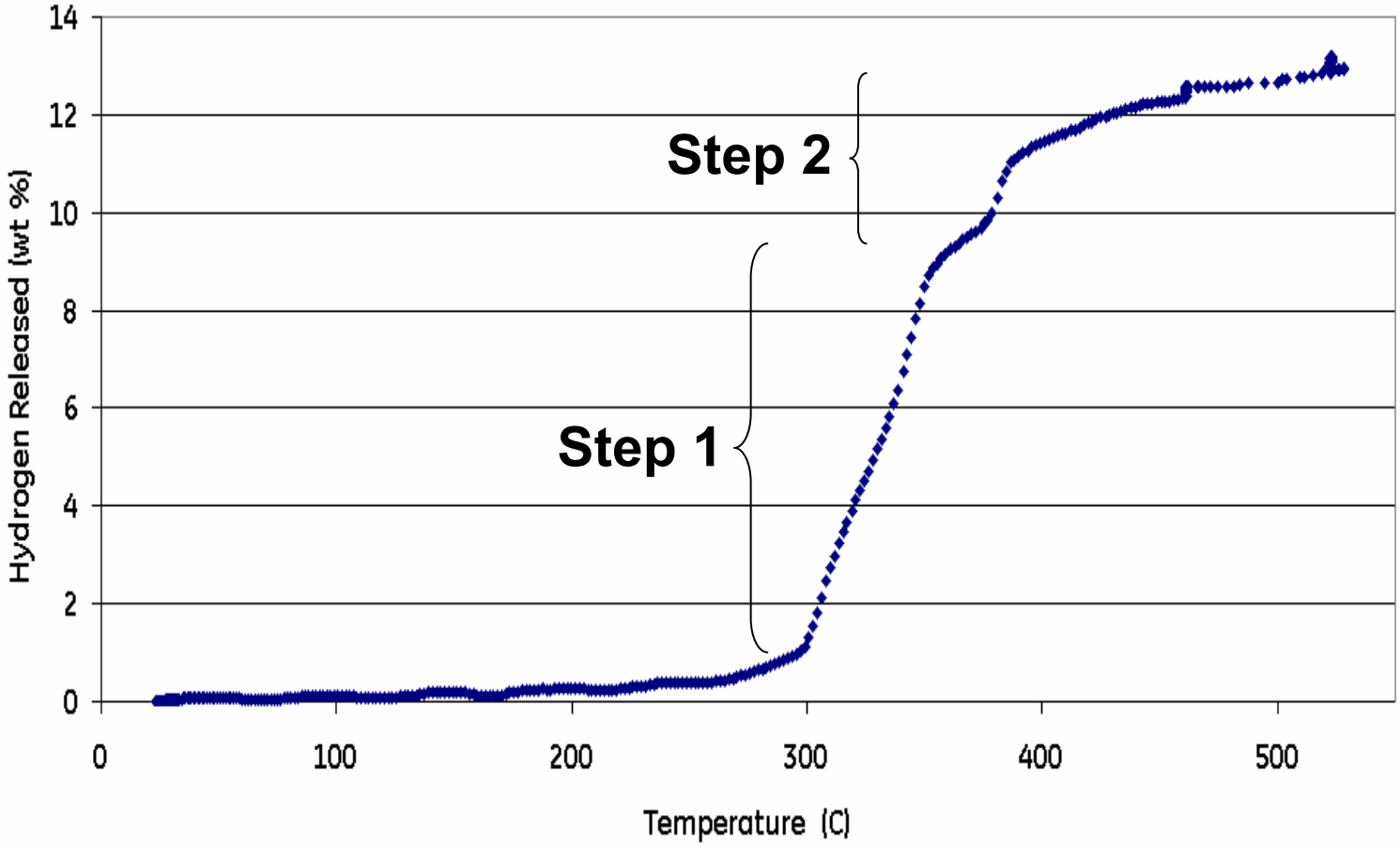


- $Mg(BH_4)_2$: one of the only few hydrides that may meet the DOE 2015 wt.% target
- ΔH much more favorable than $LiBH_4$

$Mg(BH_4)_2$



1st desorption
13.2 wt.%

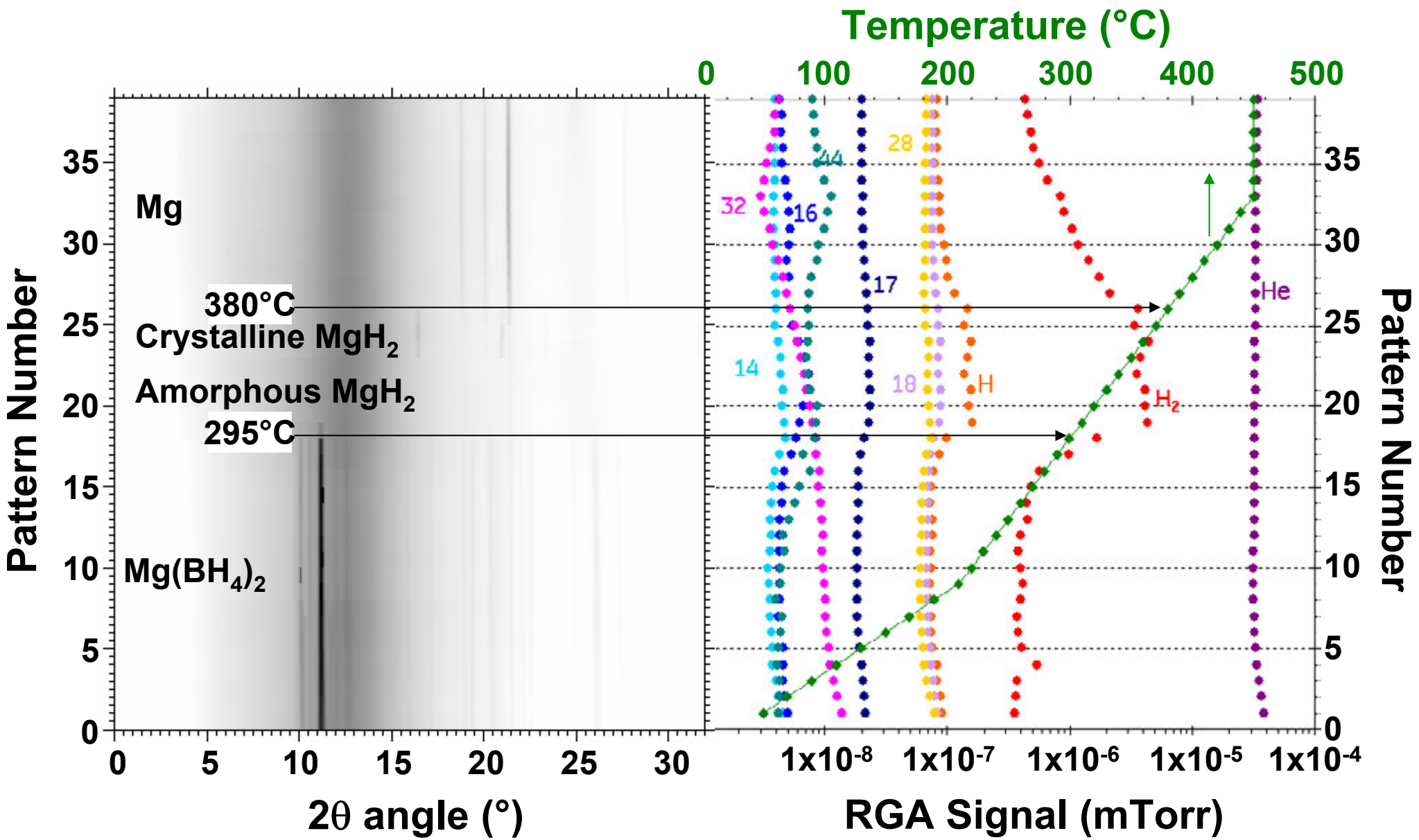


Step 1. $Mg(BH_4)_2 \rightarrow 2\ B + MgH_2 + 3\ H_2$ (11.2 wt % H_2)

Step 2. $MgH_2 \leftrightarrow Mg + H_2$ (3.7 wt % H_2)

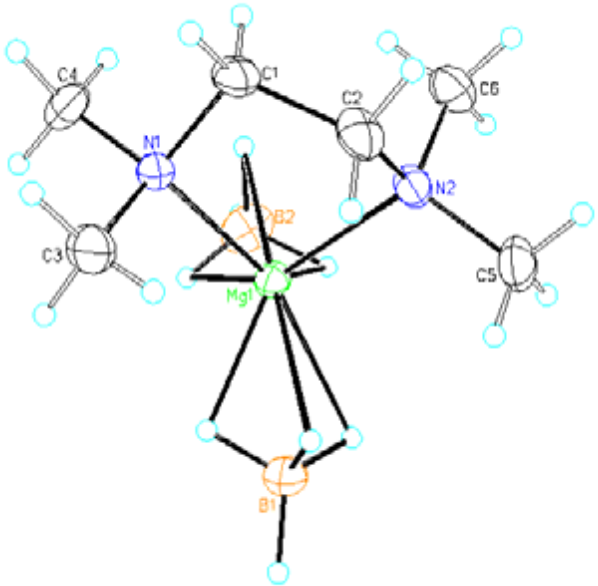
- Only Step 2 is currently reversible (~3 wt % H_2)
- Need better structural & catalyst understanding to make Step 1 reversible

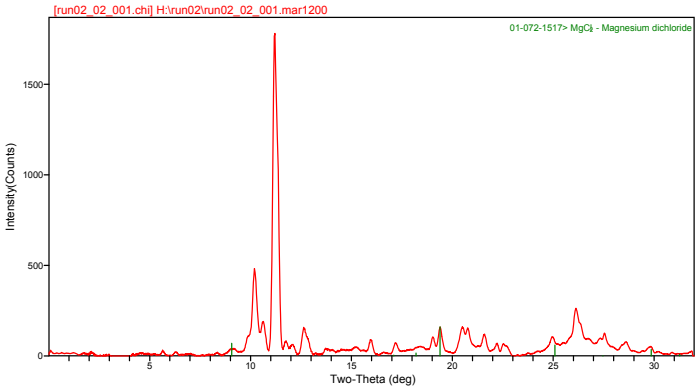
$Mg(BH_4)_2$ desorption



$Mg(BH_4)_2$

- Have determined the crystal structure of the solvated (TMEDA) form
- Desolvated compound may have a different Mg:BH_4 ration (i.e., <2:1)
- Isotope labeling of $Mg(^{11}BD_4)_2$ near completion.
  - Necessary for high quality neutron diffraction
- DFT modeling needed for structure checking and confirmation
- Doping & catalyst study ongoing





Structural identification is essential to doping & catalyst study

Future Work

FY06

- Combinatorial screening of dopants and catalysts for $Mg(BH_4)_2$
- Crystal structure identification of $Mg(BH_4)_2$ – BNL, NIST, UIUC
- Computational prediction of dopants for $Mg(BH_4)_2$ – UIUC, CMU, U Pitt
- Thermal conductivity measurements (Sandia) & Vapor pressure measurements (Univ. Nevada)

FY07

- Continue on catalyst and doping study of $Mg(BH_4)_2$ to improve reversibility
- Perform system-level evaluation of properties such as cycling stability/degradation
- Go/No-Go for $Mg(BH_4)_2$ reversibility: < 450°C & < 200 bar

Summary

- Robust combinatorial/HTS methodology developed – met our ’05 deliverable
- Focus on $Mg(BH_4)_2$ in FY06-07
- Use combi/HTS expertise to identify dopants/catalysts
- Use unique in-situ capabilities to understand and then tailor reaction pathways
- Collaborate with MHCoE partners to explore $Mg(BH_4)_2$ as a potential high-capacity H_2 storage material

imagination at work

ecomagination℠

Publications & Presentations

- Job Rijssenbeek presented a poster "Characterization of the titanium catalyst in $NaAlH_4$", at IPHE International Hydrogen Storage Technology Conference, Lucca, Italy, June '05.
- John Lemmon presented a poster "High-throughput hydride discovery" at Metal - Hydrogen Gordon Conference (July '05)
- Job Rijssenbeek presented a poster "Phase formation and reaction pathway of $Mg(NH_2)_2$ + 2 LiH mixtures for reversible hydrogen storage" at Metal - Hydrogen Gordon Conference (July '05)
- Job Rijssenbeek gave a talk "Crystal structure determination and reaction pathway of amide-hydride mixtures" the MRS Fall Meeting, Boston (Nov '05)
- J.-C. Zhao attended the IEA Task 17 meeting in Takeshita, Japan & presented talk on "Lightweight intermetallics for hydrogen storage" (Oct '05)
- J.-C. Zhao attended the TMS meeting in San Antonio and presented an invited talk on "Reversible hydrogen storage in mixtures of $Mg(NH_2)_2$ and LiH studied by X-ray and neutron diffraction" (March '06)
- Our paper on "Crystal structure determination and reaction pathway of amide-hydride mixtures" is in the final stage of preparation