

# Lightweight Intermetallics for Hydrogen Storage

DOE Award #: DE-FC3605GO15062

J.-C. Zhao

Matt Andrus, Jun Cui, Yan Gao, John Lemmon, Tom Raber,  
Job Rijssenbeek, Gosia Rubinsztajn, & Grigorii Soloveichik

GE Global Research

May 17<sup>th</sup>, 2006

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

# 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)

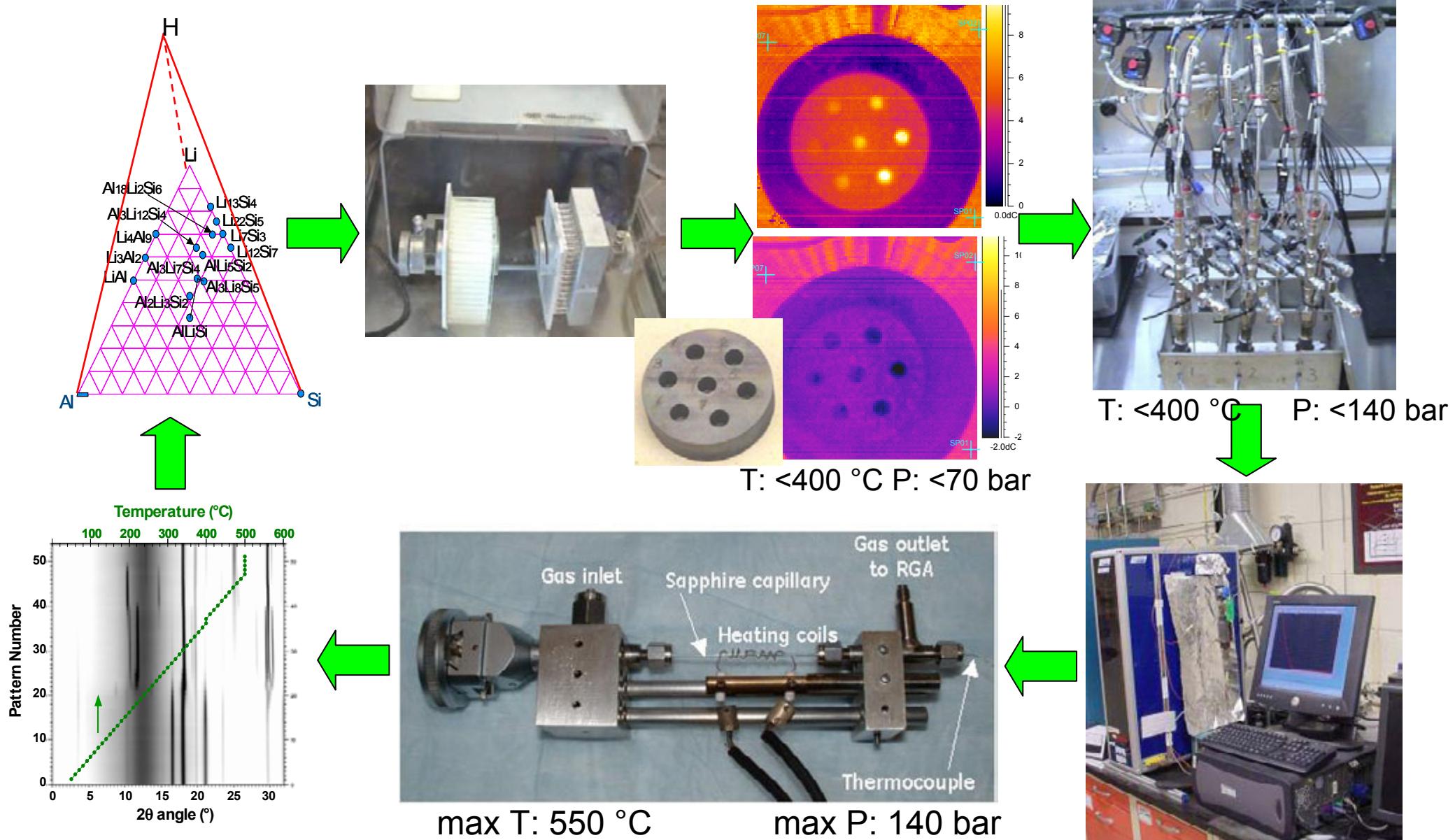
## Partners/Collaborations

- 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	<ul style="list-style-type: none"><li>• Develop a high-efficiency combinatorial synthesis and high-throughput screening methodology for metal hydride discovery</li><li>• Identify hydrides from combinatorial samples and validate them through gram-quantity sample tests</li></ul>
FY06	<ul style="list-style-type: none"><li>• Identify the crystal structures of Mg(BH<sub>4</sub>)<sub>2</sub> using XRD, neutron diffraction and computer modeling</li><li>• Perform combinatorial and computational screening of catalysts and dopants for Mg(BH<sub>4</sub>)<sub>2</sub></li></ul>

# Approach



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

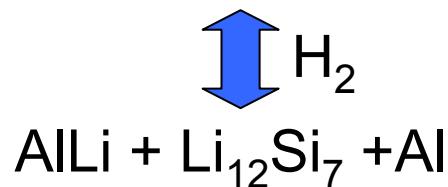
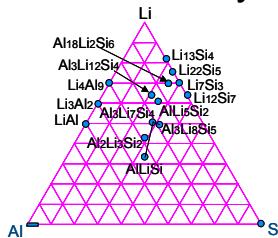


imagination at work

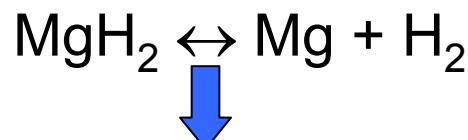
Lemmon, Rubinsztajn, Cui, Rijssenbeek, Gao & Zhao



# Combi findings in aluminides & silicides



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



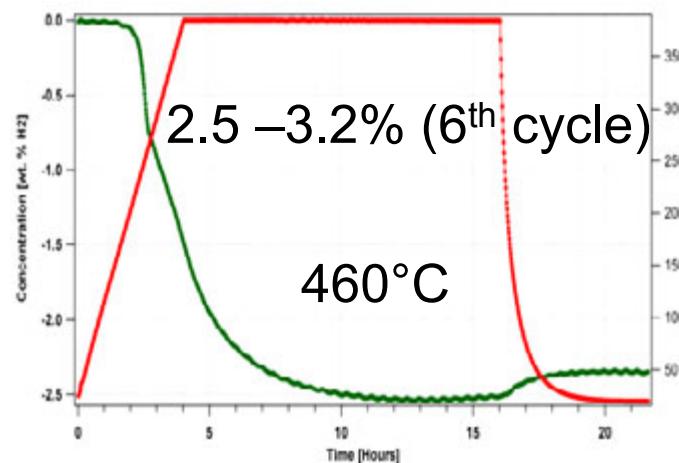
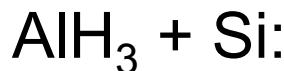
7.0 wt % 300°C

- Reduced T & wt.%



4.4 wt % 230°C

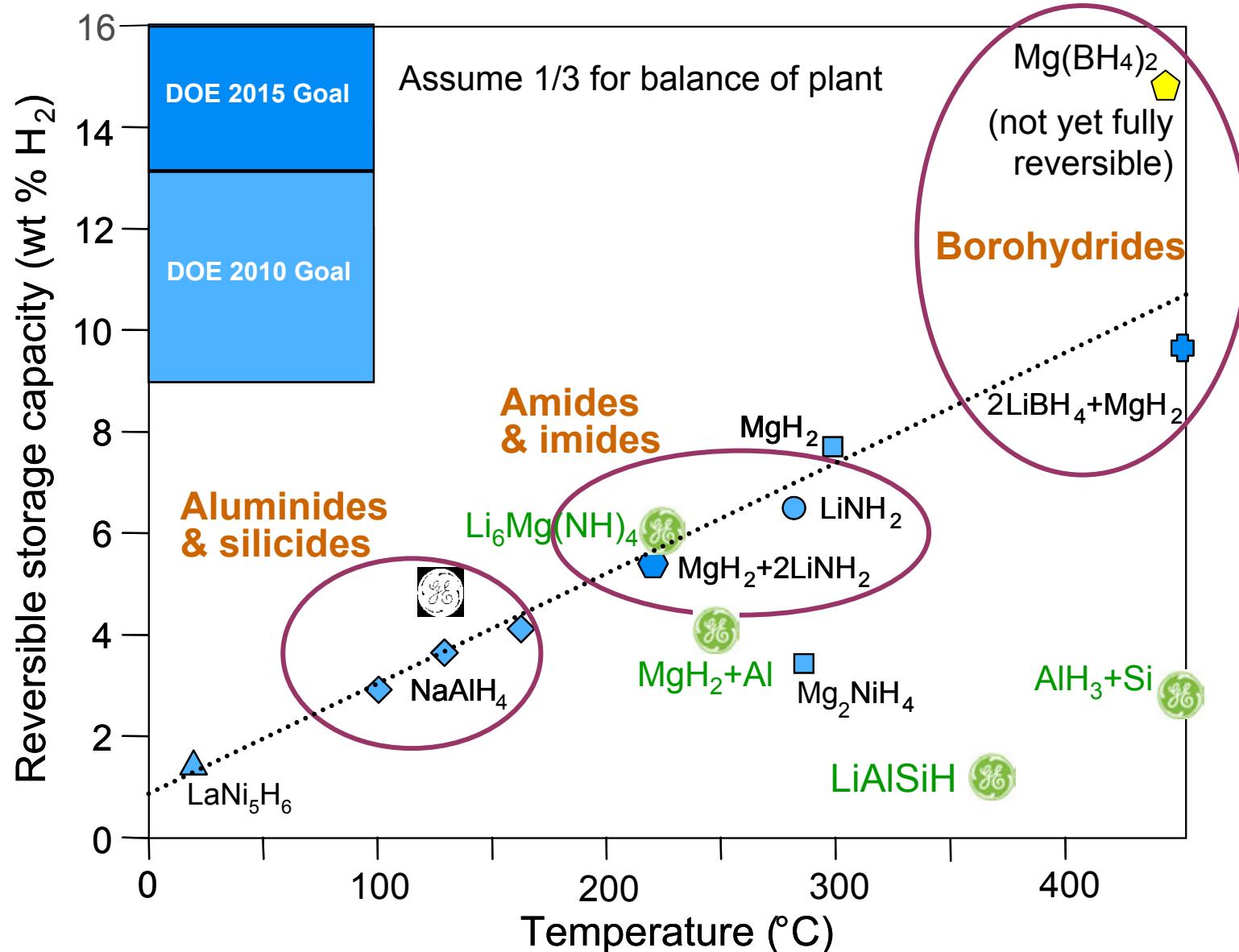
- Faster kinetics
- Found using shaker
- Known in literature



- 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

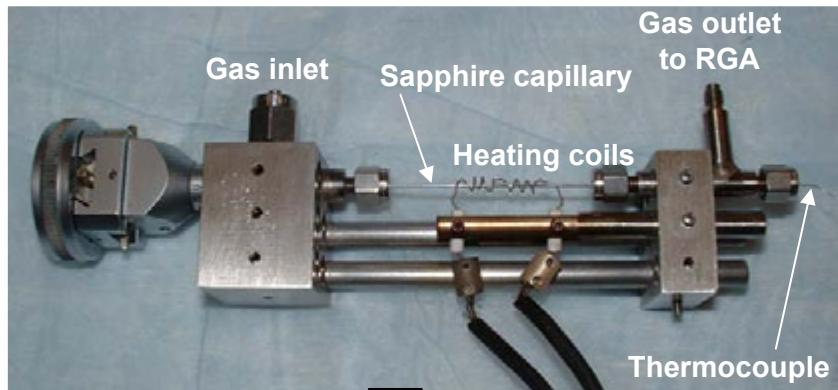
- Screened > 10 ternary systems (Al-Li-Si, Al-Mg-Ti, Al-Si-Ti, Al-Li-Mn, Li-Na-Si, etc.)
- No promising hydrides found, suspending efforts in this area

# Metal hydrides against DOE targets



# Combined *In-situ* XRD and gas analysis

Sample holder



max T: 550 °C

max P: 140 bar

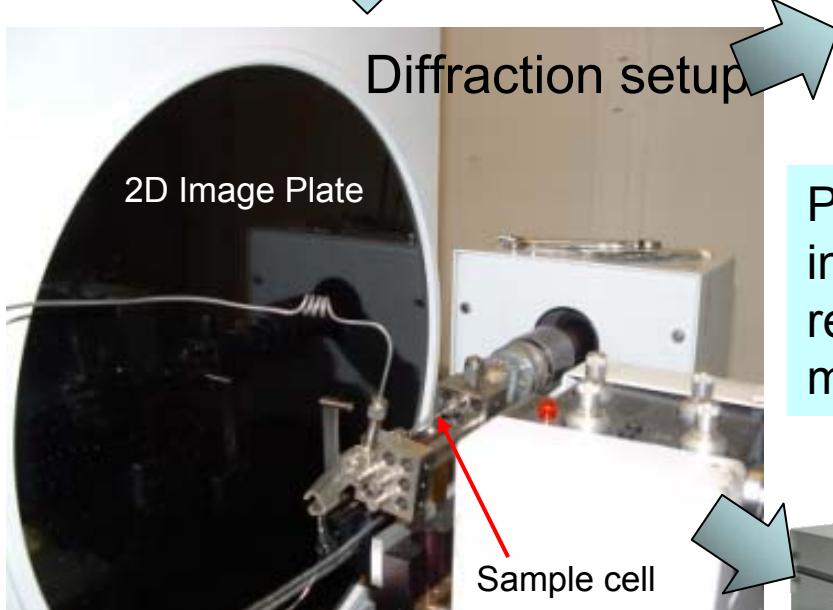
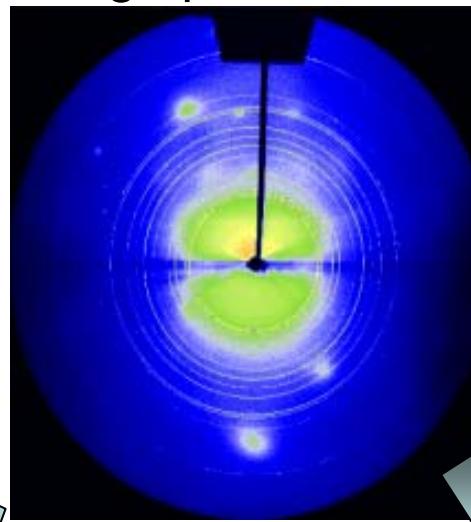
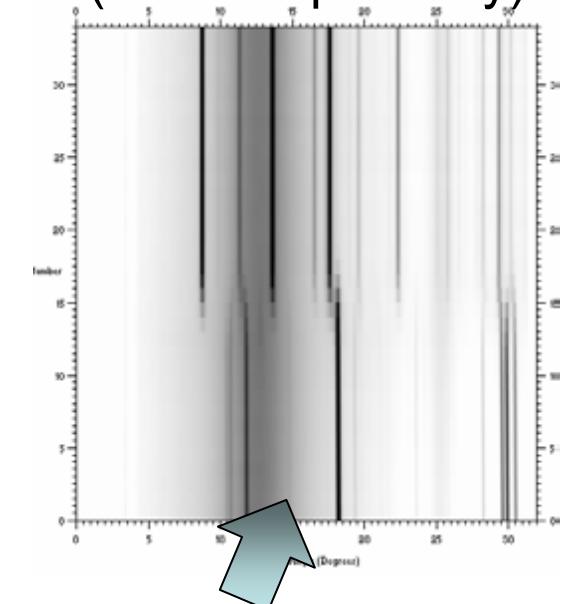


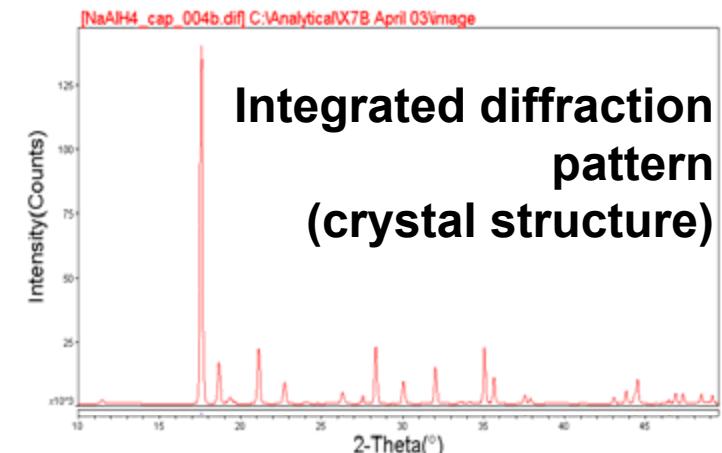
Image plate readout



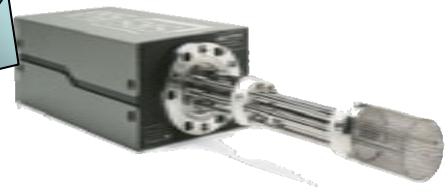
Time resolved patterns  
(reaction pathway)



Provides unmatched information about reaction pathways / mechanism



RGA (gas analysis)



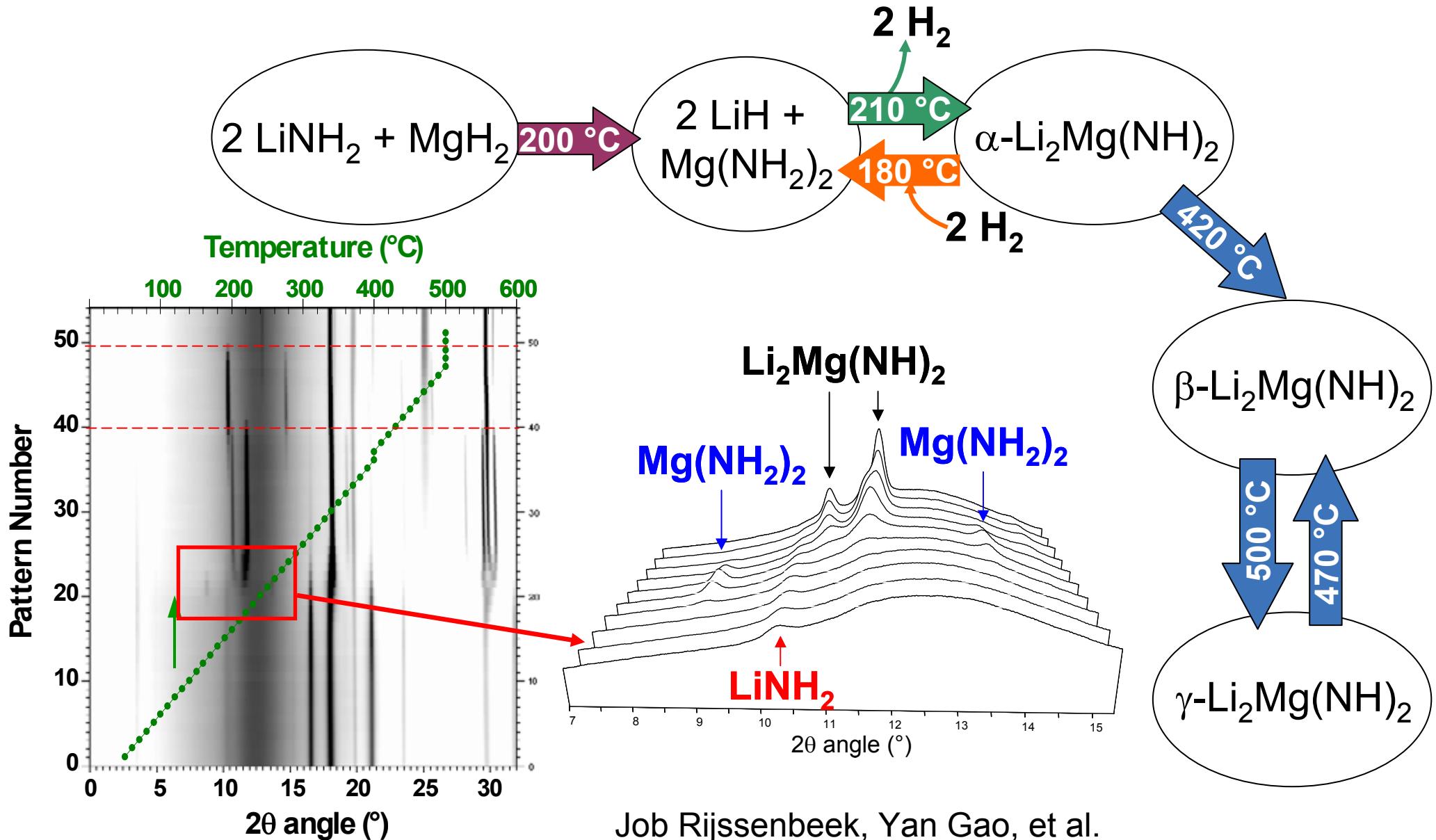
imagination at work

Yan Gao & Job Rijssenbeek

**BROOKHAVEN**  
NATIONAL LABORATORY

METAL HYDRIDE CENTER OF EXCELLENCE

# Looking inside amide-hydride reactions



Job Rijssenbeek, Yan Gao, et al.

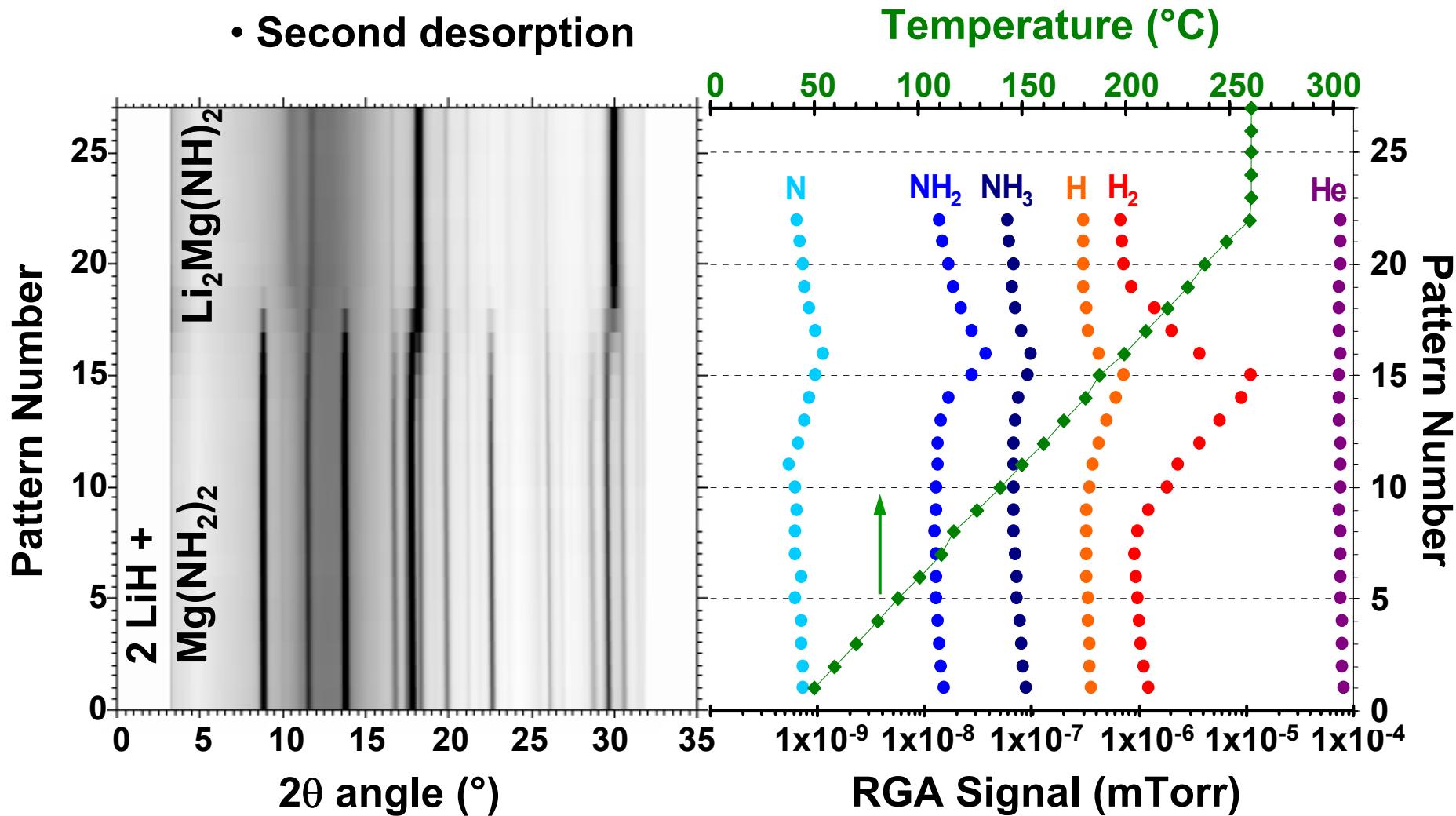


imagination at work

Entire reaction pathway from one experiment

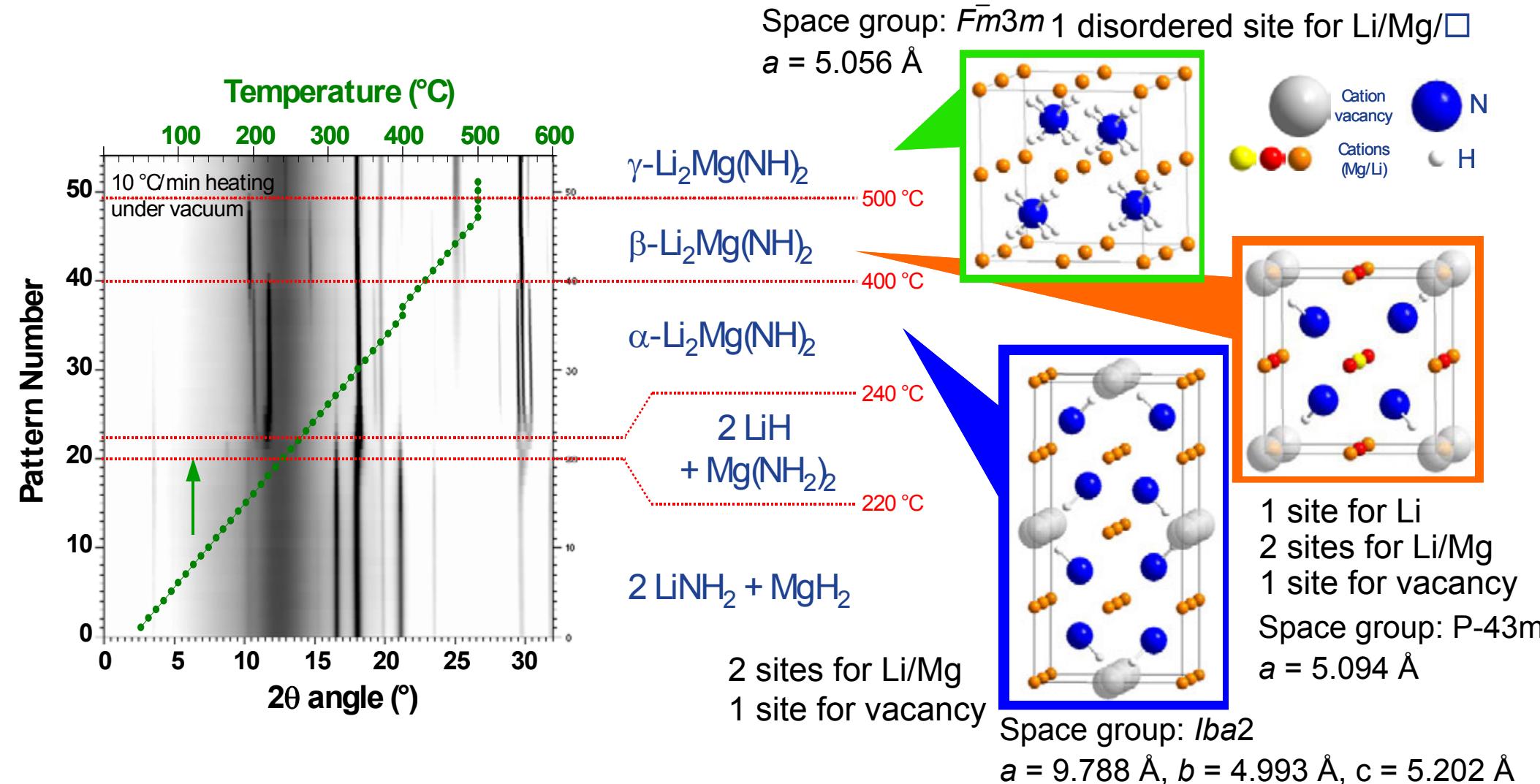


# Gas analysis during H<sub>2</sub> release reaction



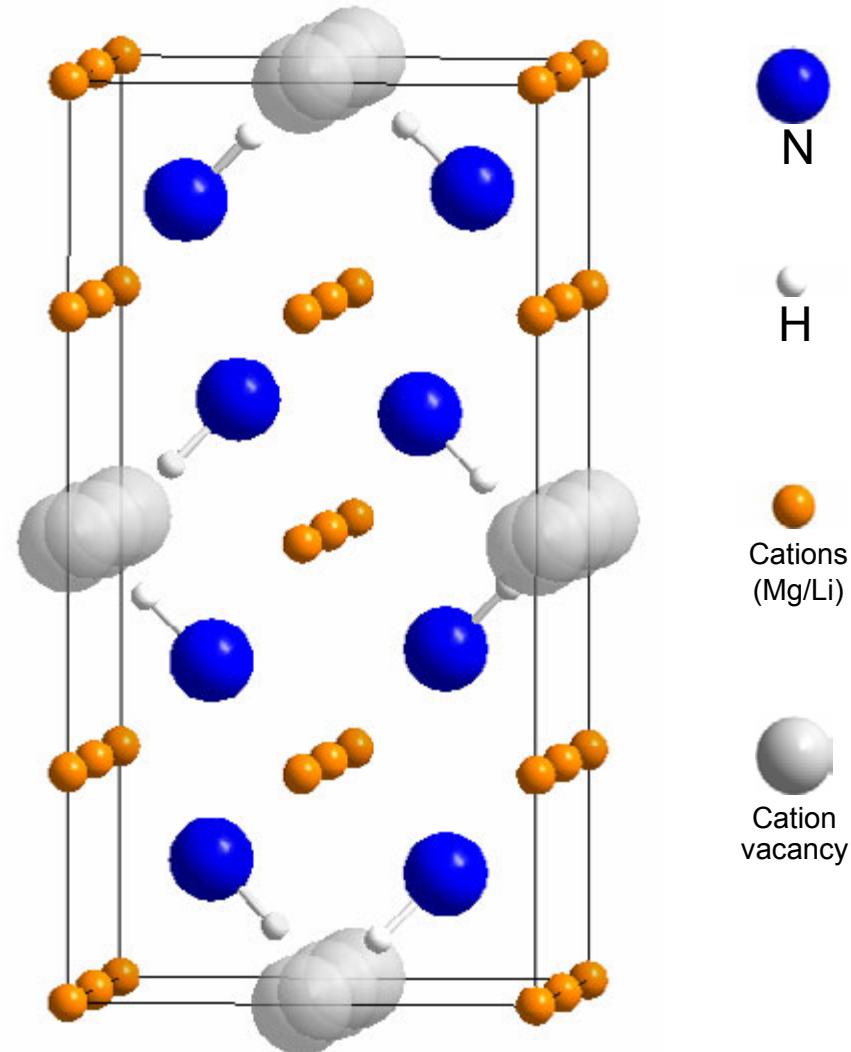
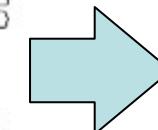
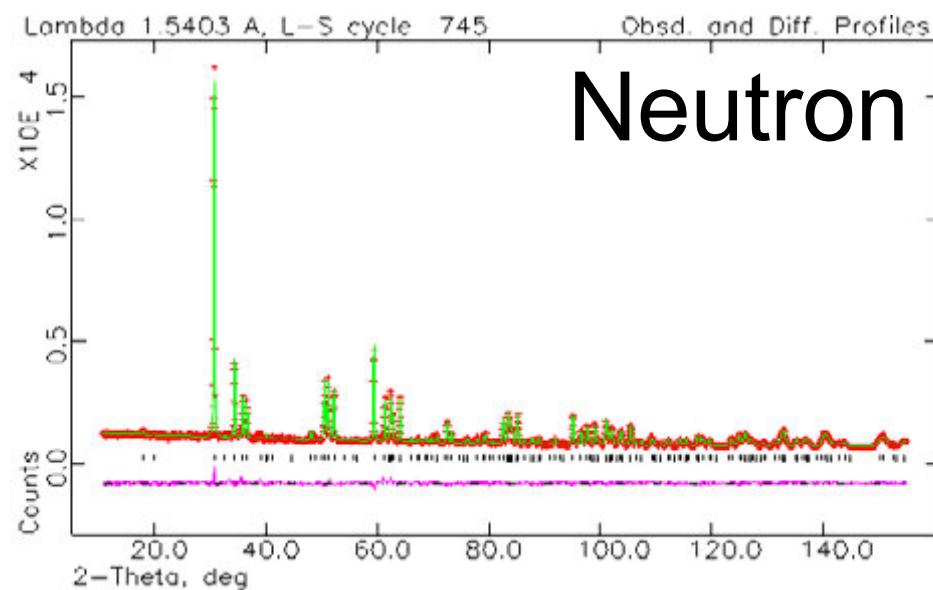
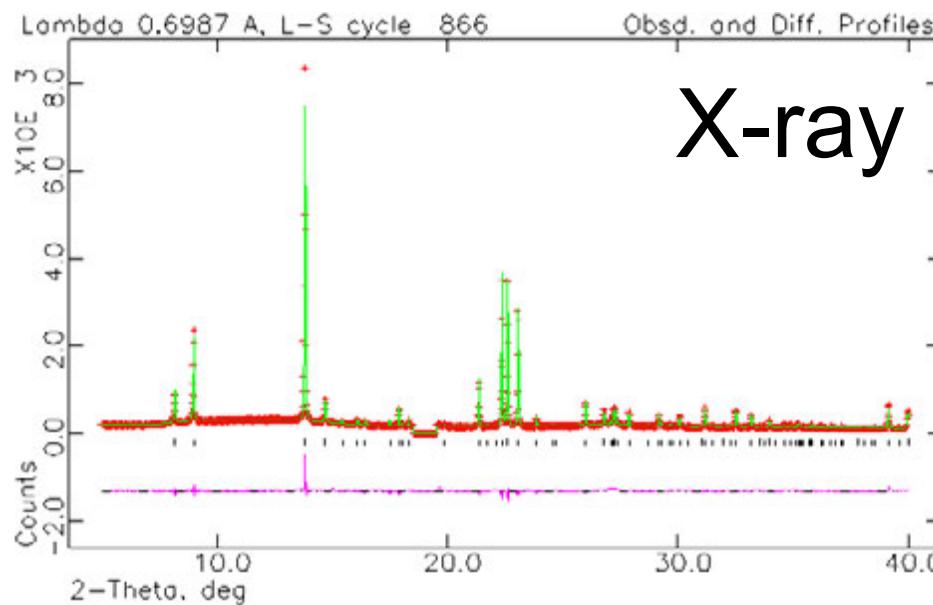
- Combined RGA & in-situ XRD provide unmatched information about reaction pathways
  - Studied  $\text{NH}_3$  formation in the hydride-imide systems
  - $\text{NH}_3$  still there at low level at 2<sup>nd</sup> and subsequent desorption

# Vacancy ordering determines structure



- Determined 3 new imide crystal structures using high-resolution X-ray & neutron diffraction
- Identified a new family of imides with formula  $\text{Li}_{4-2x}\text{Mg}_x(\text{NH})_2$  (up to 6 wt %  $\text{H}_2$  @  $\sim 220 \text{ }^{\circ}\text{C}$ )

# Crystal structure of $\alpha\text{-Li}_2\text{Mg}(\text{NH})_2$



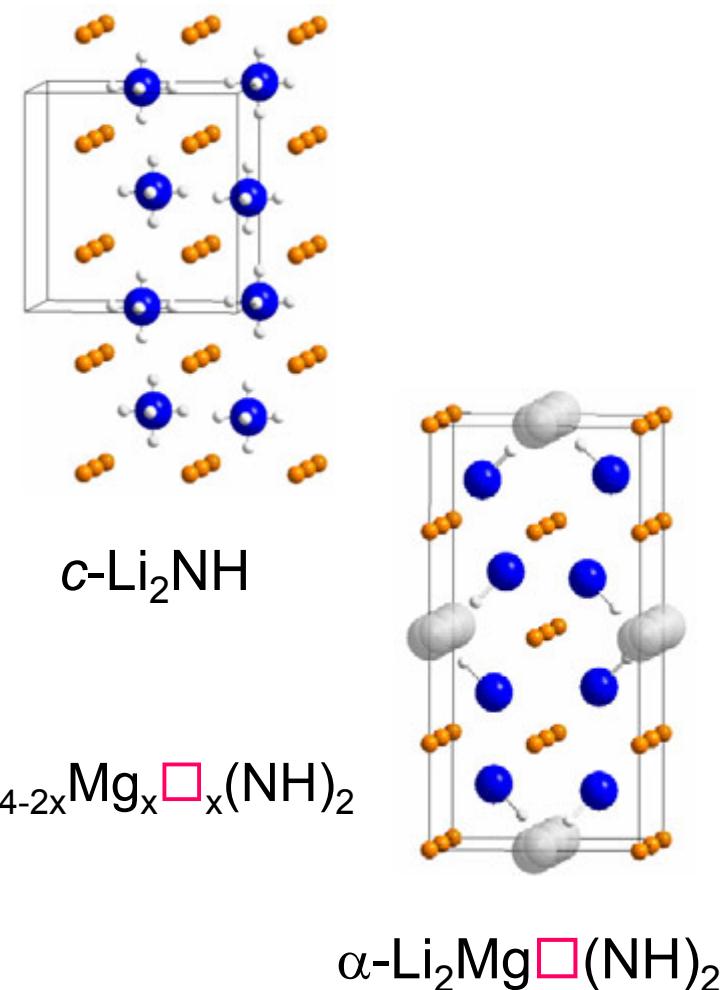
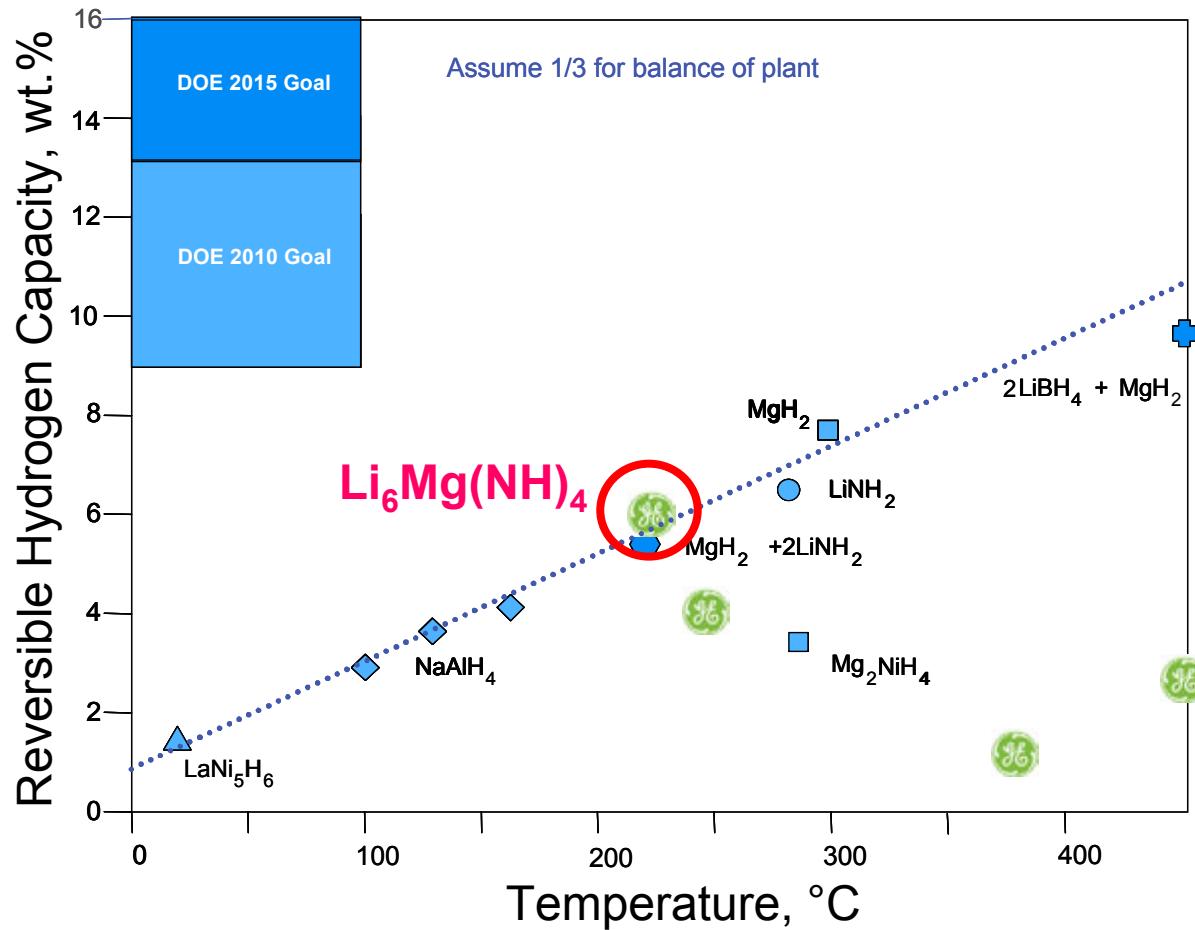
Job Rijssenbeek, & Yan Gao, et al.



imagination at work

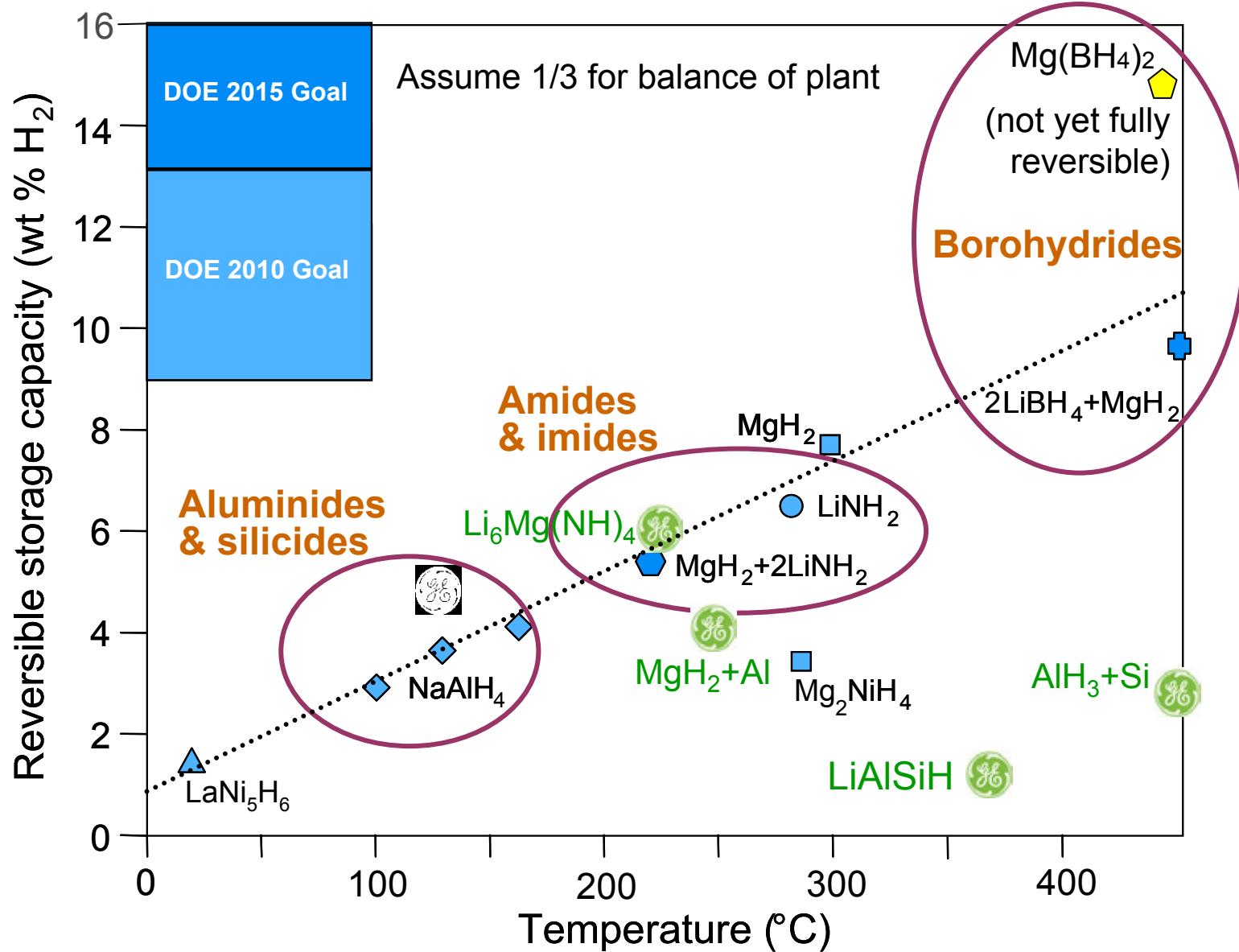


# Imide-amide systems

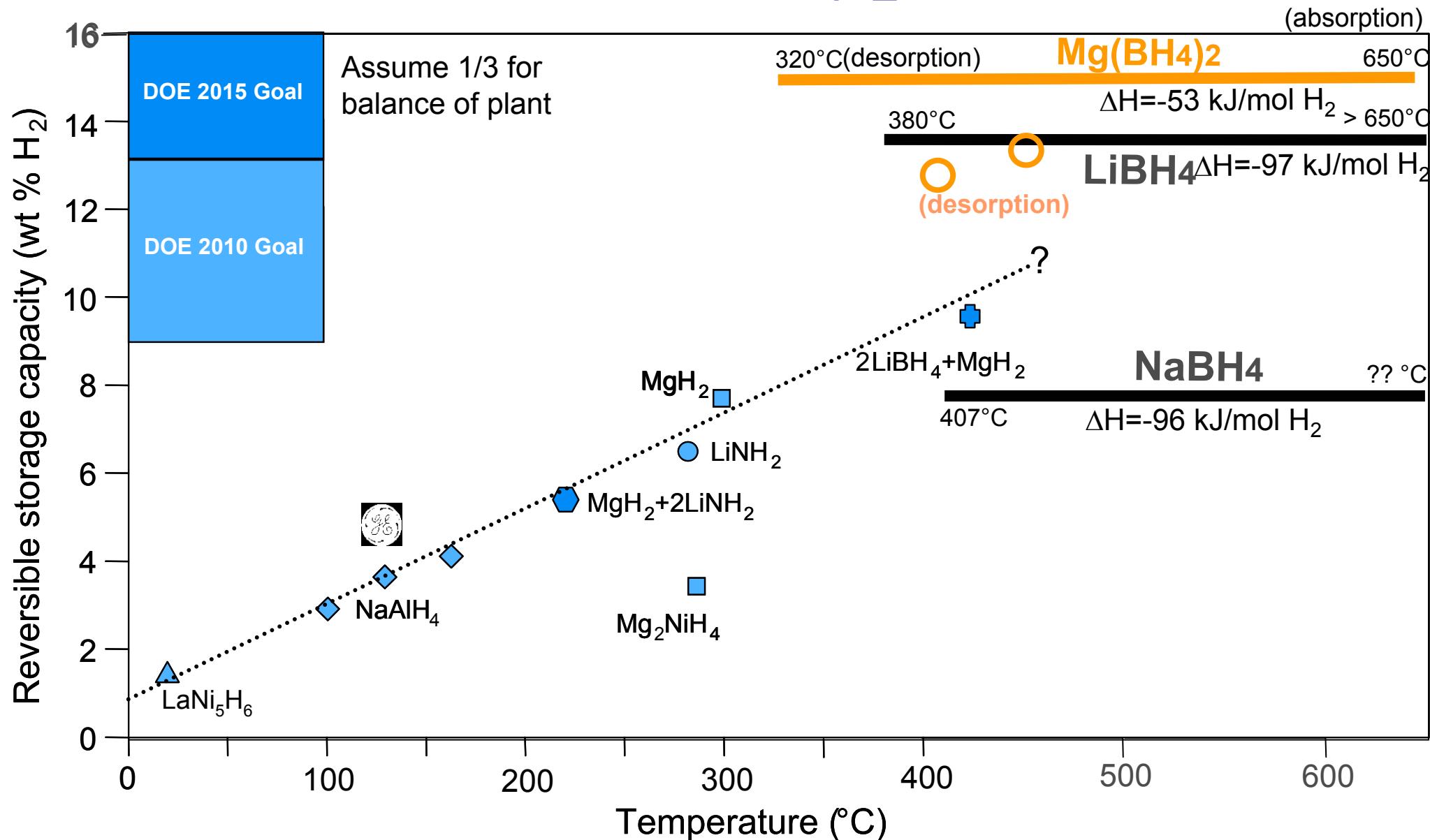


- Crystal structure understanding led to  $\text{Li}_6\text{Mg}(\text{NH})_4$ : 6 wt. % @  $\sim 220^\circ\text{C}$
- No effective catalysts found from combinatorial screening work
- Higher (6.9) wt. % (i.e.,  $8\text{LiH} + 3\text{Mg}(\text{NH}_2)_2 \rightarrow 4\text{Li}_2\text{NH} + \text{Mg}_3\text{N}_2 + 8\text{H}_2$ ) only at  $> \sim 340^\circ\text{C}$
- Suspended effort at GE – available to help the amide-imide group in MHCoE

# Metal hydrides against DOE targets

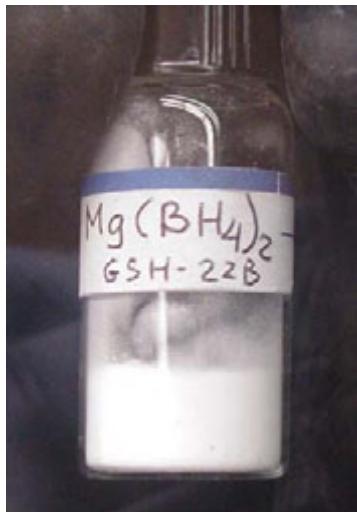


# Mg(BH<sub>4</sub>)<sub>2</sub>

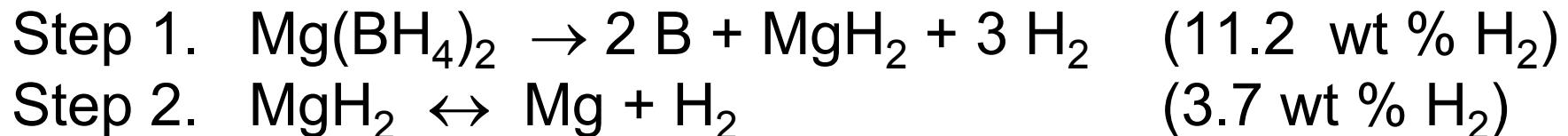
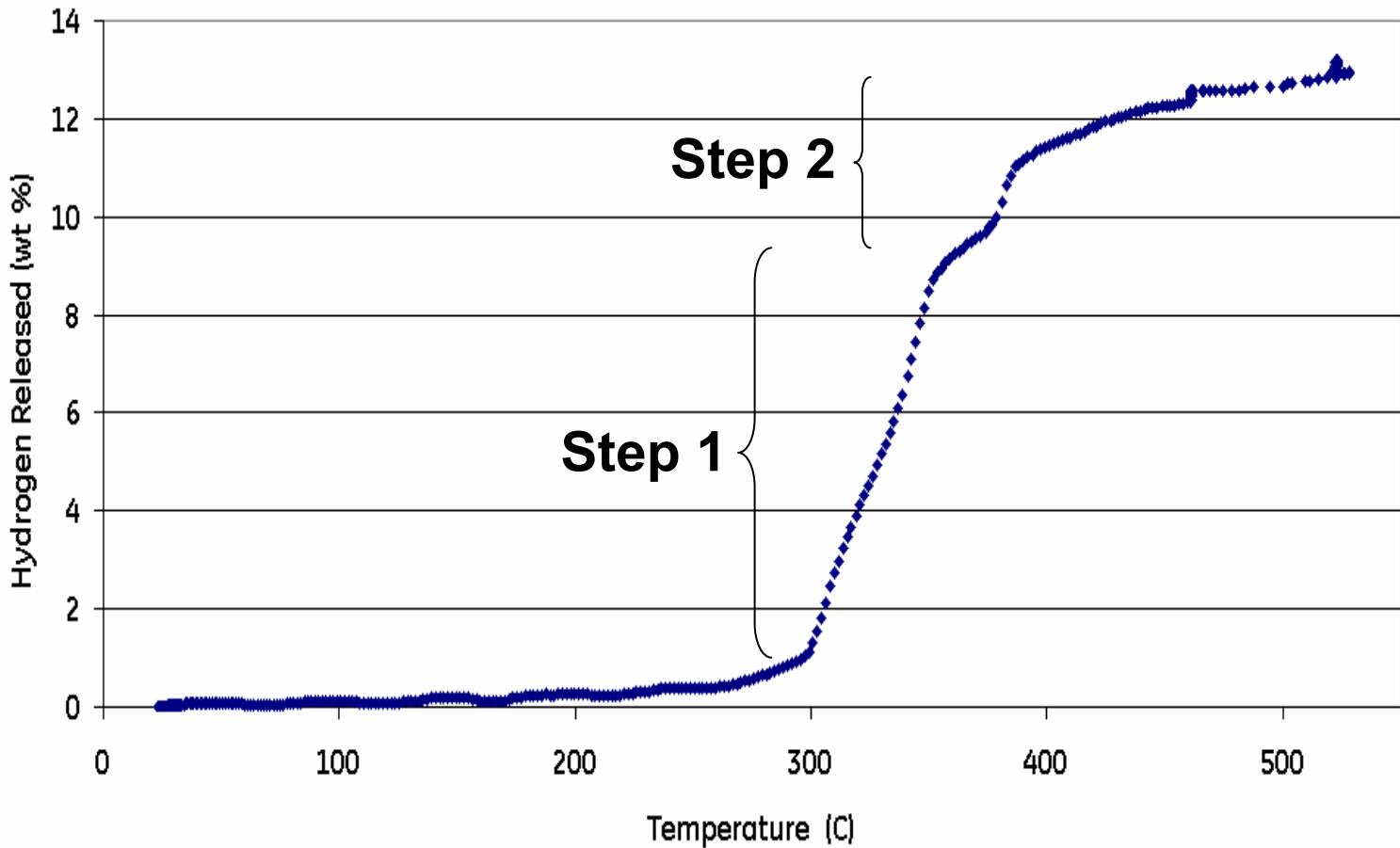


- Mg(BH<sub>4</sub>)<sub>2</sub>: one of the only few hydrides that may meet the DOE 2015 wt.% target
- ΔH much more favorable than LiBH<sub>4</sub>

# Mg(BH<sub>4</sub>)<sub>2</sub>

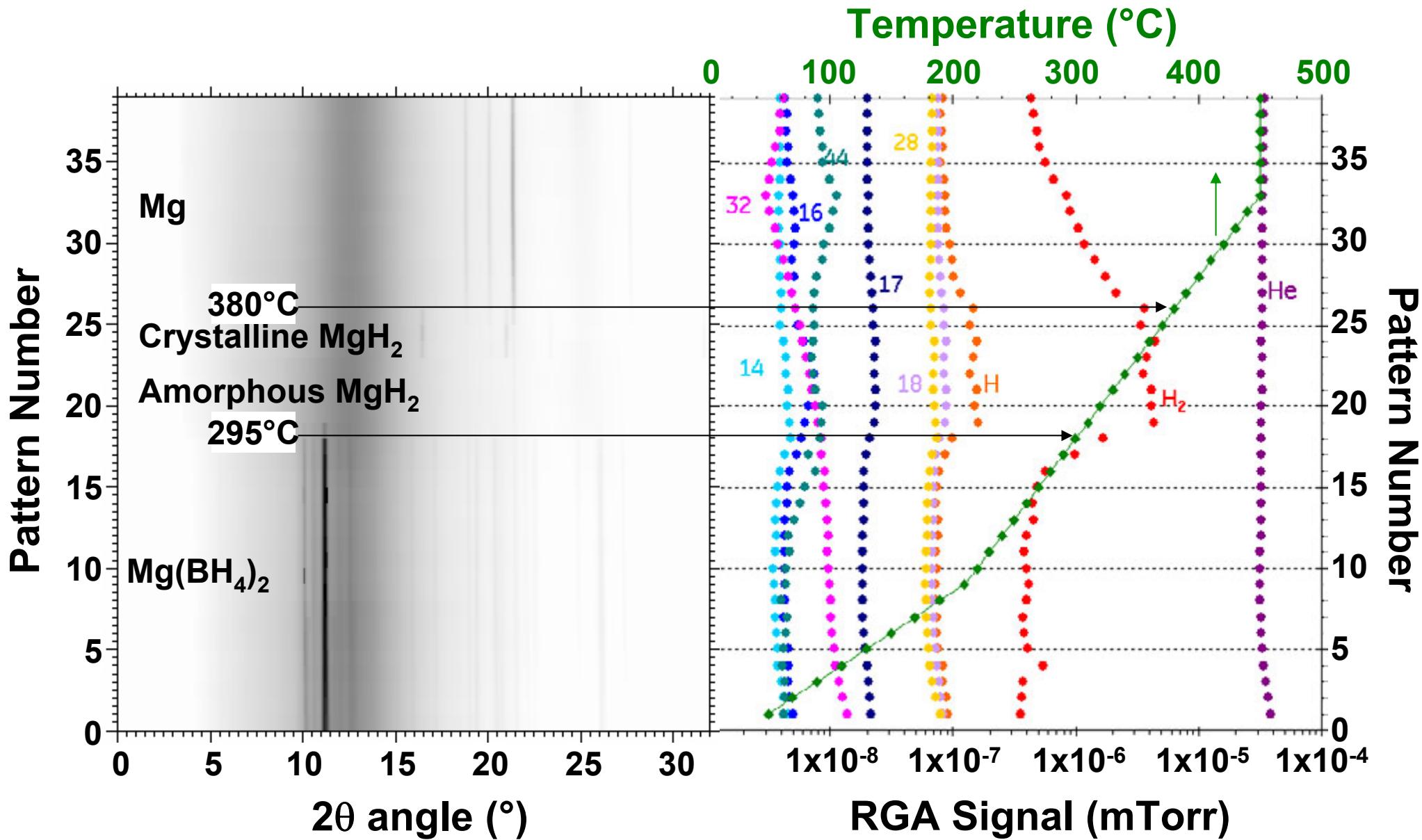


1<sup>st</sup> desorption  
13.2 wt.%



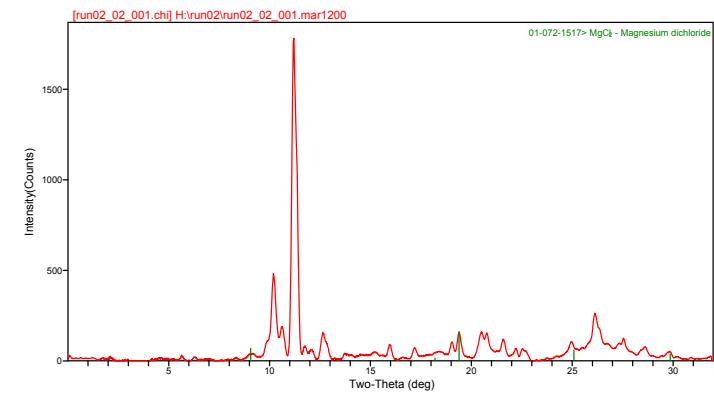
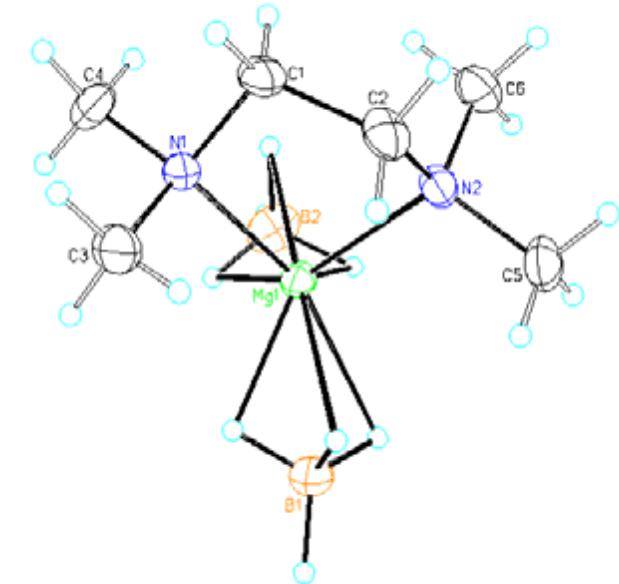
- Only Step 2 is currently reversible (~3 wt % H<sub>2</sub>)
- Need better structural & catalyst understanding to make Step 1 reversible

# Mg(BH<sub>4</sub>)<sub>2</sub> desorption



# Mg(BH<sub>4</sub>)<sub>2</sub>

- Have determined the crystal structure of the solvated (TMEDA) form
- Desolvated compound may have a different Mg:BH<sub>4</sub> ration (i.e., <2:1)
- Isotope labeling of Mg(<sup>11</sup>BD<sub>4</sub>)<sub>2</sub> 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<sub>4</sub>)<sub>2</sub>
- Crystal structure identification of Mg(BH<sub>4</sub>)<sub>2</sub> – BNL, NIST, UIUC
- Computational prediction of dopants for Mg(BH<sub>4</sub>)<sub>2</sub> – UIUC, CMU, U Pitt
- Thermal conductivity measurements (Sandia) & Vapor pressure measurements (Univ. Nevada)

## FY07

- Continue on catalyst and doping study of Mg(BH<sub>4</sub>)<sub>2</sub> to improve reversibility
- Perform system-level evaluation of properties such as cycling stability/degradation
- Go/No-Go for Mg(BH<sub>4</sub>)<sub>2</sub> reversibility: < 450°C & < 200 bar

# Summary

- Robust combinatorial/HTS methodology developed – met our '05 deliverable
- Focus on  $\text{Mg}(\text{BH}_4)_2$  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  $\text{Mg}(\text{BH}_4)_2$  as a potential high-capacity  $\text{H}_2$  storage material



imagination at work

**ecomagination<sup>SM</sup>**



imagination at work



# Publications & Presentations

- Job Rijssenbeek presented a poster "Characterization of the titanium catalyst in NaAlH<sub>4</sub>", 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<sub>2</sub>)<sub>2</sub> + 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<sub>2</sub>)<sub>2</sub> 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