

# Discovery and Development of Metal Hydrides for Reversible On-board Hydrogen Storage

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Sandia National Laboratories

June 10, 2010



**Project ID: ST033**

## *Timeline*

- Project started in March '05
- Project end June 2010
- Percent complete 100%

## *Barriers*

- A. System Weight & Volume, B. Cost, C. Efficiency, D. Durability
- E. Charge/discharge rates
- P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

## *SNL R&D Budget*

- FY08 Funds: \$2.4M
- FY09 Funds: \$3.1M
- FY10 Funds: \$1.9M

## *MHCoE Partners*

BNL, JPL, NIST, ORNL, SRNL, Caltech, GA Tech, OSU, PITT, Stanford, UH, UIUC, UNR, UNB, Utah, HRL, UTRC

## *Collaborators*

V. Ozolins (UCLA), J. Herberg (LLNL), Y. Filinchuk (ESRF),  
C. Wolverton (Northwestern), J-H Her (U. Maryland)

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**Technical POC and MHCoE Director:** Lennie Klebanoff

## Core Technical Team

**Mark Allendorf:** *Theory, Theory Group Coordinator*

**Eric Majzoub:** *PEGS theory, experiments (Sandia/UMSL)*

**Vitalie Stavila:** *New materials (borohydrides, ammine complexes)*

**Joe Cordaro:** *New materials (P materials, bulk syntheses)*

**Weifang Luo:** *New materials (Li-N-Mg-H materials)*

**Mitch Anstey:** *P-containing materials*

## Other Key Contributors

Rich Behrens, Ida Nielsen

## Ph.D. Students

Rebecca Newhouse, Leo Seballos (UC Santa Cruz),  
Godwin Severa (U. Hawai'i), David Peaslee (UMSL)

## Undergraduate Student

Natchapol Poonyayant (Mahidol University, Thailand)

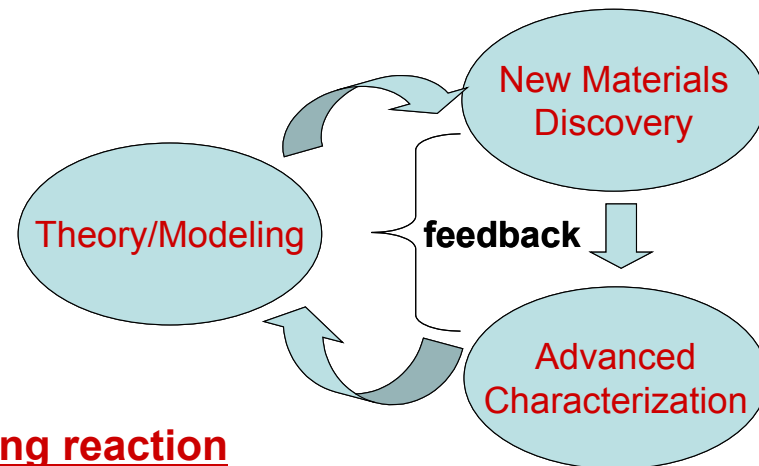
Discover, develop and validate “**reversible**” on-board metal hydride storage materials with potential to meet the DOE 2010 targets and a clear path to meeting the 2015 targets. Use theory-directed synthesis and characterization

## Prediction of crystal structures:

- ✓ Prototype Electrostatic Ground State (PEGS) technique for structure predictions and rapid  $\Delta H$  estimates
- ✓ First-principles Density Functional Theory (DFT) is used for accurate thermodynamics calculations

## Synthesis/sample preparation:

- ✓ Solid-state and solution routes
- ✓ High-energy ball-milling (SPEX), cryo-milling
- ✓ Hot-sintering at high-P (600 C, 2000 bar)



## Understanding structural properties / Probing reaction mechanisms / Additives/dopants/catalysts modification:

Powder/Synchrotron XRD, Neutron diffraction, STMBMS, PCT/Sieverts, Raman, FTIR, TGA/DSC, TEM, SEM, EDAX, EELS

## Theory Status in June 2009:

- Established Multiphase Equilibria (MPE) Theory:
  - applied to  $\text{LiNH}_2$  (+LiH);  $\text{LiBH}_4$  /C
- Coordinated the MHCoe Theory Group (TG)
- Used PEGS to predict structures of  $\text{LiSc}(\text{BH}_4)_4$ ,  $\text{M-Ti}(\text{BH}_4)_x$ ,  $[\text{B}_{12}\text{H}_{12}]^{2-}$
- Predicted  $\Delta H$  dehydrogenation for borohydride destabilized reactions

## Theory Focus During FY09/10:

- MPE Theory applied to  $\text{LiBH}_4$  and the formation of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$
- MPE Theory applied to  $\text{LiBH}_4 + \text{MgH}_2$ : Pressure-dependent mechanism
- MPE Study of  $2\text{LiNH}_2 + \text{C} \rightarrow \text{Li}_2\text{CN}_2 + 2\text{H}_2$ , a rxn. predicted by MHCoe TG
- $\text{Mg}(\text{BH}_4)_2 + 2\text{C} \rightarrow \text{MgB}_2\text{C}_2 + 4\text{H}_2$ , another predicted destabilized Rxn.
- PEGS studies of  $\text{Ti}(\text{BH}_4)_3$ ,  $\text{M}[\text{PB}_2\text{H}_8]_x$  for  $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Mg}, \text{Ca}$
- Continued Coordination of the MHCoe Theory Group

Phase equilibrium calculations can reveal complex hydride decomposition chemistry to better predict gas-phase and solid products...

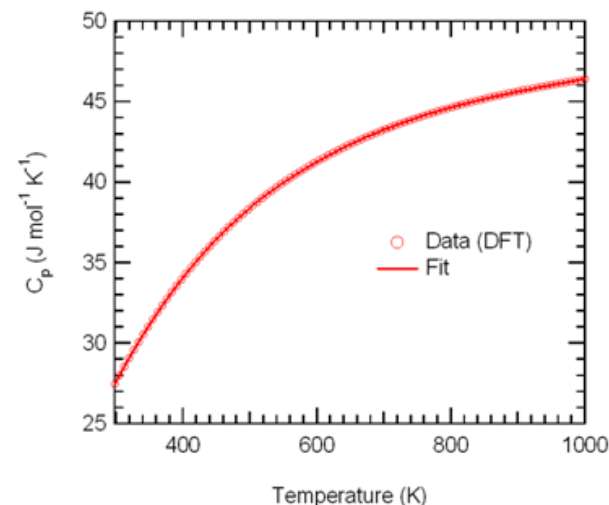
## Approach: DFT/Gibbs Free Energy Minimization

- Compute hydride thermodynamics
  - DFT: Ground-state energies (0 K)
  - PHONON: finite-temperature thermodynamics ( $C_p^\circ$ ,  $S^\circ$ ,  $\Delta H^\circ$ )
  - Fit  $C_p^\circ$  to polynomial
- Compute equilibrium at constant T,P
  - FactSage package (commercial software)
  - Include all relevant gas- and solid-phase species:
    - Gas phase: *JANAF Tables*
    - $B_xH_y$  -  $B_{10}H_{14}$
    - Li-B-C-Mg crystalline phases
    - Some liquids

$$C_p = a + bT + cT^2 + dT^3$$

Polynomial fit to  $C_p$  for  $MgH_2$ . Data from DFT and phonon calculation

$$G = \sum_{\substack{\text{ideal} \\ \text{gas}}} n_i (g_i^\circ + RT \ln P_i) + \sum_{\substack{\text{pure} \\ \text{condensed} \\ \text{phases}}} n_i g_i^\circ$$



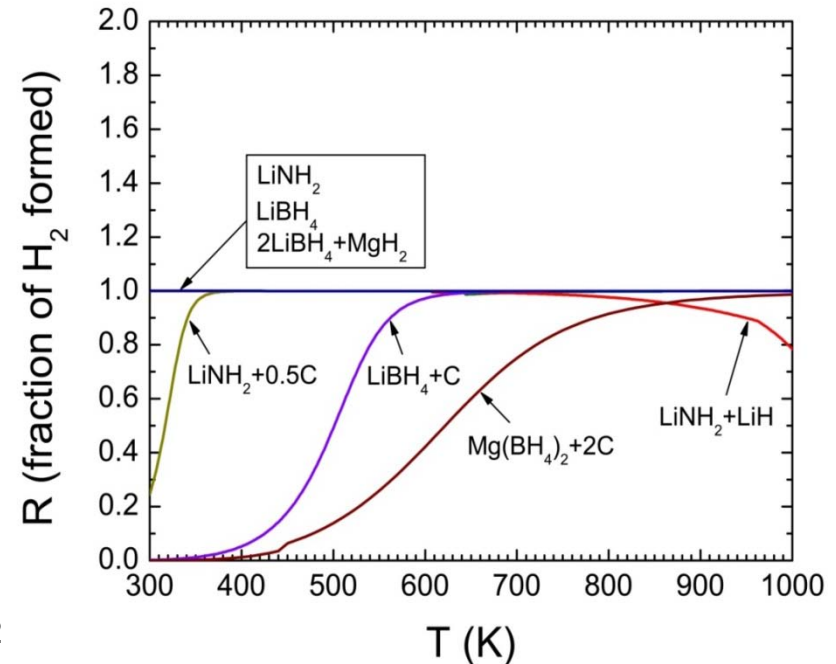
Representative MH systems considered to assess the importance of full-scale equilibrium

## MPE Theory Results Last Year:

- **LiNH<sub>2</sub> (+ LiH):** NH<sub>3</sub>, N<sub>2</sub> formation; thermodynamic vs. kinetic products
- **LiBH<sub>4</sub> + C:** Hydrocarbon formation

## MPE Theory Results This Year:

- **LiBH<sub>4</sub>:** Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> intermediate formation
- **2LiNH<sub>2</sub> + C → Li<sub>2</sub>CN<sub>2</sub> + 2H<sub>2</sub>, 31.4 kJ/mol H<sub>2</sub>**
- **LiBH<sub>4</sub> + MgH<sub>2</sub>:** Pressure-dependent mechanism\*
- **Mg(BH<sub>4</sub>)<sub>2</sub> + 2C → MgB<sub>2</sub>C<sub>2</sub> + 4H<sub>2</sub>, 43.1 kJ/mol H<sub>2</sub>\***



R = 1: only H<sub>2</sub> forms

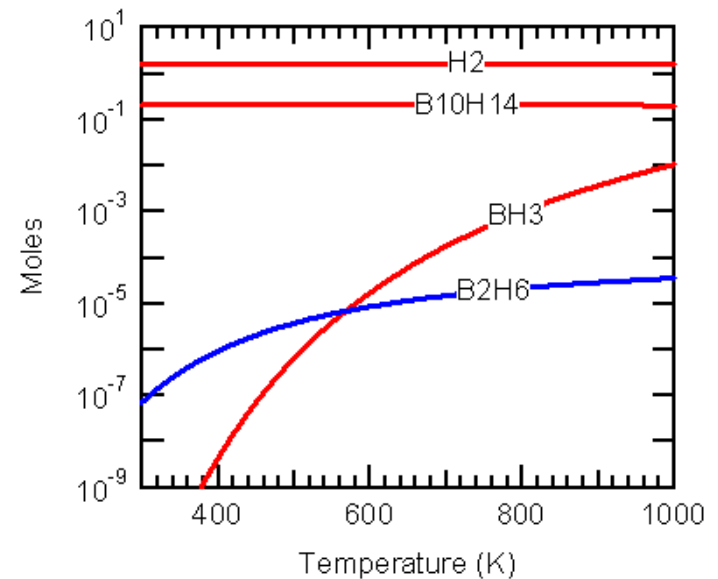
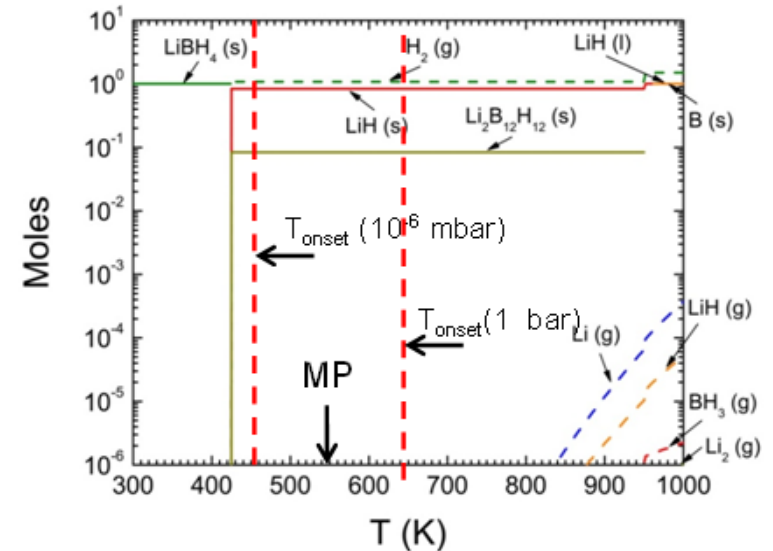
R < 1: significant gas-phase byproducts

\* -- see our additional slides

# LiBH<sub>4</sub>: condensed-phase intermediate formation

- Predicted overall reaction:  

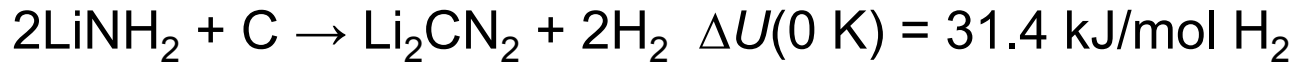
$$\text{LiBH}_4 \rightarrow 1/12(\text{Li}_2\text{B}_{12}\text{H}_{12}) + 5/6\text{LiH} + 13/12\text{H}_2$$
(426K)
- Small kinetic barrier suggested
  - 440 K onset Kostka et al.,  $P_{\text{tot}} = 10^{-6}$  mbar
  - ~ 600 K Pinkerton et al.,  $P_{\text{tot}} = 1$  atm
- B<sub>2</sub>H<sub>6</sub> formation:
  - Detected by Kostka et al. (*JPCOC* 2007)
  - B<sub>2</sub>H<sub>6</sub>(g) is not stable; converts to B<sub>x</sub>H<sub>y</sub>
  - B<sub>2</sub>H<sub>6</sub> probably not detectable at 1 atm
- Effect of nanoconfinement
  - Gross et al. no Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> (*JPCOC* 2008)
  - Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> stability reduced?
  - Alternative kinetic pathway?



B<sub>2</sub>H<sub>6</sub> gas-phase equilibrium (1 atm)

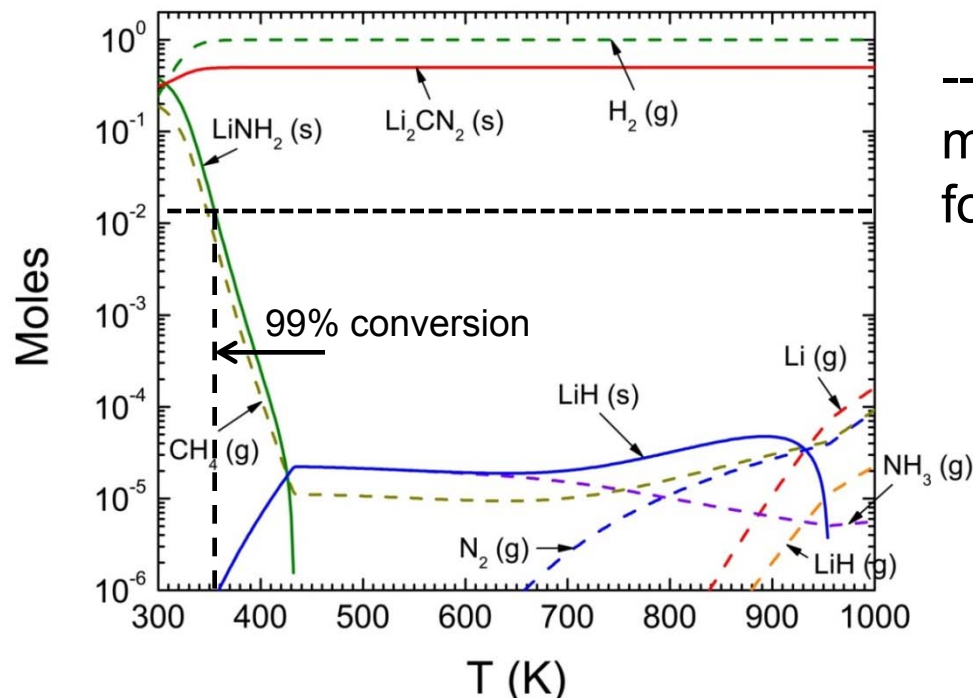


## MHCoE TG Prediction (Alapati et al. (JPCC 2008))



Reactions predicted by MPE Theory:

- $\text{LiNH}_2 + 0.5\text{C} \rightarrow 0.4\text{LiNH}_2 + 0.3\text{Li}_2\text{CN}_2 + 0.25\text{H}_2 + 0.2\text{CH}_4$  ( $T < 350 \text{ K}$ )
- $\text{LiNH}_2 + 0.5\text{C} \rightarrow 0.5\text{Li}_2\text{CN}_2 + \text{H}_2$  ( $T > 350 \text{ K}$ )



--  $\text{CH}_4$  predicted to be a major gas-phase by-product for  $\text{H}_2$  release below 350 K

--  $\text{Li}_2\text{CN}_2 + \text{H}_2$  are predicted to be major products at  $T > 350 \text{ K}$ , avoiding  $\text{CH}_4$  formation

Month/year	Milestone or Go/No-Go decision: <b>Al-Adduct Theory, MPE Theory</b>
May-08 ✓	Milestone: Complete BAC calculations of alane-amine complexes
Sep-08 ✓	Milestone: Complete BAC calculations on alane-adduct complexes
Dec-08 ✓	No-go: Model reactions of alane-amine surface interactions
May-09 ✓	Milestone: Complete calculations on alanate-amine complexes
Sep-09 ✓	Milestone: Complete calculations on alanate-ether adducts
Apr-10 ✓	Milestone: Evaluate gas-phase species formation in C-containing materials
Jun-10 ✓	Milestone: Evaluate gas-phase species formation in B-containing materials
Month/year	Milestone or Go/No-Go decision: <b>Borohydride Theory</b>
Oct-09 ✓	Milestone: Complete PEGS searches for new high-H <sub>2</sub> content mixed alkali-TM borohydrides
Feb-09 ✓	No-go: Discontinue surfactant templating for nano-scale alanates/borohydrides
Mar-10 ✓	Milestone: Complete PEG searches for new mixed cation alkaline-earth TM borohydrides
May-10 ✓	Go/no-go: Discontinue alkali-TM borohydrides if no suitable materials found

## Status in June 2009:

- Completed  $\text{Ca}(\text{BH}_4)_2$ , made “downselect” decision (no further work)
- Synthesized and characterized ammine adducts of borohydrides
- Synthesized and examined *closo*-borates ( $[\text{B}_{12}\text{H}_{12}]^{2-}$ ) predicted by PEGS
- Initiated work on P-based hydrogen storage materials

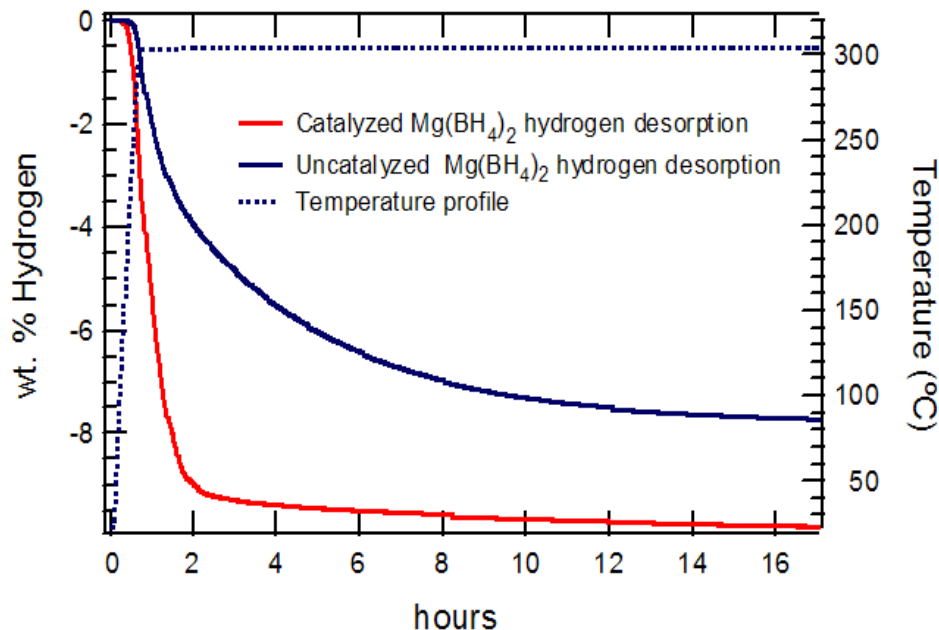
***Final Year Goals: Improve our understanding of high wt. % borohydrides, find new materials based on P and optimize  $2\text{LiNH}_2/\text{MgH}_2$  -- recommended by the MHCoe to the HSECoE as a preferred “near-term” material.***

- Additive studies of  $\text{Mg}(\text{BH}_4)_2$
- Destabilization of  $\text{CaB}_{12}\text{H}_{12}$  with  $\text{CaH}_2$
- Rehydrogenation of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  and  $\text{Na}_2\text{B}_{12}\text{H}_{12}$
- Hydrogen storage properties of P-containing metal hydrides
- Catalysis of  $2\text{LiNH}_2/\text{MgH}_2$  by  $\text{KH}$  and  $\text{KNH}_2$
- Synthesized and characterized  $\text{Ti}(\text{BH}_4)_3$  -- see additional slides

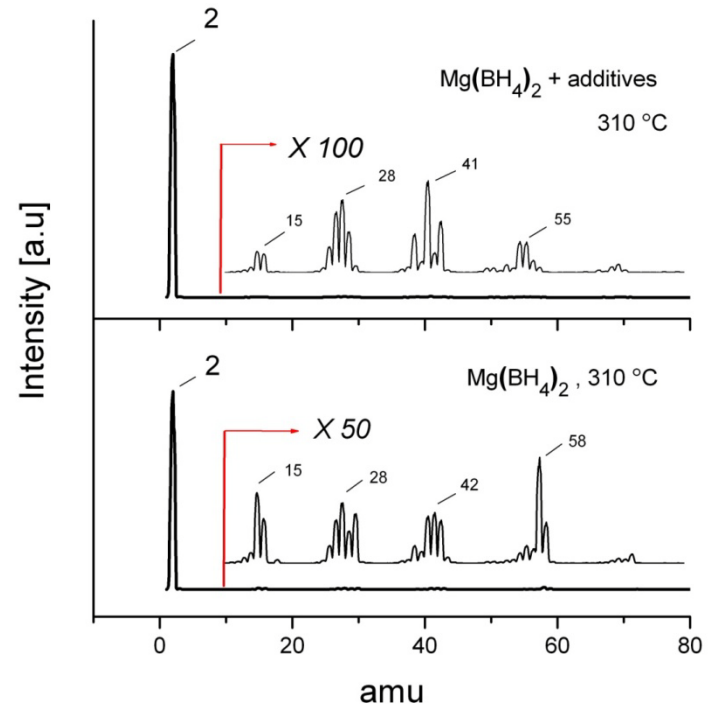
# TiF<sub>3</sub>/ScCl<sub>3</sub> Enhances H<sub>2</sub> Desorption from Mg(BH<sub>4</sub>)<sub>2</sub>


*Desorption of Mg(BH<sub>4</sub>)<sub>2</sub> ball-milled with 5mol % TiF<sub>3</sub> and 5mol% ScCl<sub>3</sub>*

**Desorption Sievert's data**



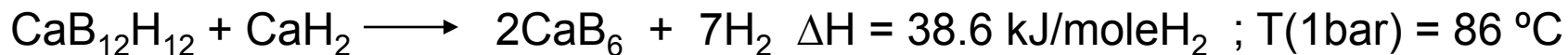
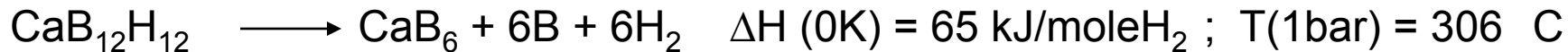
**RGA data**



 R. Newhouse, V. Stavila, S. Hwang, L. Klebanoff, J.Z. Zhang  
*J. Phys. Chem. C* **2010**, *114*, 5224-5232.

- Small amounts of boron hydrides (15 – 58 amu) (<0.2wt%) are released
- Other transition metal chlorides (Mn(II), V(III), Ni(II) and Cu(II)) alone or in combination with Ti(III) and Sc(III) salts were not as effective as TiF<sub>3</sub>/ScCl<sub>3</sub>
- The transition metal additives generally degrade reversibility.

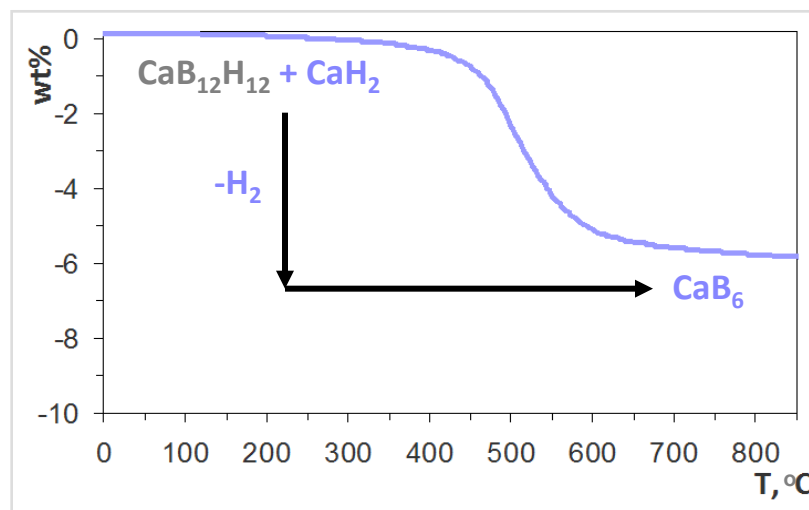
# Understanding $[B_{12}H_{12}]^{2-}$ Intermediates



-- predicted by Ozolins, Majzoub and Wolverton, JACS, 2009, 131, 230.

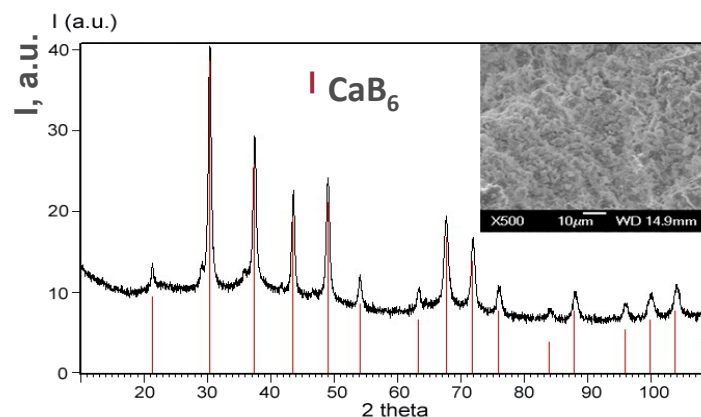
Experimentally, we see no  $H_2$  release from  $CaB_{12}H_{12}$  heated to  $700 \text{ }^\circ\text{C}$

$CaB_{12}H_{12} + CaH_2$  releases  $H_2$  at  $\sim 500 \text{ }^\circ\text{C}$



The presence of  $CaH_2$  decreases the  $T$  required to release  $H_2$  from  $CaB_{12}H_{12}$  by  $> 200 \text{ }^\circ\text{C}$ , in good agreement with prior theory

We also see a slight destabilization of  $Li_2B_{12}H_{12}$  and  $Na_2B_{12}H_{12}$  by  $MgH_2$

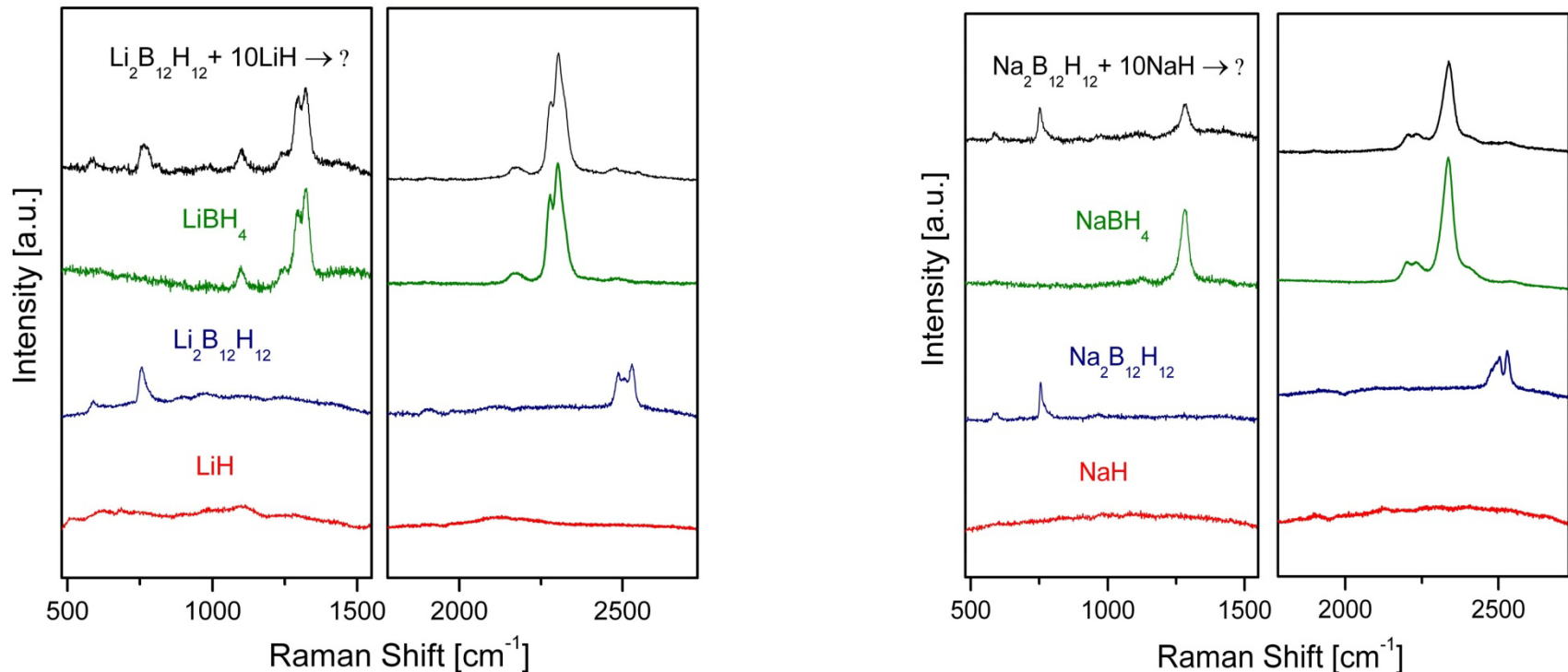


$CaB_6$  confirmed



# Reversibility of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ , $\text{Na}_2\text{B}_{12}\text{H}_{12}$ Demonstrated at High $\text{H}_2$ Pressure

$p(\text{H}_2) = 70\text{--}90$  MPa ( $>10,150$  psi),  $t = 400\text{--}500$  C, reaction time: 16–72 hours

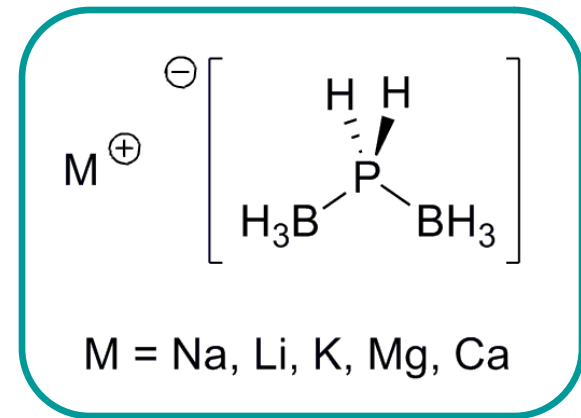


$[\text{B}_{12}\text{H}_{12}]^{2-}$  compounds can be converted quantitatively into borohydrides in the presence of the corresponding metal hydride at high  $\text{H}_2$  pressure.

*Conclusion confirmed by solid-state NMR (Caltech) and neutron vibrational spectroscopy (NIST).*

## Bis(borano)hypophosphites are:

- Air and water tolerant
- Soluble in most organic solvents
- Form concentrated solutions/gels
- Theoretical Weight % of H<sub>2</sub> is 8-12 %

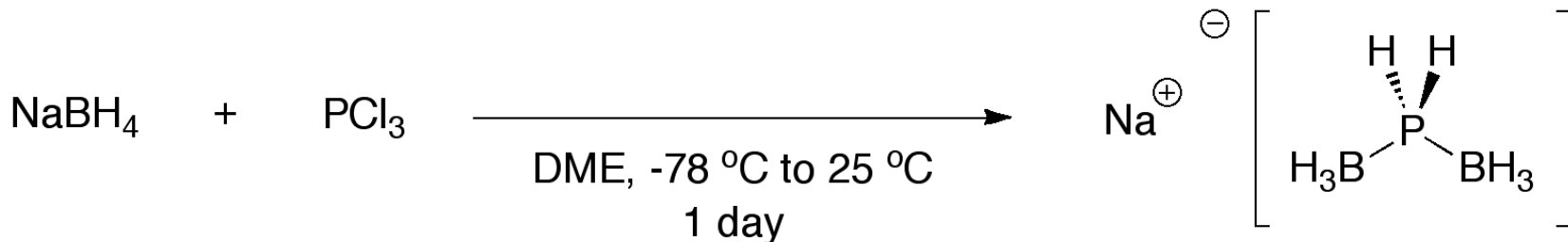


Gilmont, P. and coworkers, *J. Am. Chem. Soc.* **1940**, 62, 717.

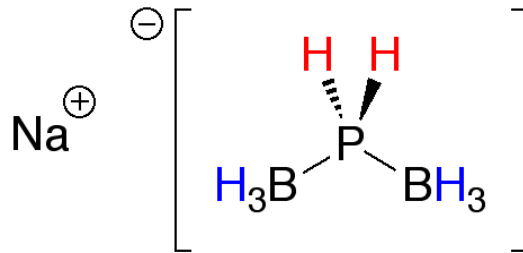
Parry, R. W. and coworkers, *Inorg. Chem.* **1967**, 6, 1761.

Previous synthetic methods used PH<sub>3</sub>, PH<sub>3</sub>-BH<sub>3</sub>, or PH<sub>4</sub>I as the source of phosphorus, which are dangerous precursors

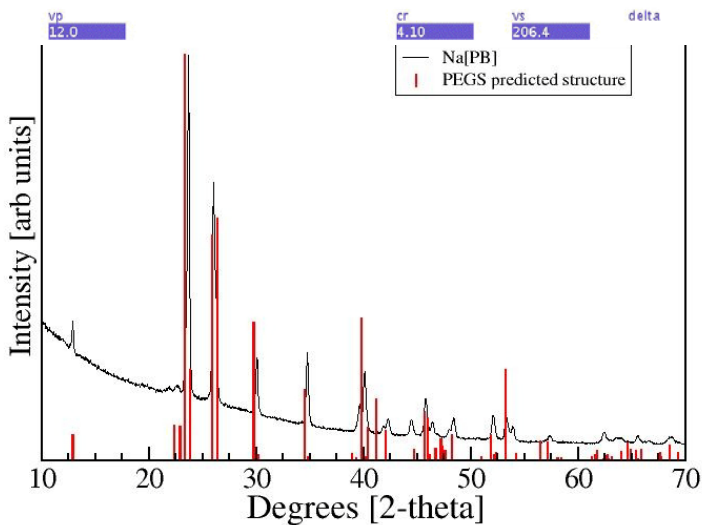
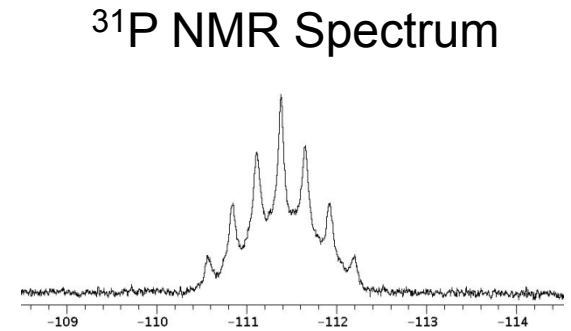
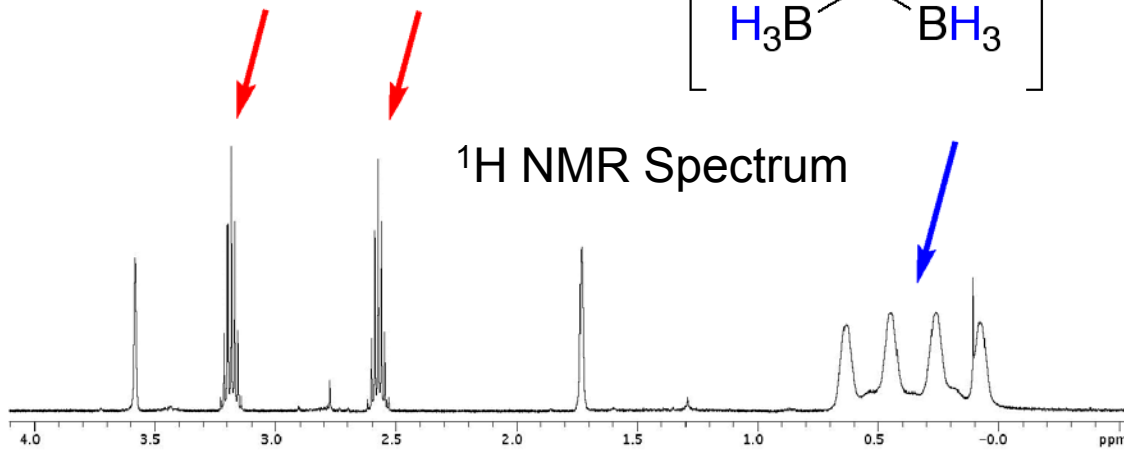
We developed a safe route to M[PB]<sub>x</sub> Na[PB], Na[PB]-d<sub>8</sub>, Li[PB], and Ca[PB]<sub>2</sub>



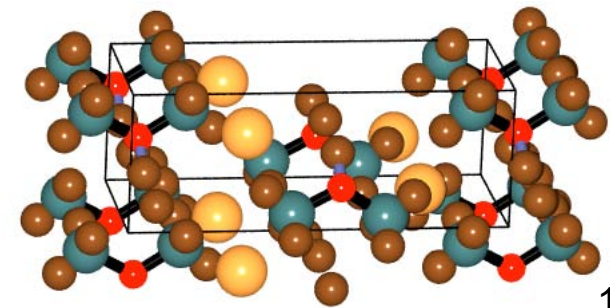
# Na[PB] Structure Understood Theoretically, Experimentally



*Identity of the anionic species confirmed by solution NMR*



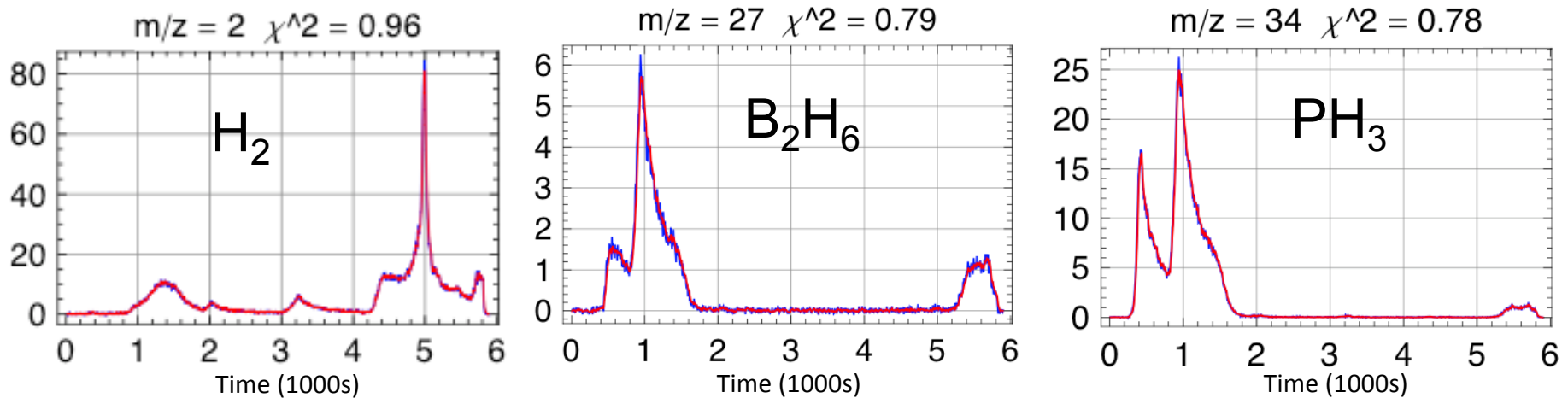
PEGS Predicted Crystal Structure in Agreement with Experiment



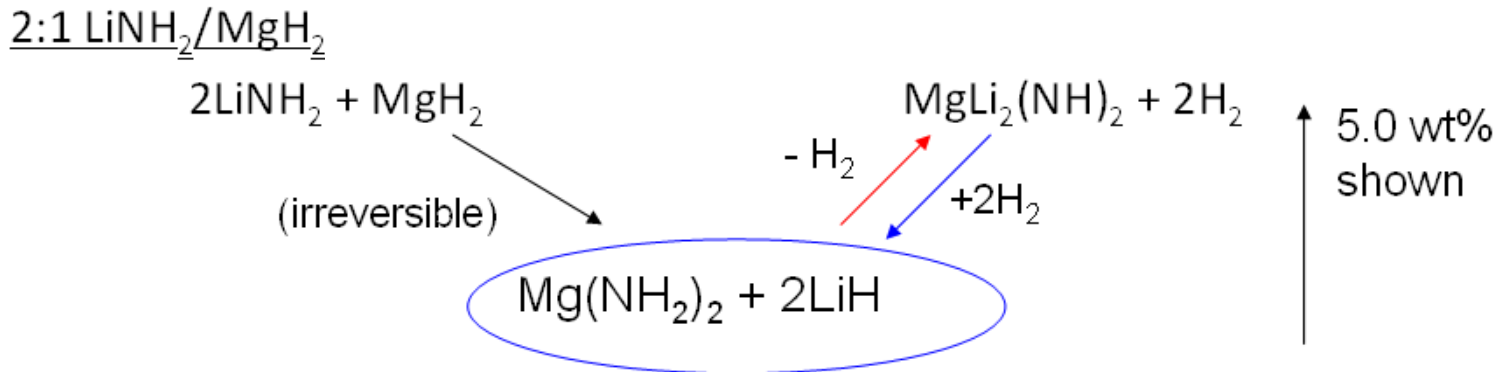


- ~ 6 wt. % H<sub>2</sub> desorbed from the Na[PB] material
- Reasonable H<sub>2</sub> desorption temperature of ~165°C is observed
- Faster heating rates yield more endothermic melting, slower heating rates favor exothermic H<sub>2</sub> release.
- Attempts to rehydrogenate desorbed material have so far been unsuccessful

## Simultaneous Thermogravimetry Modulated Beam Mass Spectrometry (STMBMS):



Release of PH<sub>3</sub> and B<sub>2</sub>H<sub>6</sub> combined with lack of reversibility lead us to downselect Na[PB], removing from further consideration.



W. Luo and S. Sicksafoose, *J. Alloys and Compounds*, 407 (2006) 274-281

-- honored as a "Top Cited" paper by this journal in 2009

-- recommended by the MHCoE as a "near term" material for the HSECoE

- Potassium doping dramatically improves absorption rate.
- $\Delta H_{\text{des.}} = 42 \text{ kJ/mole H}_2$
- Proven reversible hydrogen capacity of 5wt%, 1wt% more than  $\text{NaAlH}_4$
- Excellent Cyclability: 264 cycles demonstrated, with 23% loss in capacity
- Manageable  $\text{NH}_3$  release (200 ppm at 180 °C), but needs improvement

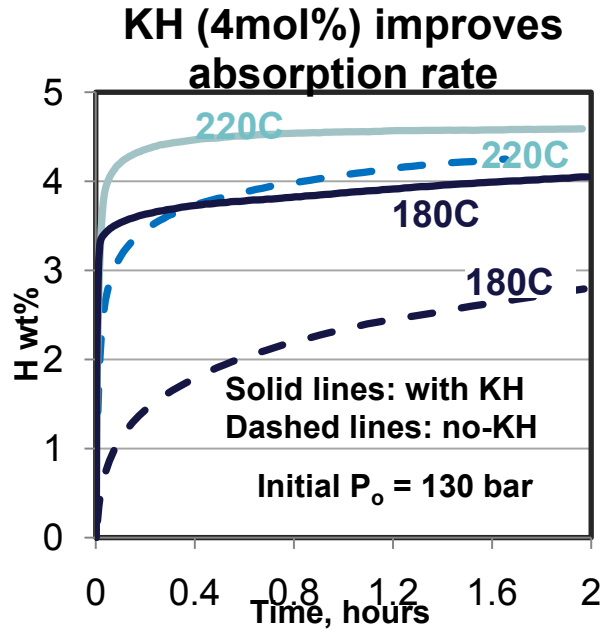
**More capacity possible with 1:1  $\text{LiNH}_2/\text{MgH}_2$  material, but need to improve pressure of 1st plateau region, cyclability**

# KH, KNH<sub>2</sub> Promote Absorption

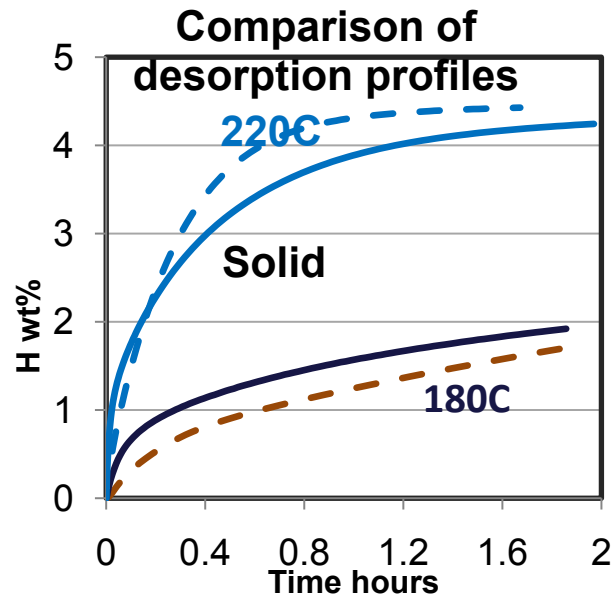
## Kinetics of 2LiNH<sub>2</sub>+MgH<sub>2</sub>

Motivation: P. Chen *et. al.* show that KH can aid kinetics in Li-Mg-N-H systems (Angew. Chem. Int. Ed. 2009, 48, 1-5)

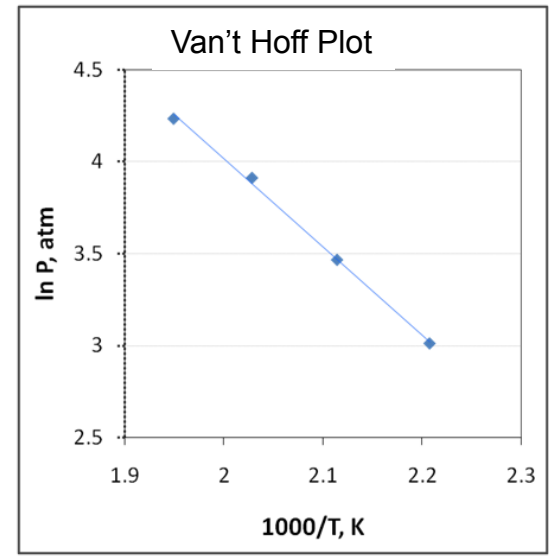
Our Work: Both KH and KNH<sub>2</sub> aid absorption kinetics (K<sup>+</sup> catalytic agent)



KH dramatically aids absorption kinetics



Little catalytic effect on desorption



$$\Delta H_{\text{des}} = 42 \text{ kJ/mole H}_2$$

-- results support prior work by Chen. *et. al*

# Experimental Milestones Are Completed

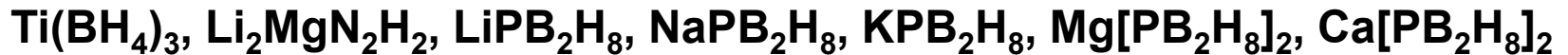
Month/year	Milestone or Go/No-Go decision
Jan-09 ✓	Milestone: Synthesize $\text{Ca}(\text{BH}_4)_2/\text{NH}_3$ system No-go: On further work on $\text{Ca}(\text{BH}_4)_2/\text{NH}_3$ system Milestone: Complete STMBMS characterization of $\text{Ca}(\text{BH}_4)_2$
Mar-09 ✓	Milestone: Lowering of $\text{Ca}(\text{BH}_4)_2$ desorption temperature No-go decision made on $\text{Ca}(\text{BH}_4)_2$
June-09	Go/no-go: Continue with mixed $\text{Ca}_{(1-x)}\text{M}_x(\text{BH}_4)_z$ materials if reversibility has been shown at improved P and T compared to $\text{Ca}(\text{BH}_4)_2$ : No-Go Decision Made
Sep-09 ✓	Milestone: Incorporation of hydride material in catalyzed nano-frameworks
Dec-09 ✓	Isolate and assess the $\text{H}_2$ storage properties of new mixed cation alkali-TM borohydrides
Dec-09 ✓	Synthesize and characterize $\text{NaPB}_2\text{H}_8$ and $\text{LiPB}_2\text{H}_8$ .
Jan-10 ✓	Complete mechanistic study of the hydrogenation/dehydrogenation of $\text{LiMgN}$
Feb-10 ✓	Go/no-go on $\text{A-TM}(\text{BH}_4)_x$ : No-Go decision made on alkali transition metal borohydrides
Apr-10 ✓	Characterize the $\text{H}_2$ desorption properties of modified $\text{Mg}(\text{BH}_4)_2$
Apr-10 ✓	Determine the $\text{H}_2$ desorption properties of $\text{NaPB}_2\text{H}_8$ and $\text{LiPB}_2\text{H}_8$
Apr-10 ✓	Synthesize and characterize $\text{Mg}[\text{PB}_2\text{H}_8]_2$ and $\text{Ca}[\text{PB}_2\text{H}_8]_2$

## Theory:

Gained a better mechanistic understanding of H<sub>2</sub> release and the role of impurity gas formation in high wt. % borohydride and amide materials:



Predicted MH structures, allowing DFT calculations of reaction thermodynamics:



Successfully Coordinated the MHCoE Theory Group

## New Materials:

- Improved the desorption kinetics of Mg(BH<sub>4</sub>)<sub>2</sub>
- Developed a route for releasing H<sub>2</sub> from B<sub>12</sub>H<sub>12</sub> compounds, confirmed prior theory
- Demonstrated hydrogenation of Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> and Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> at high H<sub>2</sub> pressure
- Successfully synthesized and characterized H<sub>2</sub> storage properties of NaPB<sub>2</sub>H<sub>8</sub>
- Confirmed remarkable catalysis of 2LiNH<sub>2</sub>/MgH<sub>2</sub> by KH and KNH<sub>2</sub>
- Successfully synthesized and characterized Ti(BH<sub>4</sub>)<sub>3</sub>

## ***MHCoE Partners:***

- BNL: J. Wegrzyn, J. Graetz
- Caltech: S.-J. Hwang, C. Ahn
- HRL: J. Vajo, P. Liu
- GA Tech: D. Sholl
- JPL: J. Reiter, J. Zan
- NIST: T. Udovic, U. Kattner
- OSU: J.-C. Zhao
- SRNL: D. Anton, R. Zidan
- U. Hawai'i: C. Jensen
- U. Illinois: I. Robertson, D. Johnson
- UNR: D. Chandra
- U. Pitt: K. Johnson
- U. Utah: Z. Fang
- UTRC: X. Tang, D. Mosher, S. Opalka

## ***Other Collaborations:***

- ESRF: Y. Filinchuk
- LLNL: J. Herberg
- Northwestern: C. Wolverton
- UCLA: V. Ozolins
- U. Geneva: K. Yvon
- U. Maryland: J.-H. Her

# Additional Slides

# 2LiBH<sub>4</sub>+MgH<sub>2</sub>: pressure-dependent mechanisms

$P_{\text{tot}} = 1 \text{ atm H}_2$  (2-step mechanism):

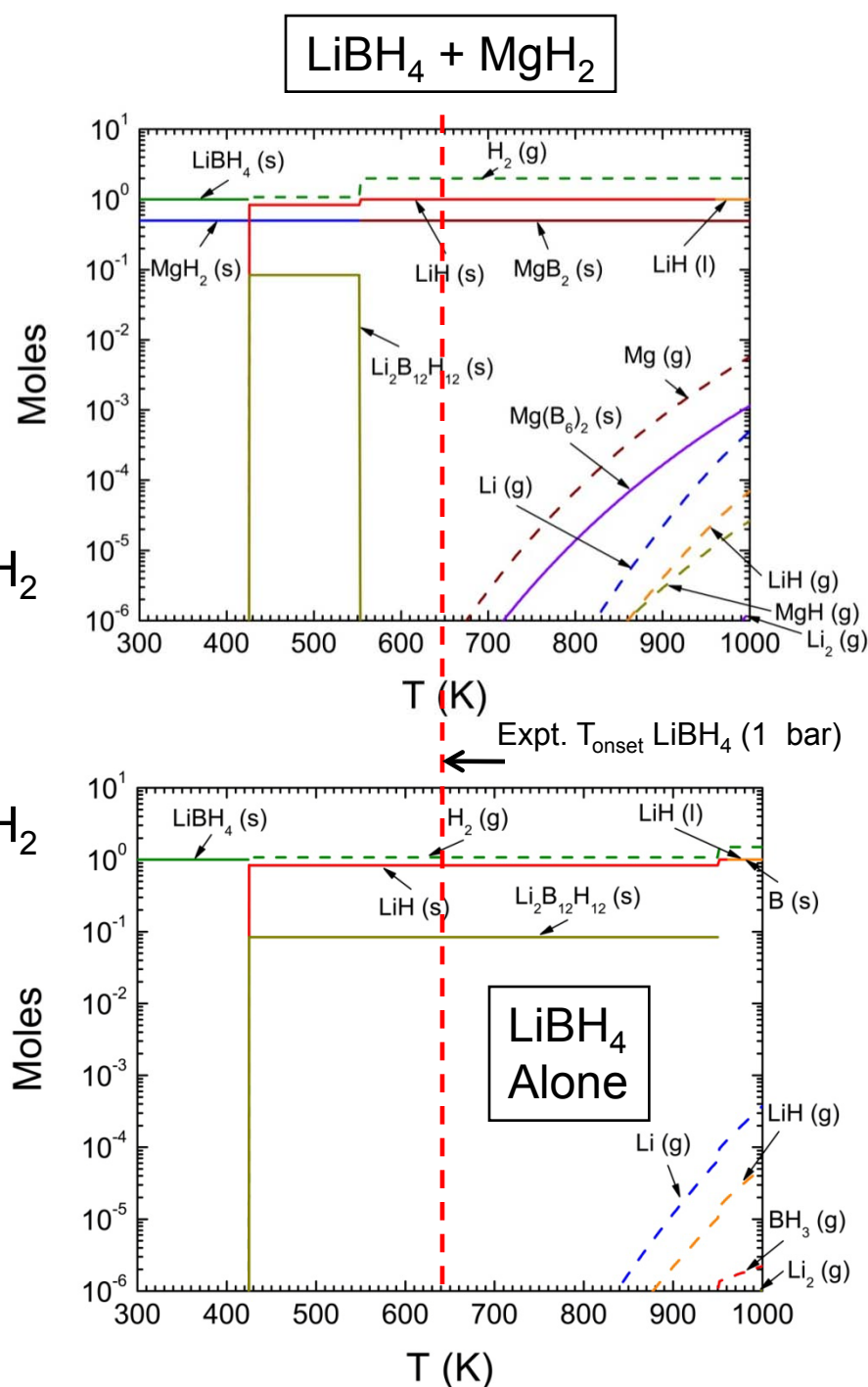
- $\text{LiBH}_4 \rightarrow 1/12(\text{Li}_2\text{B}_{12}\text{H}_{12}) + 5/6\text{LiH} + 13/12\text{H}_2$
- $\text{Li}_2\text{B}_{12}\text{H}_{12} + 6\text{MgH}_2 \rightarrow 2\text{LiH} + 6\text{MgB}_2 + 11\text{H}_2$

100 atm H<sub>2</sub> (3-step mechanism):

- $\text{LiBH}_4 \rightarrow 1/12(\text{Li}_2\text{B}_{12}\text{H}_{12}) + 5/6\text{LiH} + 13/12\text{H}_2$
- $\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$  (782 K)
- $\text{Li}_2\text{B}_{12}\text{H}_{12} + \text{Mg} \rightarrow \text{LiH} + \text{MgB}_2 + \text{H}_2$

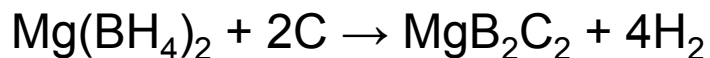
→ Kinetic limitation to Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> determines decomposition

→ Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> is thermodynamically 'destabilized' in the presence of MgH<sub>2</sub>





# Mg(BH<sub>4</sub>)<sub>2</sub> (+ 2C): thermodynamic and kinetic effects

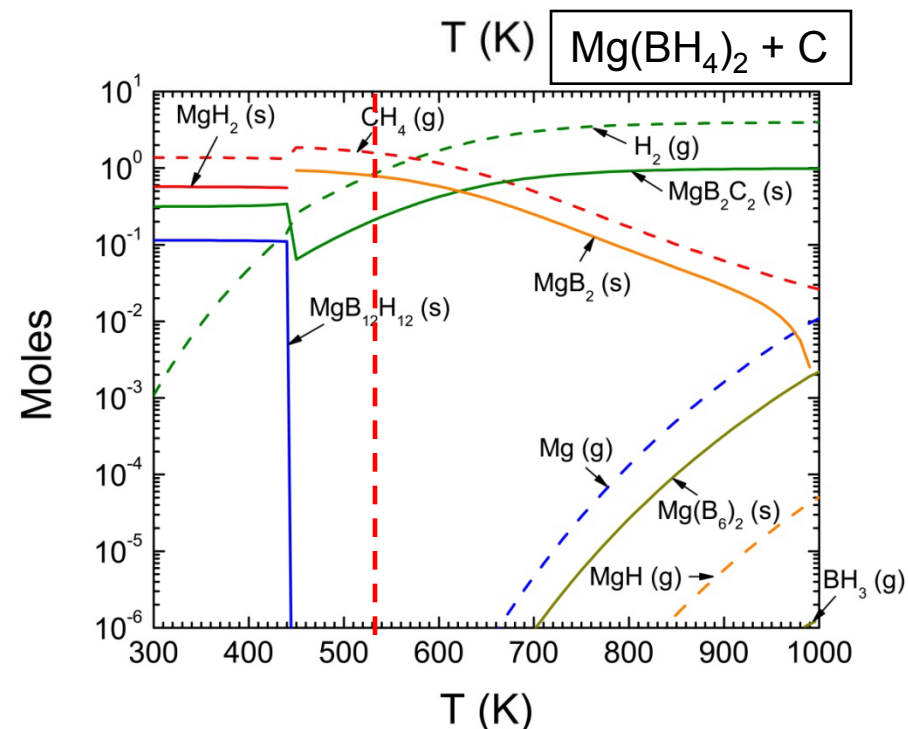
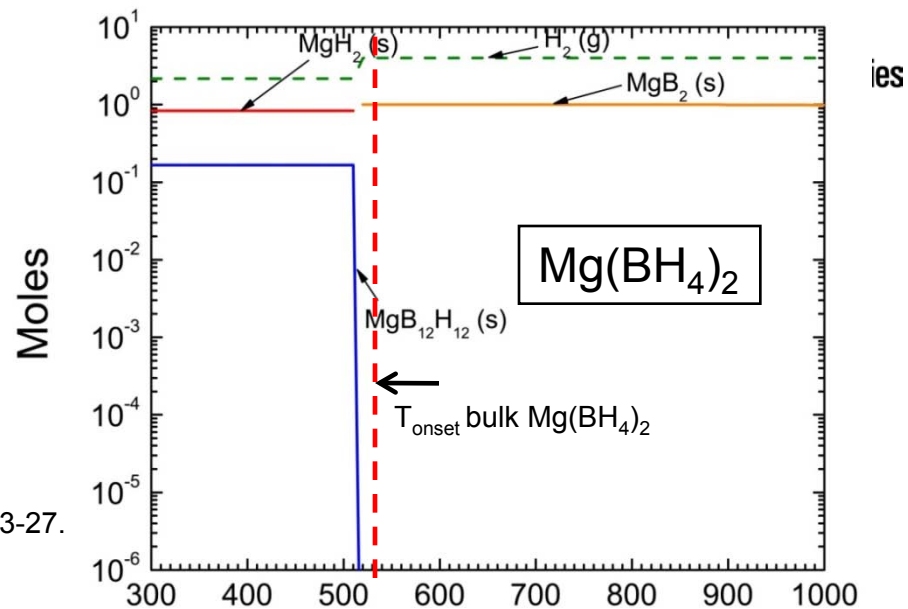


$$\Delta U(0 \text{ K}) = 43.1 \text{ kJ/mol H}_2$$

Alapati, S. V.; Johnson, J. K.; Sholl, D. S., *J. Alloys Compd.* **2007**, 446, 23-27.

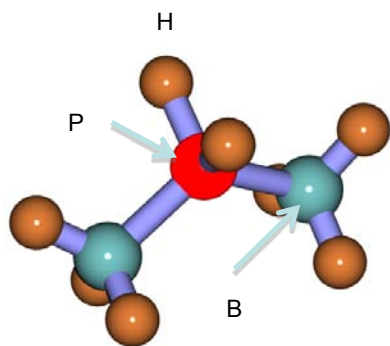
- Newhouse et al. *JPCCC* 2010
  - $T_{\text{onset}} = 540 \text{ K}$
  - MgB<sub>12</sub>H<sub>12</sub> is detected
- Thermodynamic advantage to C addition as well as kinetic
- Nanoconfinement
  - Infiltrated C aerogel reduces  $E_a$
  - H<sub>2</sub> release suggests no CH<sub>4</sub> forms

Fichtner et al., *Nanotechnology*, **2009**, 204029.

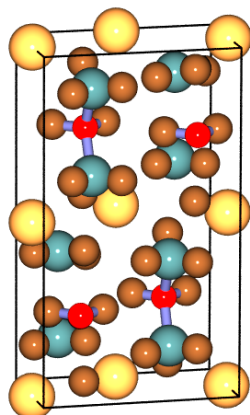


## Stability Trends Assessed Using PEGS\*-generated Crystal Structures

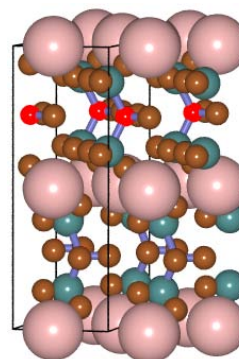
$\text{PH}_2(\text{BH}_3)_2$  complex



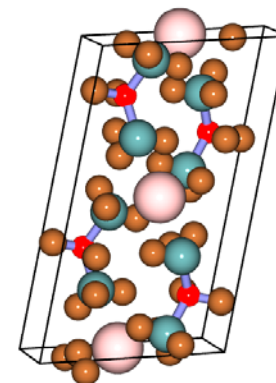
$\text{NaPH}_2(\text{BH}_3)_2$



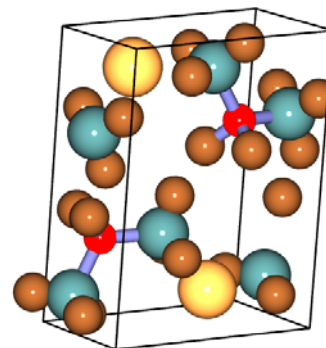
$\text{KPH}_2(\text{BH}_3)_2$



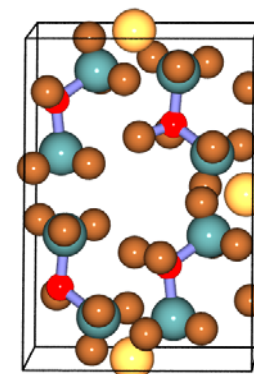
$\text{Ca}[\text{PH}_2(\text{BH}_3)_2]_2$



$\text{LiPH}_2(\text{BH}_3)_2$



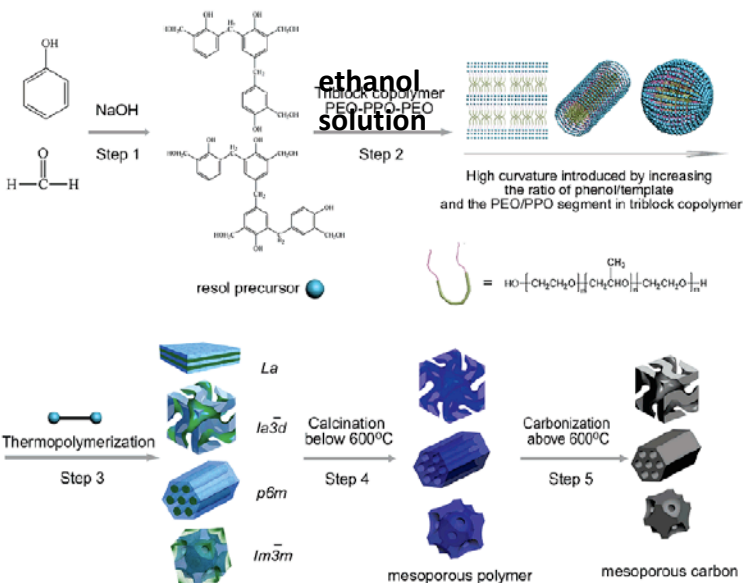
$\text{Mg}[\text{PH}_2(\text{BH}_3)_2]_2$



- Several high symmetry candidates identified
- Preliminary stability of the salts indicates:  $\text{Na} < \text{Li} < \text{K}$ ;  $\text{Ca} < \text{Mg}$

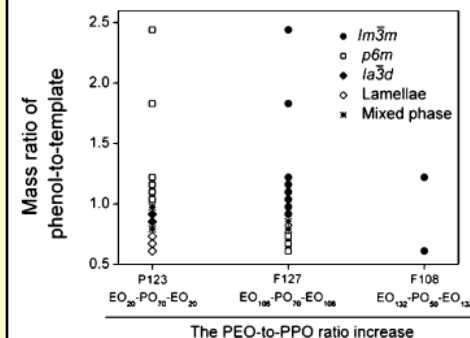
\*E.H. Majzoub, V. Ozolins, Phys. Rev. B, 77, 104115 (2008)

## Synthesis From Block-polymer And Cross-linked Phenolic Resins



### Advantages:

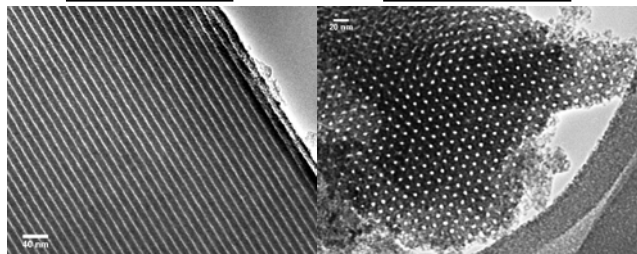
- versatile and easily controlled mesostructure
- narrow pore size distribution
- large volumes: 0.8 cc/g
- tunable pore size: 2-20 nm
- resol polymer template OR carbon-only template
- variety of morphologies
- potentially monolithic



Meng, et al., *Chem. Mater.*, **18**, 4447-4464, (2006)

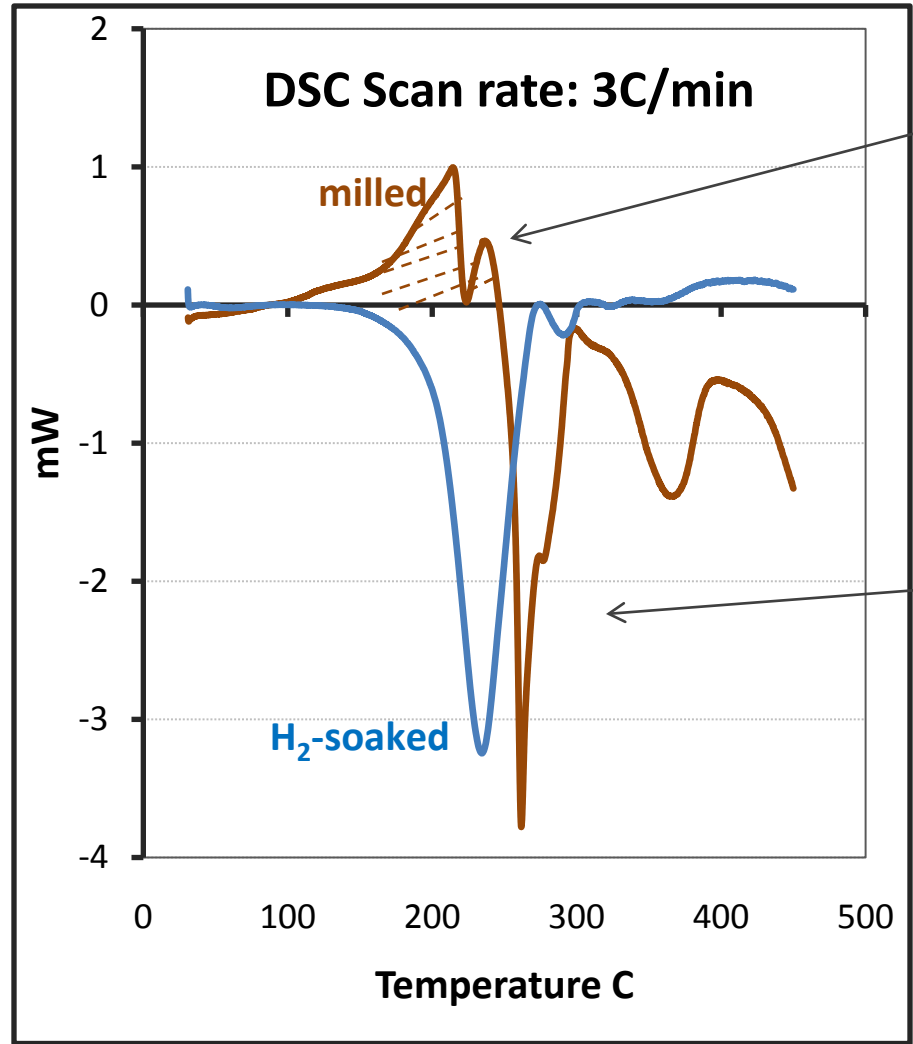
edge-on

top down



Templates are being used for  $\text{Mg}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{BH}_4)_2$  infiltration

# Developed Method to Convert $2\text{LiNH}_2/\text{MgH}_2$ into $2\text{LiH} + \text{Mg}(\text{NH}_2)_2$



Exothermic process from conversion of



milled

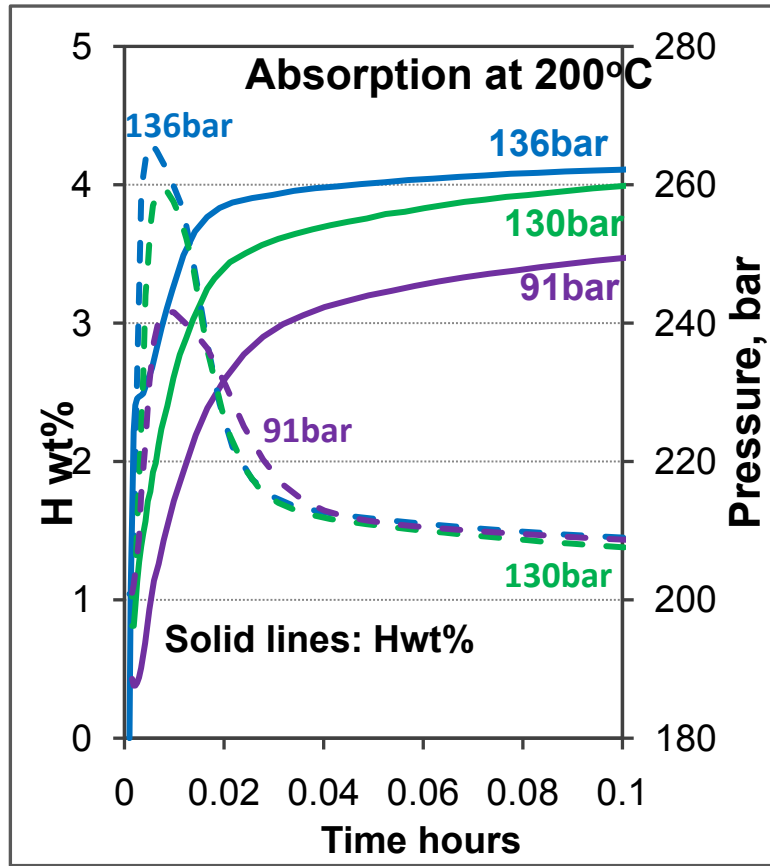
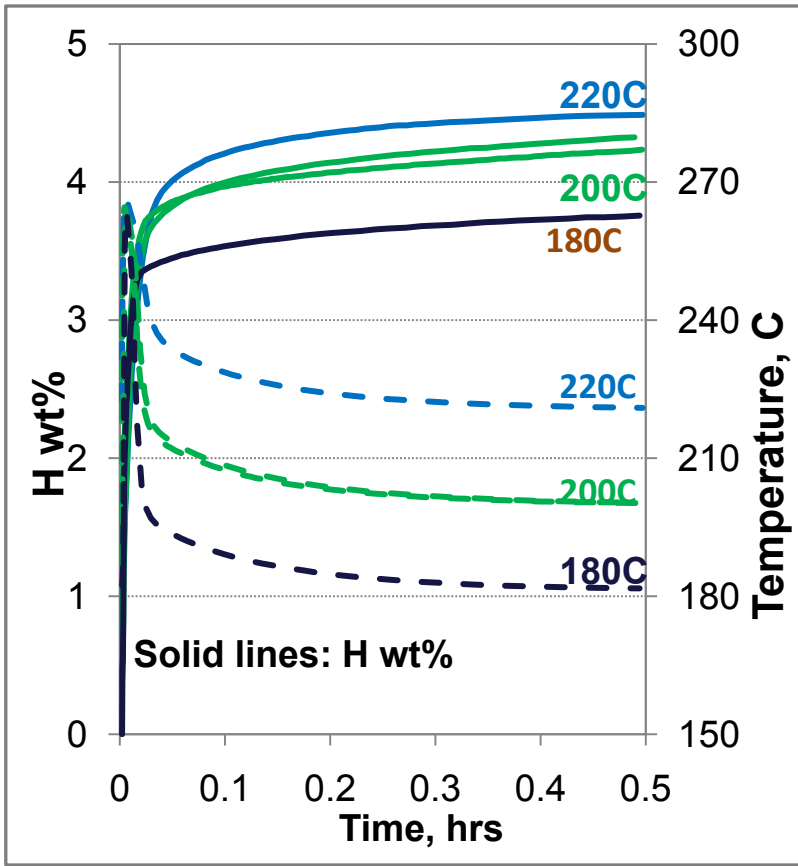
$\text{H}_2$  soaked at 120bar and 220C

$\text{H}_2$  release at different temperatures

$2\text{LiH} + \text{Mg}(\text{NH}_2)_2$  demonstrates cleaner  $\text{H}_2$  desorption, and lower T (which also helps suppress  $\text{NH}_3$  formation)

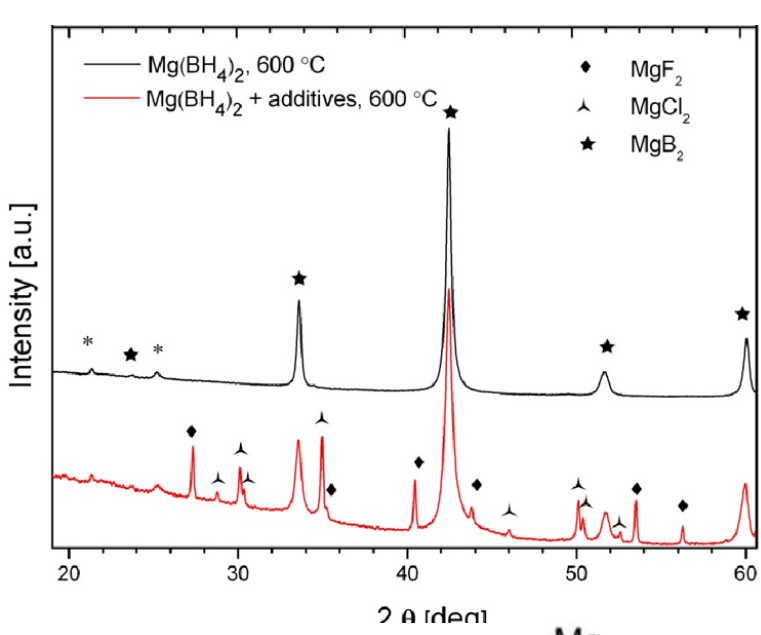
# Absorption kinetics of $MgLi_2(NH)_2/KH$

Initial pressure: 130 bar

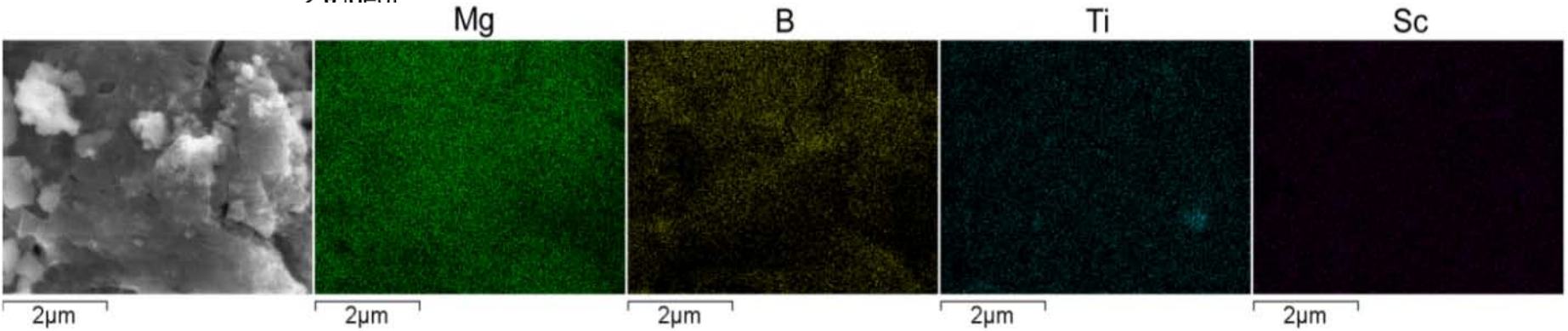
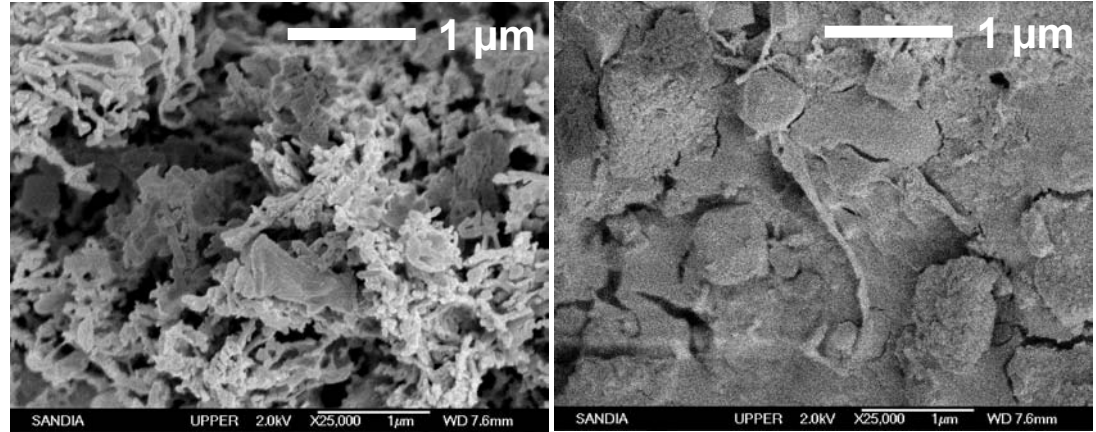
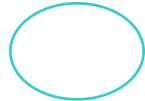


KH aids the absorption kinetics of the  $2LiNH_2/MgH_2$  material system

# Mg(BH<sub>4</sub>)<sub>2</sub> Compositional Studies with SEM/EDX

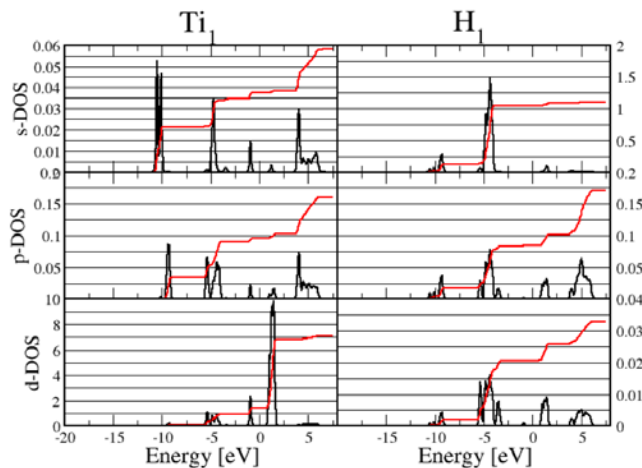


14.9 wt%

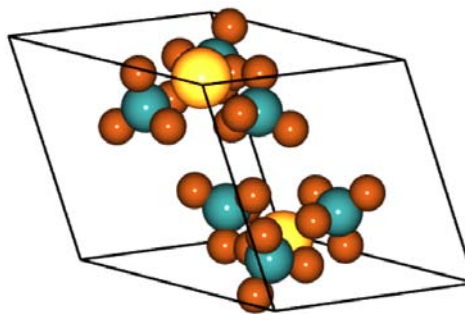


MgB<sub>2</sub> almost exclusively formed upon heating up to 600 °C  
 Additives are distributed relatively uniformly throughout the boride sample

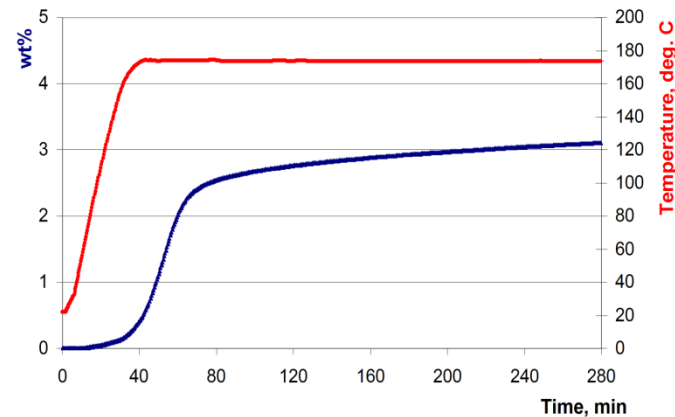
G.S. Girolami, *Inorg. Chem.* v45, p1380 (2006)



$Ti(BH_4)_3$   
PEGS structure

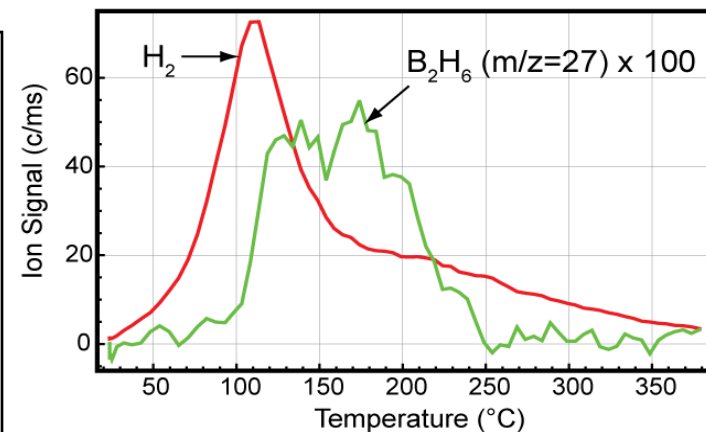


TPD & STMBMS data



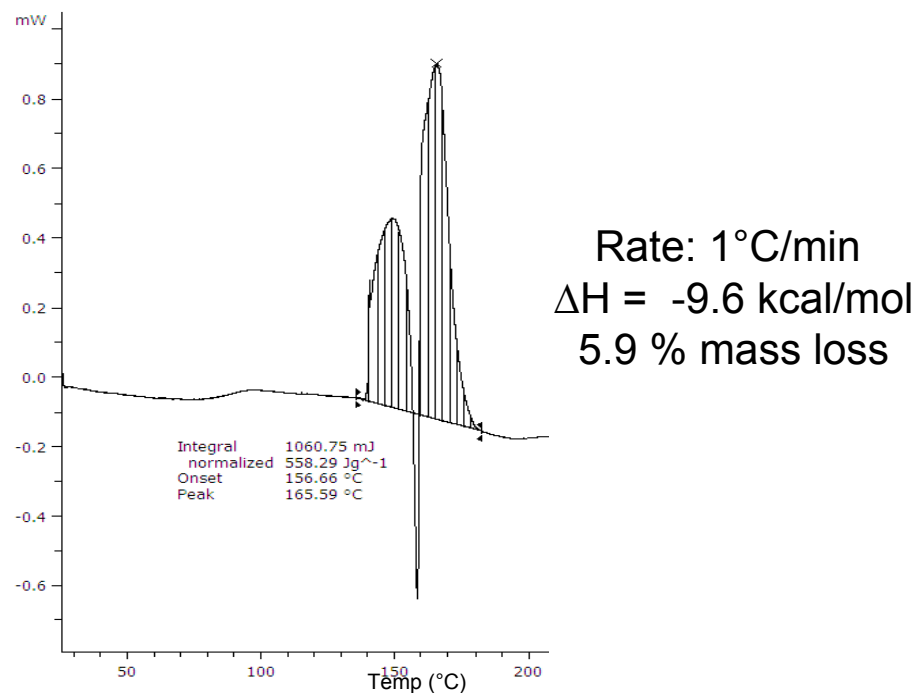
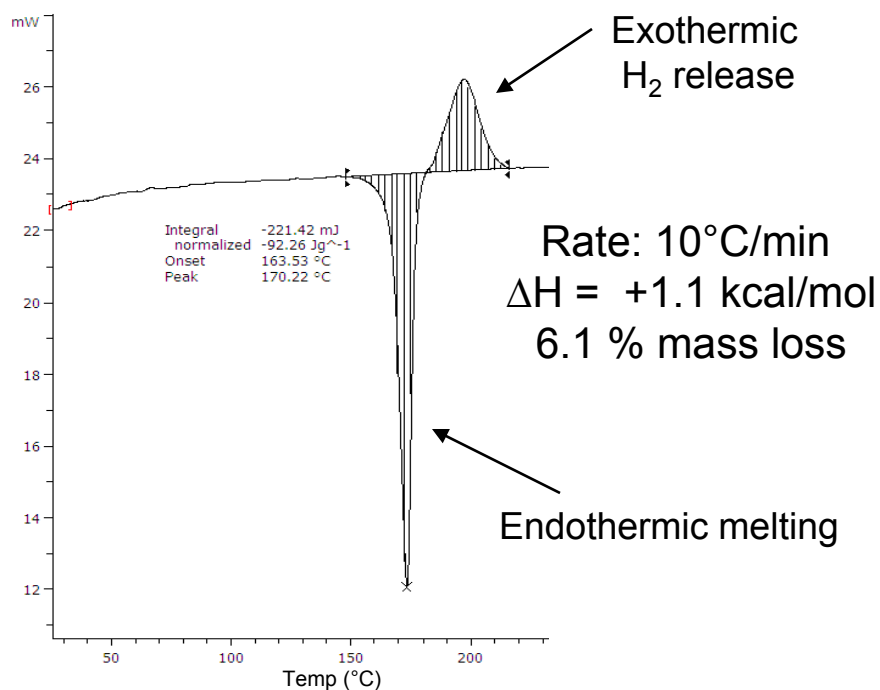
Partial electronic density of states for  $Ti(BH_4)_3$ . Yellow spheres represent Ti, which is coordinated to the  $[BH_4]^-$  anions. The partial DOS indicate Ti-H d-s hybrid orbital.

- Theory shows that  $Ti(BH_4)_4$  is unstable with respect to decomposition into  $Ti(BH_4)_3$ .
- $Ti(BH_4)_3$  predicted to be unstable at RT (in agreement with expt.).



- Dehydrogenation from  $Ti(BH_4)_3$  occurs between  $22\text{ }^\circ\text{C} < T < 140\text{ }^\circ\text{C}$ .
- Problems include poor reversibility, and gas-phase impurities ( $B_2H_6 / H_2 \sim 1:100$ ).

- ~ 6 wt. % H<sub>2</sub> desorbed from the Na[PB] material
- Reasonable H<sub>2</sub> desorption temperature of ~165°C is observed
- Faster heating rates yield more endothermic melting, slower heating rates favor exothermic H<sub>2</sub> release.
- Attempts to rehydrogenate desorbed material have so far been unsuccessful



Melting and decomposition occur near the same temperature; more decomposition means less Na[PB] left to melt, smaller endothermic peak



\* Simultaneous thermo-gravimetric modulated-beam mass spectrometer

*This instrument, developed for our national security work, is used to study reaction kinetics of complex systems*

## Instrument details:

- Knudsen effusion cell installed within a furnace and upon a microbalance
- Simultaneous modulated molecular beam mass spectrometer provides time-dependent species info
- High accuracy FTMS for species identification

## Data:

- Species
- Number density
- Rate of evolution
- Partial pressure
- Temperature

*Data is correlated and analyzed to determine reaction processes and kinetics*

