

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

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Sandia National Laboratories

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**Project ID: ST\_03\_Allendorf**

## *Timeline*

- Project started in March '05
- Project end June 2010
- Percent complete 80%

## *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
- Planned FY09 Funds: \$2.3M

## *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)*

**Tim Boyle:** *Nanoconfinement (liquid-phase syntheses)*

**Mutlu Kartın:** *New materials (borohydrides, amides)*

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

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

**Weifang Luo:** *New materials, since 03/02/2009*

**Ewa Rönnebro:** *Departed 02/20/2009*

## Other Key Contributors

**Rich Behrens, Leo Seballos, Ida Nielsen**

## Ph.D. Students

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

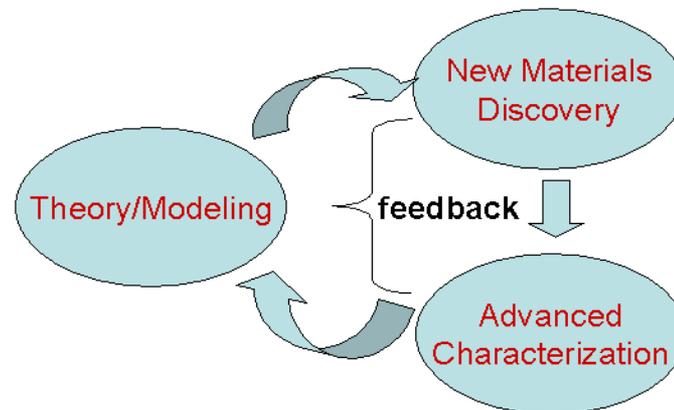
Discover, develop and validate “**reversible**” on-board metal hydride storage materials with potential to meet the DOE 2010 targets and a clear path to meeting the 2015 targets. Use theory-directed synthesis with characterization

## Prediction of crystal structure prototypes:

- ✓ 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)
- ✓ Hot-sintering at high-P (600°C, 2000 bar)



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

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

## Status in June 2008:

- Modeled structure and thermodynamics in alkali-, and transition metal(TM)-borohydrides using PEGS / first-principles DFT
- Used quantum chemical methods to calculate bond energies of alane complexes (in support of BNL  $\text{AlH}_3$  regeneration studies)
- Modeling of alanate energetics in solution initiated

## Focus during FY08/FY09:

- Impact of *closo*-borates formation on thermodynamics of Li-, Ca- and Mg-borohydrides
- Reaction pathways in complex multi-component systems
- Role of gas phase in determining reaction pathways
- Continue the coordination of MHCoe Theory Group (Allendorf)

## Collaboration -- SNL / GA Tech / U. Pittsburg

Phase equilibrium calculations can provide valuable insight into complex hydride decomposition chemistry

### ➤ Gas phase:

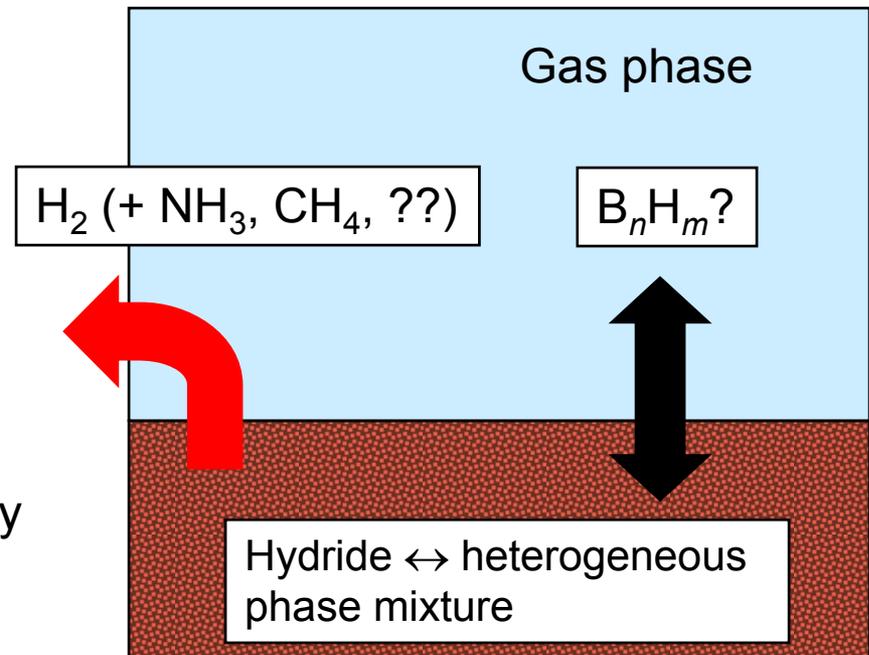
- Fuel-cell poisons (e.g.  $\text{NH}_3$ )
- Storage capacity, reversibility
- Safety (e.g.,  $\text{H}_2\text{O}$  or  $\text{O}_2$  reactions)
- Possible kinetic role

### ➤ Condensed phase:

- Multiple stable products
- Parasitic reactions
- Effects of T, P, reaction stoichiometry

### ➤ Useful results of equilibrium modeling:

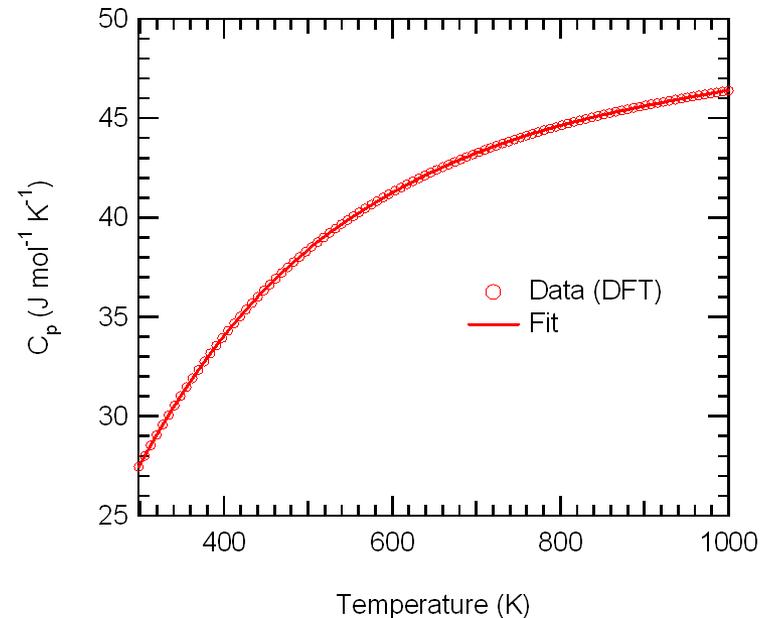
- Identify most stable products
- Predict undesirable gas-phase species
- System design and optimal operating conditions



Ki Chul Kim & David Sholl (GA Tech.)  
Bo Zhang & Karl Johnson (U. Pittsburgh)  
Mark Allendorf (SNL)

# Comprehensive Multi-phase Equilibrium Modeling is Advancing Our Understanding of Metal Hydride Systems

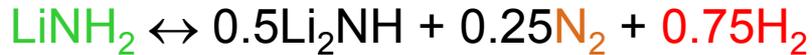
- Gibbs Free Energy minimization
- FactSage package (commercial software)
- Thermodynamic data sources:
  - Gas phase: *JANAF Tables*
  - Gas-phase  $B_nH_m - B_{10}H_{14}$   
(Yu & Bauer, *J. Phys. Chem. Ref. Data* 1998)
- Custom hydride data base
  - Li-B-C-Mg condensed phases
  - $\Delta H_f^\circ(298)$   $\Delta S^\circ(298)$ ,  $C_p(T)$ 
    - DFT + phonon calculation  
(Kim & Sholl results, 2008)
- Examples of possible calculations:
  - Constant (T,p), (T,V), (T,H)
  - Phase diagrams
  - Thermodynamics of individual reactions



Polynomial fit to  $C_p$  for  $MgH_2$   
Data from DFT and phonon calculation  
(Kim & Sholl, 2008)

# LiNH<sub>2</sub> (+ LiH): Prediction of Significant Gas-phase Impurities

## ➤ Nominal reactions:

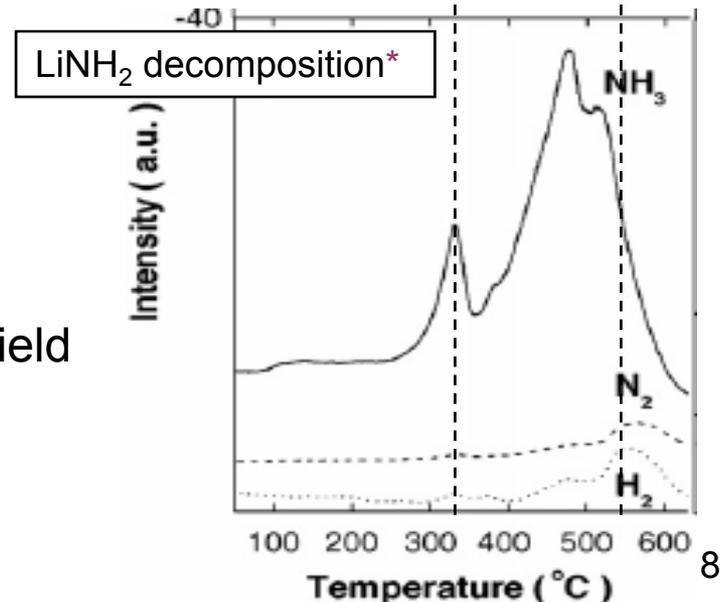
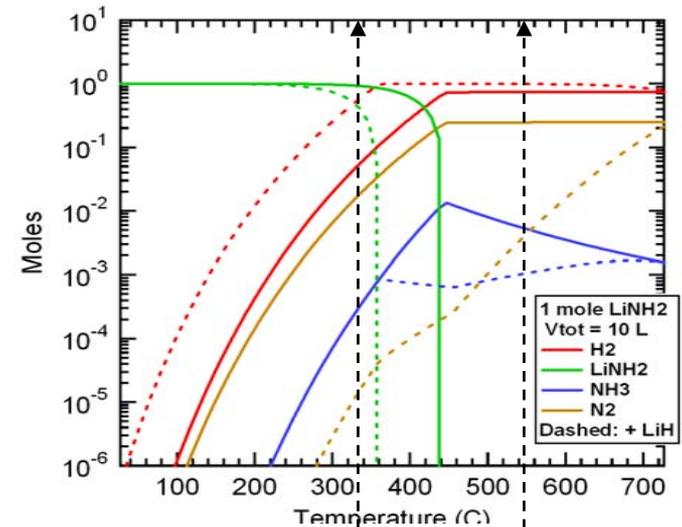


## ➤ Conditions for calculation:

- 1 mole LiNH<sub>2</sub> (+1 mole LiH)
- Constant T, Constant V (10 L)
- Gas phase: H<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>, Li, Li<sub>2</sub>, LiH

## ➤ Results:

- N<sub>2</sub> and NH<sub>3</sub> predicted to be significant byproducts
- LiH addition:
  - Scavenges nitrogen to enhance H<sub>2</sub> yield
  - Reduces NH<sub>3</sub>, but only at T > 360 °C
- Experiments confirm NH<sub>3</sub> formation but suggest kinetic barrier to N<sub>2</sub> formation



- Model phase equilibria for general hydride categories:



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- Hydride + C
- Nitrogen-containing hydrides
- Boron-containing hydrides

- Model the following destabilized reactions:



Georgia Institute  
of Technology



- $2\text{LiNH}_2 + \text{C} \rightarrow \text{Li}_2\text{CN}_2 + 2\text{H}_2$   $\Delta U(0 \text{ K}) = 31.4 \text{ kJ/mol H}_2$
- $2\text{C} + \text{Mg}(\text{BH}_4)_2 \rightarrow \text{MgB}_2\text{C}_2 + 4\text{H}_2$   $\Delta U(0 \text{ K}) = 43.1 \text{ kJ/mol H}_2$
- $\text{BN} + 4\text{Mg}(\text{BH}_4)_2 \rightarrow 3\text{MgH}_2 + \text{MgB}_9\text{N} + 13\text{H}_2$   $\Delta U(0 \text{ K}) = 51.2 \text{ kJ/mol H}_2$

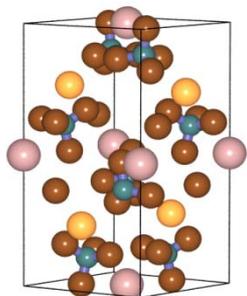
- *Incorporate multiple gas-phase species approach into U. Pittsburgh / Georgia Tech screening code*

*-- see more details in ST08 by K. Johnson (Univ. Pittsburgh)  
-- see our additional slide #30*

- Journal article describing results is in preparation

## Investigation of LiSc(BH<sub>4</sub>)<sub>4</sub> Validates PEGS method with TM-borohydrides

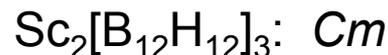
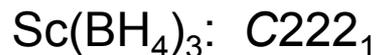
### Collaboration -- SNL / JPL / Caltech / UCLA



*I*-4

LiSc(BH<sub>4</sub>)<sub>4</sub>

- Solid-state NMR indicates formation of ScB<sub>2</sub>, [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> on desorption
- PEGS predicted structures:



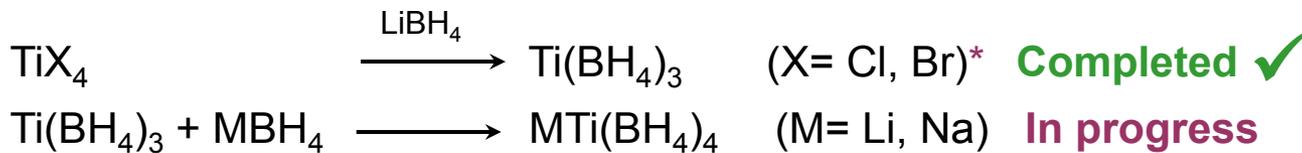
Complicated decomposition pathway predicted using PEGS structures consistent with experimental measurements

Ref: C Kim, S-J Hwang, RC Bowman, Jr., JW Reiter, JA Zan, JG Kulleck, H Kabbour, EH Majzoub, V Ozolins, *J. Phys. Chem C*, accepted (2009)

### Exploring:

NaTi(BH<sub>4</sub>)<sub>4</sub>  
Na<sub>2</sub>Ti(BH<sub>4</sub>)<sub>5</sub>  
LiTi(BH<sub>4</sub>)<sub>4</sub>  
Li<sub>2</sub>Ti(BH<sub>4</sub>)<sub>5</sub>

### Synthesis:



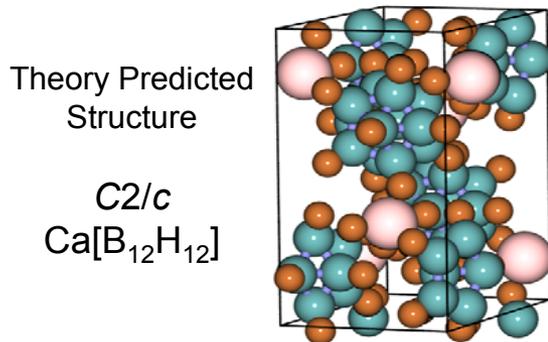
## Theoretical and Experimental Search for Alkali-Ti-(BH<sub>4</sub>)<sub>x</sub>

### Collaboration -- SNL / UTRC

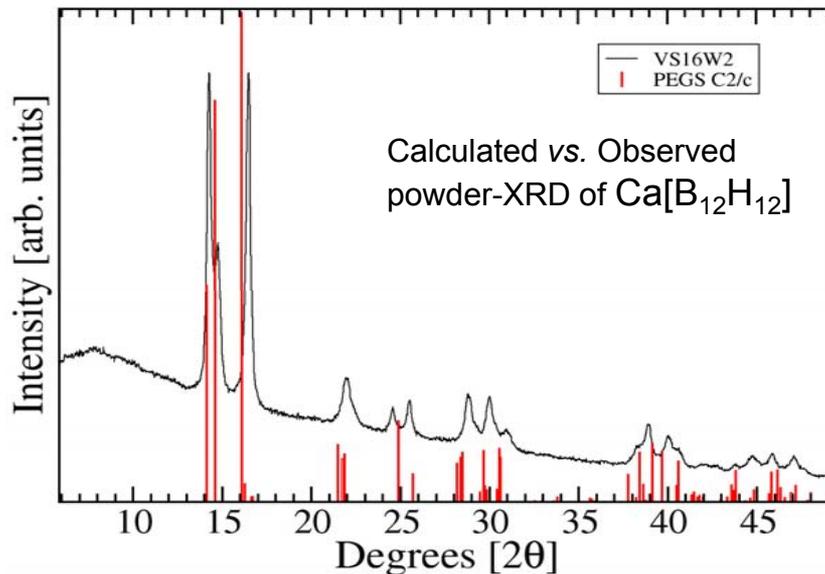
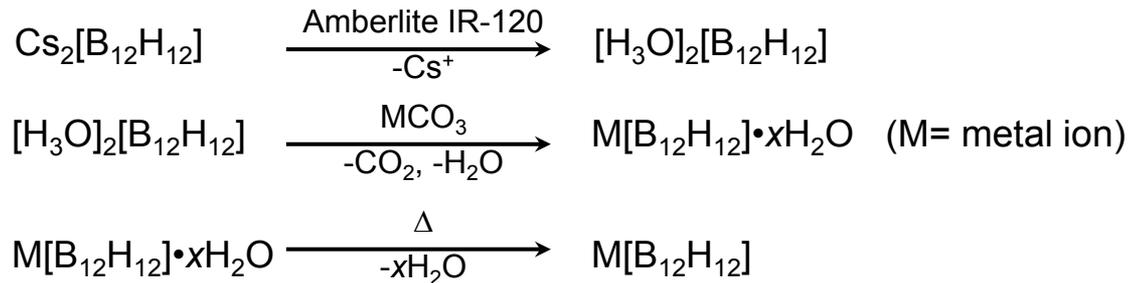
- Stabilize Ti(BH<sub>4</sub>)<sub>3</sub> through addition of alkali metals, and/or confinement in nano-frameworks

## Collaboration -- SNL / NIST

- Evidence of diborane and *closo*-borates formation during borohydride desorption reactions prompts further analysis of  $[B_{12}H_{12}]^{2-}$  salts\*



### \*\*Synthesis:



Compound	PEGS Structures	SNL/NIST Data
$Li_2[B_{12}H_{12}]$	$C2/m$ (#12)	$Pa-3$
$Na_2[B_{12}H_{12}]$	$P2_1/n$ (#14)	$P2_1/n$
$Ca[B_{12}H_{12}]$	$C2/c$ (#15)	$C2/c$
$Mg[B_{12}H_{12}]$	$C2/m$ (#12)	Amorphous
$Sc_2[B_{12}H_{12}]_3$	$Cm$ (#8)	Amorphous

## *Collaboration -- SNL / UMSL / UCLA / Northwestern*

- First-principles DFT calculations determine compound thermodynamics while Gibbs' free energy calculations determine reaction critical temperature ( $T_c = T_{1bar}$  of  $H_2$ ),  $\Delta H$  and thermodynamically possible products

**Desired desorption products for  $Ca(BH_4)_2$  and  $Mg(BH_4)_2$  are  $CaB_6$  and  $MgB_2$**   
**But:**

- $Mg[B_{12}H_{12}]$  formation lowers capacity of  $Mg(BH_4)_2$  from 14.9 to 8.1 wt%  $H_2$
- $Ca[B_{12}H_{12}]$  formation lowers capacity of  $Ca(BH_4)_2$  from 9.6 to 6.3 wt%  $H_2$

Ref: V Ozolins, EH Majzoub, C Wolverton, *J. Am. Chem. Soc.*, v131(1), p 230 (2009)

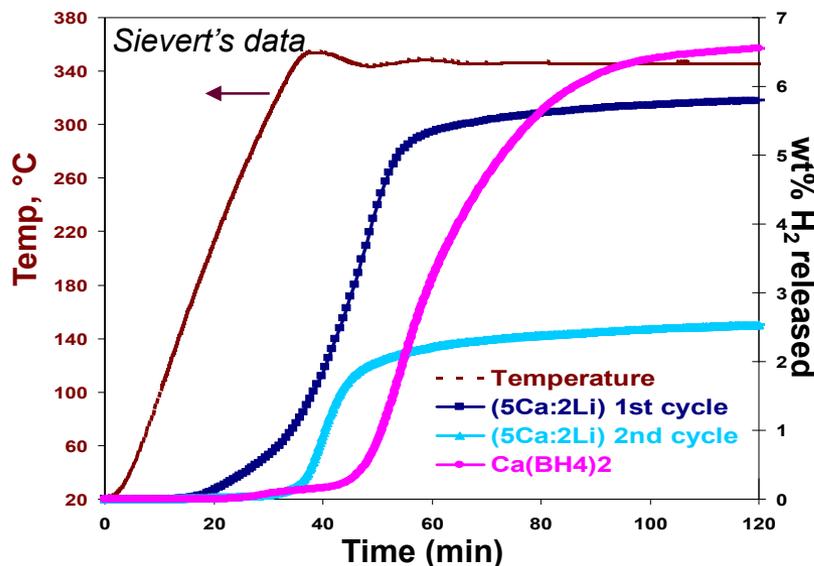
Possible Reactions	Theoretical wt% $H_2$	$\Delta H^{300K}$	$T_c$ (°C)
$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2$	14.9	38.8	75
$6Mg(BH_4)_2 \rightarrow Mg[B_{12}H_{12}] + 5MgH_2 + 13H_2$	8.1	29.3	20
$3Ca(BH_4)_2 \rightarrow CaB_6 + 2CaH_2 + 10H_2$	9.6	40.8	94
$6Ca(BH_4)_2 \rightarrow Ca[B_{12}H_{12}] + 5CaH_2 + 13H_2$	6.3	39.2	99

A predicted desorption pathway of  $Ca(BH_4)_2$  involves  $Ca[B_{12}H_{12}]$ , and is therefore consistent with loss of capacity on each cycle observed in sorption experiments

Entropy of H<sub>2</sub> gas (130 J/Kmol H<sub>2</sub> at 20 °C, 1 bar) commonly dominates. Products with fewer anions or tightly bound bulk phase reduce the number of low frequency phonon branches and decreases ΔS to ~ 100 J/K mol H<sub>2</sub> for the following reactions:

**New Candidate Destabilized Reactions:** Ref: V Ozolins, EH Majzoub, C Wolverton, *J. Am. Chem. Soc.*, v131(1), p 230 (2009)

Predicted Reactions	Theoretical wt% H <sub>2</sub>	ΔH <sup>300K</sup> kJ/mol H <sub>2</sub>	T <sub>c</sub> (°C)	SNL Data: wt% H <sub>2</sub> (350°C, 4h)
5Mg(BH <sub>4</sub> ) <sub>2</sub> + 2LiBH <sub>4</sub> → Li <sub>2</sub> [B <sub>12</sub> H <sub>12</sub> ] + 5MgH <sub>2</sub> + 13H <sub>2</sub>	8.4	24.4	-29	<b>6.0</b>
5Mg(BH <sub>4</sub> ) <sub>2</sub> + Ca(BH <sub>4</sub> ) <sub>2</sub> → Ca[B <sub>12</sub> H <sub>12</sub> ] + 5MgH <sub>2</sub> + 13H <sub>2</sub>	7.7	25.7	-18	<b>4.4</b>
5Ca(BH <sub>4</sub> ) <sub>2</sub> + 2LiBH <sub>4</sub> → Li <sub>2</sub> [B <sub>12</sub> H <sub>12</sub> ] + 5CaH <sub>2</sub> + 13H <sub>2</sub>	6.7	37.9	83	<b>6.2</b>



**Kinetic barriers for new reactions are unknown**

**Experimental Comparison of 5Ca(BH<sub>4</sub>)<sub>2</sub> + 2LiBH<sub>4</sub> vs Ca(BH<sub>4</sub>)<sub>2</sub> Systems:**

Although the kinetics improved slightly and the desorption temperature was lowered ~50 °C, a significant capacity loss *via* cycling still remains

# Theory Milestones

Month/year	Milestone or Go/No-Go decision: <b>Al-Adduct 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

Month/year	Milestone or Go/No-Go decision: <b>Alanate/Borohydride Theory</b>
Jan-09 ✓	Milestones: (1) Structural modeling of TM-containing borohydrides. (2) Extension of PEGS method to nanoparticle hydrides
Feb-09 ✓	* No-go: Discontinue surfactant templating for nano-scale alanates/borohydrides
Jul-10	Milestone: Finish alkali-TM borohydride structure and stability calculations
Nov-10	Go/no-go: Discontinue alkali-TM borohydrides if no suitable materials found

## Status in June 2008:

- Determined the phase transitions of  $\text{Ca}(\text{BH}_4)_2$  polymorphs at different temperatures (*--see our additional slide #32*)
- Demonstrated the partial reversibility of  $\text{Ca}(\text{BH}_4)_2$  at 100 bar and  $350^\circ\text{C}$
- Initiated additive screening for  $\text{Ca}(\text{BH}_4)_2$
- Theory predicted bi-alkali borohydrides,  $\text{AK}(\text{BH}_4)_2$  (A= Li, Na), were synthesized but not pursued further due to poor thermodynamics

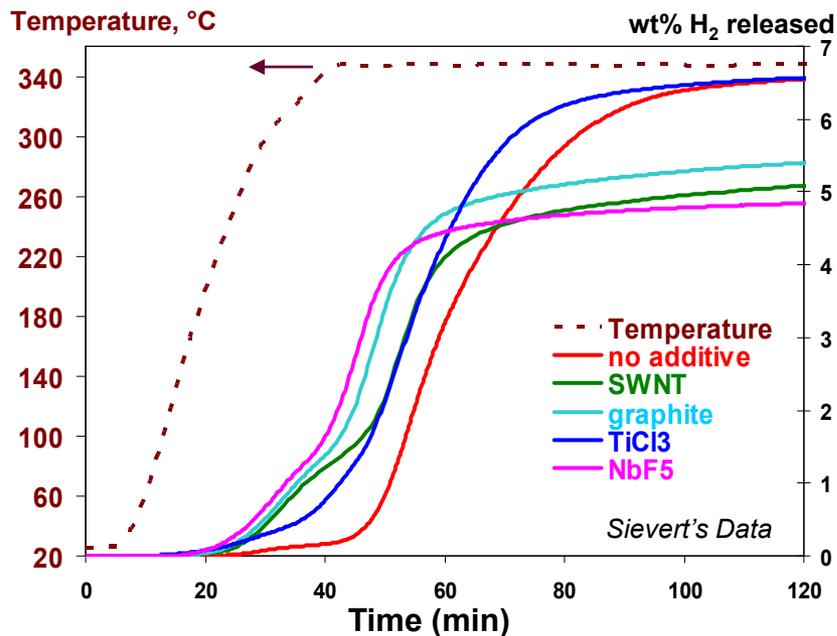
## Focus during FY08/FY09:

- Elucidate the reaction mechanism and decomposition products of  $\text{Ca}(\text{BH}_4)_2$
- Complete  $\text{Ca}(\text{BH}_4)_2$  additive study,  $\Delta\text{H}$  determination: Make go/no-go decision
- Syntheses and characterization of PEGS-predicted *closo*-borates and new  $\text{BH}_4/\text{NH}_3$ ,  $\text{BH}_4/\text{NH}_2$ ,  $\text{BH}_4/\text{AlH}_4$  systems
- Re-hydrogenation of  $\text{Mg}(\text{BH}_4)_2$  utilizing Sandia high-pressure capability (*--see our additional slide #33, --see ST07-UH*)
- Incorporation of hydride materials in catalyzed nano-framework structures (NFS) to improve kinetics (*--see our additional slide #34, --see ST10-UTRC*)

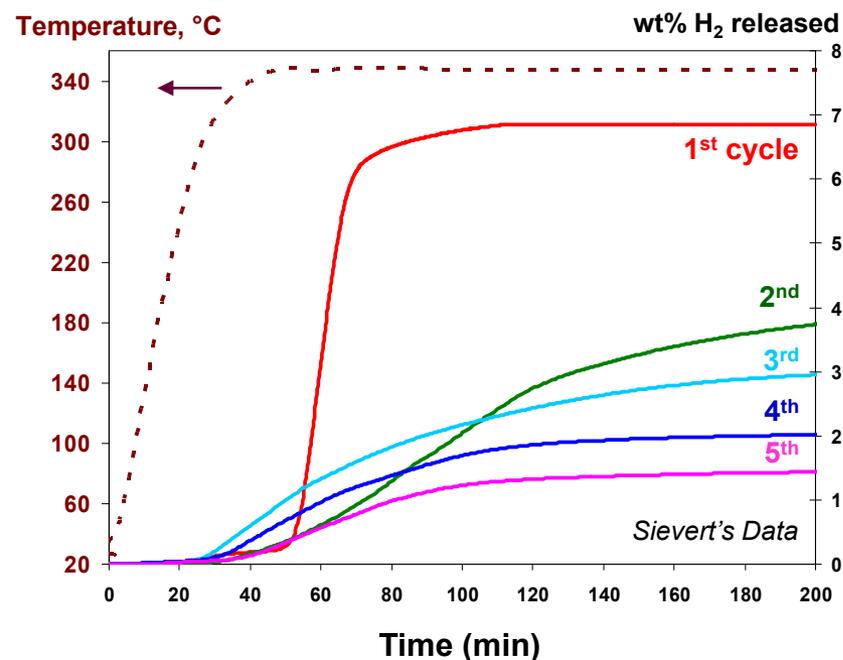
# Effect of Additives on Cycling Capacity and Kinetics of $\text{Ca}(\text{BH}_4)_2$

- 30 different additives screened
- ~6 wt%  $\text{H}_2$  released in 1 hour at 350 °C

## Additive Effect on $\text{Ca}(\text{BH}_4)_2$ Desorption



## Life-cycle of $\text{Ca}(\text{BH}_4)_2$ with 4wt% $\text{PdCl}_2$ Additive



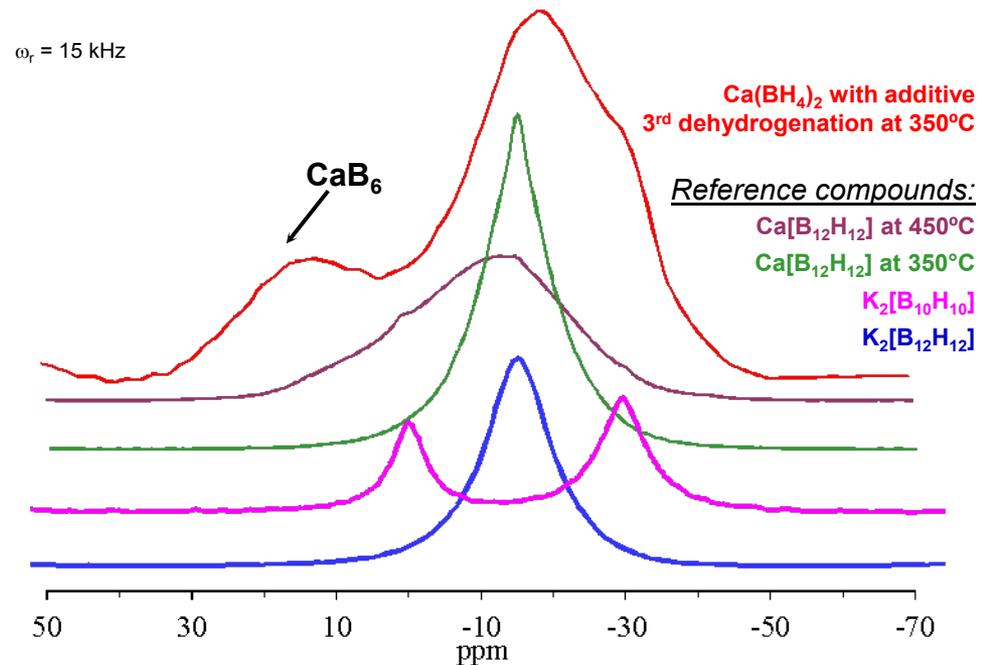
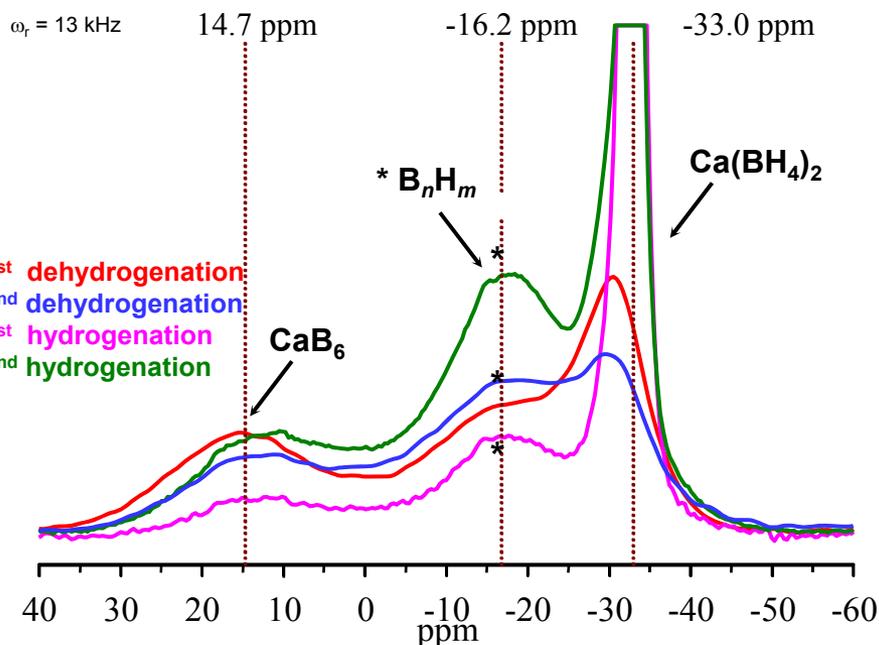
- Additives do not significantly improve kinetics of  $\text{Ca}(\text{BH}_4)_2$
- Significant capacity loss observed on subsequent cycles

## Collaboration -- SNL / Caltech - JPL

" $\text{B}_n\text{H}_m$ " species formed during the dehydrogenation

$\text{Ca}(\text{BH}_4)_2$  with Additive-A

$\text{Ca}(\text{BH}_4)_2$  with Additive-B



➤  $^{11}\text{B}$  NMR reveals the presence [ $\text{B}_n\text{H}_m$ ] species and their accumulation upon cycling  
 (-- see also our additional slide #35)

➤ Separate experiments show that  $\text{Ca}[\text{B}_{12}\text{H}_{12}]$  cannot be hydrogenated or dehydrogenated under the conditions tested (-- see our additional slide # 36)

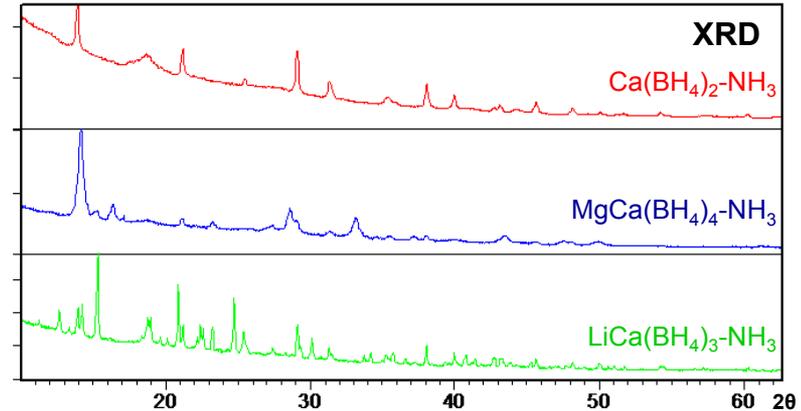
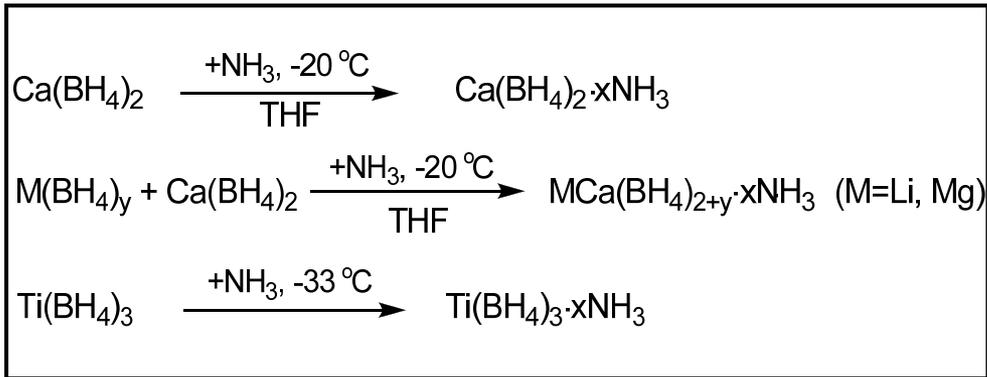
Although the thermodynamics for  $\text{Ca}(\text{BH}_4)_2$  are reasonable (measured  $\Delta H_{\text{desorption}} = 20 - 30 \text{ kJ/mol H}_2$  by DSC)\*, we have made a decision to “down-select”  $\text{Ca}(\text{BH}_4)_2$  as a hydrogen storage material, because:

- It is only partially reversible due to “ $\text{B}_n\text{H}_m$ ” formation
- It is kinetically limited
- Catalysts do not improve the rate of hydrogen desorption below 300 °C
- The observed maximum desorption capacity, up to 350 °C, is less than ~ 7 wt %

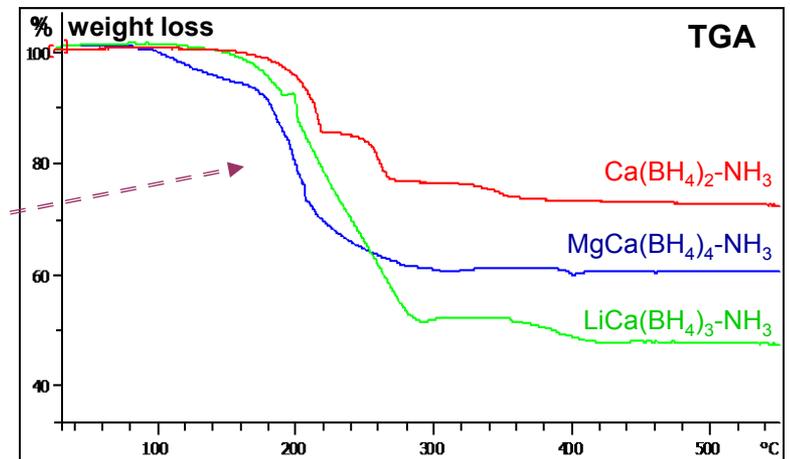
∴ We will not pursue  $\text{Ca}(\text{BH}_4)_2$  further as a hydrogen storage material

# New $M(\text{BH}_4)\text{-NH}_3$ Materials Synthesized and Characterized

**Motivation:** Based on promising results reported for  $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$  (Zhao *et al.*) other metal-borohydride-ammonia systems were investigated



- The  $\text{BH}_4\text{-NH}_3$  compounds display increased air- and moisture stability compared to the initial borohydrides
- $\text{Ca}(\text{BH}_4)_2 \cdot \text{NH}_3$ ,  $\text{MgCa}(\text{BH}_4)_4 \cdot \text{NH}_3$  and  $\text{LiCa}(\text{BH}_4)_3 \cdot \text{NH}_3$  adducts release significant amounts of  $\text{NH}_3$  upon heating, confirmed by gas phase analysis
- New systems based on transition metals (e.g. Ti(III)) are currently under investigation



Month/year	Milestone or Go/No-Go decision
Oct-08 ✓	Go: Successfully coated the catalyzed NFS substrate with metal hydride via solution route. Milestone: Complete PCT isotherms for $\text{Ca}(\text{BH}_4)_2$ to determine reaction enthalpy
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 $\text{Ca}(\text{BH}_4)_2$ No-go: La-doped $\text{CaB}_6$ , but the efforts shifted towards C-doping of $\text{MgB}_2$
Mar-09 ✓	Milestone: Lowering of $\text{Ca}(\text{BH}_4)_2$ desorption temperature No-go decision made on $\text{Ca}(\text{BH}_4)_2$
April-09 ✓	Milestone: Complete additive screening study of MHCoe borohydride Milestone: Discover new borohydride related materials <b>In progress</b>
May-09	Go/no-go on A-TM- $(\text{BH}_4)_x$ : Reversibility of alkali transition metal borohydrides
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 $\text{Ca}(\text{BH}_4)_2$ Go/no-Go: to incorporate the hydride material into the NFS <i>via</i> a solid-state route, (50% loading of a hydride material with a hydrogen storage capacity greater than 5% in NFS)
Sep-09	Milestone: Incorporation of hydride material in catalyzed nano-frameworks
Oct-09	Milestone: Complete additive screening study of MHCoe of mixed amide/borohydride

## Theory:

- Developed phase equilibria theoretical technique, applied to  $\text{LiNH}_2$  (+LiH) and  $(\text{LiBH}_4 + \text{C})$
- Predicted structures of  $[\text{B}_{12}\text{H}_{12}]^{2-}$  intermediates and their effect on reaction pathways
- PEGS structure predictions of transition-metal borohydrides

## Calcium Borohydride:

- Completed additive screening of  $\text{Ca}(\text{BH}_4)_2$  and studied the cycling behavior
- Revealed that  $\text{B}_n\text{H}_m$  species limit the reversibility of  $\text{Ca}(\text{BH}_4)_2$
- Probed reaction pathway and kinetics of  $\text{Ca}(\text{BH}_4)_2$  using STMBMS (*-- see our additional slides #38, 39*)
- Made No-Go decision on  $\text{Ca}(\text{BH}_4)_2$

## New Materials:

- Synthesized  $[\text{B}_{12}\text{H}_{12}]^{2-}$  salts with various cations to examine their influence on the hydrogen release in borohydride systems in conjunction with theoretical predictions (*-- see our additional slide #36*)
- Synthesized new  $\text{MM}'(\text{BH}_4)_x/(\text{NH}_3)_y$  and  $\text{MM}'(\text{BH}_4)_x/(\text{NH}_2)_y$  compounds and assessed their hydrogen storage properties (*-- see our additional slide #40*)
- Synthesized  $\text{Ca}(\text{AlH}_4)/(\text{BH}_4)$  and predicted high symmetry solid-state structure (*-- see our additional slide #41*)
- Examined C-dopant effects on  $\text{MgB}_2$  hydrogenation (*-- see our additional slide #35*)
- Initiated the incorporation of  $\text{Ca}(\text{BH}_4)_2$  in a C-aerogel and characterized hydrogen release

## **Theory:**

- Model phase equilibria for promising metal hydride materials
- Complete calculations on alanate-ether adducts
- Examine phase stability and the reactions of TM-containing borohydrides
- Conduct PEGS search for mixed-anion borohydride materials

## **New Materials:**

- Synthesis and characterization of PEGS predicted new  $\text{BH}_4/\text{NH}_3$ ,  $\text{BH}_4/\text{NH}_2$  and  $\text{BH}_4/\text{AlH}_4$  compounds (*-- see our additional slides #40,41*)
- Explore new mixed-metal borohydride systems

## **Incorporation of Hydrides into Nano-frameworks:**

- Metal borohydride incorporation into nano-frameworks *via* solution routes
- Characterize metal borohydride incorporation into catalyzed and uncatalyzed nano-frameworks (*-- see ST10-UTRC*)

## ***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. Kettner
- 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

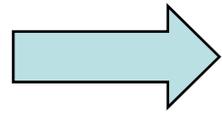
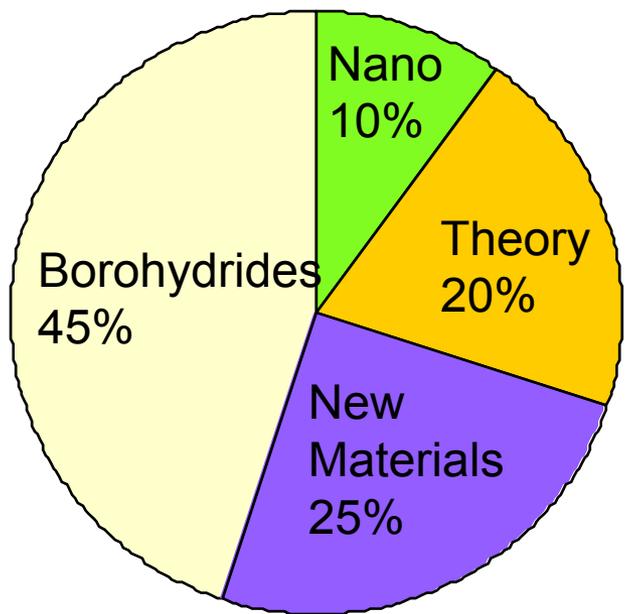
## ***Other Collaborations:***

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

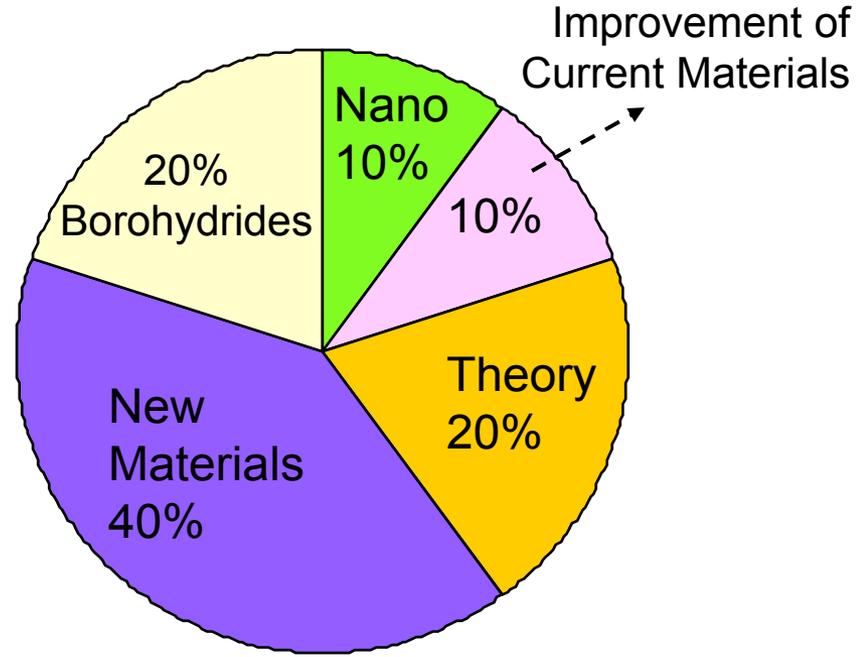
# Additional Slides

# SNL Major Technical Emphases 2009/2010

2008/2009



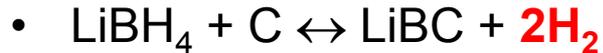
2009/2010



# LiBH<sub>4</sub> + C: Predict Initial Formation of LiBC + H<sub>2</sub> at Low T

**Motivation:** MHCoe Theory (Sholl) predicts LiBH<sub>4</sub> + C has favorable desorption thermodynamics ( $\Delta H = 45.1$  kJ/mol H<sub>2</sub>)

## ➤ Nominal reaction



## ➤ Also possible:

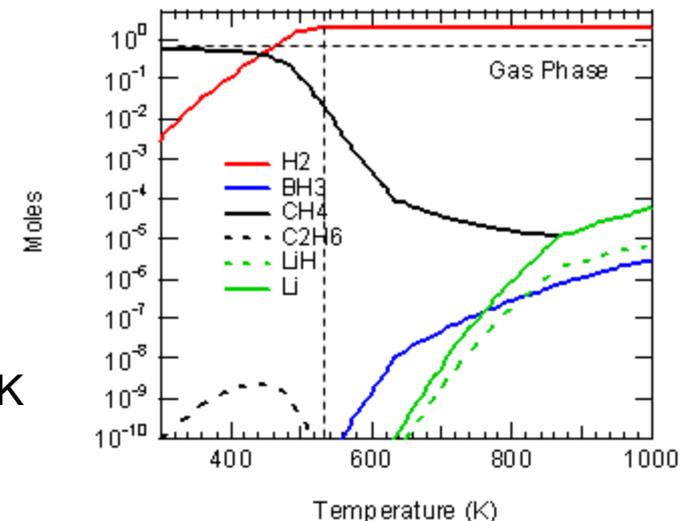
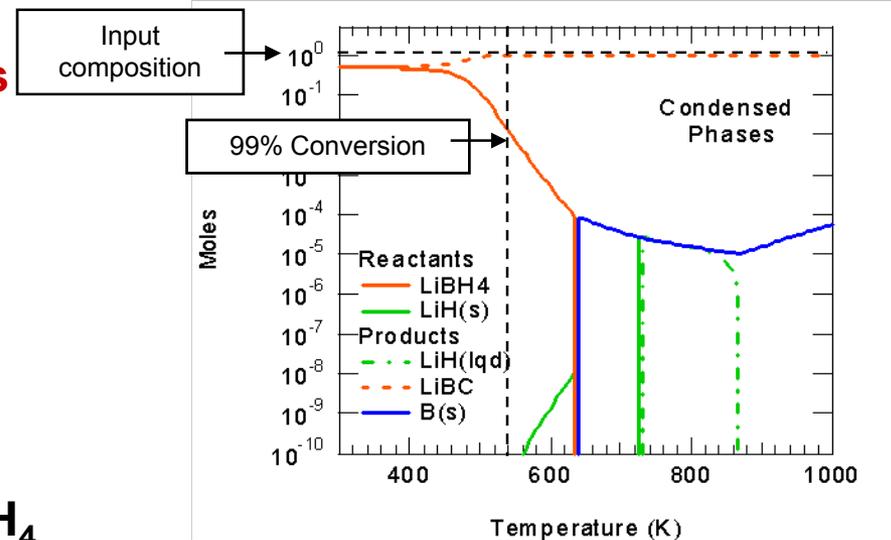


## ➤ Conditions for each calculation

- 1 mole LiBH<sub>4</sub> + 1 mole C as graphite
- Constant P (1 atm), constant T

## ➤ Results

- LiH and C(s) not stable 300-640 K
  - Converted to **CH<sub>4</sub>** and **LiBC**
- Complete conversion to **LiBC+H<sub>2</sub>** only at T > 540 K
- **BH<sub>3</sub>** is only significant B-containing gas-phase species

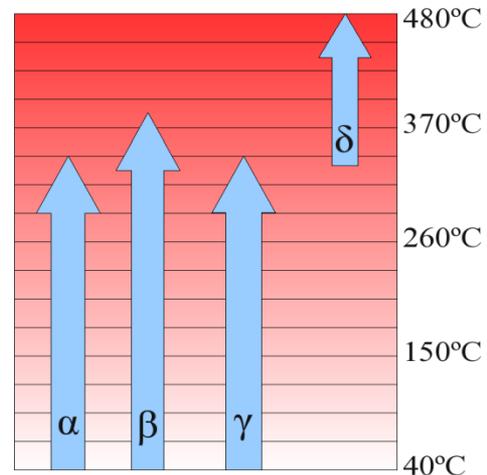
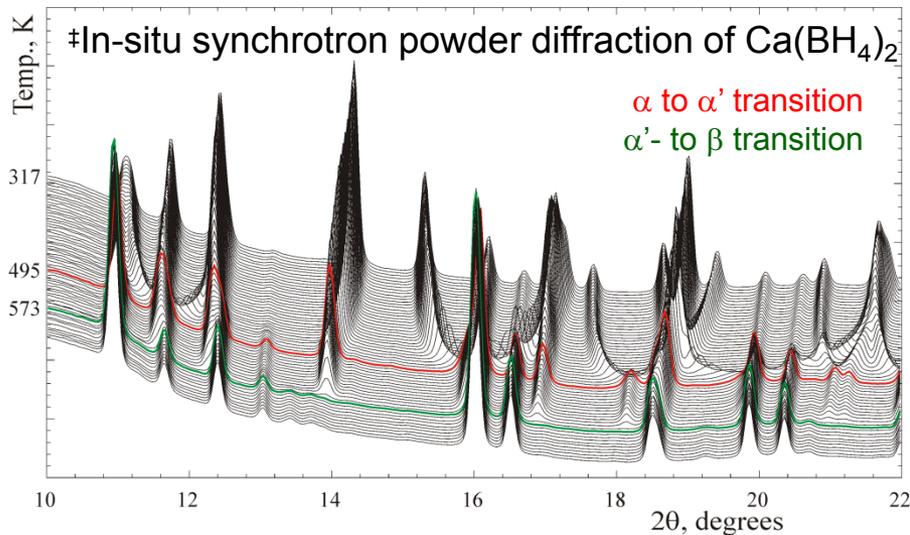
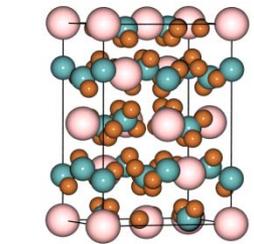
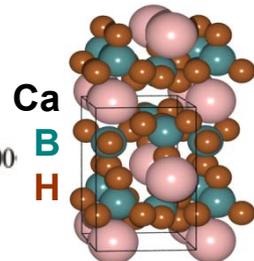
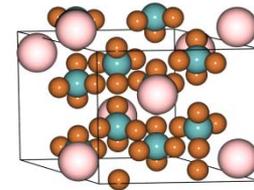
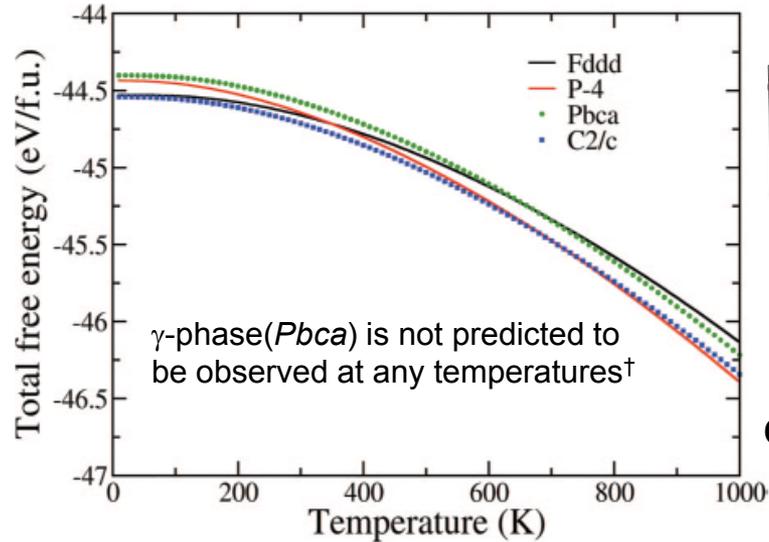
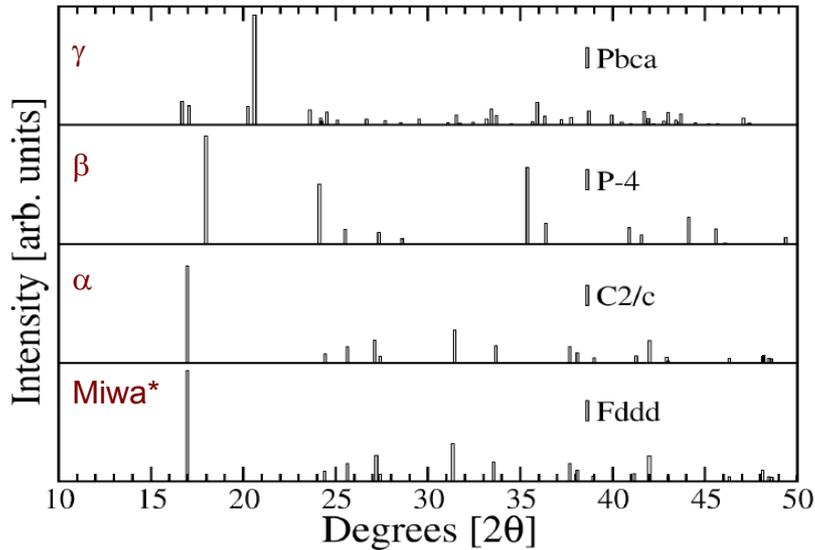


## **Motivation: Surfactant micelles offer potential for incorporation of MH in the nanoscale**

- Nanoparticle Production *via* Surfactant Templating
  - H<sub>2</sub>O/AOT/decane solutions with NaBH<sub>4</sub>/H<sub>2</sub>O produced ~10nm particles
  - No suitable THF/surfactant analogs found for alanates/borohydride inclusion
  - Problems with scalability and separation of surfactant excess prevents quantitative characterization

Method down-selected, do not pursue further

# Identified Phase Transitions of Four Polymorphs of $\text{Ca}(\text{BH}_4)_2$

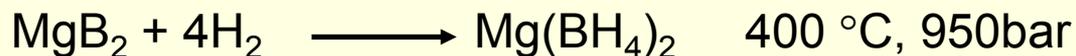


\*K Miwa et al, *Phys. Rev. B*, v74, p155122 (2006)

† EH Majzoub, E Ronnebro, *J. Phys Chem C*, 113 (8), pp 3352 (2009)

‡ Y Filinchuk, E Ronnebro, D Chandra, *Acta Materialia*, 57, p732 (2009)

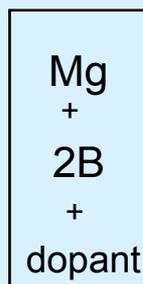
- I. Demonstrated the reversibility of the decomposition products by hydrogenation (Sandia high-pressure capability), in collaboration with U. Hawaii:



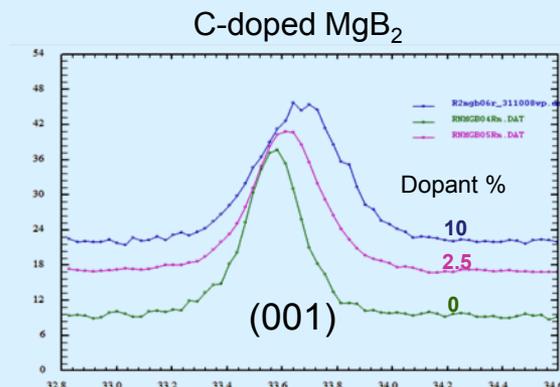
- II. Destabilizing  $\text{Mg}(\text{BH}_4)_2$  with C-doping to improve hydrogen storage properties

**Current Status:** Synthesized doped- $\text{MgB}_2$  from  $\text{Mg} + \text{B} + \text{C}$  (dopant-level) and hydrogenated  $\text{MgB}_{(2-x)}\text{C}_x$  precursor to form  $\text{Mg}(\text{BH}_4)_2$  structure

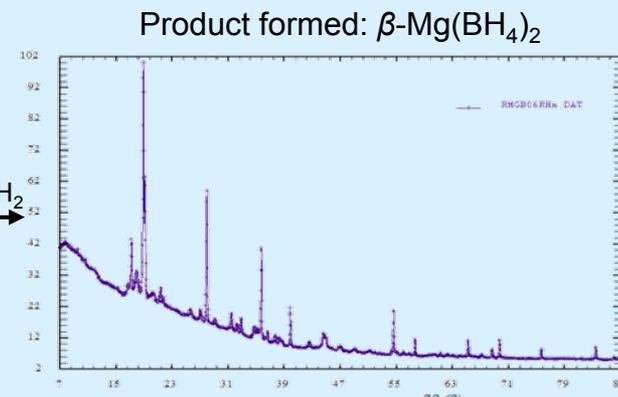
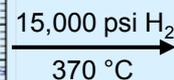
### Synthesis:



Powders milled and pressed into pellets



XRD confirmation of C-doped  $\text{MgB}_2$  from (001) peak shift



XRD of 10% C-doped  $\text{MgB}_2$  after hydrogenation showing formation of  $\beta\text{-Mg}(\text{BH}_4)_2$

**Summary:**  $\text{MgB}_2$  successfully doped with C, subsequently hydrogenated to make  $\text{Mg}(\text{BH}_4)_2$

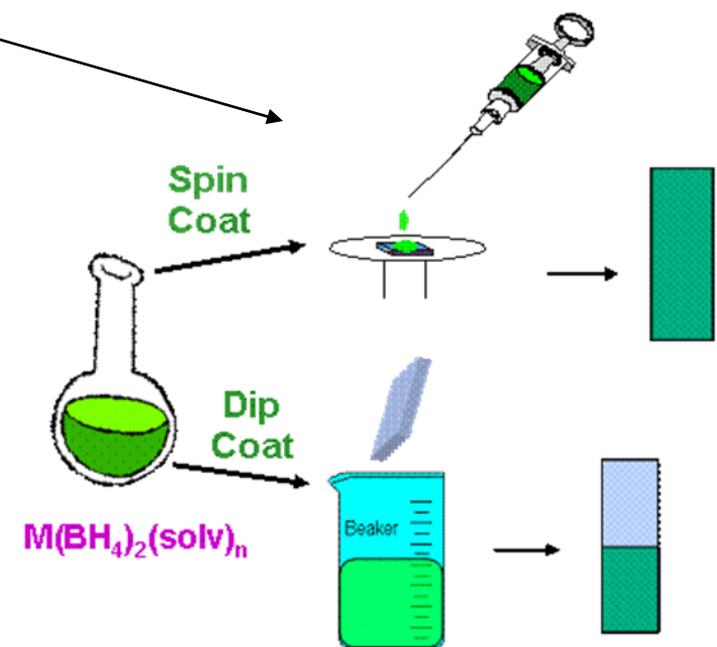
**Future Work:** – Confirm the presence of carbon in  $\text{Mg}(\text{BH}_4)_2$  (NMR, XPS)

– Improve the yield to measure the hydrogen capacity of C-doped  $\text{Mg}(\text{BH}_4)_2$

– Doping  $\text{Mg}(\text{BH}_4)_2$  with transition metals

## Current Status: *Collaboration -- SNL / UTRC / Albemarle Corp.*

- Solution deposition of hydride materials
  - Porous materials (YSZ, C-aerogel) were treated with concentrated solutions of metal hydride
  - Varied solvent (THF, DME, pyridine), exposure time, and drying conditions
  - Results indicate that a super saturated solution can yield up to 50% incorporation by weight, however, H<sub>2</sub> desorption was low
- Solid-state (incipient or melting) incorporation
  - Selected three porous materials (C-aerogel, YSZ, SiO<sub>2</sub>) and exposed to metal hydride melt
  - Used high-energy ball milling or high temperature/pressure to mix
  - Ca(BH<sub>4</sub>)<sub>2</sub> wets surface of carbon aerogel but retention in the nano-framework structure has not been confirmed



*-- see more details in ST10 by X. Tang (UTRC)*

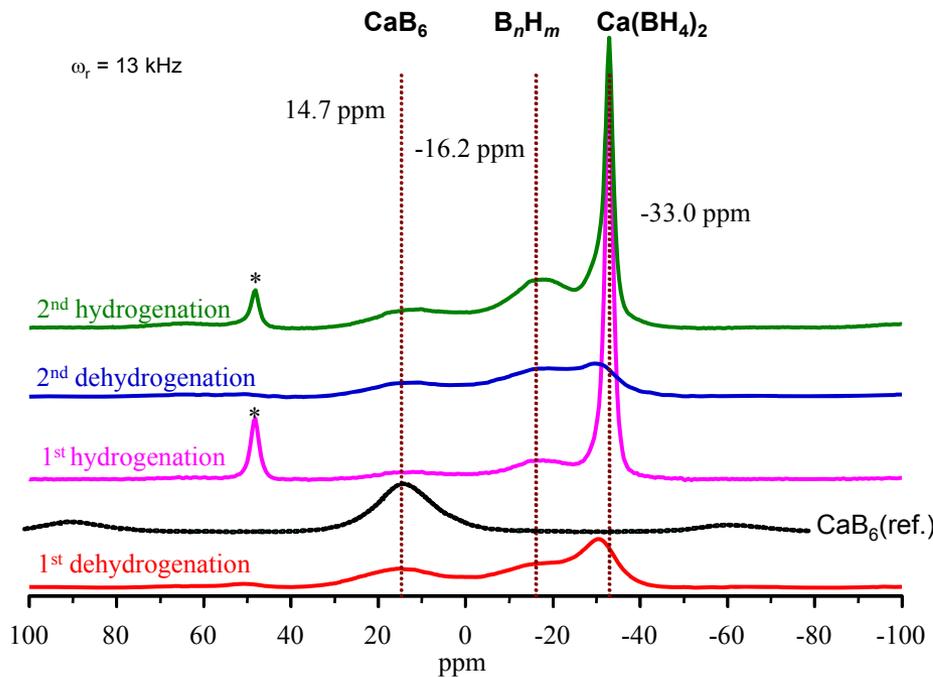
## Future Work:

- *Determination of incipient wetting via melting experiments*
- *Solution deposition gives highest loading but effects on hydrogen desorption are marginal – propose alternative NFS or hydride materials*

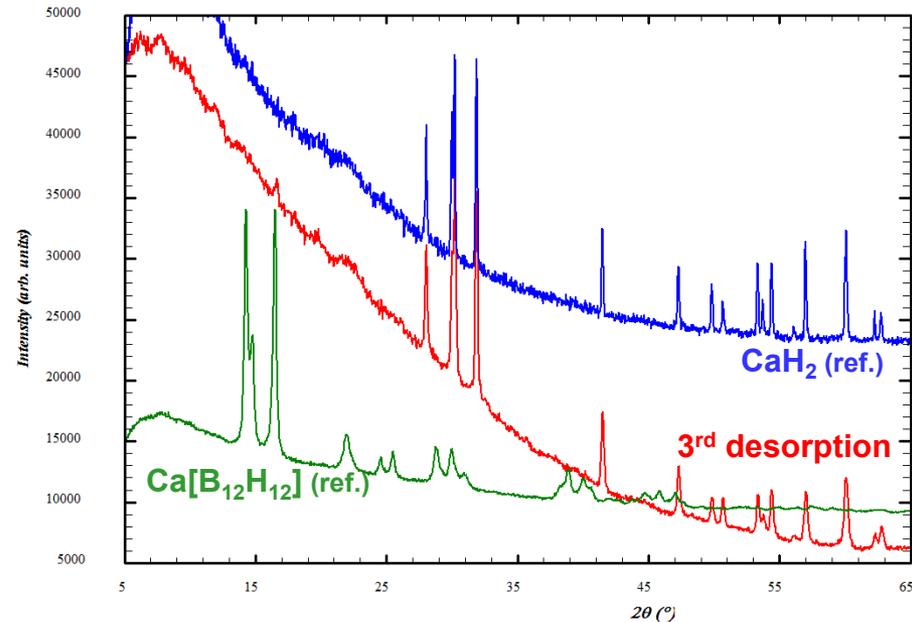
# Cycling Capacity Loss of $\text{Ca}(\text{BH}_4)_2$ Due to Formation of “ $\text{B}_n\text{H}_m$ ” Species

Theory predicts that  $\text{Ca}(\text{BH}_4)_2$  releases  $\text{H}_2$  to form  $\text{Ca}[\text{B}_{12}\text{H}_{12}]$  upon heating

$^{11}\text{B}$  MAS-NMR of  $\text{Ca}(\text{BH}_4)_2$  with Additive-A



XRD of  $\text{Ca}(\text{BH}_4)_2$  with Additive-B After 3<sup>rd</sup> Desorption



XRD indicates crystalline component is largely  $\text{CaH}_2$  in desorbed product, while  $^{11}\text{B}$  NMR indicates the presence of amorphous  $\text{CaB}_6$  and “ $\text{B}_n\text{H}_m$ ” species

# Can $\text{Ca}[\text{B}_{12}\text{H}_{12}]$ Absorb/Release $\text{H}_2$ ?

## Hydrogenation:

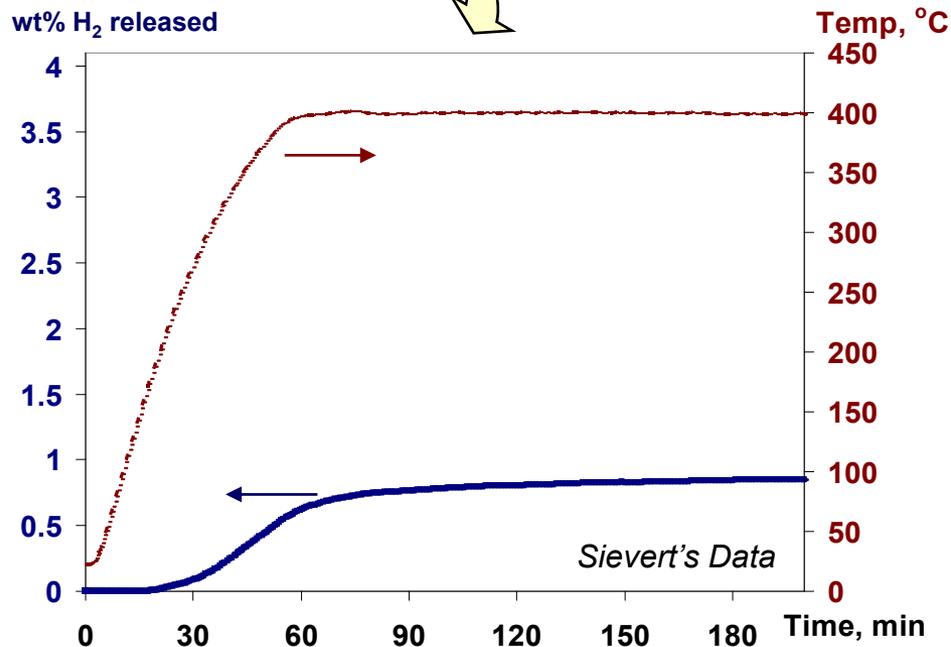
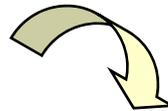
$\text{Ca}[\text{B}_{12}\text{H}_{12}] + x\text{CaH}_2 + \text{H}_2 \longrightarrow$  No reaction at  $400^\circ\text{C}$ , 1000 bar  $\text{H}_2$

$\longrightarrow$  At  $450^\circ\text{C}$ , 1000 bar  $\text{H}_2$  traces of  $\text{Ca}(\text{BH}_4)_2$  form

$\text{Ca}[\text{B}_{12}\text{H}_{12}] + \text{H}_2 \longrightarrow$  No reaction at  $400^\circ\text{C}$  1000 bar  $\text{H}_2$

## Dehydrogenation:

$\text{Ca}[\text{B}_{12}\text{H}_{12}] + \text{CaH}_2$



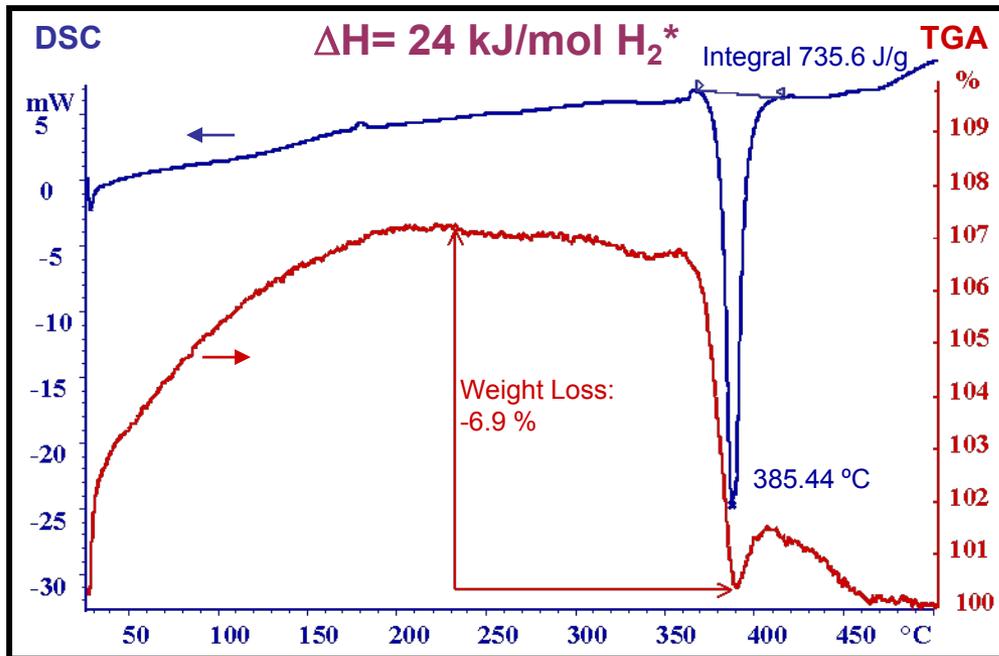
We found that  $\text{CaB}_{12}\text{H}_{12}$  is kinetically stable and the formation of it would hinder  $\text{Ca}(\text{BH}_4)_2$  reversibility

# Enthalpy Measurements of $\text{Ca}(\text{BH}_4)_2$ Complicated by Slow Kinetics

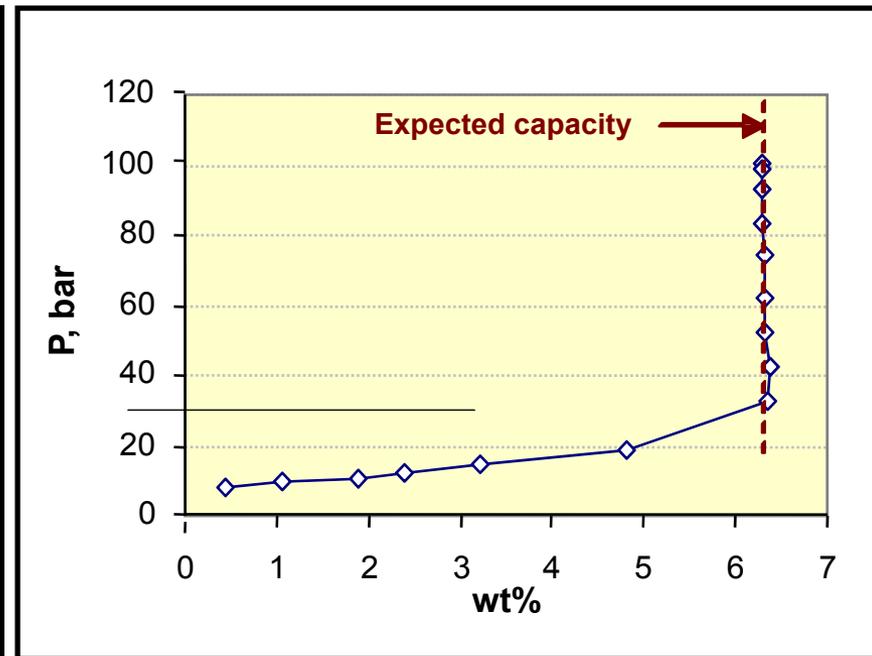
Enthalpy measurements for the decomposition have been measured using Differential Scanning Calorimetry (DSC)

Pressure-Composition-Isotherms (PCI) measurements are ongoing

## TGA-DSC of $\text{Ca}(\text{BH}_4)_2^*$



## Desorption Isotherm at 354 °C\*\*



\*Assuming  $\text{H}_2$  is the only gaseous species released upon heating:  
 $6\text{Ca}(\text{BH}_4)_2 \rightarrow \text{CaB}_{12}\text{H}_{12} + 5\text{CaH}_2 + 13\text{H}_2$  (6.3 wt%  $\text{H}_2$ )

\*\*Ongoing measurement

\* Simultaneous thermo-gravimetric modulated-beam mass spectrometer

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

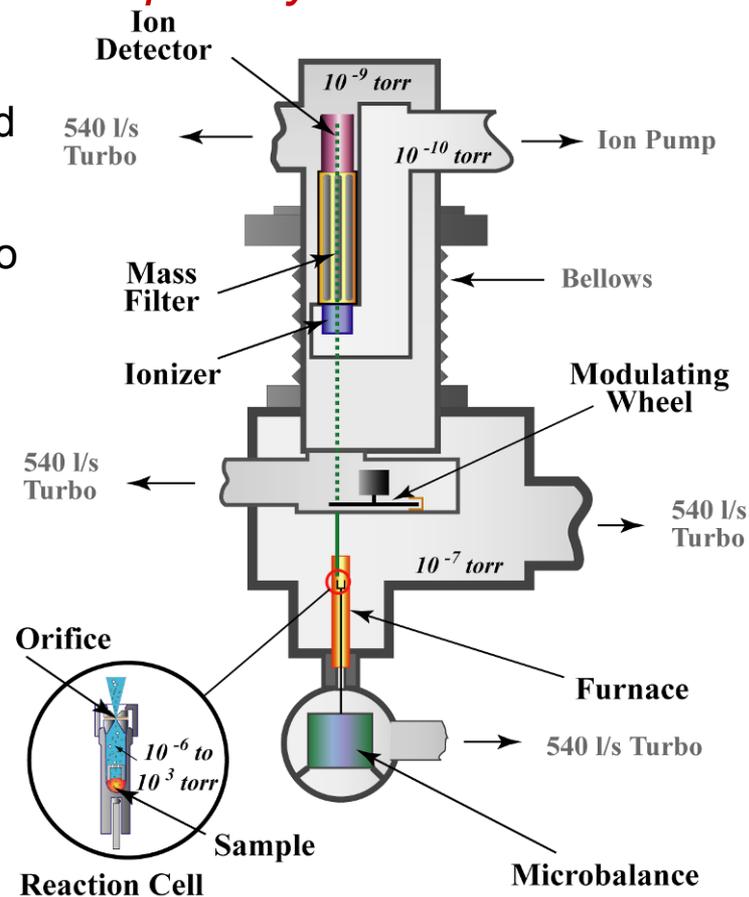
## Instrument details:

- 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:

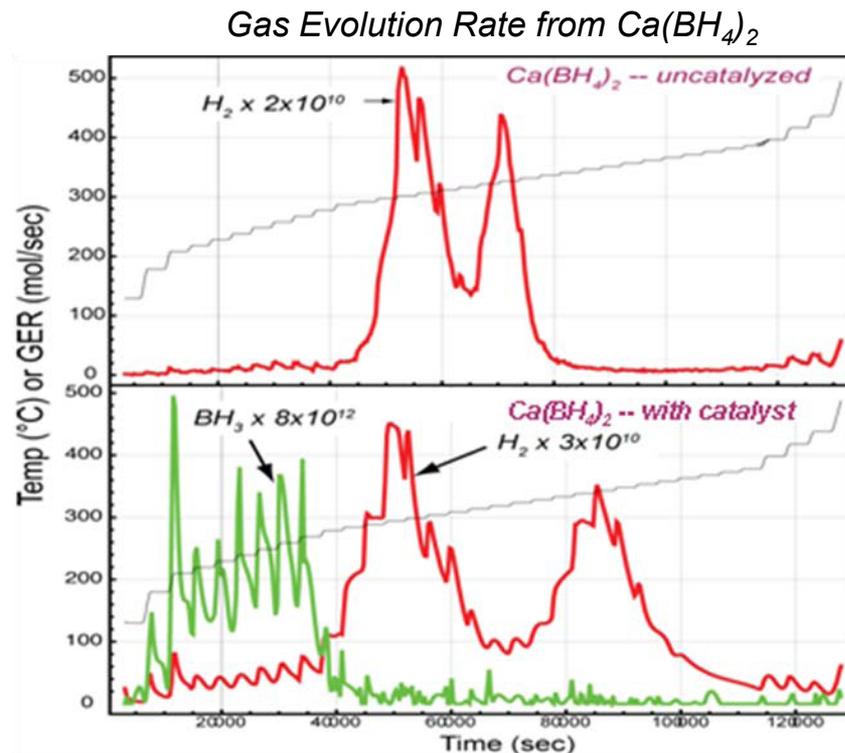
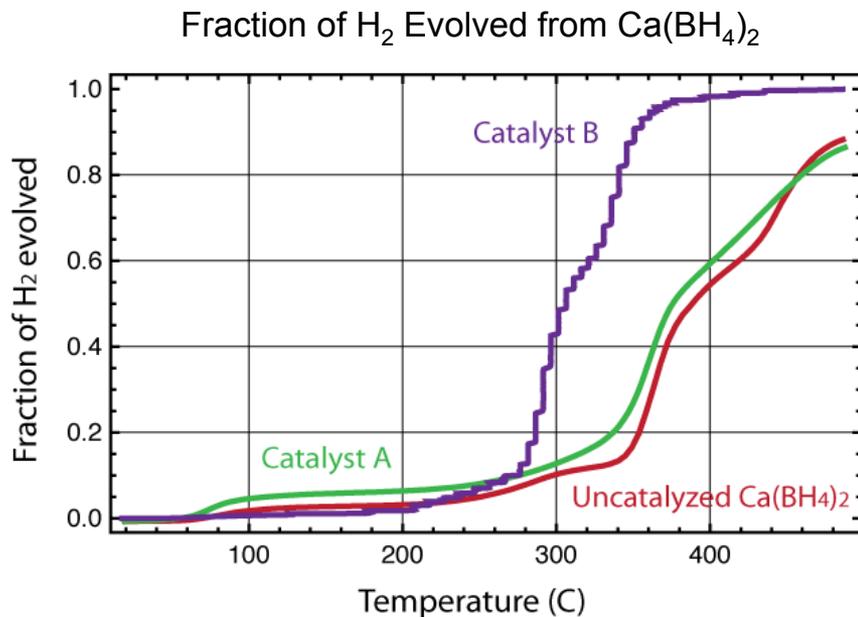
- Species
- Number density
- Rate of evolution
- Partial pressure
- Temperature

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



# STMBMS Results of $\text{Ca}(\text{BH}_4)_2$ Gaseous Decomposition Products

- A variety of gaseous species observed during decomposition process (*i.e.*  $\text{BH}_3$ )
- Lower temperature hydrogen release observed for catalyzed- $\text{Ca}(\text{BH}_4)_2$

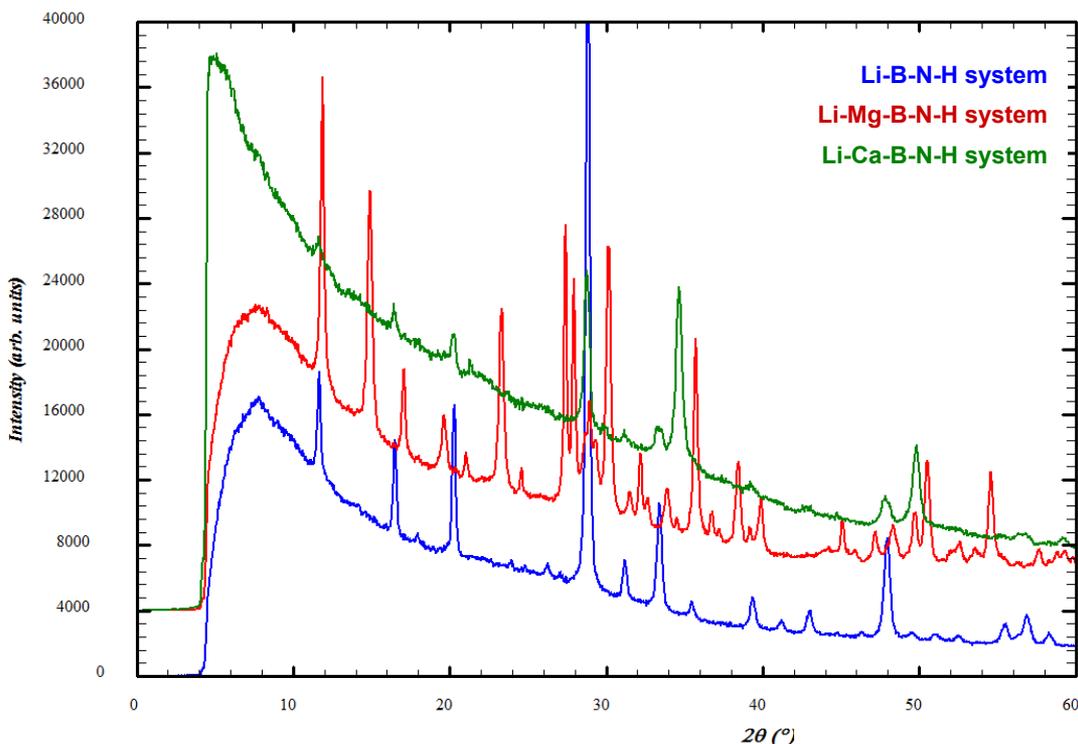


- $\text{H}_2$  released in multiple steps from  $\text{Ca}(\text{BH}_4)_2$
- Additives modify the kinetics and increase the amount of  $\text{BH}_3$  released ( $\sim 1\%$  of  $\text{H}_2$  stream)

## Motivation: Search for new high capacity hydrogen storage materials

Ball-milled various molar-ratio mixtures of borohydride, amides and binary hydrides to form compounds with intermediate hydrogen capacities

### Selected XRD Results:



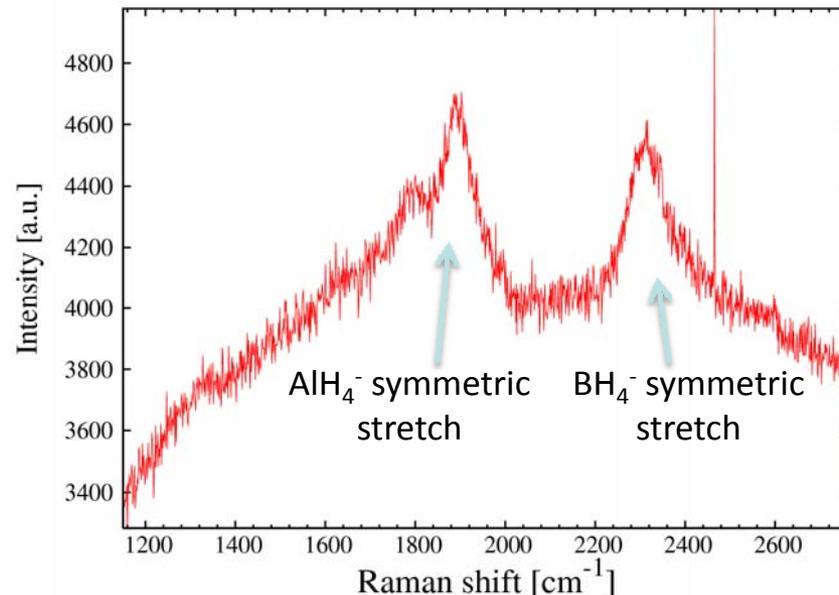
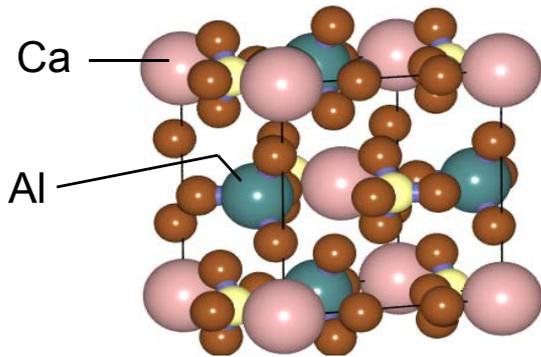
- XRD indicates that the starting materials,  $\text{M}(\text{BH}_4)_x$  and  $\text{M}'(\text{NH}_2)_y$ , are no longer present and new phases form
- Raman spectroscopy indicates the presence of  $(\text{BH}_4)^-$  and  $(\text{NH}_2)^-$  anions,  $\sim 2300$  and  $\sim 3250$   $\text{cm}^{-1}$ , respectively

Characterization of hydrogen storage properties is on-going

## **Motivation: Alanates generally have better reversibility compared to pure borohydrides**

- Synthesis:  $\text{LiAlH}_4 + \text{LiBH}_4 + \text{CaCl}_2 \rightarrow \text{Ca}(\text{AlH}_4)(\text{BH}_4) + 2 \text{LiCl}$
- XRD indicates no  $\text{LiBH}_4$  or  $\text{LiAlH}_4$
- Raman spectroscopy indicates  $(\text{BH}_4^-)$ ,  $(\text{AlH}_4^-)$  anions present in product
- Initial studies show no reversibility at  $200^\circ\text{C}$ , 65 bar  $\text{H}_2$  pressure, experiments ongoing

Predicted high  
symmetry structure



$\text{M}(\text{AlH}_4)/(\text{BH}_4)$  are promising new hydrogen storage materials