METAL HYDRIDE CENTER OF EXCELLENCE

DOE Hydrogen Program

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

Mark Allendorf, Eric Majzoub, Vitalie Stavila

Sandia National Laboratories

May 19, 2009

Sandia National Laboratories

Project ID: ST_03_Allendorf

Overview of Sandia Program

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)

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

Sandia Team (~ 6 FTEs)

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 Kartin: *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)

Objectives/Relevance/Approach

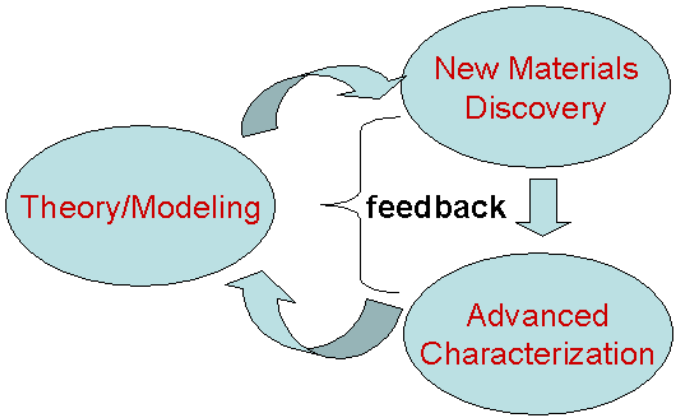
Discover, develop and validate "**reversible**" on-board metal hydride storage materials with potential to meet the DOE 2010 targets and a clear path to meeting the 2015 targets. Use theory-directed synthesis with characterization

Prediction of crystal structure prototypes:

- ✓ Prototype Electrostatic Ground State (PEGS) technique for structure predictions and rapid ΔH 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 of Theory in June 2008 and Current Focus

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 AlH_3 regeneration studies)
- Modeling of alanate energetics in solution initiated

Focus during FY08/FY09:

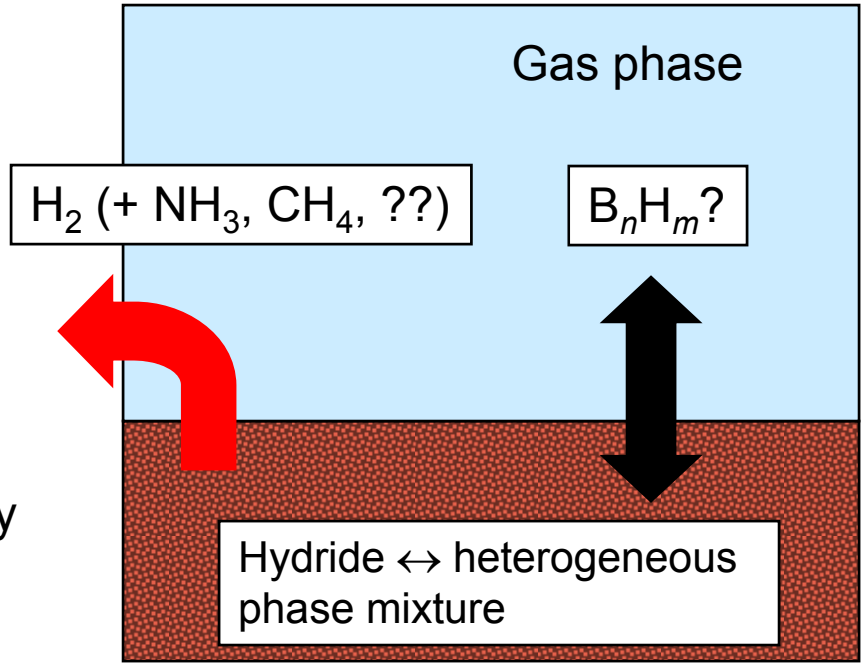
- Impact of *closo*-borates formation on thermodynamics of Li-, Ca- and Mg-borohydrides
- Reaction pathways in complex multi-component systems
- Role of gas phase in determining reaction pathways
- Continue the coordination of MHCoE Theory Group (Allendorf)

Metal Hydride Theory Needs to Address Multiple Phases and Gas Composition

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.* NH_3)
  - Storage capacity, reversibility
  - Safety (*e.g.*, H_2O or 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



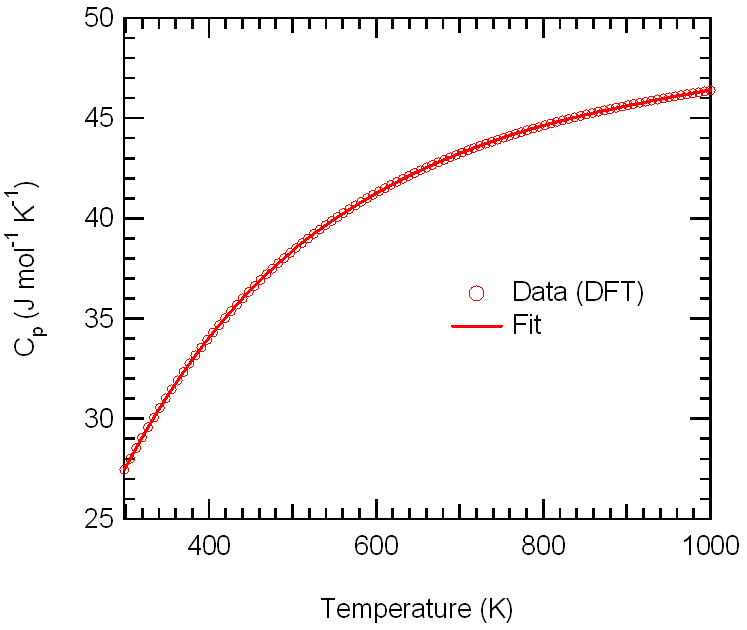
Ki Chul Kim & David Sholl (GA Tech.)
Bo Zhang & Karl Johnson (U. Pittsburgh)
Mark Allendorf (SNL)

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)

$LiNH_2$ (+ LiH): Prediction of Significant Gas-phase Impurities

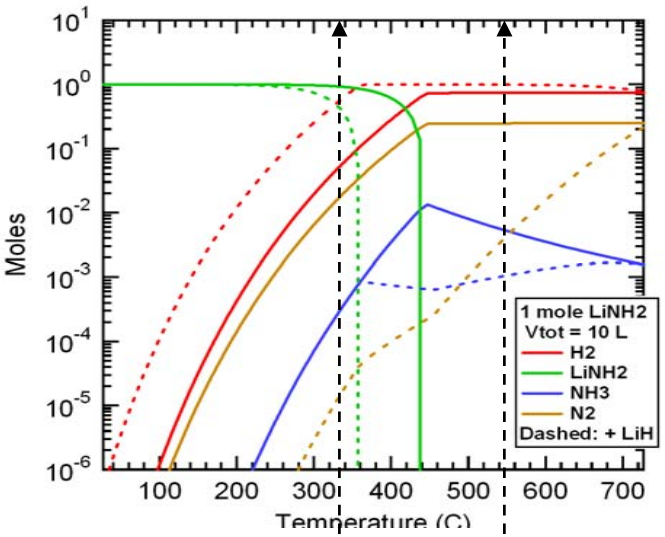
- **Nominal reactions:**

  $LiNH_2 \leftrightarrow 0.5Li_2NH + 0.25N_2 + 0.75H_2$

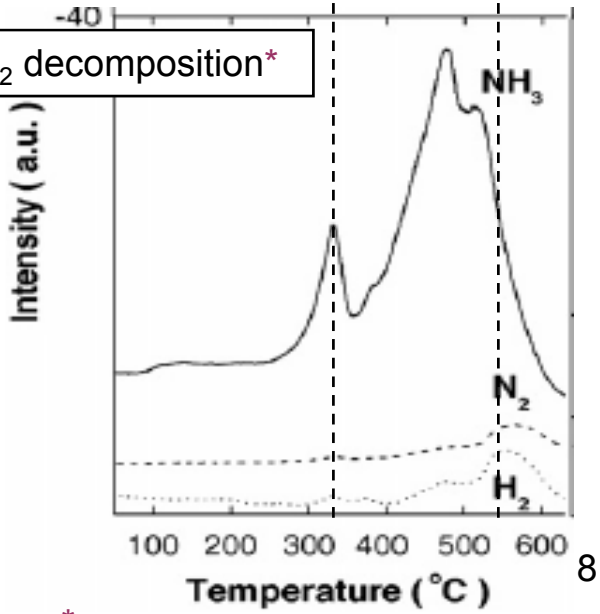
  $LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$

  $2LiNH_2 \leftrightarrow Li_2NH + NH_3$

- **Conditions for calculation:**
  - 1 mole $LiNH_2$ (+1 mole LiH)
  - Constant T, Constant V (10 L)
  - Gas phase: H_2, NH_3, N_2, Li, Li_2, LiH
- **Results:**
  - N_2 and NH_3 predicted to be significant byproducts
  - LiH addition:
    - Scavenges nitrogen to enhance H_2 yield
    - Reduces NH_3, but only at T > 360 ºC
  - Experiments confirm NH_3 formation but suggest kinetic barrier to N_2 formation



$LiNH_2$ decomposition*



* Ref: Yao *et al. J. Alloy Comp. v432, p277* (**2007**)

Future Work: Model Equilibria for Most Important Metal Hydride Materials

- Model phase equilibria for general hydride categories:
  - Hydride + C
  - Nitrogen-containing hydrides
  - Boron-containing hydrides
- Model the following destabilized reactions:
  - $2LiNH_2 + C \rightarrow Li_2CN_2 + 2H_2$ $\Delta U(0\ K) = 31.4\ kJ/mol\ H_2$
  - $2C + Mg(BH_4)_2 \rightarrow MgB_2C_2 + 4H_2$ $\Delta U(0\ K) = 43.1\ kJ/mol\ H_2$
  - $BN + 4Mg(BH_4)_2 \rightarrow 3MgH_2 + MgB_9N + 13H_2$ $\Delta U(0\ K) = 51.2\ kJ/mol\ H_2$

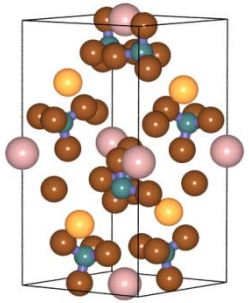
- *Incorporate multiple gas-phase species approach into U. Pittsburgh / Georgia Tech screening code*

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

- Journal article describing results is in preparation

Alkali-TM-$(BH_4)_x$ Explored for Low-Temperature Desorption

Investigation of $LiSc(BH_4)_4$ Validates PEGS method with TM-borohydrides



I-4
$LiSc(BH_4)_4$

Collaboration -- SNL / JPL / Caltech / UCLA

- Solid-state NMR indicates formation of ScB_2, $[B_{12}H_{12}]^{2-}$ on desorption
- PEGS predicted structures:

$Sc(BH_4)_3$: *C*222$_1$ $Sc_2[B_{12}H_{12}]_3$: *Cm* $LiSc(BH_4)_4$: *I*-4

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:
$NaTi(BH_4)_4$
$Na_2Ti(BH_4)_5$
$LiTi(BH_4)_4$
$Li_2Ti(BH_4)_5$

Theoretical and Experimental Search for Alkali-Ti-$(BH_4)_x$

Collaboration -- SNL / UTRC

- Stabilize $Ti(BH_4)_3$ through addition of alkali metals, and/or confinement in nano-frameworks

Synthesis:

$$TiX_4 \xrightarrow{LiBH_4} Ti(BH_4)_3 \quad (X= Cl, Br)^*$$ **Completed** ✓

$$Ti(BH_4)_3 + MBH_4 \longrightarrow MTi(BH_4)_4 \quad (M= Li, Na)$$ **In progress**

* Ref: DM Goedde, GS Girolami, *Inorg. Chem. v45*, p1380 (**2006**)

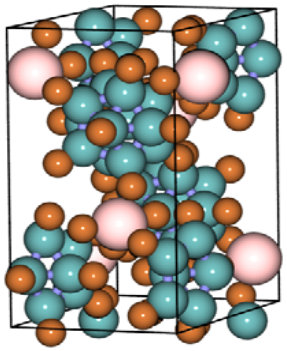
Structure of $[B_{12}H_{12}]^{2-}$ Salts Predicted with PEGS and Confirmed with XRD

Collaboration -- SNL / NIST

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

Theory Predicted Structure

*C*2/*c*
$Ca[B_{12}H_{12}]$

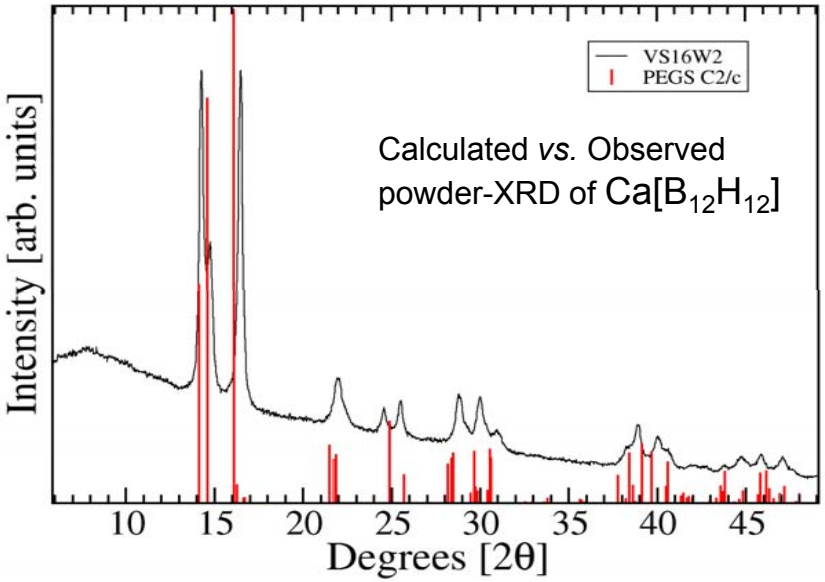


Synthesis:

$$Cs_2[B_{12}H_{12}] \xrightarrow[-Cs^+]{\text{Amberlite IR-120}} [H_3O]_2[B_{12}H_{12}]$$

$$[H_3O]_2[B_{12}H_{12}] \xrightarrow[-CO_2,\ -H_2O]{MCO_3} M[B_{12}H_{12}]\bullet xH_2O \quad (M = \text{metal ion})$$

$$M[B_{12}H_{12}]\bullet xH_2O \xrightarrow[-xH_2O]{\Delta} M[B_{12}H_{12}]$$



Compound	PEGS Structures	SNL/NIST Data
$Li_2[B_{12}H_{12}]$	*C*2/*m* (#12)	*Pa*-3
$Na_2[B_{12}H_{12}]$	$P2_1/n$ (#14)	$P2_1/n$
$Ca[B_{12}H_{12}]$	*C*2/*c* (#15)	*C*2/*c*
$Mg[B_{12}H_{12}]$	*C*2/*m* (#12)	Amorphous
$Sc_2[B_{12}H_{12}]_3$	*Cm* (#8)	Amorphous

Ref: * SJ Hwang, *et al. J. Phys. Chem. C*, *v112, p3164* **(2008)**
** I Tiritiris, T Schleid, *Z. Anorg. Allg. Chem.*, *v627*, *p1836* **(2001)**

$[B_{12}H_{12}]^{2-}$ Formation Impacts Storage Capacity in $Ca(BH_4)_2$ and $Mg(BH_4)_2$

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), ΔH 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	ΔH^{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

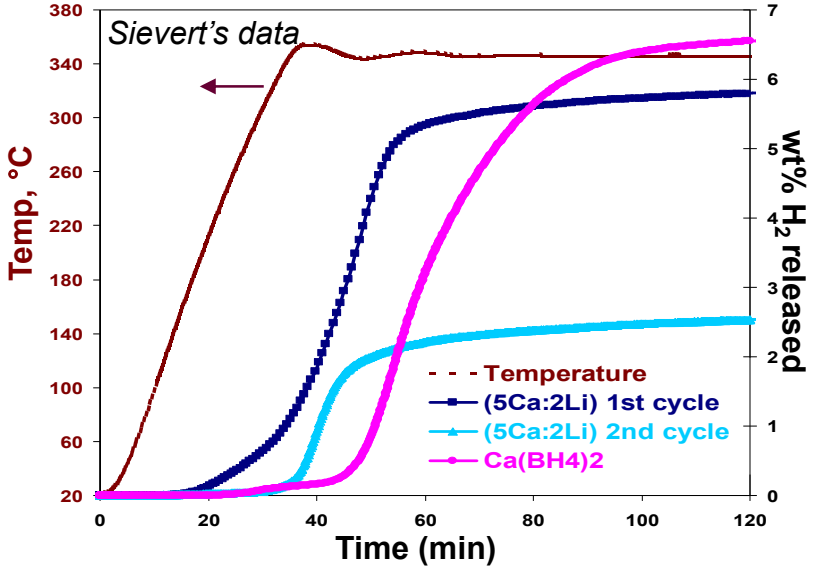
A predicted desorption pathway of $Ca(BH_4)_2$ involves $Ca[B_{12}H_{12}]$, and is therefore consistent with loss of capacity on each cycle observed in sorption experiments

Lower Entropy Reactions Allow Lower Enthalpy at the Same Pressure

Entropy of H_2 gas (130 J/Kmol H_2 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_2 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_2	ΔH^{300K} kJ/mol H_2	T_c (°C)	SNL Data: wt% H_2 (350°C, 4h)
$5Mg(BH_4)_2 + 2LiBH_4 \rightarrow Li_2[B_{12}H_{12}] + 5MgH_2 + 13H_2$	8.4	24.4	-29	**6.0**
$5Mg(BH_4)_2 + Ca(BH_4)_2 \rightarrow Ca[B_{12}H_{12}] + 5MgH_2 + 13H_2$	7.7	25.7	-18	**4.4**
$5Ca(BH_4)_2 + 2LiBH_4 \rightarrow Li_2[B_{12}H_{12}] + 5CaH_2 + 13H_2$	6.7	37.9	83	**6.2**



Kinetic barriers for new reactions are unknown

Experimental Comparison of $5Ca(BH_4)_2 + 2LiBH_4$ *vs* $Ca(BH_4)_2$ 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: Al-Adduct Theory
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: Alanate/Borohydride Theory
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

** -- see our additional slide #31*

Discovery and Characterization of New Materials

Status in June 2008:

- Determined the phase transitions of $Ca(BH_4)_2$ polymorphs at different temperatures (*--see our additional slide #32*)
- Demonstrated the partial reversibility of $Ca(BH_4)_2$ at 100 bar and 350°C
- Initiated additive screening for $Ca(BH_4)_2$
- Theory predicted bi-alkali borohydrides, $AK(BH_4)_2$ (A= Li, Na), were synthesized but not pursued further due to poor thermodynamics

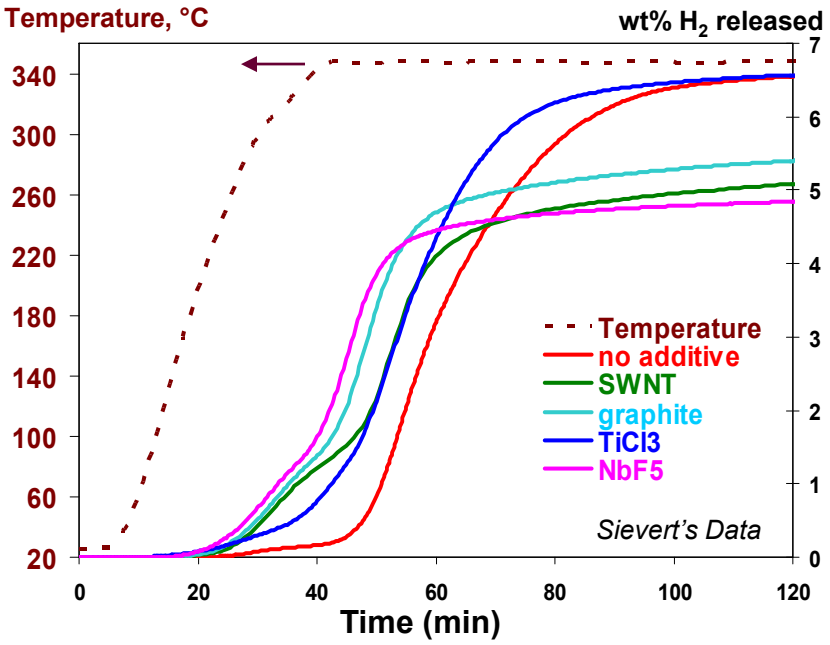
Focus during FY08/FY09:

- Elucidate the reaction mechanism and decomposition products of $Ca(BH_4)_2$
- Complete $Ca(BH_4)_2$ additive study, ΔH determination: Make go/no-go decision
- Syntheses and characterization of PEGS-predicted *closo*-borates and new BH_4/NH_3, BH_4/NH_2, BH_4/AlH_4 systems
- Re-hydrogenation of $Mg(BH_4)_2$ 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*)

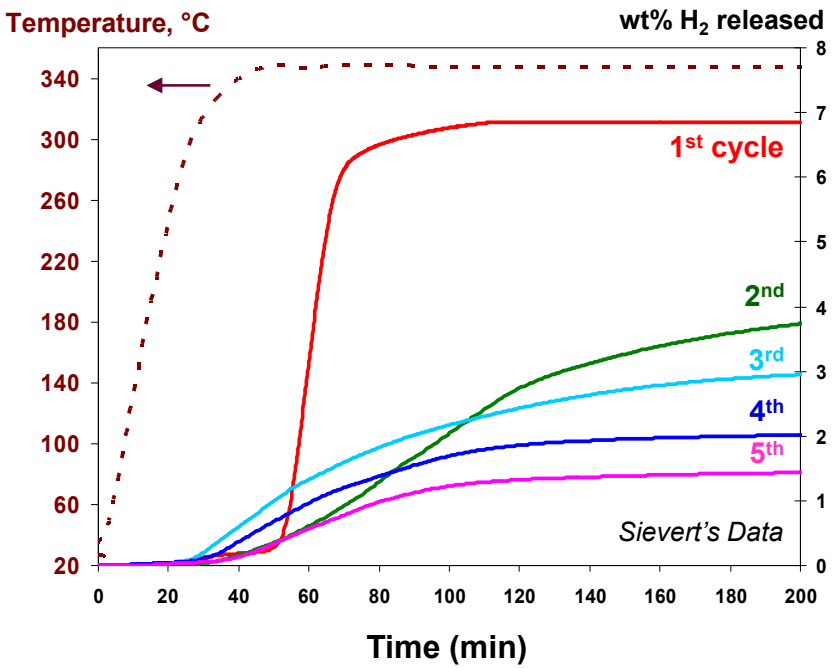
Effect of Additives on Cycling Capacity and Kinetics of $Ca(BH_4)_2$

- 30 different additives screened
- ~6 wt% H_2 released in 1 hour at 350 °C

Additive Effect on $Ca(BH_4)_2$ Desorption



Life-cycle of $Ca(BH_4)_2$ with 4wt% $PdCl_2$ Additive



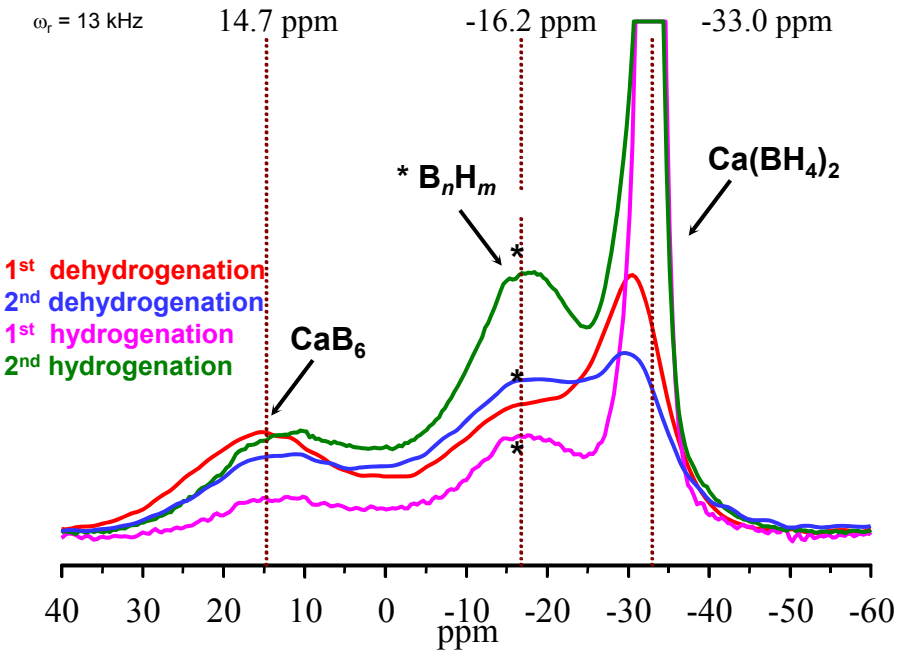
- Additives do not significantly improve kinetics of $Ca(BH_4)_2$
- Significant capacity loss observed on subsequent cycles

^{11}B MAS-NMR Confirms the Cycling Capacity Loss of $Ca(BH_4)_2$ Due to Formation of "B_nH_m" Species

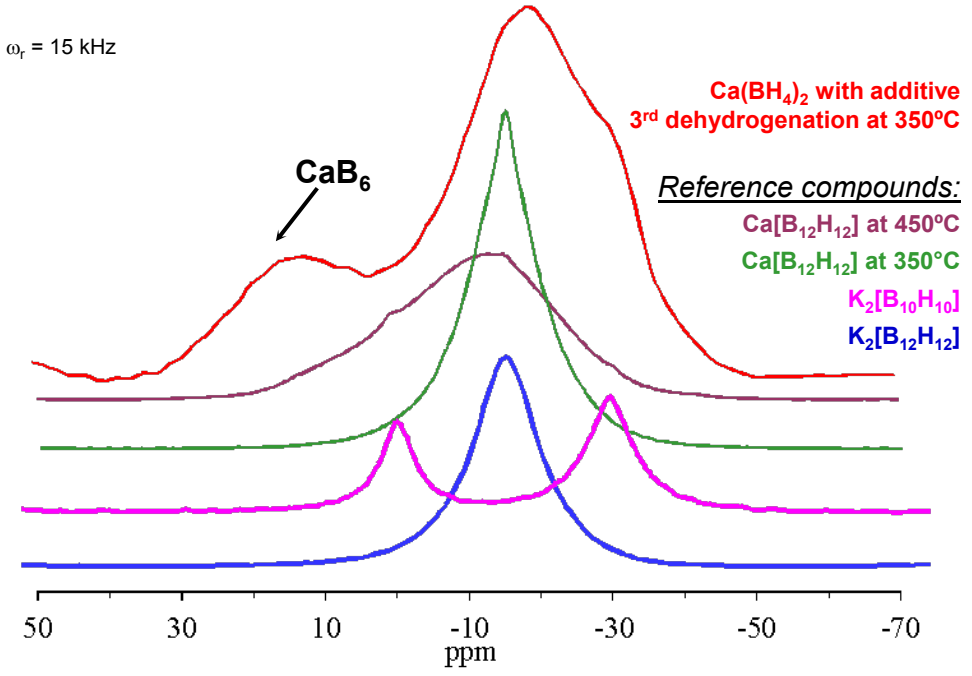
Collaboration -- SNL / Caltech - JPL

"B_nH_m" species formed during the dehydrogenation

$Ca(BH_4)_2$ with Additive-A



$Ca(BH_4)_2$ with Additive-B



- ^{11}B NMR reveals the presence [B_nH_m] species and their accumulation upon cycling (*-- see also our additional slide #35*)
- Separate experiments show that $Ca[B_{12}H_{12}]$ cannot be hydrogenated or dehydrogenated under the conditions tested (*-- see our additional slide # 36*)

No-Go Decision Made on $Ca(BH_4)_2$

Although the thermodynamics for $Ca(BH_4)_2$ are reasonable (measured $\Delta H_{desorption}$ = 20 – 30 kJ/mol H_2 by DSC)*, we have made a decision to "down-select" $Ca(BH_4)_2$ as a hydrogen storage material, because:

- It is only partially reversible due to "B_nH_m" formation
- It is kinetically limited
- Catalysts do not improve the rate of hydrogen desorption below 300 ºC
- The observed maximum desorption capacity, up to 350 ºC, is less than ~ 7 wt %

∴ We will not pursue $Ca(BH_4)_2$ further as a hydrogen storage material

* -- see our additional slide #37

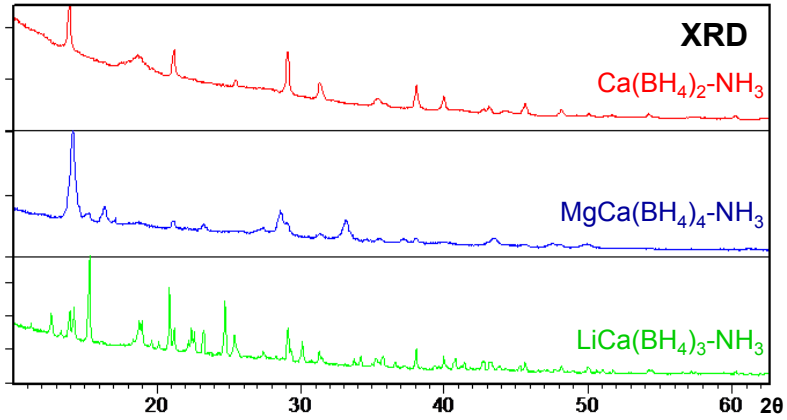
New $M(BH_4)$-NH_3 Materials Synthesized and Characterized

Motivation: Based on promising results reported for $Mg(BH_4)_2 \cdot 2NH_3$ (Zhao *et al.*) other metal-borohydride-ammonia systems were investigated

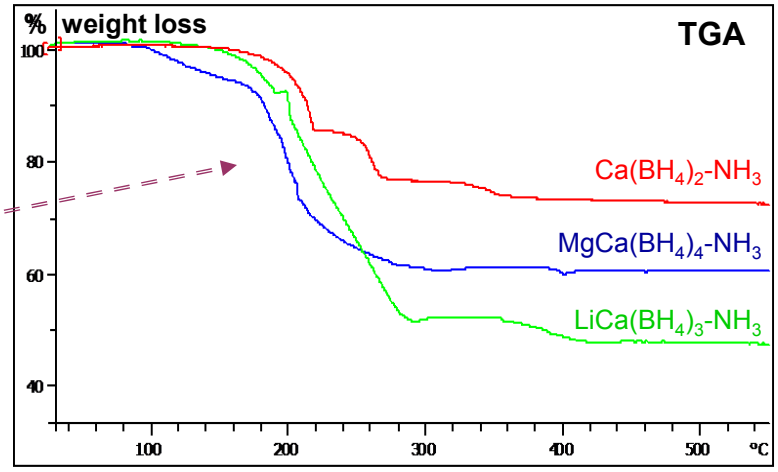
$$Ca(BH_4)_2 \xrightarrow[THF]{+NH_3,\ -20\ ^\circ C} Ca(BH_4)_2 \cdot xNH_3$$

$$M(BH_4)_y + Ca(BH_4)_2 \xrightarrow[THF]{+NH_3,\ -20\ ^\circ C} MCa(BH_4)_{2+y} \cdot xNH_3 \quad (M=Li, Mg)$$

$$Ti(BH_4)_3 \xrightarrow{+NH_3,\ -33\ ^\circ C} Ti(BH_4)_3 \cdot xNH_3$$



- The BH_4-NH_3 compounds display increased air- and moisture stability compared to the initial borohydrides
- *$Ca(BH_4)_2 \cdot NH_3$*, *$MgCa(BH_4)_4 \cdot NH_3$* and *$LiCa(BH_4)_3 \cdot NH_3$* adducts release significant amounts of NH_3 upon heating, confirmed by gas phase analysis
- New systems based on transition metals (*e.g.* Ti(III)) are currently under investigation



-- see other details on the $Ca(BH_4)_2$-NH_3 system in STP37 by G. Brown (ORNL)

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Experimental Milestones

Sandia National Laboratories

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 $Ca(BH_4)_2$ to determine reaction enthalpy
Jan-09 ✓	Milestone: Synthesize $Ca(BH_4)_2/NH_3$ system No-go: On further work on $Ca(BH_4)_2/NH_3$ system Milestone: Complete STMBMS characterization of $Ca(BH_4)_2$ No-go: La-doped CaB_6, but the efforts shifted towards C-doping of MgB_2
Mar-09 ✓	Milestone: Lowering of $Ca(BH_4)_2$ desorption temperature No-go decision made on $Ca(BH_4)_2$
April-09 ✓	Milestone: Complete additive screening study of MHCoE borohydride Milestone: Discover new borohydride related materials **In progress**
May-09	Go/no-go on A-TM-$(BH_4)_x$: Reversibility of alkali transition metal borohydrides
June-09	Go/no-go: Continue with mixed $Ca_{(1-x)}M_x(BH_4)_z$ materials if reversibility has been shown at improved P and T compared to $Ca(BH_4)_2$ Go/no-Go: to incorporate the hydride material into the NFS *via* 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

Summary of Accomplishments

Theory:

- Developed phase equilibria theoretical technique, applied to $LiNH_2$ (+LiH) and ($LiBH_4$ + C)
- Predicted structures of $[B_{12}H_{12}]^{2-}$ intermediates and their effect on reaction pathways
- PEGS structure predictions of transition-metal borohydrides

Calcium Borohydride:

- Completed additive screening of $Ca(BH_4)_2$ and studied the cycling behavior
- Revealed that B_nH_m species limit the reversibility of $Ca(BH_4)_2$
- Probed reaction pathway and kinetics of $Ca(BH_4)_2$ using STMBMS (*-- see our additional slides #38, 39*)
- Made No-Go decision on $Ca(BH_4)_2$

New Materials:

- Synthesized $[B_{12}H_{12}]^{2-}$ 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 $MM'(BH_4)_x/(NH_3)_y$ and $MM'(BH_4)_x/(NH_2)_y$ compounds and assessed their hydrogen storage properties (*-- see our additional slide #40*)
- Synthesized $Ca(AlH_4)/(BH_4)$ and predicted high symmetry solid-state structure (*-- see our additional slide #41*)
- Examined C-dopant effects on MgB_2 hydrogenation (*-- see our additional slide #35*)
- Initiated the incorporation of $Ca(BH_4)_2$ in a C-aerogel and characterized hydrogen release

Future Work in 2009

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 BH_4/NH_3, BH_4/NH_2 and BH_4/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*)

Collaborations

MHCoE Partners:

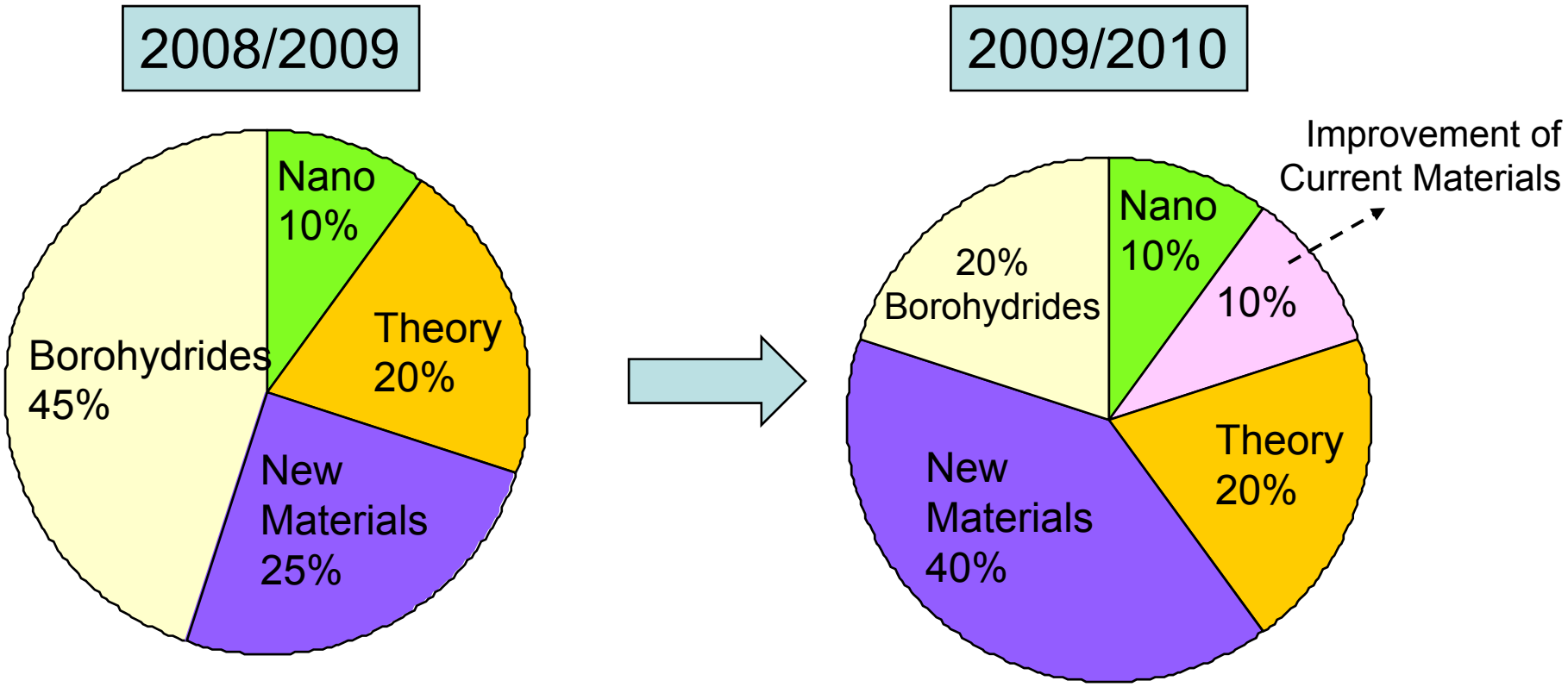
- BNL: J. Wegrzyn, J. Graetz
- Caltech: S.-J. Hwang, C. Ahn
- HRL: J. Vajo, P. Liu
- GA Tech: D. Sholl
- JPL: J. Reiter, J. Zan
- NIST: T. Udovic, U. Kettner
- OSU: J.-C. Zhao
- SRNL: D. Anton, R. Zidan
- U. Hawai'i: C. Jensen
- U. Illinois: I. Robertson, D. Johnson
- UNR: D. Chandra
- U. Pitt: K. Johnson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

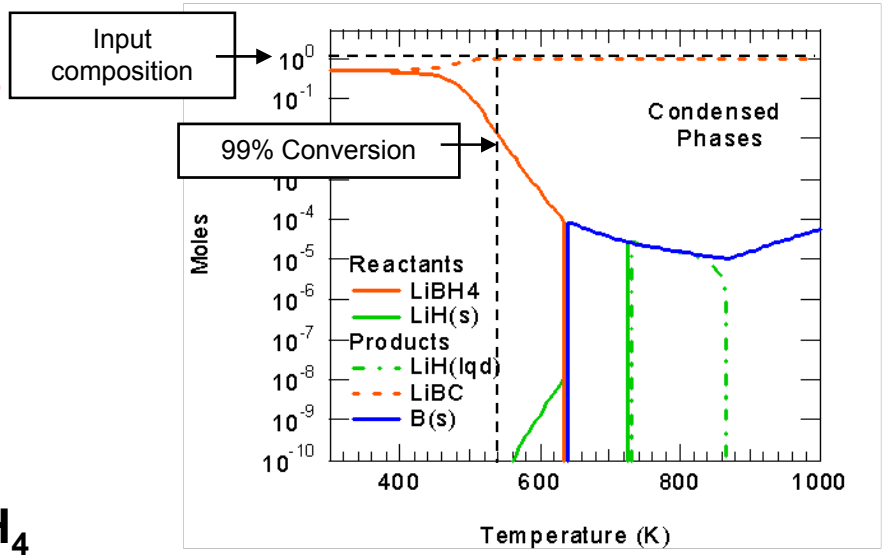
Additional Slides

SNL Major Technical Emphases 2009/2010

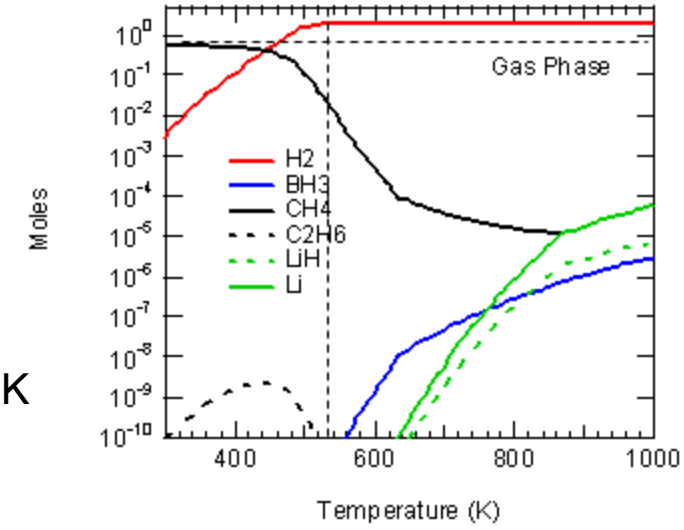


$LiBH_4$ + C: Predict Initial Formation of LiBC + H_2 at Low T

Motivation: **MHCoE Theory (Sholl) predicts $LiBH_4$ + C has favorable desorption thermodynamics (ΔH = 45.1 kJ/mol H_2)**



- **Nominal reaction**
  - $LiBH_4 + C \leftrightarrow LiBC + \mathbf{2H_2}$
- **Also possible:**
  - $LiBH_4 + 2C \leftrightarrow LiBC + \mathbf{CH_4}$
  - $LiBH_4 + 0.75C \leftrightarrow LiH + B + \mathbf{0.75\ CH_4}$
- **Conditions for each calculation**
  - 1 mole $LiBH_4$ +1 mole C as graphite
  - Constant P (1 atm), constant T
- **Results**
  - LiH and C(s) not stable 300-640 K
    - Converted to $\mathbf{CH_4}$ and LiBC
  - Complete conversion to $LiBC+H_2$ only at T > 540 K
  - BH_3 is only significant B-containing gas-phase species



-- see more details in ST08 by K. Johnson (Univ. Pittsburgh)

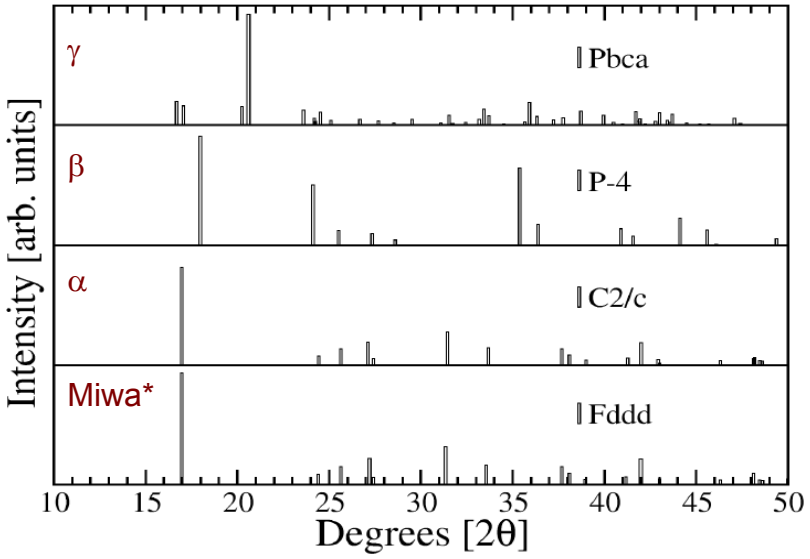
Nanoparticle Production *via* Surfactant Templating

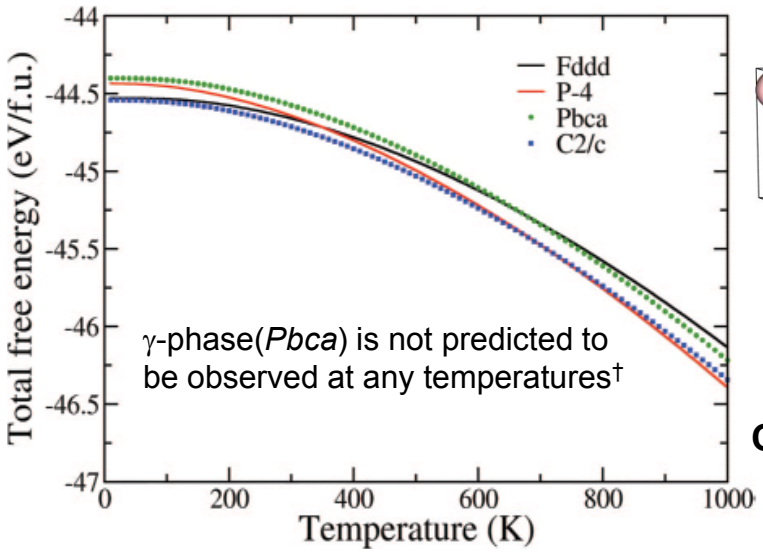
Motivation: **Surfactant micelles offer potential for incorporation of MH in the nanoscale**

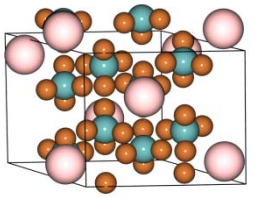
- Nanoparticle Production *via* Surfactant Templating
  - H_2O/AOT/decane solutions with $NaBH_4/H_2O$ produced ~10nm particles
  - No suitable THF/surfactant analogs found for alanates/borohydride inclusion
  - Problems with scalability and separation of surfactant excess prevents quantitative characterization

Method down-selected, do not pursue further

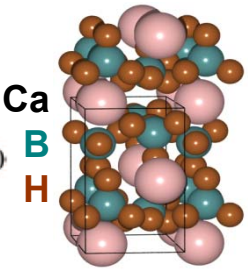
Identified Phase Transitions of Four Polymorphs of $Ca(BH_4)_2$



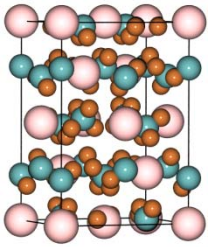




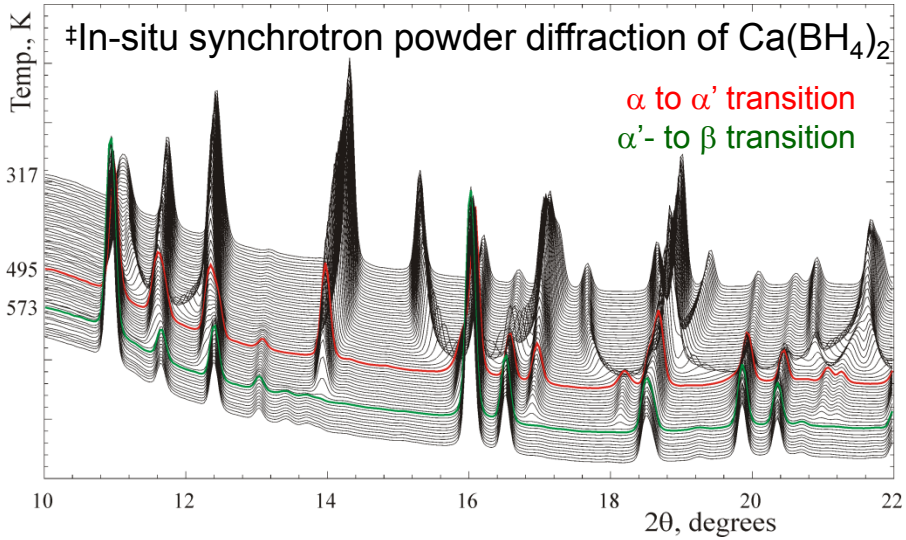
α: *Fddd*

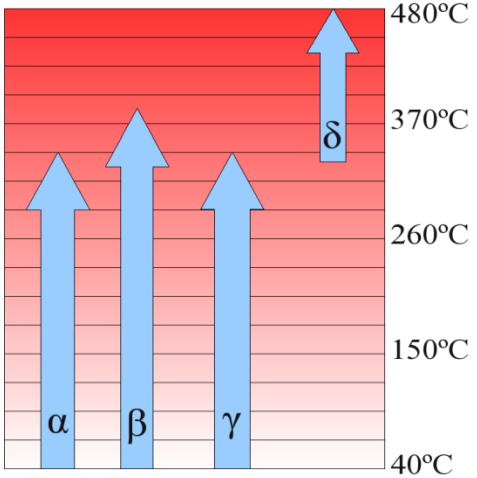


β: *P*-4



γ: *Pbca*





*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 Reversibility of $Mg(BH_4)_2$
II. Attempt to destabilize $Mg(BH_4)_2$ *via* C-doping

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

$$MgB_2 + 4H_2 \longrightarrow Mg(BH_4)_2 \quad 400\ ^\circ C,\ 950 bar$$ ✓

II. Destabilizing $Mg(BH_4)_2$ with C-doping to improve hydrogen storage properties

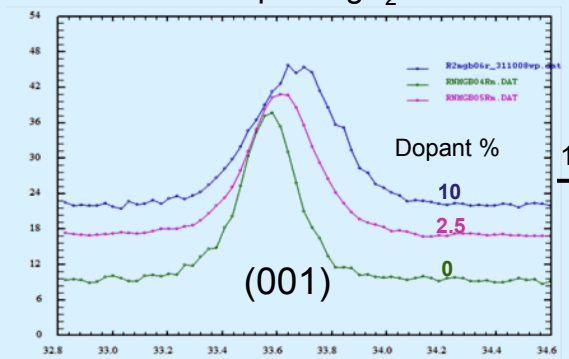
***Current Status*:** Synthesized doped-MgB_2 from Mg + B + C (dopant-level) and hydrogenated $MgB_{(2-x)}C_x$ precursor to form $Mg(BH_4)_2$ structure

Synthesis:

Mg + 2B + dopant

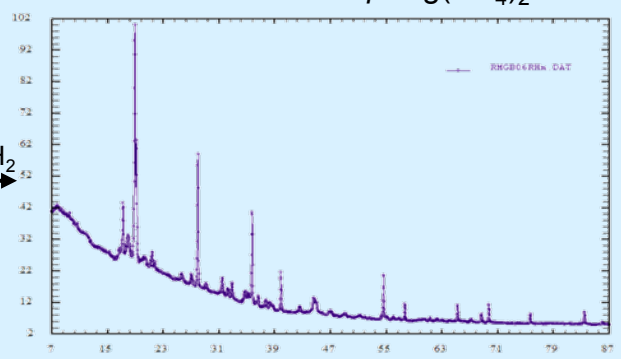
Powders milled and pressed into pellets

Argon, 720 °C



XRD confirmation of C-doped MgB_2 from (001) peak shift

15,000 psi H_2, 370 °C



XRD of 10% C-doped MgB_2 after hydrogenation showing formation of β-$Mg(BH_4)_2$

Summary: MgB_2 successfully doped with C, subsequently hydrogenated to make $Mg(BH_4)_2$

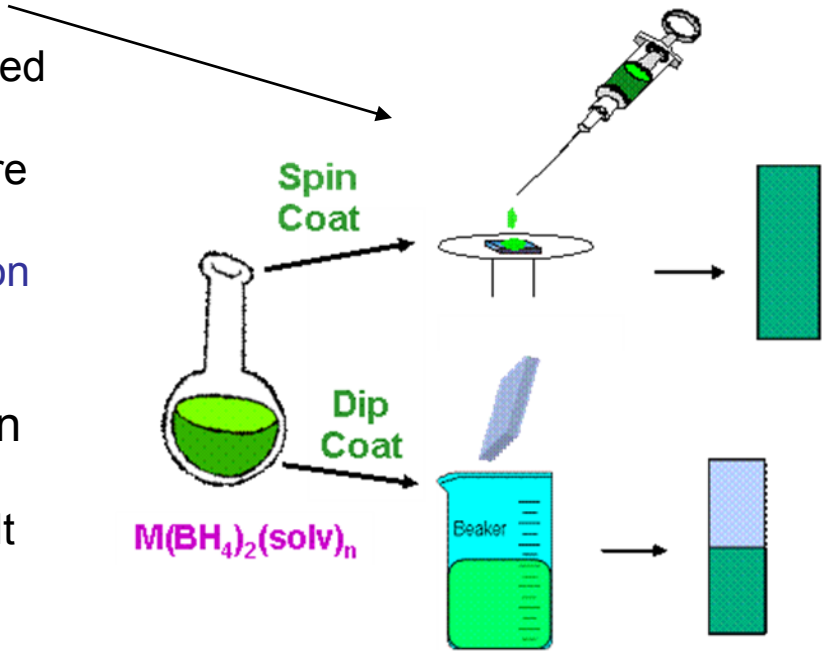
Future Work:
- Confirm the presence of carbon in $Mg(BH_4)_2$ (NMR, XPS)
- Improve the yield to measure the hydrogen capacity of C-doped $Mg(BH_4)_2$
- Doping $Mg(BH_4)_2$ with transition metals

Methods for Incorporation of Hydride Materials into NFS

Collaboration -- SNL / UTRC / Albemarle Corp.

Current Status:

- 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_2 desorption was low
- Solid-state (incipient or melting) incorporation
  - Selected three porous materials (C-aerogel, YSZ, SiO_2) and exposed to metal hydride melt
  - Used high-energy ball milling or high temperature/pressure to mix
  - $Ca(BH_4)_2$ 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)

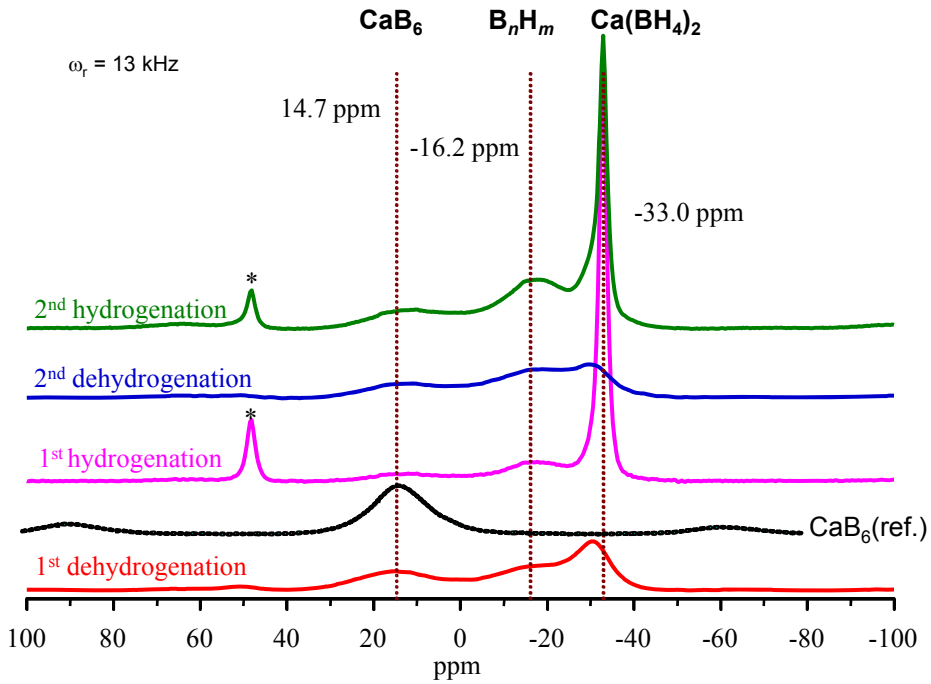
Future Work:

- *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*

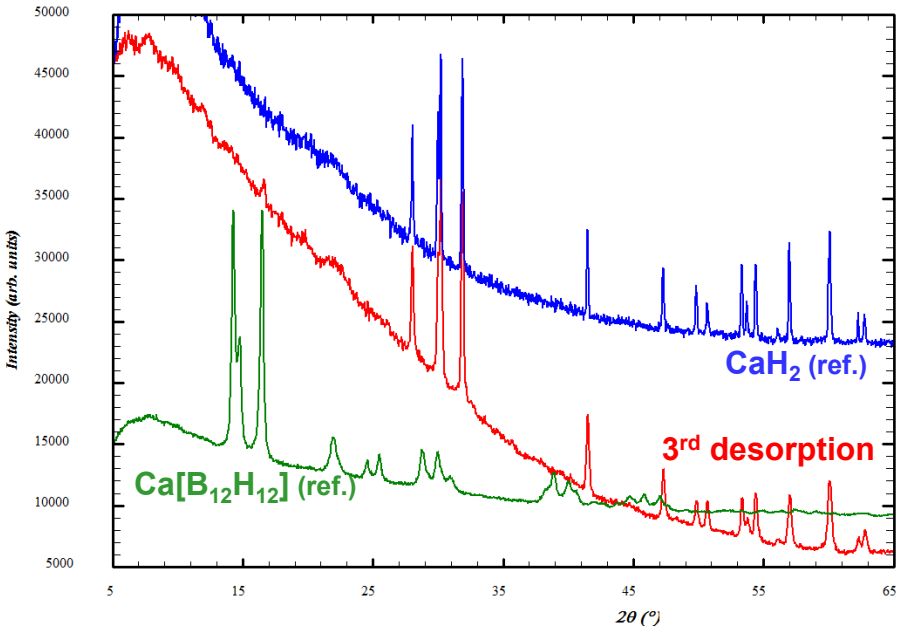
Cycling Capacity Loss of $Ca(BH_4)_2$ Due to Formation of "B_nH_m" Species

Theory predicts that $Ca(BH_4)_2$ releases H_2 to form $Ca[B_{12}H_{12}]$ upon heating

^{11}B MAS-NMR of $Ca(BH_4)_2$ with Additive-A



XRD of $Ca(BH_4)_2$ with Additive-B After 3rd Desorption



XRD indicates crystalline component is largely CaH_2 in desorbed product, while ^{11}B NMR indicates the presence of amorphous CaB_6 and "B_nH_m" species

Can $Ca[B_{12}H_{12}]$ Absorb/Release H_2?

Hydrogenation:

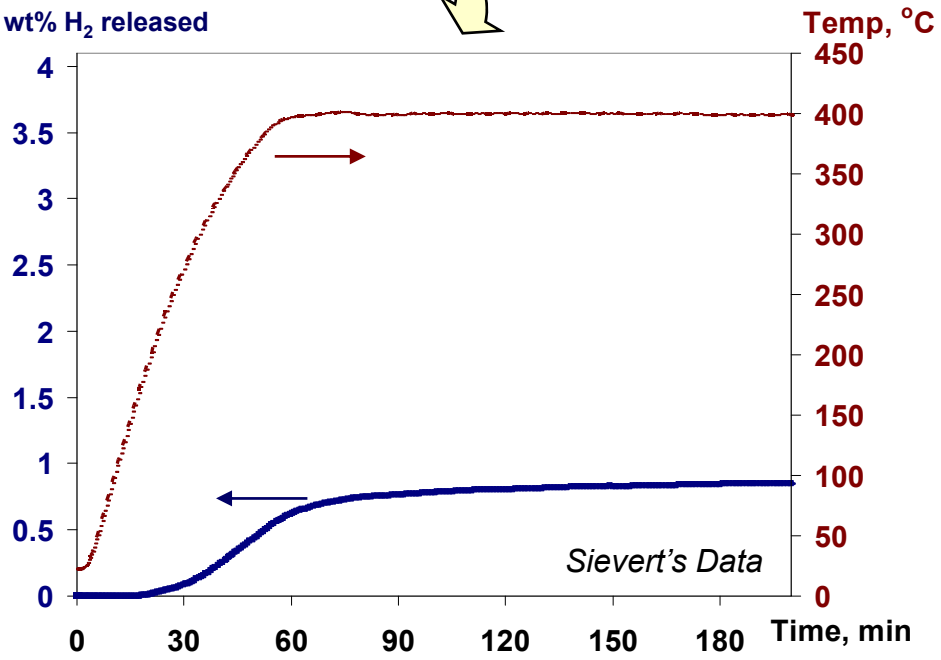
$Ca[B_{12}H_{12}] + xCaH_2 + H_2 \longrightarrow$ No reaction at 400ºC , 1000 bar H_2

$\longrightarrow$ At 450ºC, 1000 bar H_2 traces of $Ca(BH_4)_2$ form

$Ca[B_{12}H_{12}] + H_2 \longrightarrow$ No reaction at 400ºC 1000 bar H_2

Dehydrogenation:

$Ca[B_{12}H_{12}] + CaH_2$



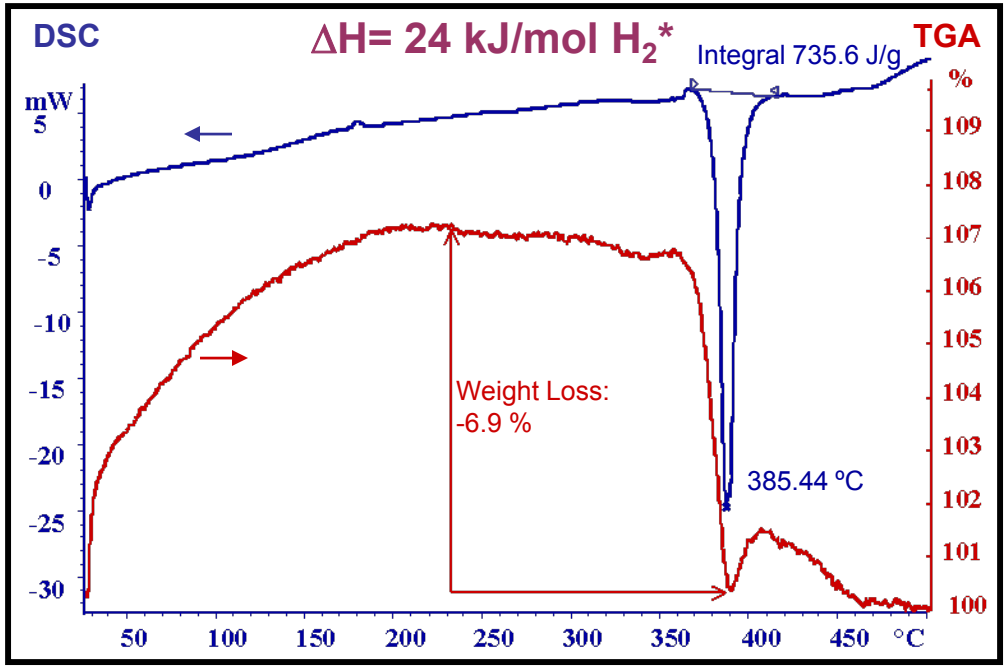
We found that $CaB_{12}H_{12}$ is kinetically stable and the formation of it would hinder $Ca(BH_4)_2$ reversibility

Enthalpy Measurements of $Ca(BH_4)_2$ Complicated by Slow Kinetics

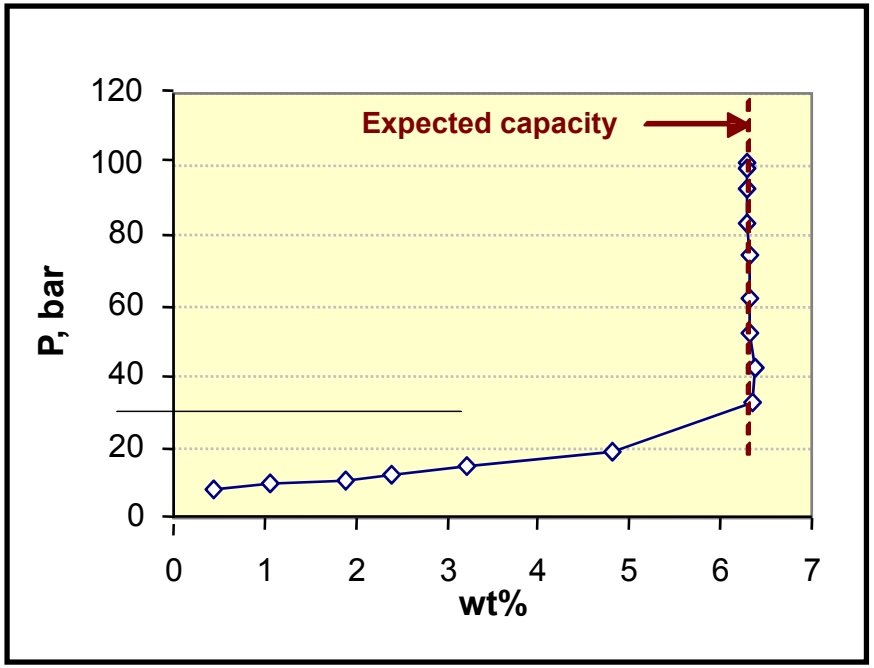
Enthalpy measurements for the decomposition have been measured using Differential Scanning Calorimetry (DSC)

Pressure-Composition-Isotherms (PCI) measurements are ongoing

TGA-DSC of $Ca(BH_4)_2$*



Desorption Isotherm at 354 °C**



*Assuming H_2 is the only gaseous species released upon heating:
$6Ca(BH_4)_2 \rightarrow CaB_{12}H_{12} + 5CaH_2 + 13H_2$ (6.3 wt% H_2)

**Ongoing measurement

STMBMS experiments confirm that H_2 is the predominant product (-- see our additional slide #39)

STMBMS*: A New MHCoE Capability to Elucidate Complex Reaction Processes

* Simultaneous thermo-gravimetric modulated-beam mass spectrometer

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

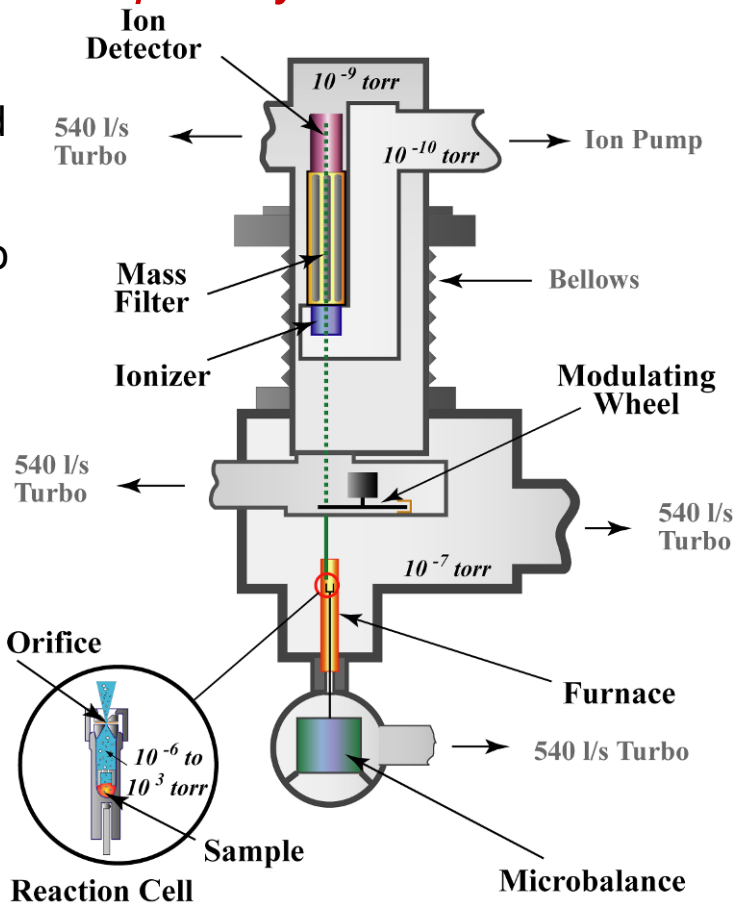
Instrument details:

- 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

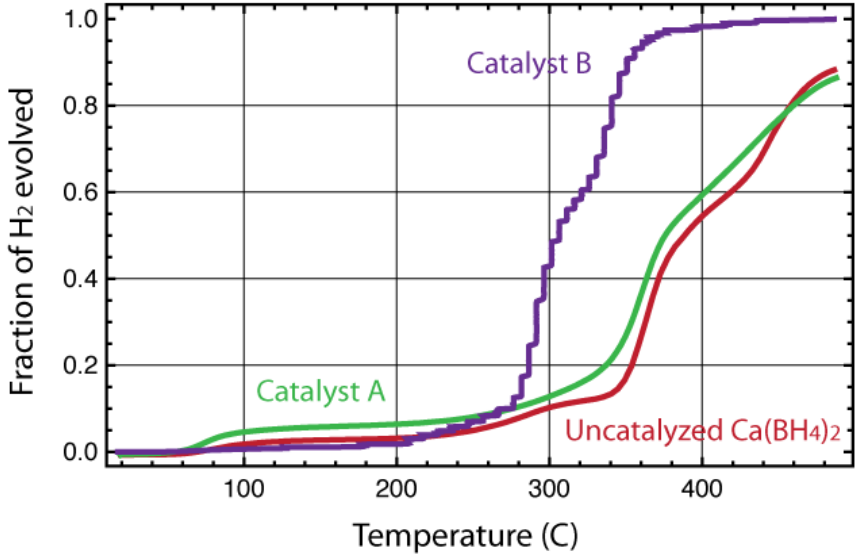


Ref: R Behrens, Jr., Review of Scientific Instruments, *58(3), p451* **(1987)**
YT Lee, *et al*, Review of Scientific Instruments, *40(11), p1402* **(1969)**

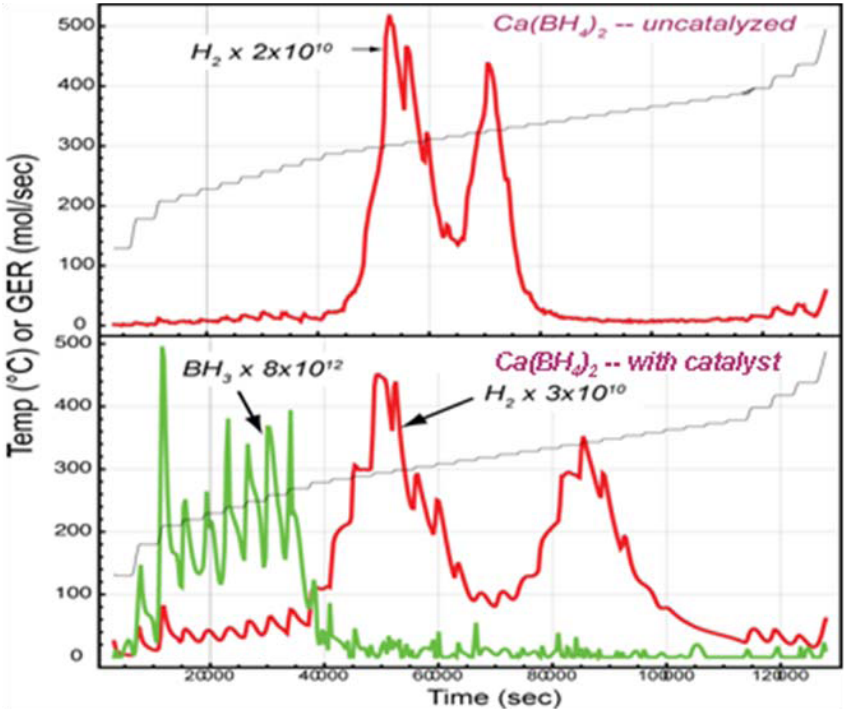
STMBMS Results of $Ca(BH_4)_2$ Gaseous Decomposition Products

- A variety of gaseous species observed during decomposition process (*i.e.* BH_3)
- Lower temperature hydrogen release observed for catalyzed-$Ca(BH_4)_2$

Fraction of H_2 Evolved from $Ca(BH_4)_2$



Gas Evolution Rate from $Ca(BH_4)_2$



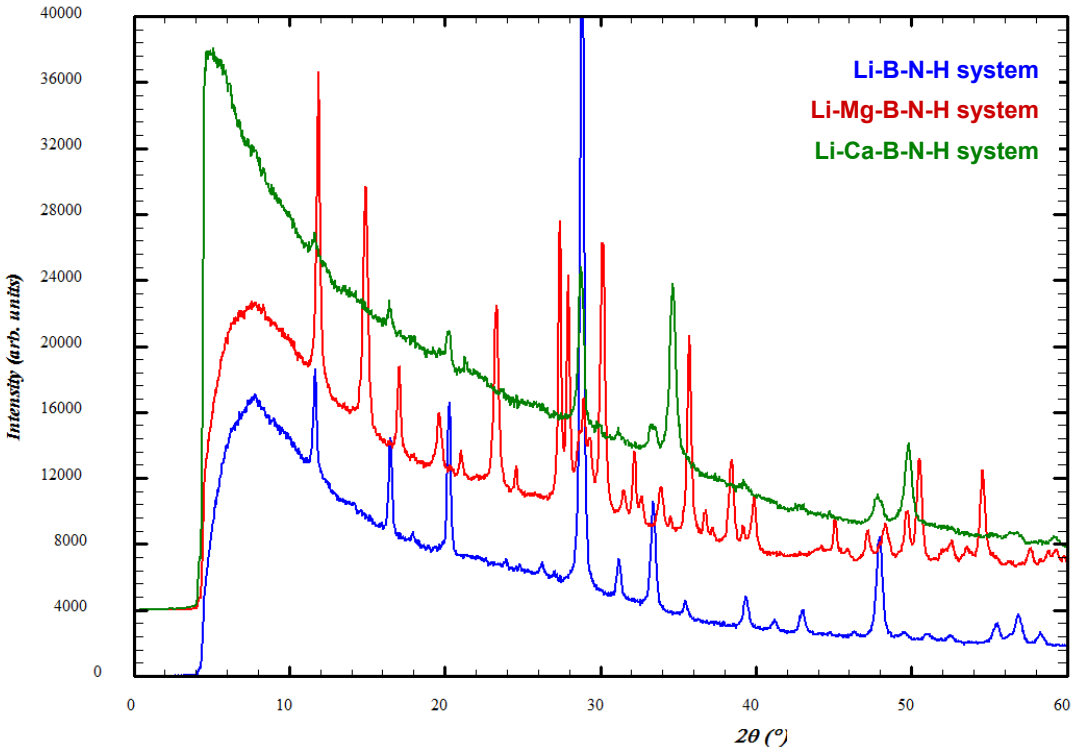
- H_2 released in multiple steps from $Ca(BH_4)_2$
- Additives modify the kinetics and increase the amount of BH_3 released (~1% of H_2 stream)

Exploration of Mixed-Anionic BH_4/NH_2 System: $AA'(BH_4)(NH_2)$

***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:



Ref: A. Sudik, *et al., J. Phys. Chem. C*, *112*, *p*4384 **(2009)**

- XRD indicates that the starting materials, $M(BH_4)_x$ and $M'(NH_2)_y$, are no longer present and new phases form
- Raman spectroscopy indicates the presence of $(BH_4)^-$ and $(NH_2)^-$ anions, ~2300 and ~3250 cm^{-1}, respectively

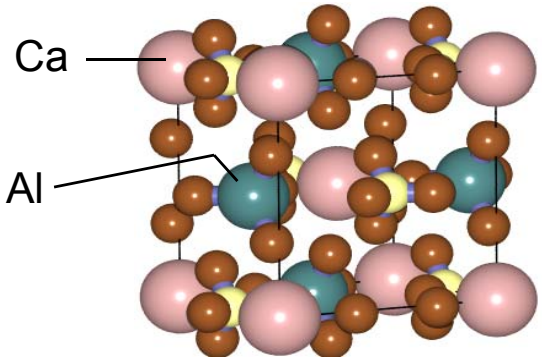
Characterization of hydrogen storage properties is on-going

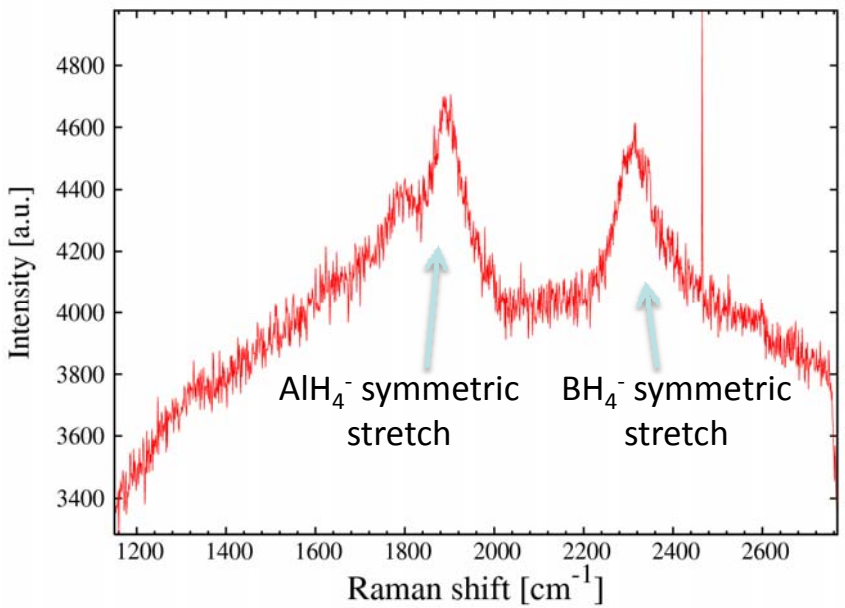
Exploration of Mixed-Anionic AlH_4/BH_4 System: $Ca(AlH_4)(BH_4)$

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

- Synthesis: $LiAlH_4 + LiBH_4 + CaCl_2 \rightarrow Ca(AlH_4)(BH_4) + 2\ LiCl$
- XRD indicates no $LiBH_4$ or $LiAlH_4$
- Raman spectroscopy indicates (BH_4) , (AlH_4) anions present in product
- Initial studies show no reversibility at 200°C, 65 bar H_2 pressure, experiments ongoing

Predicted high symmetry structure





$M(AlH_4)/(BH_4)$ are promising new hydrogen storage materials