DOE Hydrogen Program

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

Ewa Rönnebro and Eric Majzoub

Sandia National Laboratories

June 12, 2008

Project ID#ST36

Sandia Program Overview

Timeline

- Project started in March '05
- Project end ~ 2010
- Percent complete 60%

SNL R&D Budget

- $1.96M in FY '07
- $2.01M in FY '08

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

Barriers

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

MHCoE Partners

Caltech, ORNL, JPL, UNR, Stanford, UIUC, Utah, UH, PITT, SRNL, HRL, CMU, GE, NIST, BNL, Intematix, UTRC, UNB

Collaborators

V. Ozolins (UCLA), K. Yvon (U. Geneva), J. Herberg (LLNL), Y. Filinchuk (ESRF) C. Wolverton (Northwestern)

Sandia Team (~ 6 FTEs):

Technical POC (and MHCoE Director): Lennie Klebanoff

Core Technical Team

Ewa Rönnebro: ***Proj. B POC, new materials***
Eric Majzoub: ***PEGS theory, experiments (Sandia/UMSL)***
Mark Allendorf: ***Theory, Theory Group Coordinator***
Tony McDaniel: ***High-throughput screening***
Ethan Hecht***: High-throughput screening***
Mutlu Ulutagay-Kartin (since 12/07)
Vitalie Stavila (since 1/08)

Ph.D. Students

Godwin Severa: U. Hawai'i

Rebecca Newhouse, Leo Seballos: UC Santa Cruz

Other Key Contributors

Bob Bastasz, Tim Boyle, Andy Lutz, Bill Houf

Discovering New Complex Hydride Materials

Experimental

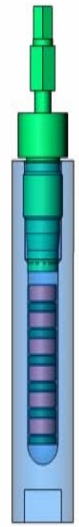
- **Established a synthesis route that combines high-energy milling followed by hot-sintering under high H_2-pressures:**

  Metal + Binary Hydride + H_2 → Complex Hydride

  Boride + Binary Hydride + H_2 → Metal Borohydride

  (Normal run: P < 700bar, T < 450°C)

- **New Start (7/1/2007): Improving kinetics, cycling life and desorption properties by incorporation of hydride materials in nanoframeworks. Teaming with UTRC (lead)**



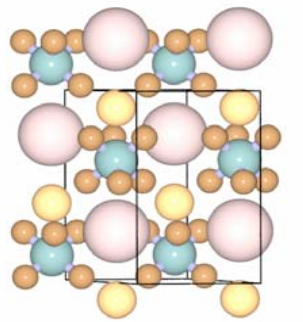
6 sample HP-autoclave

Theory

- **The Prototype Electrostatic Ground State (PEGS) technique for structure determination and ΔH estimates**

- **Provide MHCoE partners with theoretical support**

  -- provide Al-N bond energies for AlH_3 regeneration studies (BNL).



MC Structure

Synthesis Status 3/2007 and Focus Since

Status in March 2007:

- $Ca(BH_4)_2$ partially reversible at 700bar and 400-450°C
- New compounds found in the ternary Ge and Mn systems, but H-content too low
- Theory predicted bialkali borohydrides

Focus during FY07/FY08:

- Focus on re-hydriding $Ca(BH_4)_2$ at lower P and T
- Synthesis of PEGS-predicted bialkali borohydrides
- Re-hydriding low-temperature borohydrides utilizing our high-pressure capability. Teaming with Craig Jensen (UH) (in additional slides)

$Ca(BH_4)_2$ as H-storage Material

Motivation: In FY06, theory predicts $Ca(BH_4)_2$ has nearly ideal thermodynamics ($\Delta H \sim 40$ kJ/mol H_2), 9.6 wt. %

Ozolins, Majzoub and Wolverton, in preparation

Status 3/07:

$$CaB_6 + 2CaH_2 + 10\ H_2 \rightarrow 3Ca(BH_4)_2 \text{ @700bar, 400°C, 48hours}$$

- Starting with anticipated decomposition products implies reversibility
  -- *Ewa Rönnebro and Eric Majzoub, J. Phys. Chem. B, **111** 12045 (2007)*

This year:

What is the decomposition reaction mechanism?

Can $Ca(BH_4)_2$ be re-hydrided at lower pressures and temperatures?

✓ Partial reversibility observed during in situ synchrotron studies at Brookhaven by Job Rijssenbeek, Yan Gao, Ewa Rönnebro, J.-C. Zhao, unpublished data (2007)

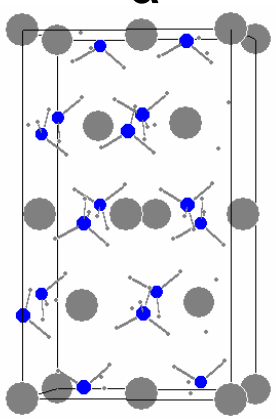
✓ Partial reversibility of 3.8 wt% at 350°C and 90 bar reported from TGA by *J.H. Kim et al, Scripta Materialia, **58**, 481 (2008)*

Identified Crystal Structures of α , α', β $Ca(BH_4)_2$ Polymorphs

***In-situ* synchrotron data from ESRF,** $Ca(BH_4)_2$ made by desolvating an Aldrich sample

$$(\alpha\ ,\ \beta) \xrightarrow[160\ °C]{} (\alpha',\ \beta) \xrightarrow[350\ °C]{-H_2} \text{desorption products}$$

α

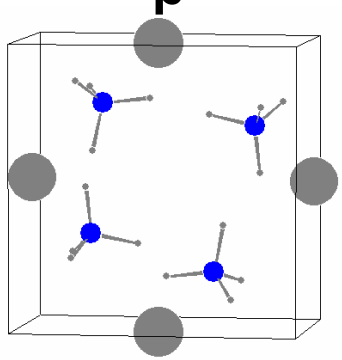


Ca

BH_4

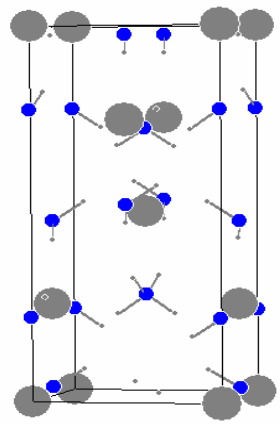
α → α' at ~160°C

β



β-phase does *not* transform into α', and decomposes at 350°C to release H_2

α'



α'-phase forms above 160°C. Decomposes at 350°C to release H_2

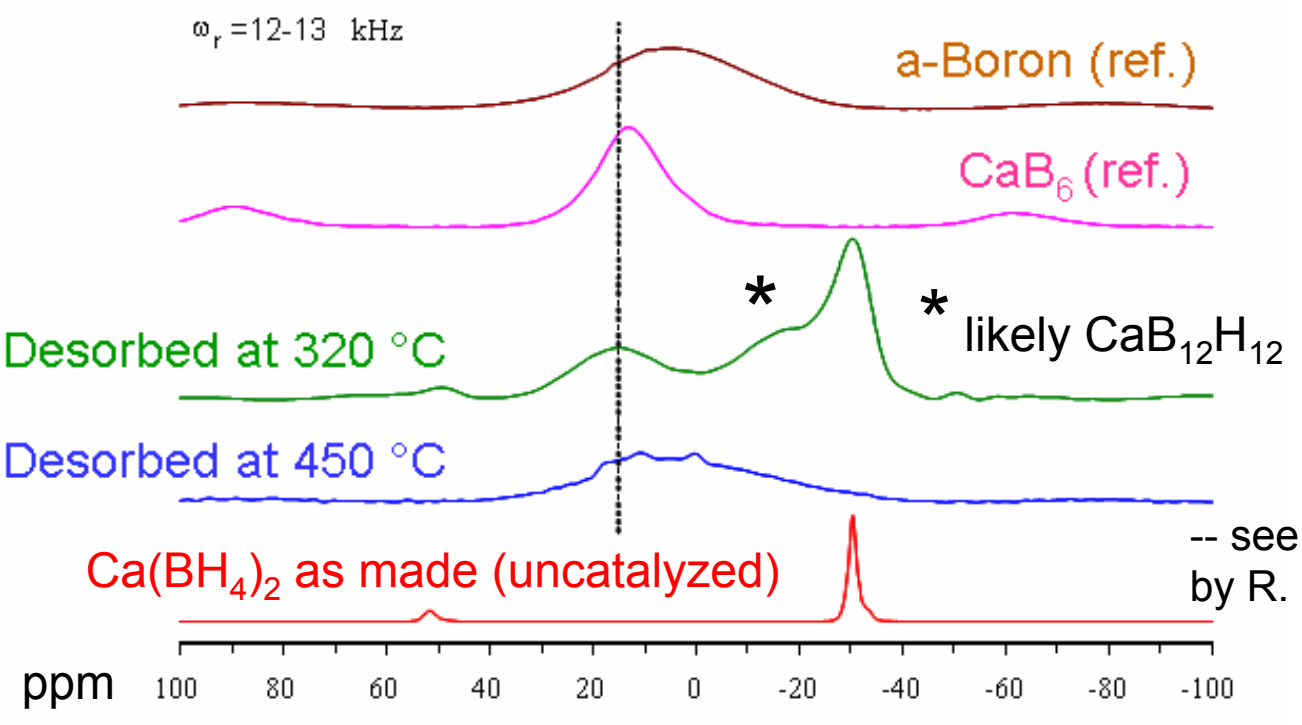
The polymorphs have different stability depending on temperature, and can be manipulated with additives

Also see ST37 D. Chandra, U. Nevada-Reno

Y. Filinchuk, E. Rönnebro, D. Chandra, submitted

^{11}B MAS-NMR Reveals $Ca(BH_4)_2$ Decomposition Products

- Desorption at 320 °C leads to CaB_6 and CaH_2
- Desorption at 450 °C leads to CaB_6 and probably a-B



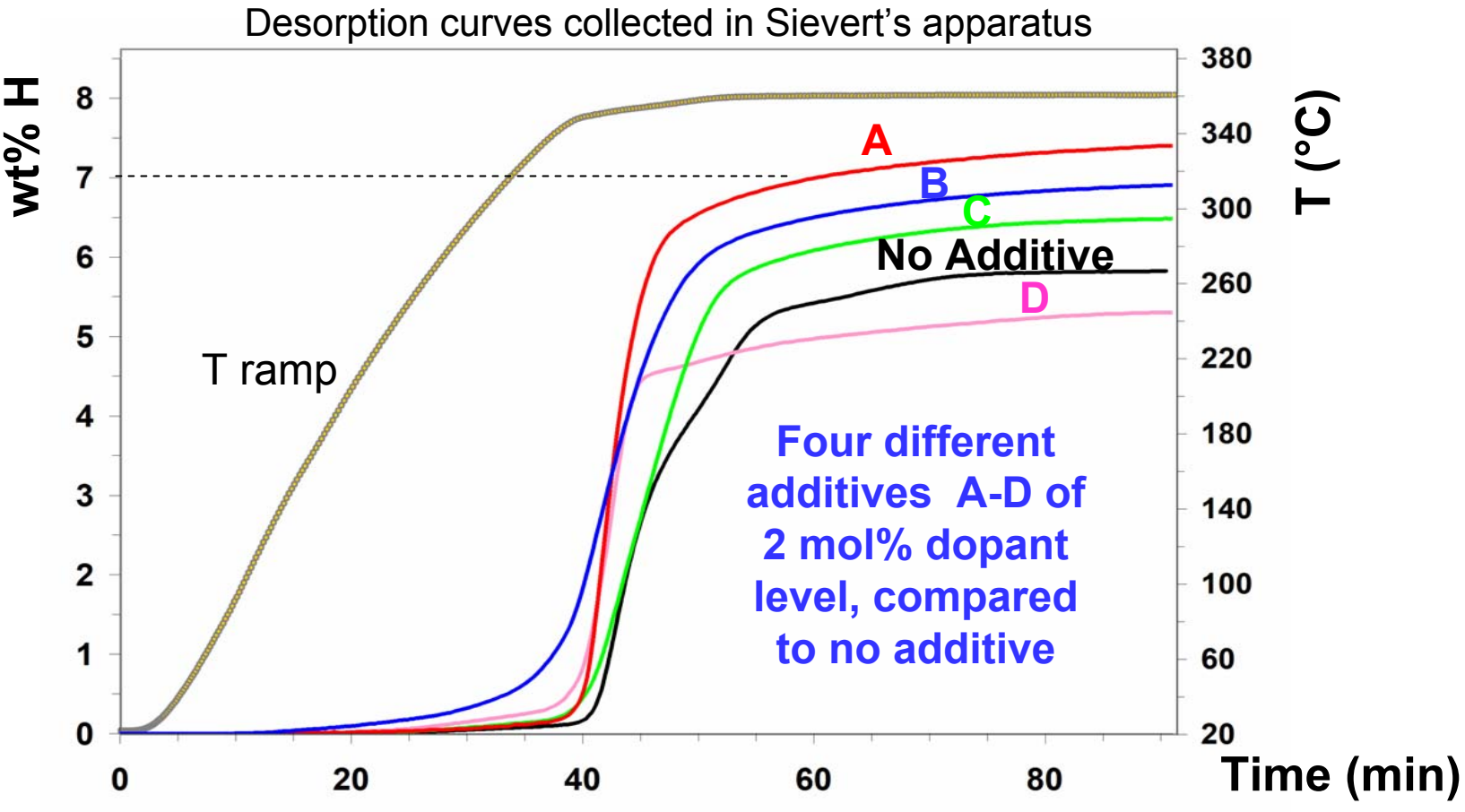
Hwang, Bowman, Kim, Reiter, Zan, Rönnebro

-- see more details in ST34 by R. Bowman, JPL

Confirmed decomposition products, and found intermediate species

Investigated Effect of Additives on Desorption Kinetics of $Ca(BH_4)_2$

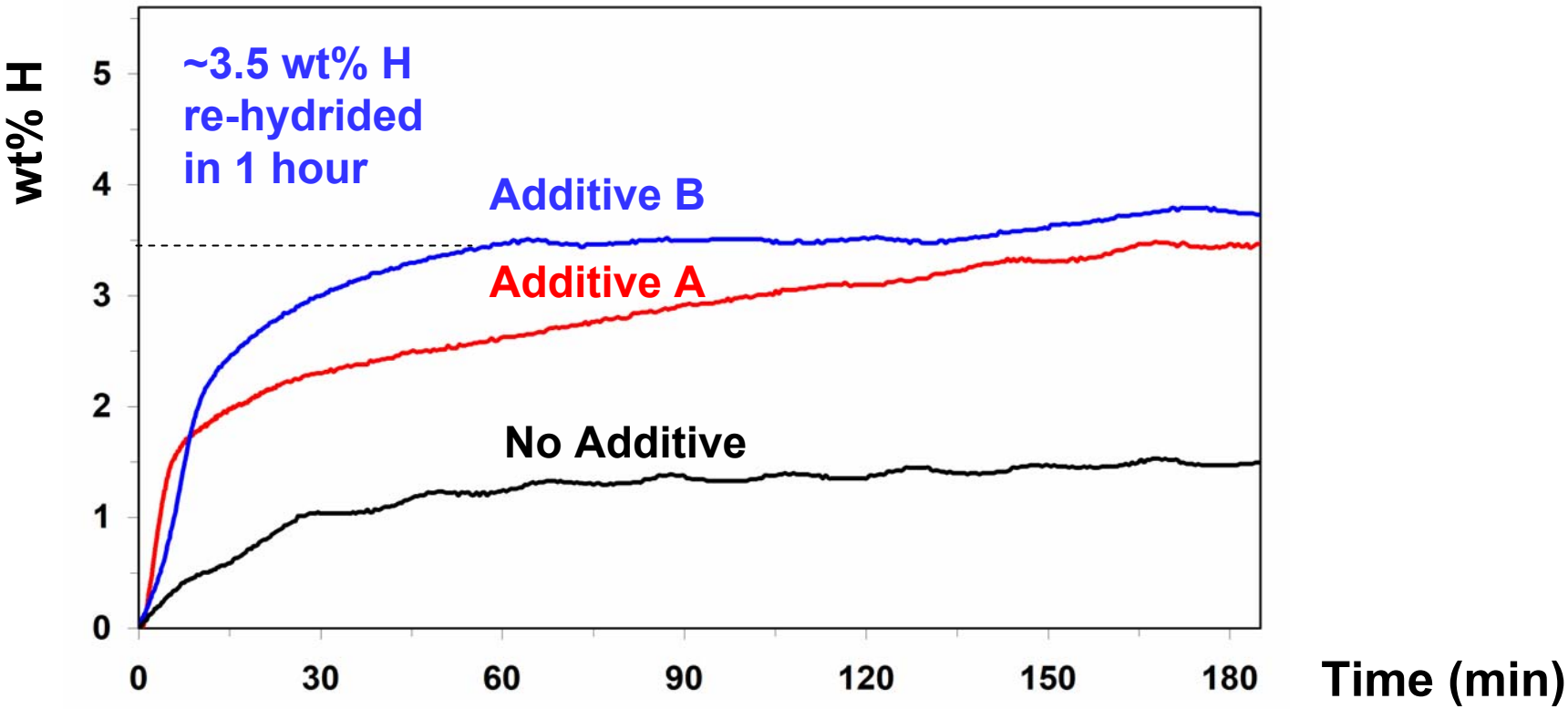
Additives change desorption kinetics and released H_2



~7 wt. % H rapidly desorbed at 360 °C

Additives Aid Reversibility of $Ca(BH_4)_2$ at lower P and T

Re-hydrided at 350°C and 120 bar to ~4.5wt% (A) in 12 hours



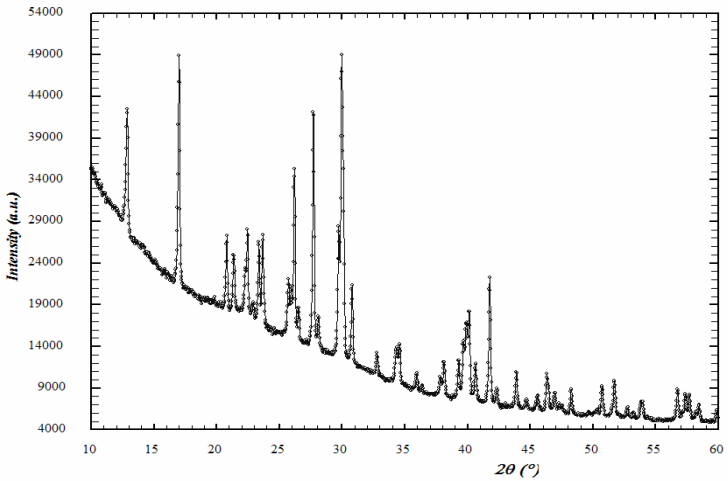
3x improvement in hydrogenation kinetics with additives

Ewa Rönnebro, Vitalie Stavila, Mutlu Ulutagay-Kartin, manuscript in progress

New $LiK(BH_4)_2$ Synthesized

Motivation: **Improving thermodynamics by changing cationic matrix**

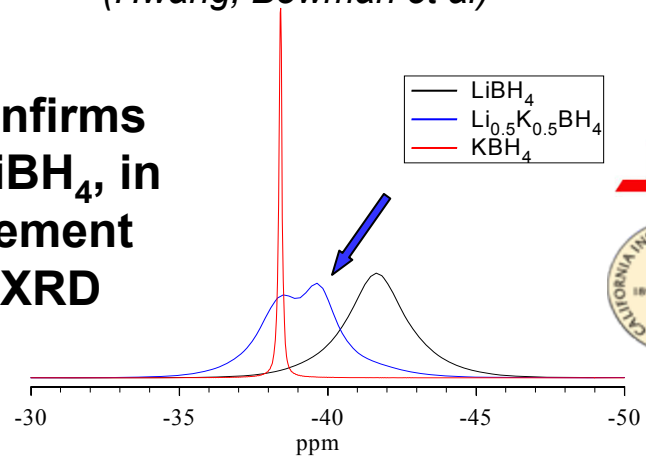
Ball Milled: $LiBH_4 + KBH_4 \rightarrow LiK(BH_4)_2$ (10.6 H wt.%)



Nuclear Magnetic Resonance

(Hwang, Bowman et al)

-- Confirms no $LiBH_4$, in agreement with XRD



- XRD shows new phase plus ~10% KBH_4, no $LiBH_4$
- Stable orthorhombic structure calculated as low-energy structure

- TGA did not show H_2 evolution below 500°C

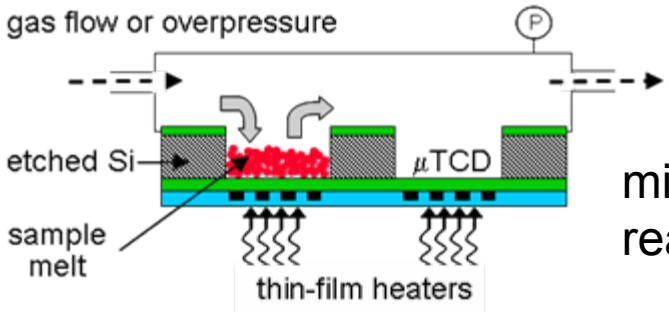
∴ **Do Not Pursue Further**

Synthesis of $LiK(BH_4)_2$ reported by P. Edwards et al, ISHE, Richmond, VA, 2007

Working to Establish High-Throughput Screening Capability

High-Throughput Screening (HiTS) of Catalysts

Tony McDaniel
Mutlu Ulutagay-Kartin
Ethan Hecht



microhotplate reactor

Completed Initial Proof of Principle Experiments using micro-hotplate reactors:

- ✓ Demonstration of in-situ calorimetry, H_2 cycling diagnostics
- ✓ Synthesis of $NaAlH_4$ from ball-milled Al + NaH precursors + H_2
- ✓ In-situ demonstration of $NaAlH_4$ catalysis by Ti

- ✓ Developed software architecture required for combinatorial work

Solved problems associated with hotplate reliability, but other hardware reliability issues emerged when examining higher T materials.

Not operational. DOE/MHCoE Coordinating Council reviewed options for materials screening, decided to pursue other methods. ∴ HiTS discontinued.

Experimental Milestones FY07&FY08

Month/year	Milestone or Go/No-Go decision
Mar-08 ✓	Milestone: Show reversibility of $Ca(BH_4)_2$ at lower pressures and temperatures. **Accomplished.**
Mar-08 X	Milestone: Acquire data on new materials and catalyst searches with HiTS methodology. **Not accomplished, activity discontinued**
Sep-08	Milestone: Complete Pressure-Composition-Temperature isotherms for $Ca(BH_4)_2$ to determine reaction enthalpy
Mar-09	Go/no-go on $Ca(BH_4)_2$: Characterize and improve $Ca(BH_4)_2$ kinetics properties with additives (Teaming with JPL, Caltech, NIST) Milestone: Discover new borohydride related materials (Teaming with U. Ohio and U. Utah)
May-09	Milestone: Lowering of $Ca(BH_4)_2$ desorption temperature Go/no-go on $AkTm(BH_4)_x$: Reversibility of alkali transition metal borohydrides (Teaming with U. Hawaii)
Sep-09	Milestone: Incorporation of hydride material in catalyzed nanoframeworks (Teaming with UTRC)

Theory Status 3/2007 and Focus Since

Status in March 2007:

- Validated PEGS method with known compounds
- Predicted stable bialkali borohydrides with PEGS

Focus during FY07/FY08:

- Predicting structures and thermodynamics of $Ca(BH_4)_2$, $NaK(BH_4)_2$, and other promising compounds
- Quantitative evaluation of PEGS versus ICSD
- Explore use of PEGS with alkali-transition metal borohydrides such as $LiSc(BH_4)_4$ (teaming with JPL and Caltech)
- Use quantum chemical methods to calculate bond energies of alane complexes (in support of BNL AlH_3 regeneration studies)

Crystal Structures For Materials Discovery Using PEGS or Database Searching

PEGS* - Prototype Electrostatic Ground States

- Global optimization of electrostatic energy
- Potential energy smoothing
- Model anions as rigid units

Database searching

- Few hits for some compounds
- A new material may have a new crystal structure

*Majzoub & Ozolins, Phys. Rev. B, **77**, 104115 (2008)

First-principles density functional theory (DFT) is used for accurate energies and thermodynamics calculations

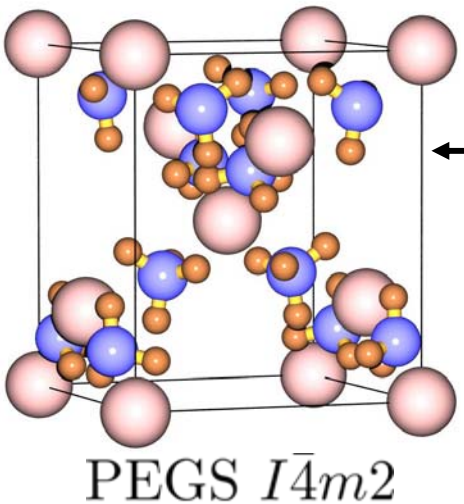
PEGS provides high-quality structures using the basic physical principles governing atomic interactions in complex hydrides

PEGS Method Produces Best Candidate for $Mg(BH_4)_2$ Ground State

Experimental $Mg(BH_4)_2$ Crystal Structures

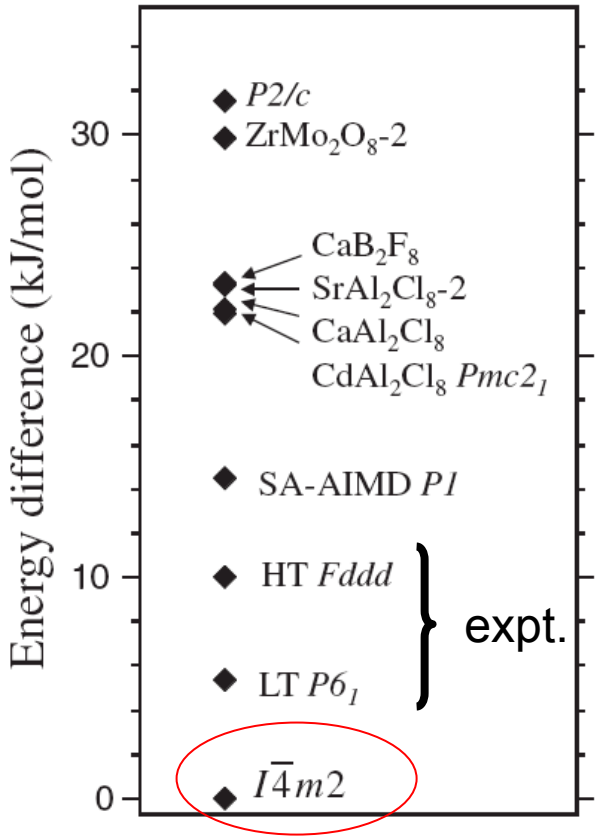
LT $P6_1$, 30 f.u./conv cell
HT *Fddd*, 64 f.u./conv cell

*Her et al, Acta Cryst, **B63,** 561 (2007)*



← **PEGS prediction LT $I\bar{4}m2$**
4 f.u. primitive cell

V. Ozolins, E. H. Majzoub, C. Wolverton
*Phys. Rev. Lett. **100**, 135501 (2008)*



- PEGS structure implies metastability of synthesized $Mg(BH_4)_2$
- Preferred decomp: $Mg(BH_4)_2$ ➔ 1/6 $MgB_{12}H_{12}$ + 5/6 MgH_2 + 13/6 H_2

($MgB_{12}H_{12}$ also predicted with PEGS method)

PEGS Predicts Weakly Metastable $NaK(BH_4)_2$

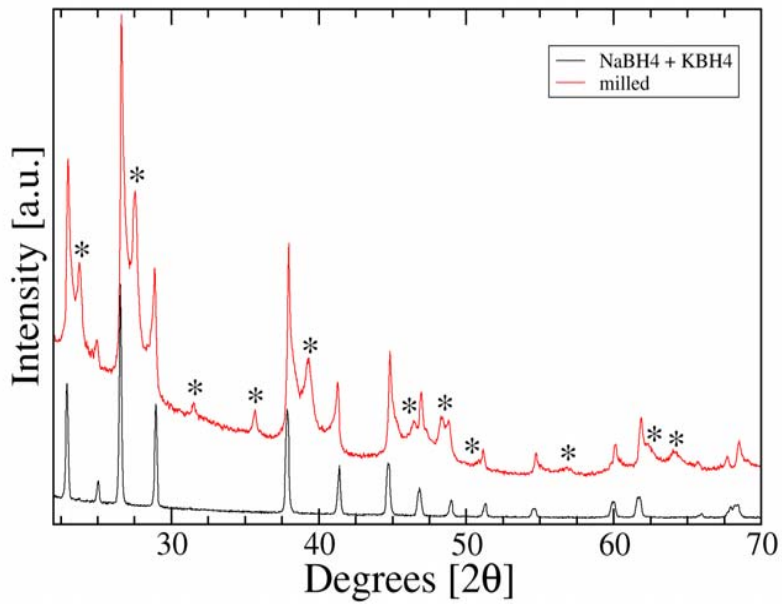
PEGS provides *several* high-symmetry candidates that may be observed as polymorphs

Space Group		$E-E_0$ [meV/f.u.]
146	$R3$	+110
148	$R\bar{3}$	+80
156	$P3m1$	+76
166	$R\bar{3}m$	0.0

$NaK(BH_4)_2$ predicted to be mildly unstable

(-3kJ/mol at T = 0K) No ZPE included!

- ✓ $NaK(BH_4)_2$ synthesized
- ✓ XRD confirms predicted new phase (metastable)



MAS NMR indicates new chemical environment for Na and K.

∴ New compound formed

J. Herberg, LLNL

PEGS Finds High-Symmetry Candidate for $LiSc(BH_4)_4$

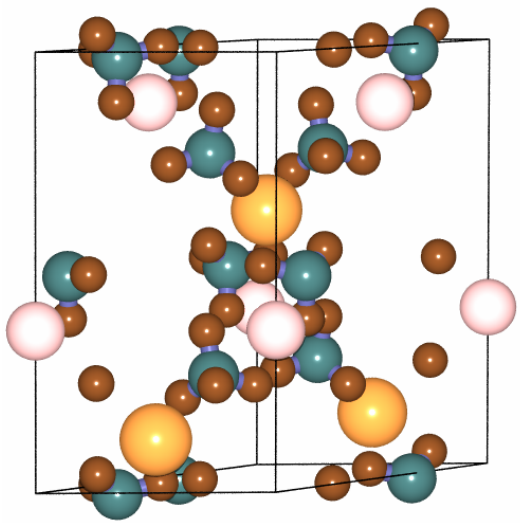
Ball milled: $ScCl_3 + 4LiBH_4 \rightarrow LiSc(BH_4)_4 + 3LiCl$ (14.5 H wt. %)

Rxn takes place, but:

- X-ray diffraction inconclusive on structure
- NMR indicates new phase
- ICSD search has very few structure candidates

Hwang, Bowman

PEGS Structure for $LiSc(BH_4)_4$



PEGS structure stable against several decomposition reactions:

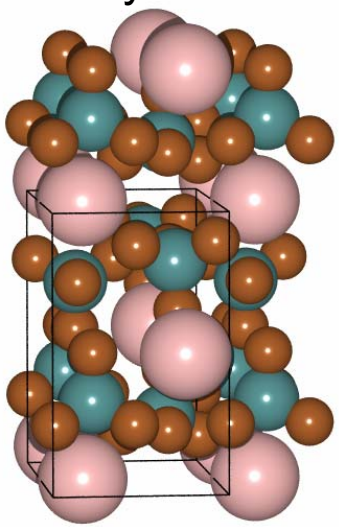
$$LiSc(BH_4)_4 \xrightarrow{x} LiBH_4 + Sc(BH_4)_3$$

$$LiSc(BH_4)_4 \xrightarrow{x} LiBH_4 + ScH_2 + 3B + 5H_2$$

PEGS applicable to transition metal borohydrides with some covalent character

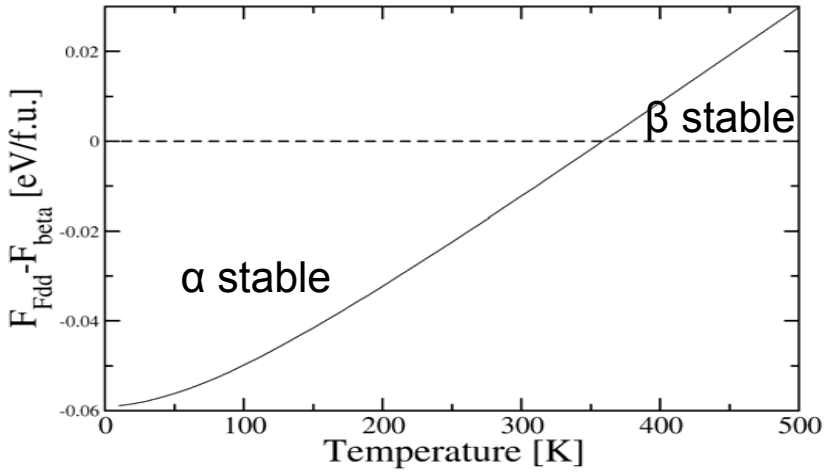
PEGS $Ca(BH_4)_2$ Search Explains Experimental Observations

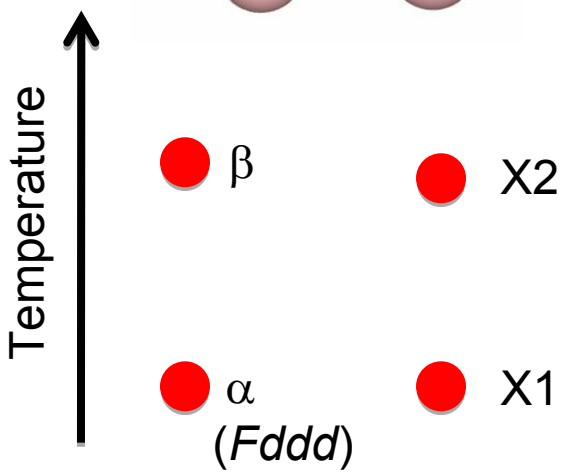
PEGS-structure of β-$Ca(BH_4)_2$
Confirmed by Rietveld refinements



Preliminary calculation shows α-to-β transition

Temperature dependence of α and β polymorphs



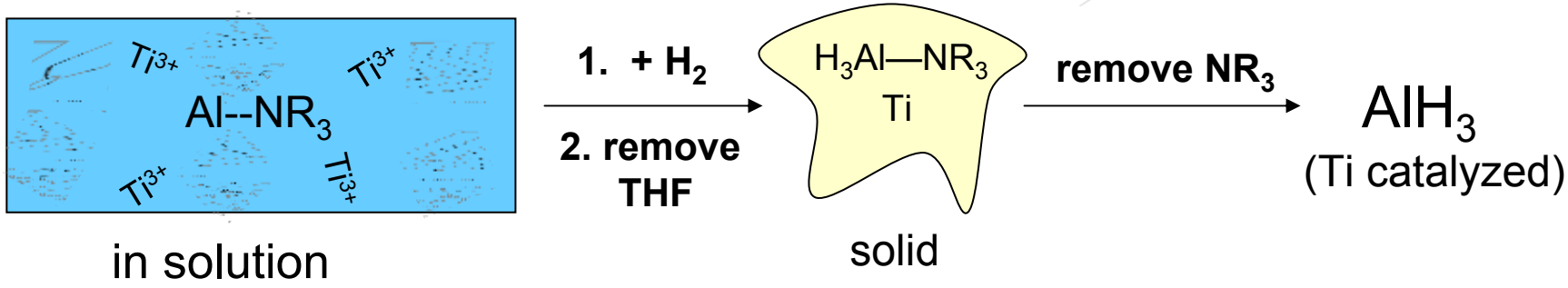


- PEGS finds four high-symmetry structures for $Ca(BH_4)_2$
- All appear to be observed in X-ray diffraction – new polymorphs!
- Rietveld refinements indicate we have found the correct beta phase structure

E. Majzoub and E. Rönnebro, manuscript submitted

Found Promising Adducts for Liquid-phase Alane Regeneration

A MHCoE collaboration between SNL and BNL



We need accurate $H_3Al—NR_3$ complexation energies to optimally choose NR_3

Our solution: Bond Additivity Correction Methods

- Sandia in-house codes based on Gaussian 03 suite
- Corrects systematic errors in computed energies
- More accurate than DFT/B3LYP
- Chemical accuracy (± 1 – 2 kcal/mol for heats of formation)
- Provides temperature-dependent thermodynamics

Comparison of BAC methods with standard DFT used by chemists

Method	Avg. error	Test set (heats of formation)
BAC-MP4	**1.25**	**93 species**
BAC-G2	**0.69**	**143 species**
DFT/B3LYP	**3.11**	**148 species**

*kcal/mol

Pyridine, Pyrazine Are Promising Adducts

TEDA-bound AlH_3 is too stable – what other amines to try?

Computed Al-N complexation energies (BAC-MP2), kJ/mol at 298 K

1:1 Complexes	Al-N BDE	1:2 Complexes	Al-N BDE
$AlH_3.NMe_3$	**147.6** (108.1)	$AlH_3.2NMe_3$	**217.9** (145.9)
$AlH_3.NEt_3$	**118.6** (89.1)	$AlH_3.2NEt_3$	**158.7** (90.9)
AlH_3.TEDA	**156.3** (115.4)	AlH_3.2TEDA	**233.8** (155.4)
AlH_3.Quinuclidine	**159.9** (118.4)	AlH_3.2Quinuclidine	**236.7** (156.0)
AlH_3.pyridine	**135.2** (109.2)	AlH_3.2pyridine	**193.3** (142.1)
AlH_3.pyrazine	**125.3**	**$(AlH_3)_2$.pyrazine**	**110.4**

BAC trends agree with DFT (McGready et al.)

Red: BAC-MP2; Blue: DFT/B3LYP (McGready et al.)

- 2:1 complexes (e.g. **$(AlH_3)_2$ • pyrazine**): significantly less stable
- 1:2 decomposition kinetics determined by Al-N bond in 1:1 complex

Computations of Al-O BDE are underway

Theory Milestones FY07&FY08

Month/year	Milestone or Go/No-Go decision: PEGS Theory
Apr-08 ✓	Milestone: Complete $Ca(BH_4)_2$ polymorph structure determination and first-principles-calculated reaction pathways. **Accomplished**
Sep-08	Milestone: Begin extension of PEGS method to nanoparticle hydrides
Mar-09	Go/no-go: Search for *mixed-anion* materials with large wt. % H
May-09	Go/no-go: Determine accuracy of PEGS method in nanoparticle energetics

Month/year	Milestone or Go/No-Go decision: Al-Adduct Theory
May-08 ✓	Milestone: Complete BAC calculations of alane-amine complexes. **Accomplished**
Sep-08	Milestone: Complete BAC calculations on alane-adduct complexes
Dec-08	Go/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

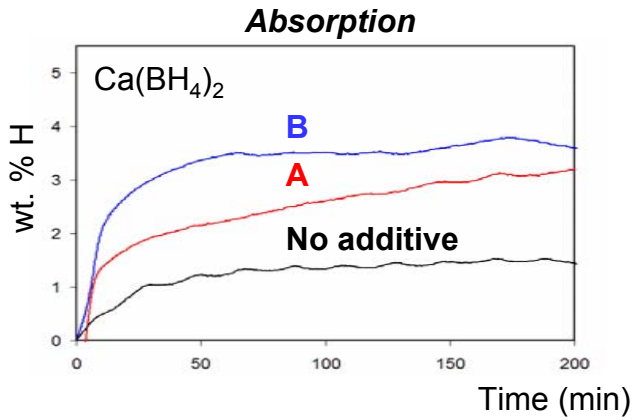
Summary FY2008 Accomplishments

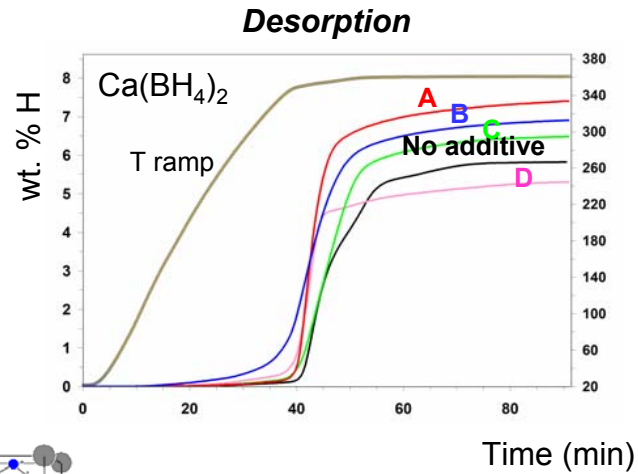
Calcium Borohydride

- Showed partial reversibility at lower P and T: 100 bar and 350°C

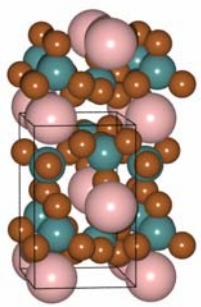
- Showed drastic improvement in kinetics by choosing right additives

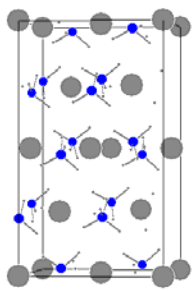
- Elucidated crystal structures of polymorphs using a combined theoretical/experimental approach, i.e. the PEGS-method and the Rietveld-method





PEGS structure for β-$Ca(BH_4)_2$



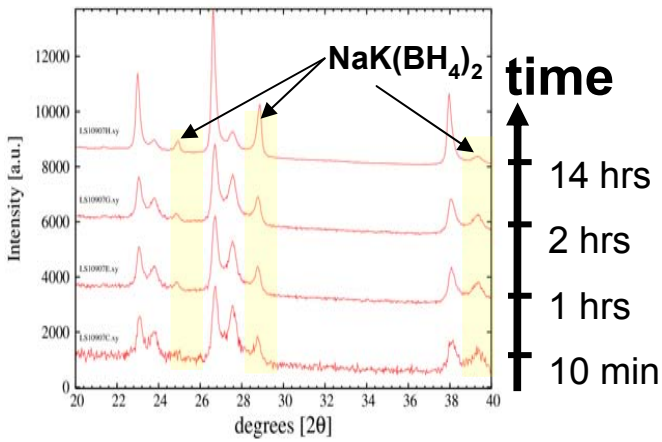


XRD α-$Ca(BH_4)_2$

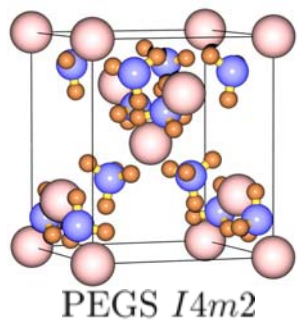
Summary FY2008 Accomplishments Cont'd

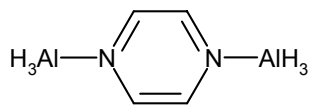
New Hydrogen Storage Materials

- Synthesized $LiK(BH_4)_2$, do not pursue further due to poor thermodynamics
- Synthesized PEGS-predicted $NaK(BH_4)_2$, do not pursue further due to instability
- Re-hydrided high-capacity material by teaming with U. Hawai'i on low-temperature borohydrides, utilizing our HP-station
- Predicted lowest-energy structure and decomposition products for $Mg(BH_4)_2$
- Showed that PEGS can provide transition metal borohydride structures
- Found promising adducts for liquid-phase AlH_3 regeneration based on bond-energy calculations

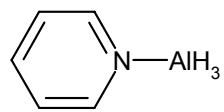


$Mg(BH_4)_2$





$(AlH_3)_2$•pyrazine



AlH_3• pyridine

Future Work in FY2008

Borohydrides

- Determine ΔH, improve kinetics and cycle life of $Ca(BH_4)_2$
- Synthesize borohydrides predicted by PEGS method
- Discover new borohydride related materials (teaming with U. Hawai'i, Ohio State and U. Utah)

Nano-structured hydrides and catalyzed nanoframeworks

- Incorporate $Ca(BH_4)_2$ into catalyzed nanoframeworks (with UTRC)
- Investigate kinetic improvements
- Synthesis of nanostructured complex hydrides

Theory

- Predict new materials with a variety of complex anions (N_nH_n, B_nH_n, etc.)
- Resolve xtal structures of polymorphic hydrides (e.g. $Mg(BH_4)_2$, $Ca(BH_4)_2$)
- Continue Al-adduct theoretical studies to optimize AlH_3 regeneration

Future Work in FY2009

Borohydrides

- Synthesize borohydride-related materials and explore their reversibility based on theoretical predictions. Continue optimizing performance of calcium borohydride and other materials

Theory

- Theory will continue guiding experiment and predict stable structures in promising systems, continue coordination of MHCoE Theory Group

Nanoengineering

- Incorporation of hydride materials in catalyzed nanoframeworks
- Explore possibilities to design alternative nanostructured metal hydrides to improve hydrogen storage properties

hydride incorporation into nanoframeworks