International Symposium on Metal Hydride Systems, MH2008, Iceland, June 24-28

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Discovery and Development of Metal Borohydrides: Calcium Borohydride, New Bialkali-and Transition Metal Borohydrides

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Sandia National Laboratories

June 24, 2008

Contributions from…

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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.

MHCoE Objectives

Research, develop and validate reversible on-board metal hydride storage materials and systems that meet the 2010 DOE system targets for hydrogen storage, with a credible path forward for meeting the 2015 DOE storage targets

Approach to Technical Targets

H Capacity: 2010 System Targets: 6 wt. %, 45gH_2/L vol. density

- Synthesize and characterize hydride materials with high hydrogen capacity and favorable thermodynamics. Use state-of-the-art theory to guide materials discovery effort.

Charge/Discharge Rates: 2010 Sys. Target: 3 min. system fill (5kg)

- Develop materials that are fully reversible, catalysts that aid reversibility, assess nanoengineering promotion of kinetics, and investigate role of contamination on reaction rates

Hydrogen Purity (from Storage) : 2010 Target: 99.99% pure

- Assess release of NH_3, B_2H_6 and other volatile species from metal hydrides during desorption and cycling

Cycle Life: 2010 Target: 1000 Desorption/Adsorption Cycles

- Investigate durability of materials, cycling behavior, effects of contaminants, structural stability, release of volatiles

Discovering New Complex Hydride Materials

Experimental

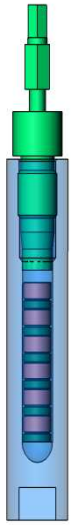
- Established a synthesis route that combines high-energy milling followed by hot-sintering under high H_2-pressures:

  Metal + Binary Hydride + H_2 → Complex Hydride

  Boride + Binary Hydride + H_2 → Metal Borohydride

  (Normal run: P < 700bar, T < 450°C)

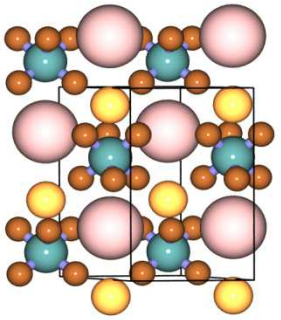
- New Start (7/1/2007): Improving kinetics, cycling life and desorption properties by incorporation of hydride materials in nanoframeworks. Collaboration with UTRC (lead)



6 sample HP-autoclave

Theory

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



MC Structure

METAL HYDRIDE CENTER OF EXCELLENCE

Contents

Sandia National Laboratories

- $Ca(BH_4)_2$ as H-storage material
- Synthesis of PEGS-predicted bialkali borohydrides
- Mixed transition metal borohydrides
- Re-hydriding low-temperature borohydrides utilizing Sandia's high-pressure capability. Teaming with Craig Jensen (UH)
- Incorporation of hydride materials in nanoframeworks

$Ca(BH_4)_2$ 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

In 2006:

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

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

In 2007:

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)*

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

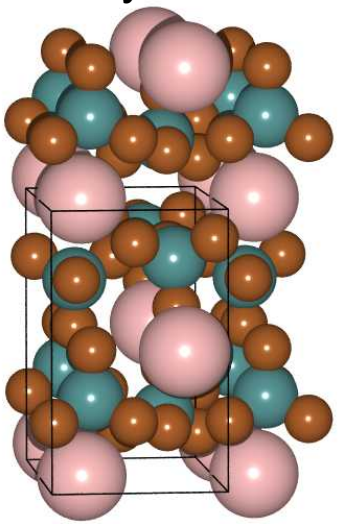
*Majzoub & Ozolins, Phys. Rev. B, **77**, 104115 (2008)

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

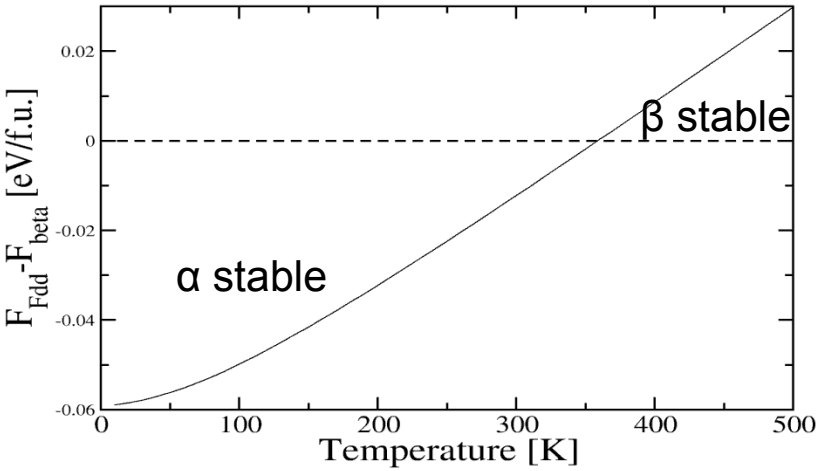
PEGS $Ca(BH_4)_2$ Search Explains Experimental Observations

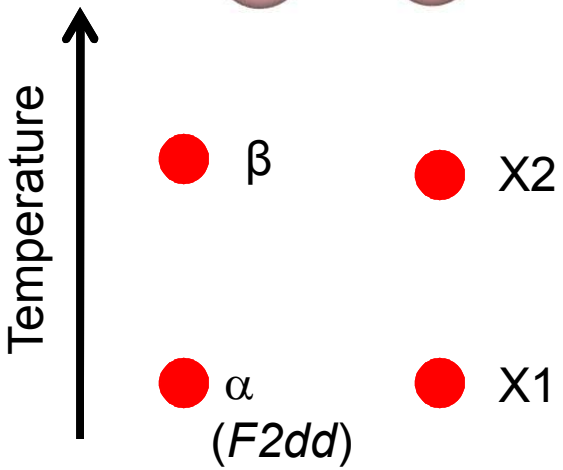
PEGS-structure of β-$Ca(BH_4)_2$
Confirmed by Rietveld refinements



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

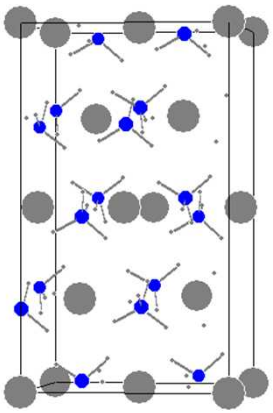
E. Majzoub and E. Rönnebro, manuscript submitted

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

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

α

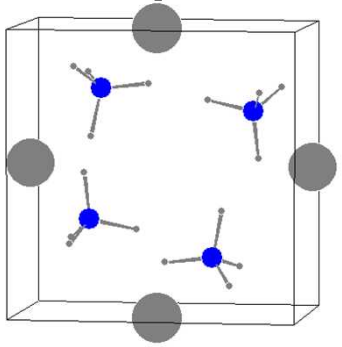


Ca

BH_4

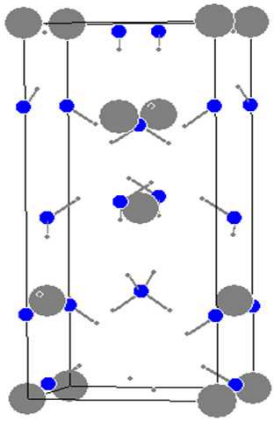
α → α' at ~160°C

β



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

α'



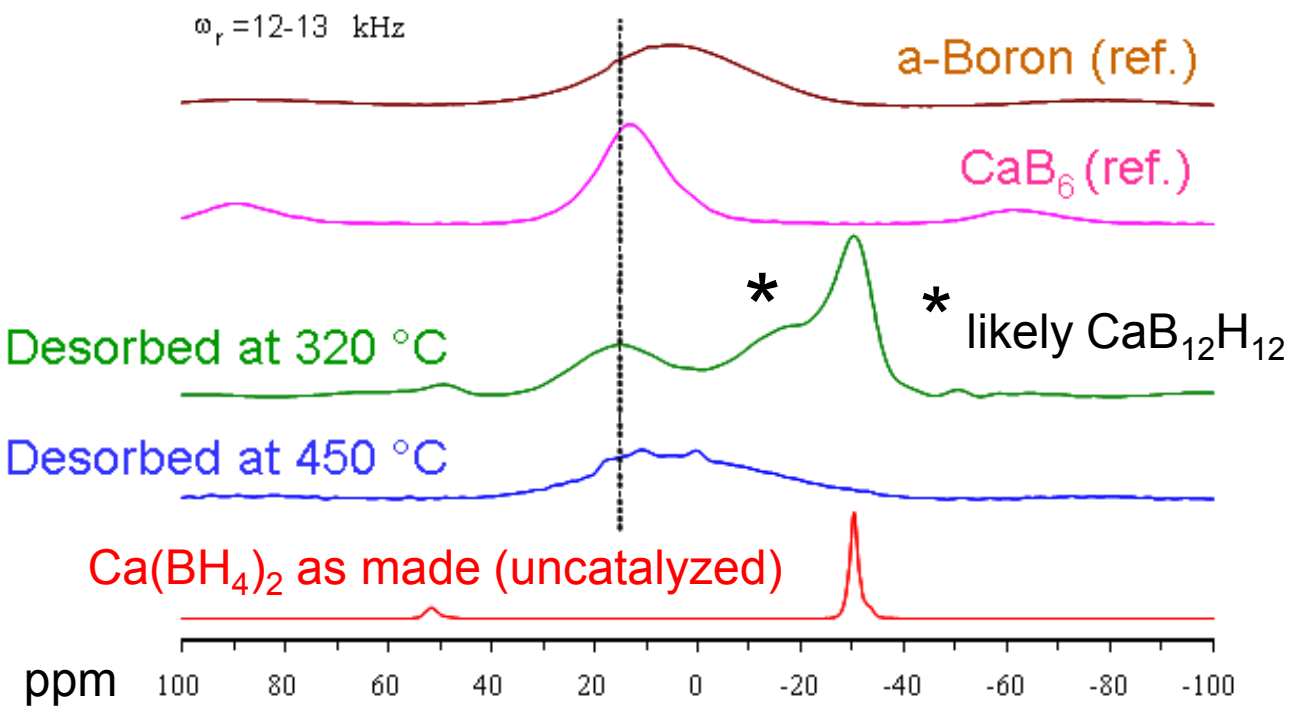
α'-phase forms above 160°C. Decomposes at 350°C to release H_2

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

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

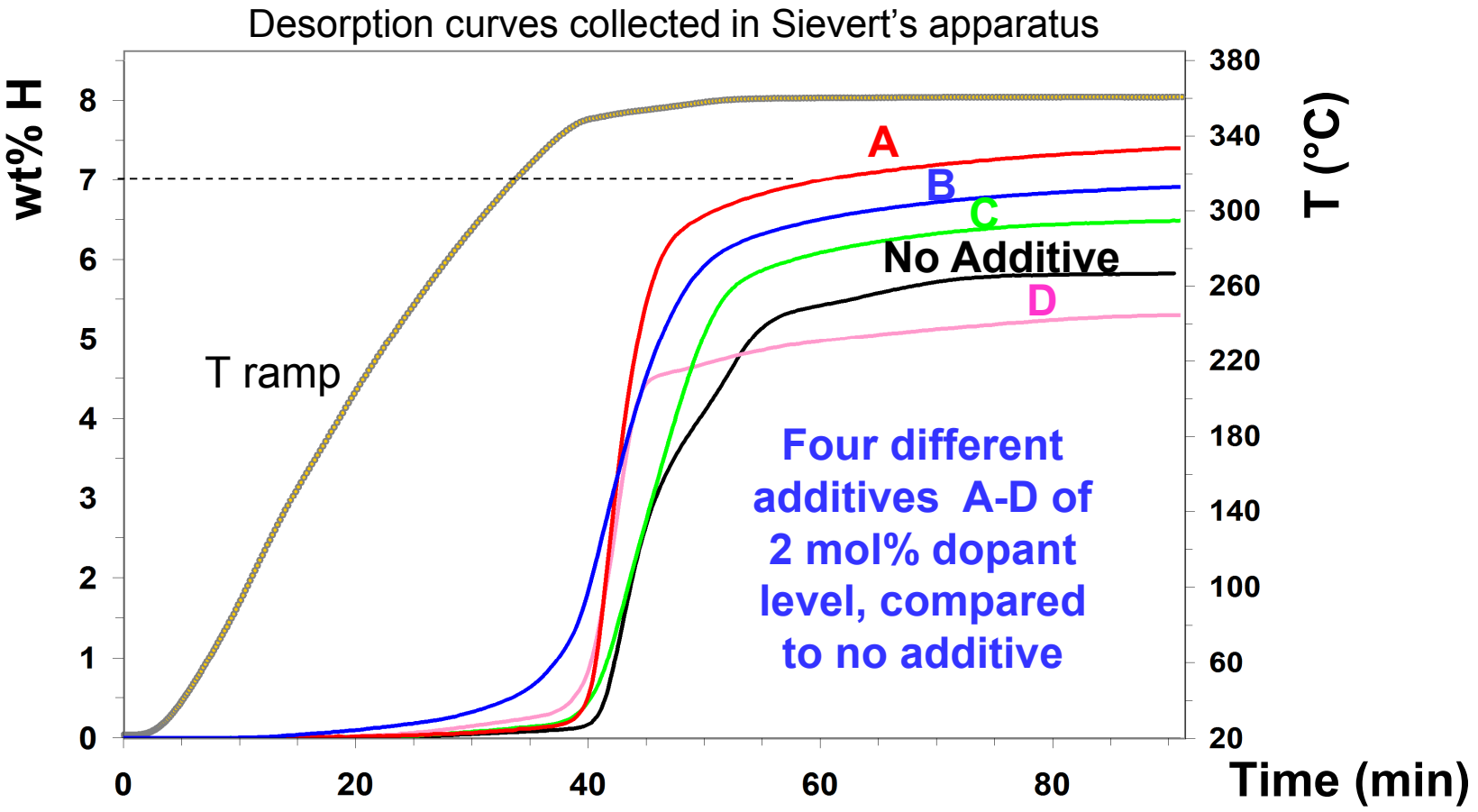


Hwang, Bowman, Kim, Reiter, Zan, Rönnebro

Confirmed decomposition products, and found intermediate species

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

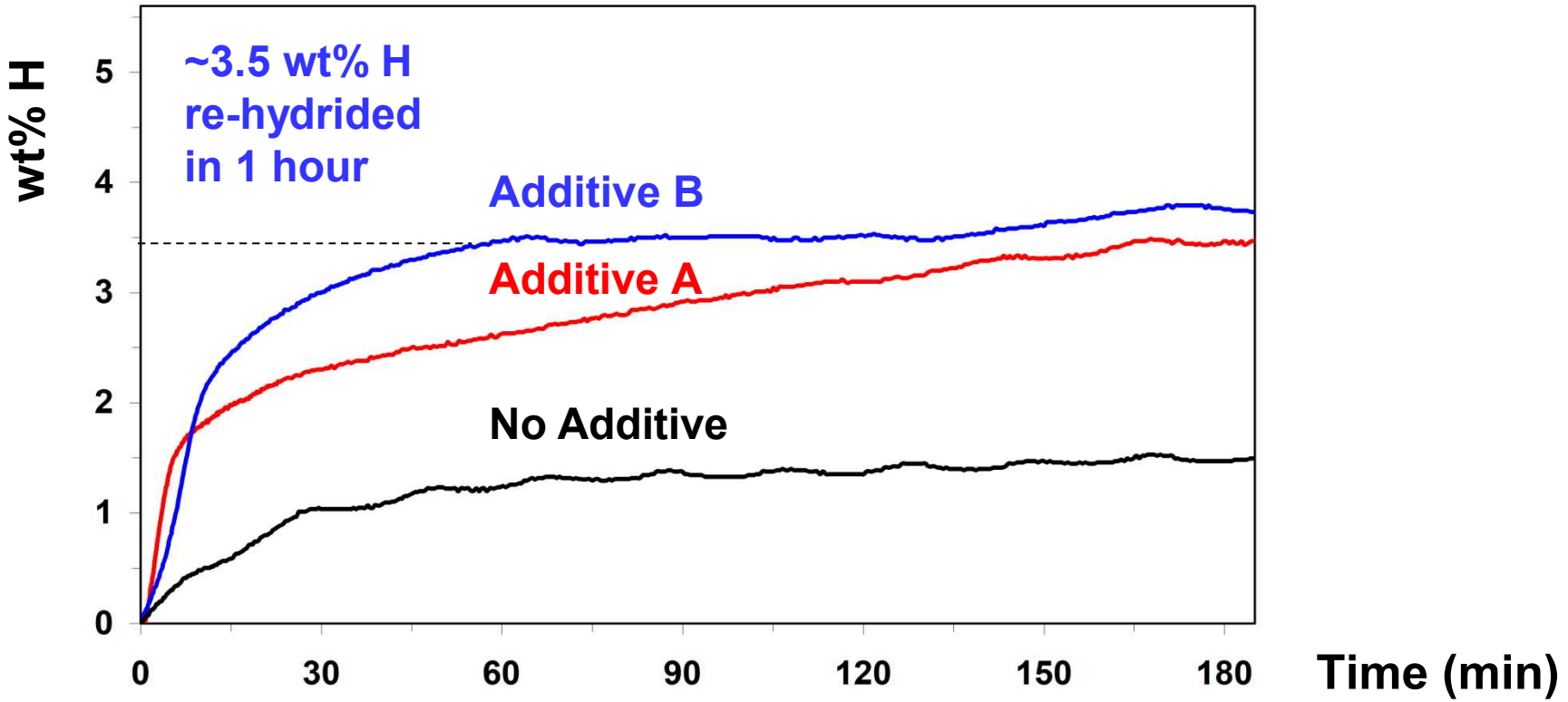
Additives change desorption kinetics and released H_2



~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

The STMBMS* is an appropriate tool to help quantify complex reaction processes

* Simultaneous thermo-gravimetric modulated-beam mass spectrometer

This is an instrument used for measuring thermodynamic properties of molecules and studying reaction kinetics of complex systems

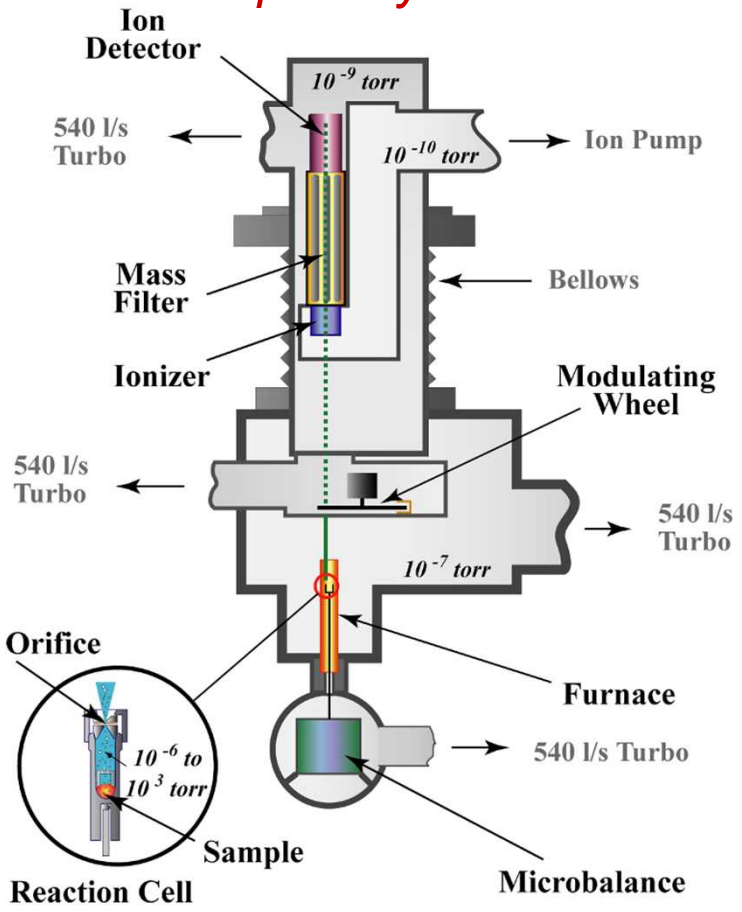
Instrument details:

- 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



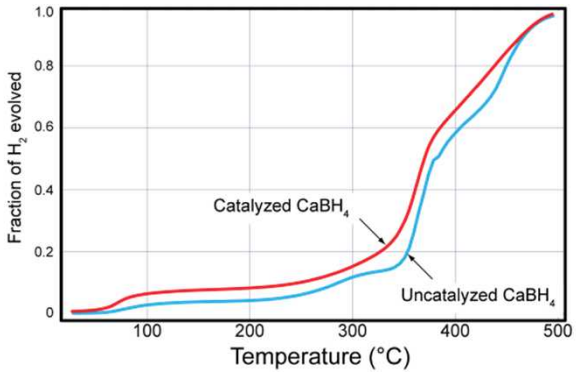
[1] Behrens, R., Jr., Review of Scientific Instruments, 1987. **58**(3): p. 451-461

[2] Lee, Y.T. et al, Review of Scientific Instruments, 1969. 40(11): P. 1402 - 1408

R. Behrens and D. Dedrick

Baseline decomposition of calcium borohydride indicates a variety of species evolving during hydrogen release

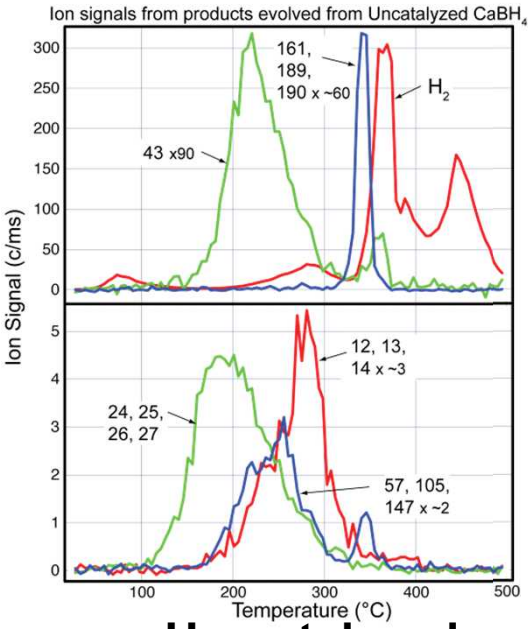
Fraction of H_2



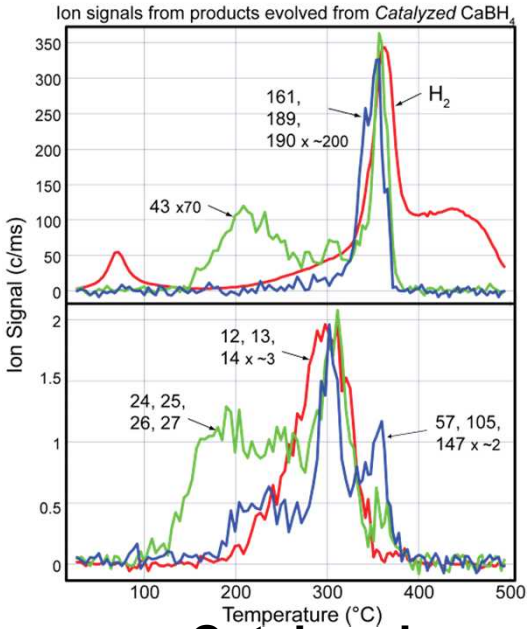
- Samples obtained from SNL (Ronnebro)
- Catalyzed $Ca(BH_4)_2$ indicates a shift in hydrogen release
- A variety of compounds are present during decomposition, these will be identified with FTICR mass spec measurements

- H_2 evolution at low temperature may give insight to reversible decomposition processes
- Di-borane (B_2H_6) complexes appear to evolve prior to H_2 evolution
- Borane (BH_3) evolves from the sample
- Differences in each of the species signals may provide insight to the role of the catalyst

MS Ion signals as a function of temperature



Un-catalyzed



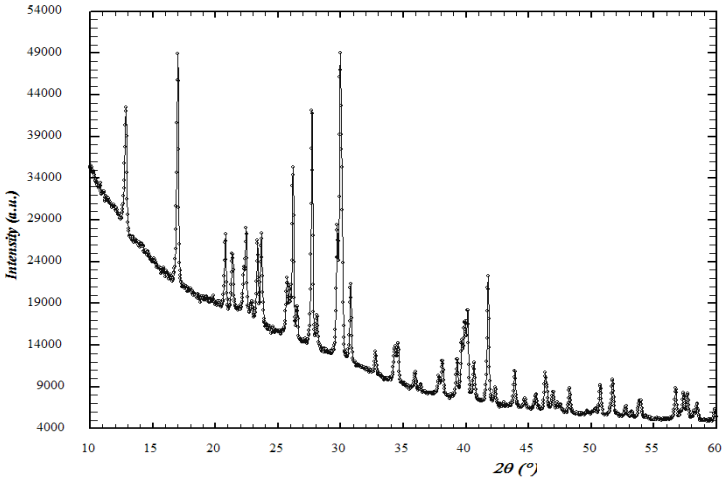
Catalyzed

R. Behrens and D. Dedrick

New $LiK(BH_4)_2$ Synthesized

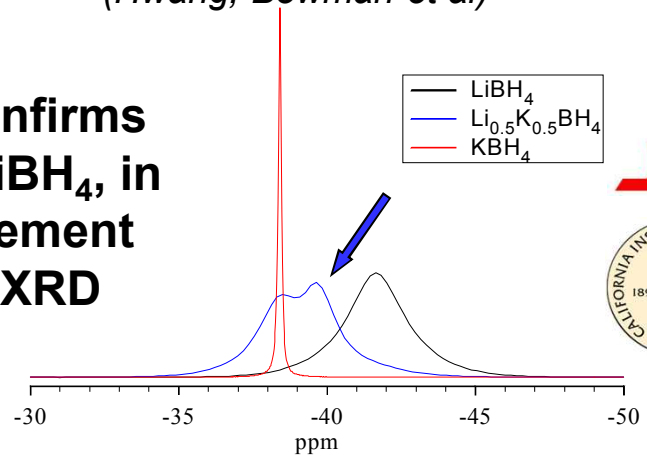
Motivation: **Improving thermodynamics by changing cationic matrix**

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 (unlike Edwards et al)

∴ **Do Not Pursue Further**

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

PEGS Predicts Weakly Metastable $NaK(BH_4)_2$

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

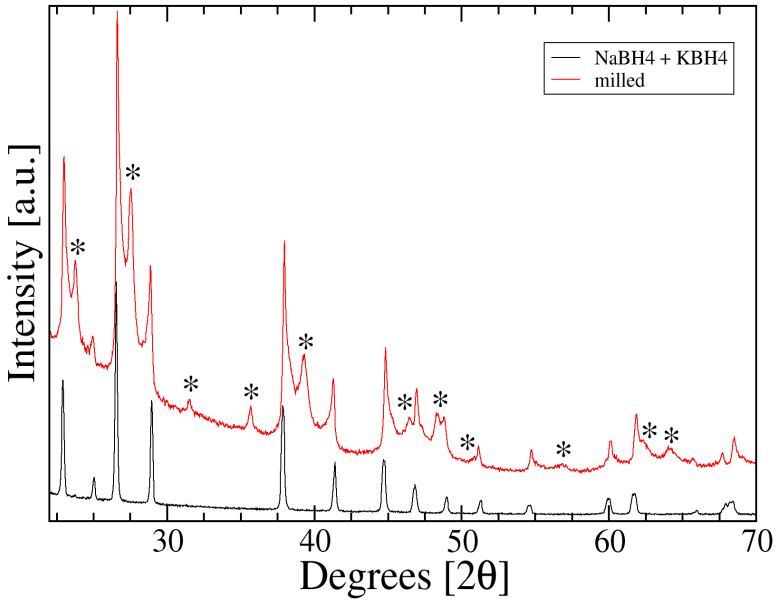
Space Group		$E-E_0$ [meV/f.u.]
146	$R3$	+110
148	$R\bar{3}$	+80
156	$P3m1$	+76
166	$R\bar{3}m$	0.0

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

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

✓ $NaK(BH_4)_2$ synthesized

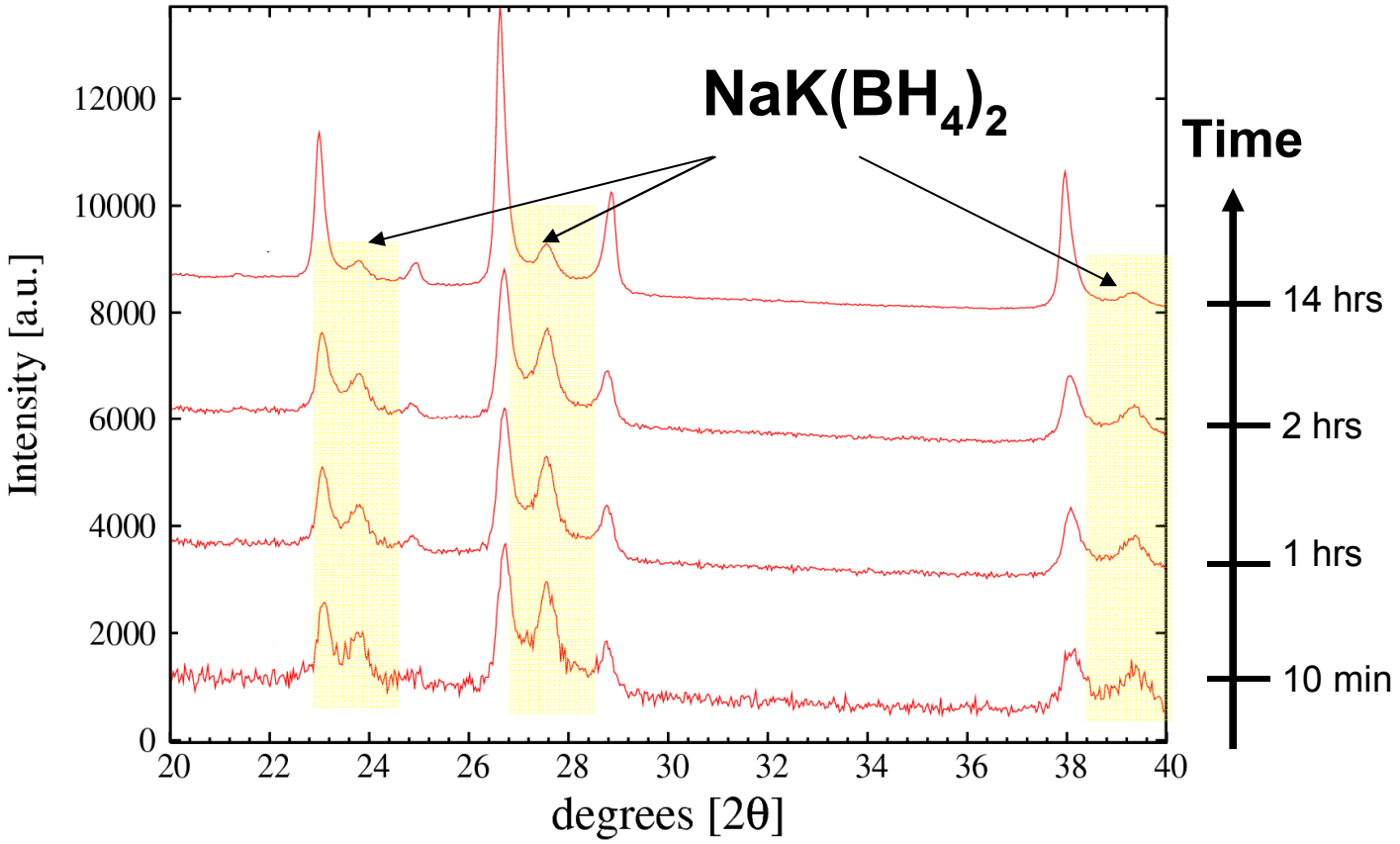
✓ XRD confirms predicted new phase (metastable)



Leo Seballos, Eric Majzoub and Ewa Rönnebro

XRD Indicates Spontaneous Decomposition of $NaK(BH_4)_2$

Ball Milling: $NaBH_4 + KBH_4 \rightarrow NaK(BH_4)_2$ (8.8 H wt%)



Decomposition takes ~ 14 hours

$NaK(BH_4)_2$ is *metastable,*

***-- consistent* with PEGS**

XRD pattern shows spontaneous decomposition: $NaK(BH_4)_2 \rightarrow NaBH_4 + KBH_4$

∴ Do not pursue further

Re-hydriding Alkali Transition Metal Borohydrides

Teaming with U. Hawai'i/ Prof. Craig Jensen

Motivation: Alkali transition metal borohydrides may have improved properties compared to the alkali borohydrides

- **Synthesis of $AkTm(BH_4)_x$** (U. Hawai'i)
  - Ball milling alkali (Ak) borohydrides with transition metal (Tm) chlorides to form high-capacity materials
  - Desorption characteristics investigated
    - Release hydrogen at low temperatures <150°C
- **Re-hydriding decomposition products** (Sandia)
  - Utilizing Sandia's high-pressure station
    - Decomposition products re-hydrided at H_2-pressures of 700-900 bar, and heating to 200-500°C
  - One material showed partial reversibility

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

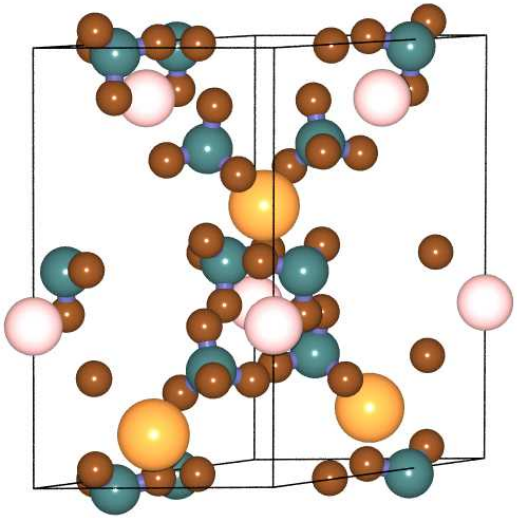
Ball milled: $ScCl_3 + 4LiBH_4 \rightarrow LiSc(BH_4)_4 + 3LiCl$ (14.5 H wt. %)

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:

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

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

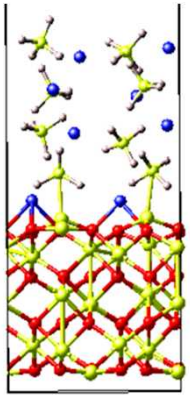
PEGS applicable to transition metal borohydrides with some covalent character

Incorporation of Hydrides in Catalyzed Nano-framework

Improve reversibility of high capacity hydride candidates by developing advanced NFS chemistries through combined modeling and experimentation

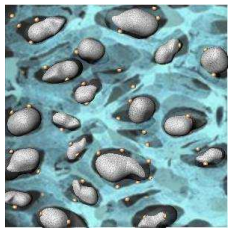
Modeling

- Simulations show interfacial NFS (nano-framework structures) interactions can alter stability of hydride and discharged products (UTRC).
- Dopants balance both NFS lattice stability and electronic NFS/hydride interfacial interactions (UTRC).



Framework and Hydride

- Synthesis of NFS: ZrO_2, Al_2O_3, SiO_2, TiO_2, Carbon (UTRC).
- UTRC / Albemarle focus on ligand stabilized: $NaTi(BH_4)_4$*DME
- Sandia focus on stable borohydride: $Ca(BH_4)_2$



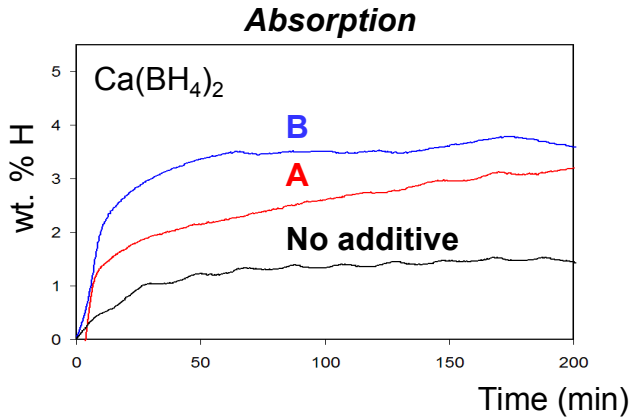
Summary

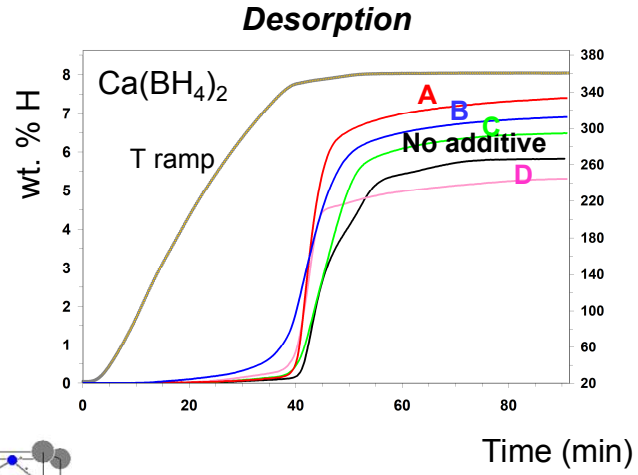
Calcium Borohydride

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

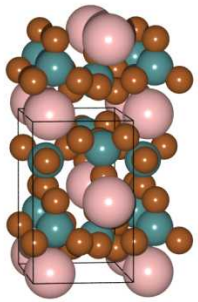
- Showed drastic improvement in kinetics by choosing right additives

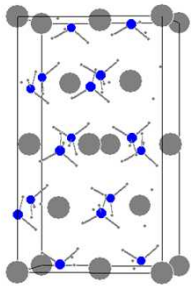
- Elucidated crystal structures of polymorphs using a combined theoretical/experimental approach, i.e. the PEGS-method and the Rietveld-method





PEGS structure for β-$Ca(BH_4)_2$



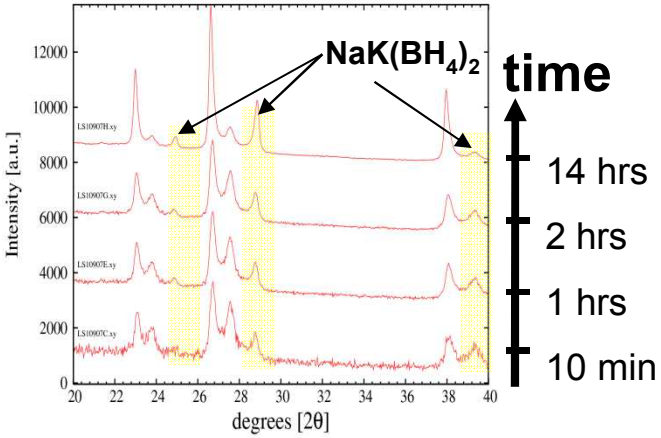


XRD α-$Ca(BH_4)_2$

Summary

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
- Showed that PEGS can provide transition metal borohydride structures



Future Work

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. $Mg(BH_4)_2$, $Ca(BH_4)_2$)