METAL HYDRIDE CENTER OF EXCELLENCE

2007 DOE Hydrogen Program Review

DOE Hydrogen Program

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

Presented by

Ewa Rönnebro, Eric Majzoub and Tony McDaniel

Sandia National Laboratories

May 15-18, 2007

Sandia National Laboratories

Project ID#ST15

Sandia Program Overview

Timeline

- Project started in March ‘05
- Project end ~ 2010
- Percent complete ~ 40%

R&D Budget

- $1.84M in FY ‘06
- $1.96M in FY ‘07

Barriers

- Weight & Volume, Cost, Efficiency, Durability
- Charge/discharge rates
- 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

Collaborators

National U. of Singapore, Tohoku U., UCLA, U. Geneva, LLNL, UTRC, IFE, ESRF

Sandia Team (~ 6 FTEs):

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

Core Technical Team

Mark Allendorf: ***Theory, coordination***
Eric Majzoub: ***MC theory, experiments***
Tony McDaniel: ***High-throughput screening***
Ewa Rönnebro: ***Proj. B POC, new materials***

- Weina Yang: 1 year visiting PhD-student from Queen Mary University of London
- In the process of interviewing postdoc candidates

Other Key Contributors

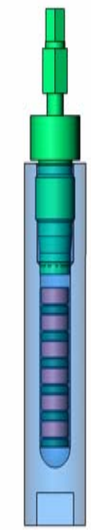
Bob Bastasz, Andy Lutz, Tim Boyle, Bill Houf
Karl Gross (Hy-Energy)

Discovering New Complex Hydride Materials

Experimental

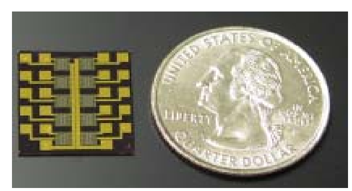
- Established a synthesis route that combines high-energy milling followed by hot-sintering under high H_2-pressures:

  Metal + Binary Hydride + H_2 → Complex Hydride
  Boride + Binary Hydride + H_2 → Metal Borohydride
  (Normal run: $P < 700$bar, $T < 450°C$)



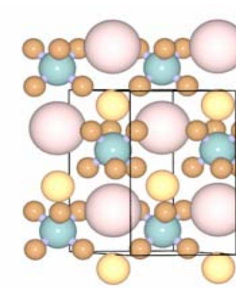
HP-autoclave

- **New Start (10/1/2007):** Developing a high-throughput combi method using micro hot-plates and *in-situ* diagnostics to rapidly synthesize and test new materials



Theory

- Theory is continuing to guide experiments. Monte Carlo (MC) technique provides minimum energy structures for subsequent enthalpy estimates. Full thermodynamics are calculated for promising materials, including bialkali borohydrides



MC Generated Structure

High-Pressure Technique Yields New Metal Hydrides

METAL HYDRIDE CENTER OF EXCELLENCE

Sandia National Laboratories

➢ Si-system:

<u>Status May 2006:</u> New materials phases found in the Na-Si-H system, but H-content was very low according to Neutron Spectroscopy (NIST) and NMR (LLNL/JPL)

<u>FY 2007:</u> We explored new synthesis routes, including reactive milling in collaboration with HRL and U. Utah. No new phases with *high*-hydrogen content were found

Therefore, made no-go decision on Na-Si-H system (Dec-06)

➢ *Other New Compounds Found in FY2007:*

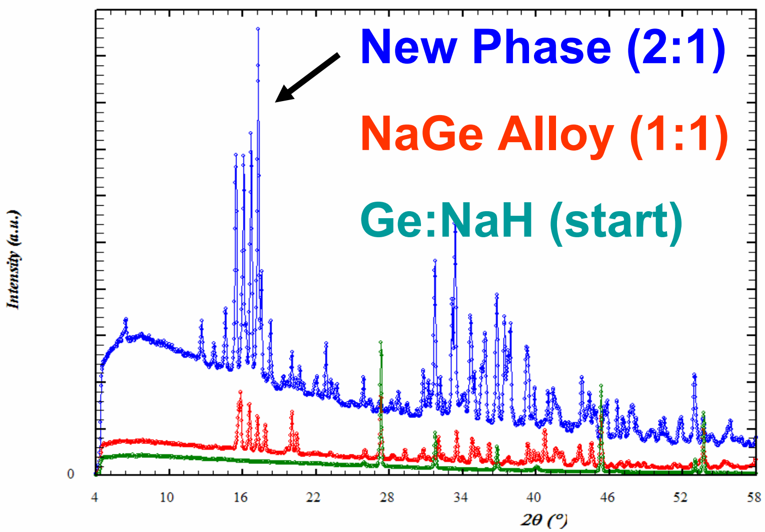
X-Ge-H
X-Mn-H

} ***XRD, PCT measurements in progress***

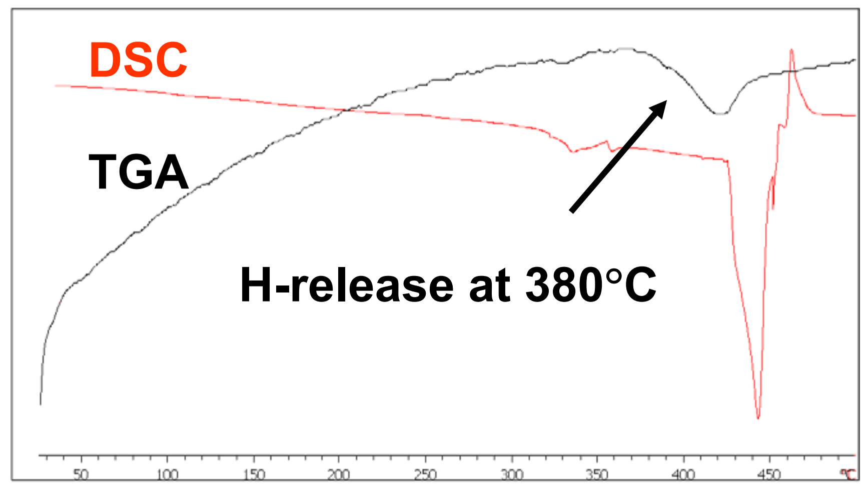
Future Directions: A-X-H systems
(A = Ti, Nb, Cr, Mn; X = Li, Na, Mg, Ca)

XRD Shows New Na-Ge-H Compound

Motivation: X-Ge-H; X = alkali or alkaline earth metals, are unexplored compounds with potential for 5 - 7 mat. wt% H_2



XRD shows that a molar ratio of NaH:Ge 2:1 results in a new hydride by HP-sintering



DSC and TGA shows gas release upon exothermic phase transition

- **Synthesis condition to be optimized. PCT-measurements will reveal H_2 storage performance**

New Solid-state Synthesis of $Ca(BH_4)_2$

Motivation: Theory predicts $Ca(BH_4)_2$ has promising thermodynamics ($\Delta H \sim 53$ kJ/mol), 9.6 wt. %

Status May 2006:

- Solid-state HP-sintering yielded unidentified Ca-B-H compound, but product yield was low, slow kinetics

FY2007:

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

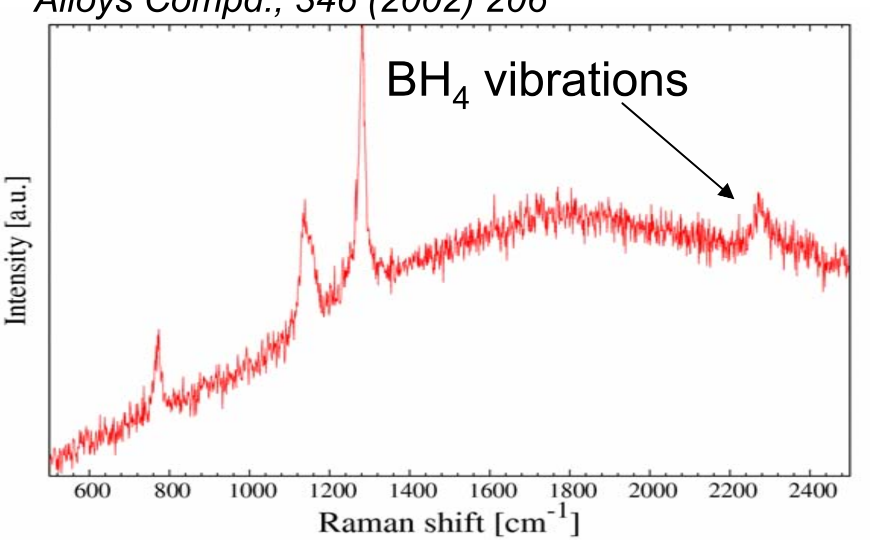
- By trying several additives, the product yield from HP-sintering was improved to ~ 80%, while improving kinetics (Patent filed)
- Identified the Ca-B-H compound as $Ca(BH_4)_2$ by thorough characterization teaming with our partners and collaborators
- Prepared pure, crystalline $Ca(BH_4)_2$ from Aldrich $Ca(BH_4)_2 \cdot 2THF$ for PCT-desorption characterizations with different additives

Notes: Other recently reported non-reversible solid-state routes:

- $2LiBH_4 + CaCl_2 \rightarrow Ca(BH_4)_2 + 2LiCl$ (Nakamori, Orimo et al, J. Alloys Compd, in press)
- $MgB_2 + CaH_2 + 4H_2 \rightarrow Ca(BH_4)_2 + MgH_2$ » 8.3 wt% calc (Dornheim, Klassen et al, J. Alloys Compd, in press)

Characterization of $Ca(BH_4)_2$

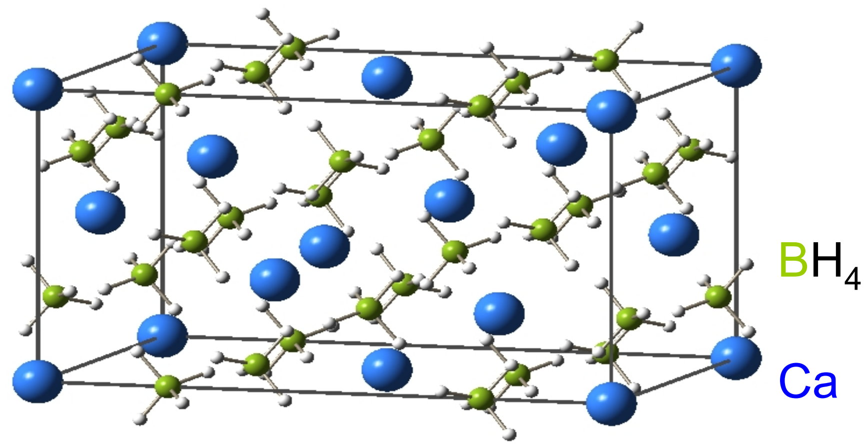
Raman of solvent-free $Ca(BH_4)_2$:
Observed BH_4 vibrations that are consistent with literature data on $LiBH_4$: *S. Gomes, H. Hagemann, K. Yvon, J. Alloys Compd., 346 (2002) 206*



From synchrotron XRD data (ESRF) of RT structure:

Space group: Fddd (No. 70)

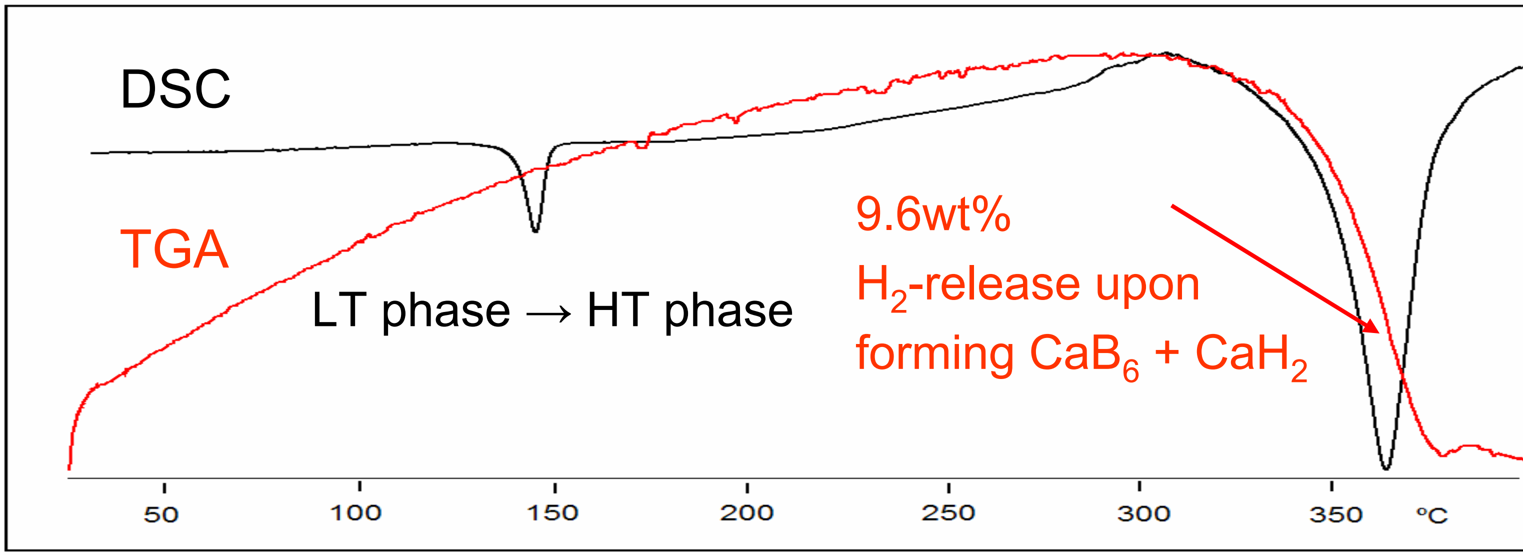
a = 8.769 Å, b = 13.104 Å, c = 7.492 Å



Results:
- Synchrotron-XRD (SNL, UNR, ESRF) preliminary indicates a structure similar to Miwa et al., PRB. 74, (2006), 155122(1-5)
- Neutron Spectroscopy identifies $Ca(BH_4)_2$ (NIST)
- Direct B-H bonding confirmed with ^{11}B NMR (JPL, LLNL)

Desorption Behavior of $Ca(BH_4)_2$

TGA and DSC of $Ca(BH_4)_2$ as prepared by solid-state synthesis at high-H_2 pressures from a mixture of CaB_6 + $2CaH_2$



- XRD@160ºC shows a phase transition from low temp. (LT) to high temp. (HT) $Ca(BH_4)_2$, confirmed by *in-situ* XRD by U. Nevada
- XRD@400ºC shows dehydrogenation to CaB_6 + CaH_2, i.e. $Ca(BH_4)_2$ was fully decomposed upon releasing 9.6 wt% H

$Ca(BH_4)_2$ Is Reversible

Dehydrogenation:

$$3Ca(BH_4)_2 \xrightarrow[350\ ^\circ C\ (TGA)]{} CaB_6 + 2CaH_2 + 10H_2$$

(9.6 wt. % H released)

Hydrogenation:

$$CaB_6 + 2CaH_2 \xrightarrow[390\ ^\circ C]{100\ bar\ H_2} 1\%\ Ca(BH_4)_2\ yield$$

However,

$$CaB_6 + 2CaH_2 \xrightarrow[400\ ^\circ C]{700\ bar\ H_2} 80\%\ Ca(BH_4)_2\ yield$$

Calcium borohydride appears to be a reversible high-pressure, high-capacity system

FY07/FY08 Borohydride Plans

Calcium Borohydride

- Thermodynamics, kinetics and cycle life to be explored
- Optimize re-hydriding conditions at *lower* pressures
- Explore impact of additives on required T, P for use
- Assess B_2H_6 release upon H_2 desorption

Bialkali And Other Borohydrides

- Explore bialkali borohydrides guided by MC theory
- Teaming with our partners to explore reversibility of other metal borohydrides at our high-hydrogen pressure facility

Theoretical Guide for New Materials: Monte Carlo Structure Searching

Status May 2006: Approach created and validated

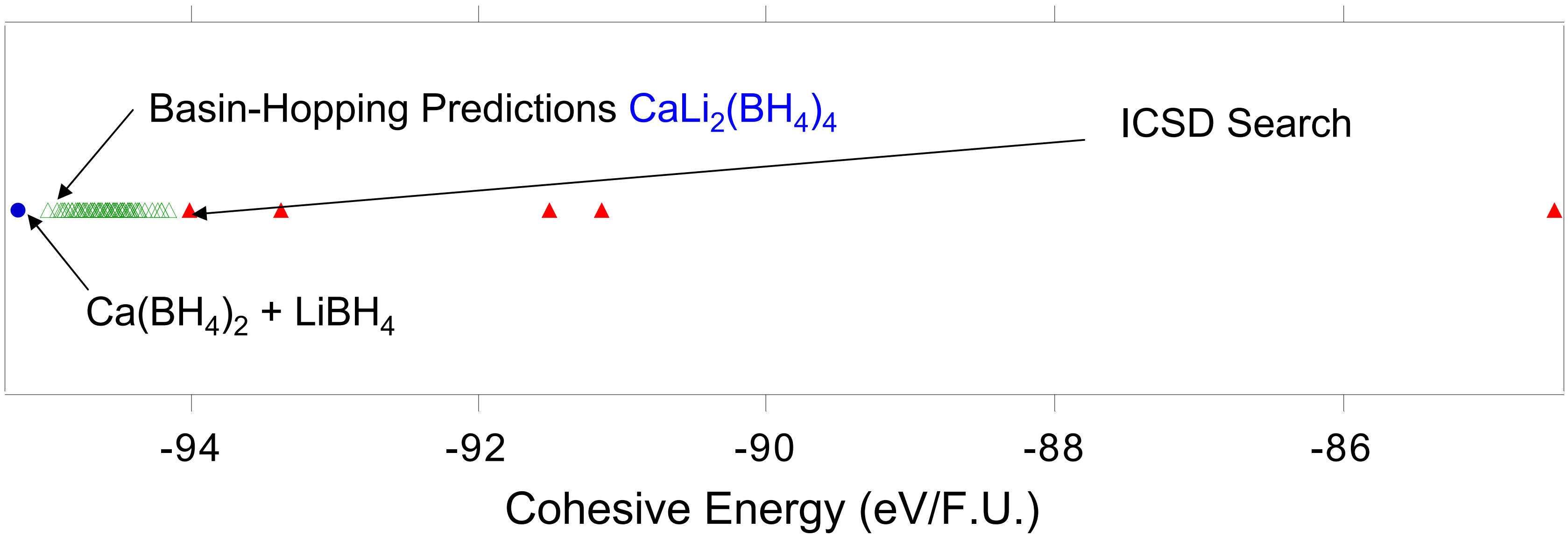
FY2007: Code improvements and exploring mixed cation borohydrides

Examples:

	$NaAlH_4$	$LiAlH_4$
Experimentally Observed structure	$I4_1/a$	$P2_1/c$
MC search	$I4_1/a$	C2/m
$E_{expt} - E_{MC}$ [kJ/mol f.u.]	0.0	+4.8
	Finds ground state!	**Lower than expt. structure!**

Improvements allow MC to access ground-state structures

$CaLi_2(BH_4)_4$ is Unstable w.r.t. Separate Borohydrides



- **Monte Carlo basin hopping easily beats the ICSD search**
- **Unfortunately, the lowest energy structure is unstable w.r.t. to phase separation to $Ca(BH_4)_2$ and $LiBH_4$**

We will not attempt to make $CaLi_2(BH_4)_4$

Bialkali Borohydride Stability

- Stability assessed with respect to phase mix of alkali borohydrides (kJ/mol formula unit)

Example: $LiMg(BH_4)_3 \rightarrow LiBH_4 + Mg(BH_4)_2$

We are half-way through approx. 100 potential high-capacity compounds

$LiMg(BH_4)_3$ (-22,16.0 wt%)	$Li_2Mg(BH_4)_4$ (-44,16.5 wt%)	
$LiK(BH_4)_2$ (-15,10.7 wt%)	$Li_2K(BH_4)_3$ (-20, 12.4 wt%)	$LiK_2(BH_4)_3$ (-20, 9.3 wt%)
$LiNa(BH_4)_2$ (-16, 13.5 wt%)	$Li_2Na(BH_4)_3$ (-24,14.9 wt%)	$LiNa_2(BH_4)_3$ (-16,12.4 wt%)
$AB(BH_4)_2$ (-3)	$A_2B(BH_4)_3$ (-13)	**$AB_2(BH_4)_3$ (-6)**

We have identified two potentially stable mixed cation borohydrides and will attempt synthesis

FY07/FY08 Theory Work

Metal Borohydrides

- Perform full first-principles thermodynamics calculations in the promising $AB(BH_4)_2$ system identified through the MC screening process
- Use MC screening to complete evaluation of mixed cation borohydride stability
- Theoretical investigation of phase stability in the reversible reaction $CaB_6 + 2CaH_2 + 10H_2 \leftrightarrow 3Ca(BH_4)_2$ and the possible importance of oxygen in this system
- Collaboration with UIUC to understand the orthorhombic to hexagonal phase transformation in $LiBH_4$ (possibly important for understanding the recent experimental results of HRL, and $LiBH_4$ in nanoporous carbon structures)

New Hydrogen Storage Materials

- Begin study of ABH_x compounds, with A = Li, Na, K and B = Si, Ge and assess ability to use MC screening

Theoretical Work Prospects

- Evaluate future theoretical work prospects: nanoparticle synthesis, hydrogenation, and thermodynamic constraints

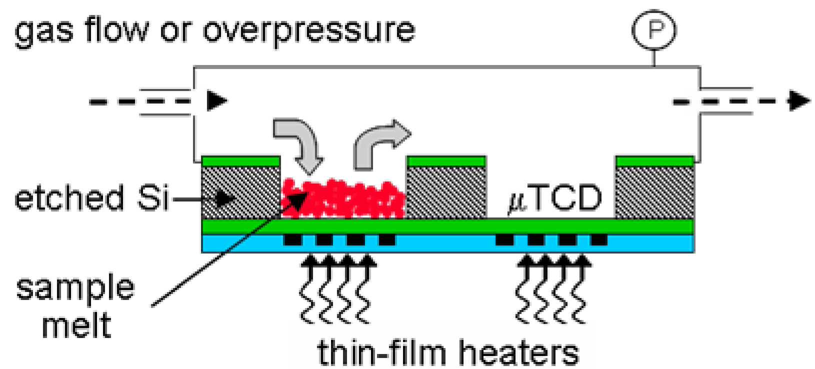
Project Started Oct. 2007
New Combinatorial Method For Center

METAL HYDRIDE CENTER OF EXCELLENCE

Sandia National Laboratories

Motivation: A breakthrough material is needed….

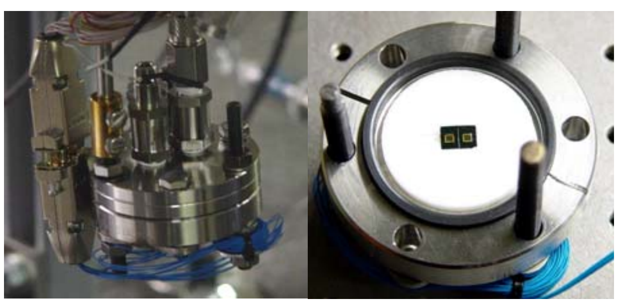
- Utilize arrays of micro-hotplates to synthesize and characterize materials
  - High-temperature and high-pressure processing of precursors
    - *800 °C and 2000 bar H_2*
  - Micro-scale in-situ diagnostics
    - *calorimetry and H_2 gas detection*
- Statistical methods to formulate and analyze the sample space



Prototype 130 bar H_2 fully instrumented system

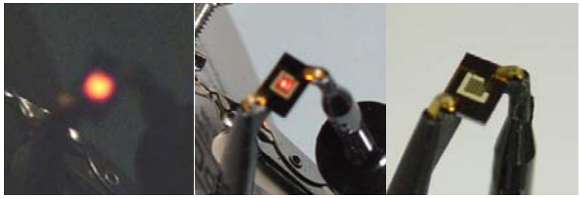
- ✓2 micro-hotplates
- ✓Calorimeter and gas composition diagnostics
- Proof Materials: MgH_2, $NaAlH_4$ (in progress)
- Target: Bialkali Borohydrides

internal chamber

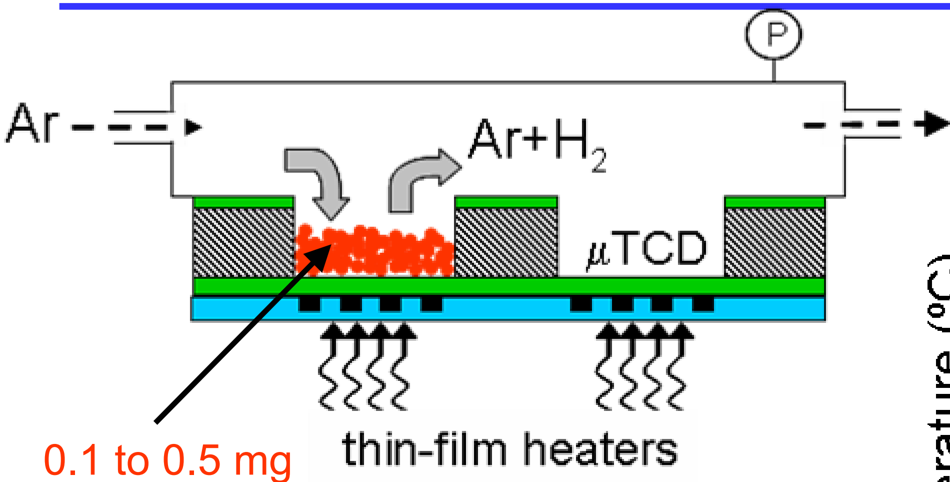


2 micro hot plates in 2.75" OD flange

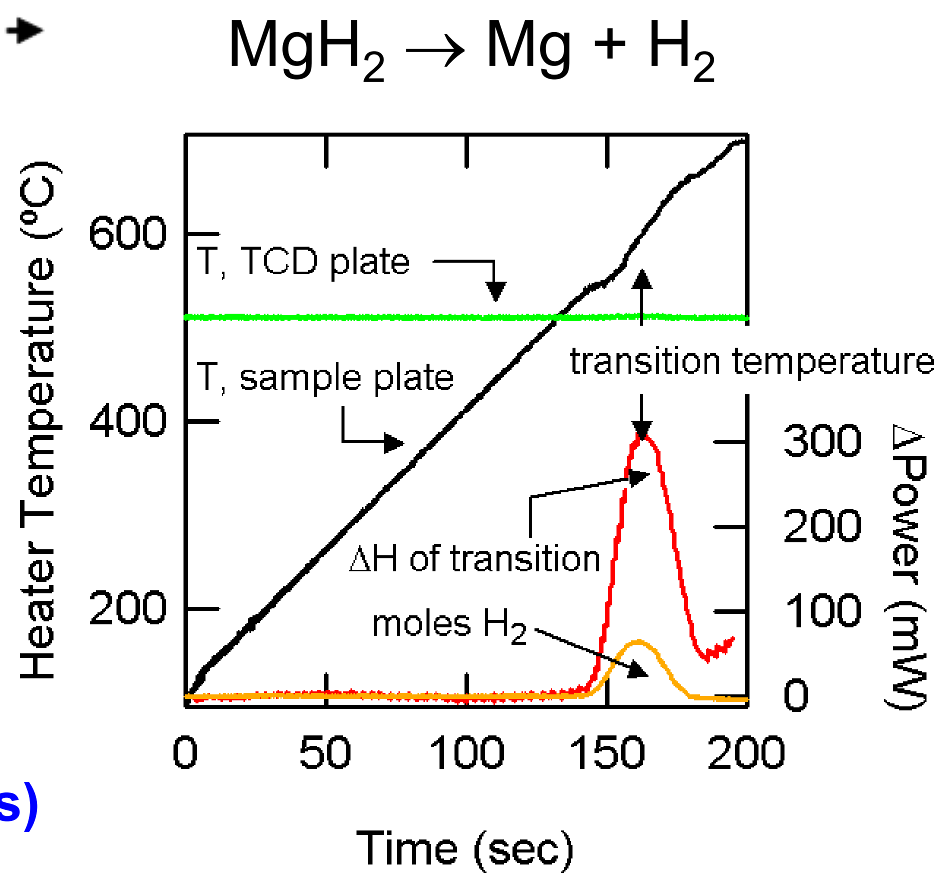
hotplate in air at 1000 K



ΔH Desorption, H_2 Release from MH Detected With In-Situ Diagnostics

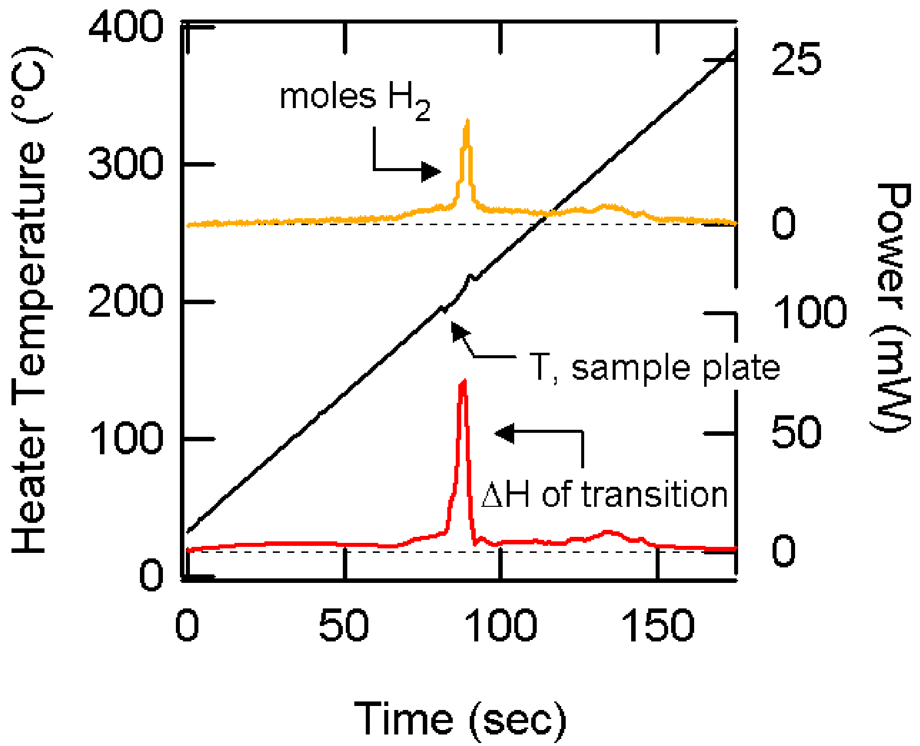


TCD = thermal conductivity detector (for H_2 detection)



- ✓ **Rapid thermal characterization with high sensitivity**
  - **Transition temperature (kinetics)**
  - **Enthalpy of transition**
  - **H_2 capacity**
- ✓ **Enables a unique combinatorial approach (information rich)**

H_2 Desorption From Ti-$NaAlH_4$



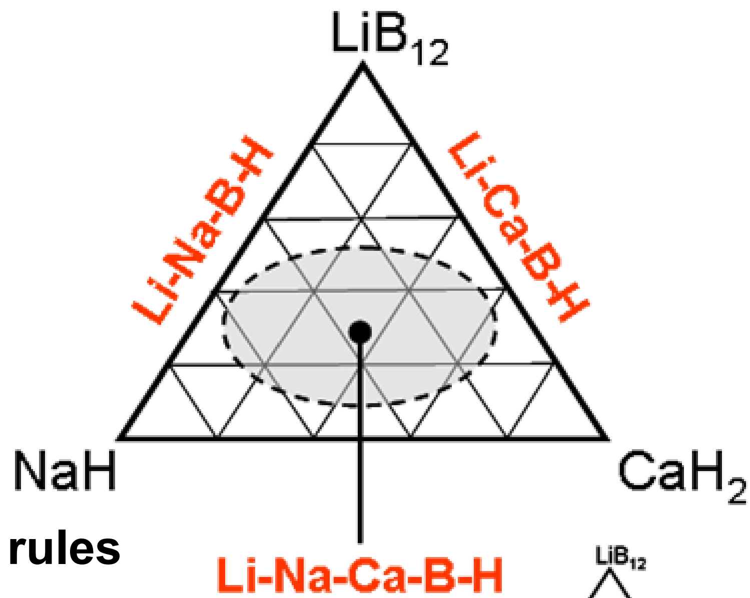
Next step: demonstrate synthesis of $NaAlH_4$ from Al and NaH powdered precursors

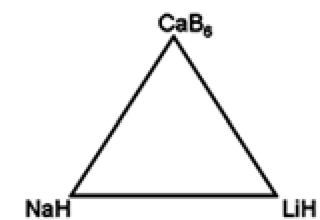
High-throughput Screening Guided By Theoretical Predictions

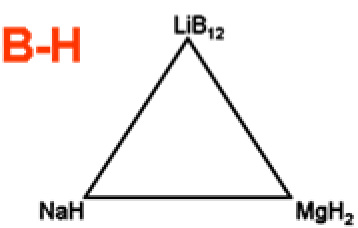
Near-term targets: Bialkali borohydrides

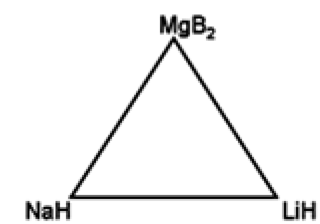
Element	Hydride	Boride
Li	LiH	LiB_2, LiB_{12}
B		
Na	NaH	
Mg	MgH_2	MgB_2
K		
Ca	CaH_2	CaB_6

$xH_2 + yNaH + zLiB_{12} + HEAT \rightarrow$ $Li_2NaB_3H_{12}$, $LiNa_2B_3H_{12}$, $LiNaB_2H_8$, ?





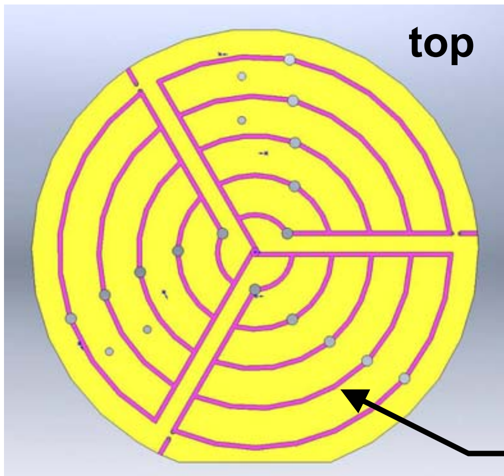


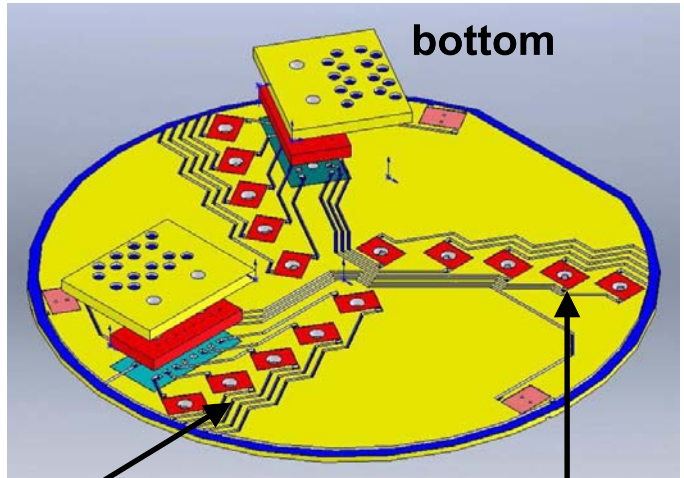


- **Statistically based mixing rules of precursor powders determine initial condition**
- **Survey hydrogen content, transition temperatures and heat fluxes with RTP**
- **Secondary analysis on promising combinations**

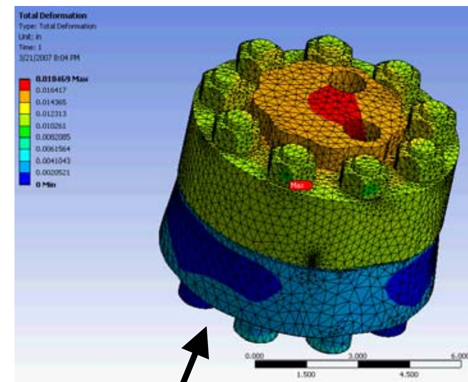
Path Forward: 15 Isolated And Fully Multiplexed Sample Wells

multiple micro-hotplates for combinatorial synthesis and characterization





internal flow paths, hotplates, and circuitry mounted on Cu-clad PTFE board



- chip mounts
- electrical traces
- isolated flow channels

- First generation 2000 bar vessel in design phase
  - 15 sample hotplates, 3 gas detectors
  - Numerical (Finite Element) stress analysis complete
- Ultra-high pressure (4000 bar) flow system assembled and in use

Summary FY2007 Accomplishments

Borohydrides

- New solid-state synthesis route and characterization of $Ca(BH_4)_2$
- Showed reversibility of $Ca(BH_4)_2$ at high H_2-pressures (<700 bar)
- Attempt to produce solvent-free adducts via solvent synthesis
- MC approach improved, ground state structures being found
- Bialkali borohydrides explored with MC method
- Completed phase stability study of Li-B-H system (with UIUC)

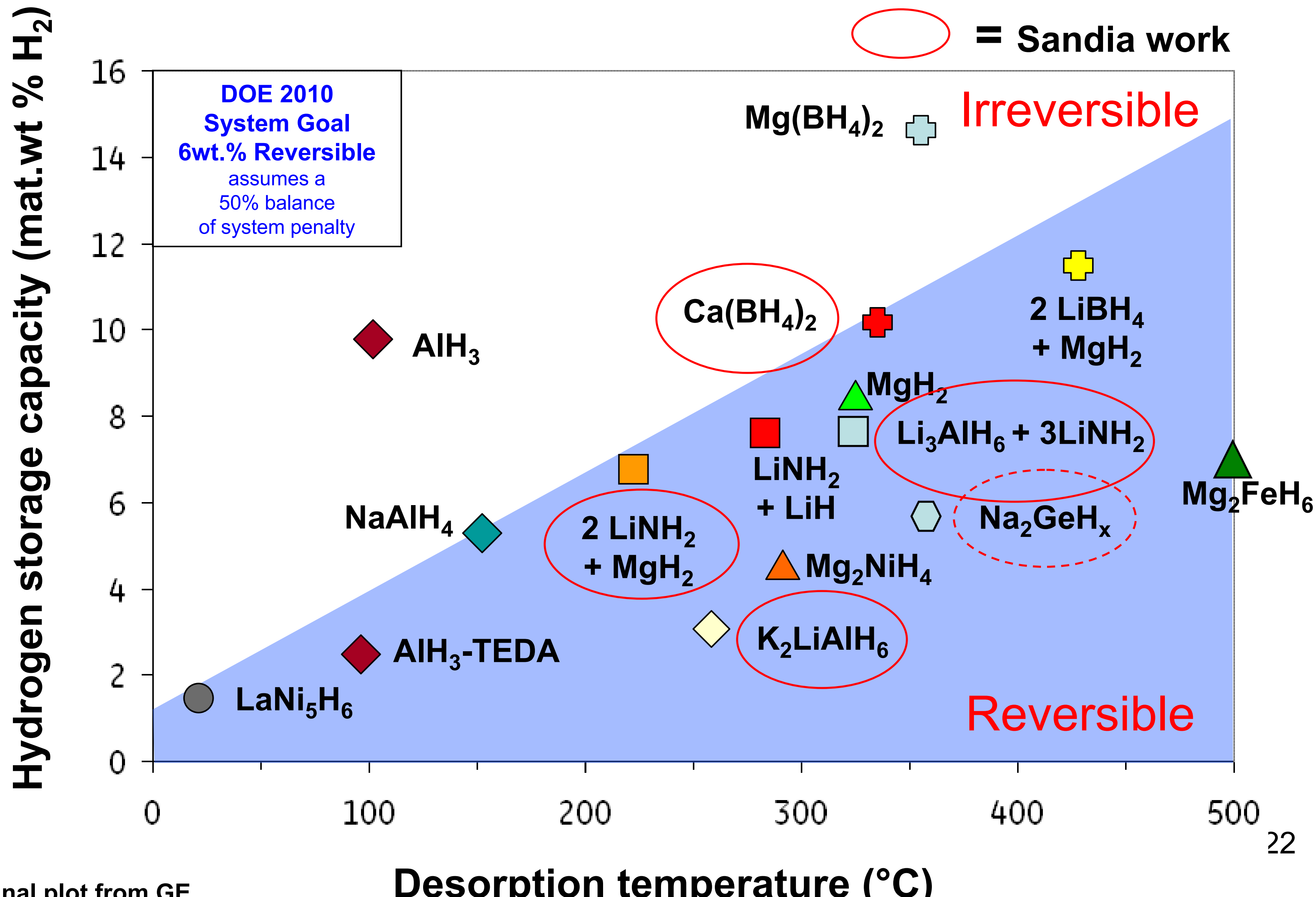
New Hydrogen Storage Materials

- New ternary Ge-H compound obtained by High P, T sintering
- Developed synthesis strategies for rapidly assessing promising hydrides
- Completed Study of $LiNH_2/LiAlH_4$ system (see extra slides)

High-throughput Screening

- Built 130 bar, 2 hotplate prototype system for initial evaluation
- Designed 2000 bar, 18 hotplate system for eventual use
- Validated Diagnostics (H_2 gas detection and calorimetry)

Status Relative to DOE Targets



Original plot from GE

Summary Future Work in FY2007

Borohydrides

- Explore kinetics, thermodynamics and cycle life of $Ca(BH_4)_2$
  Go/no-go in Dec-07
- Synthesize bialkali borohydrides predicted by MC method
- Provide high-pressure facility for MHCoE partners in exploring reversibility of other metal borohydrides

New Hydrogen Storage Materials (Na-Ge-H etc)

- Optimize solid-state synthesis routes at the high-pressure station to increase yield and to discover new materials
- Investigate structural and hydrogen sorption properties
- Go/no-go decision in Dec-07 depends on the potential of the new materials

High-throughput Screening

- Synthesize and characterize alanate from Na, NaH, and Al powders
- Synthesize and characterize bialkali borohydrides, guided by theory

Summary Future Work in FY2008

Borohydrides

- Continue optimizing performance of calcium borohydride and also synthesize bialkali borohydrides and explore their reversibility based on theoretical predictions

Synthesis of New Complex Anionic Materials

- Discover new complex anionic materials by ball milling and sintering under high H_2-pressure and down-select the most promising materials guided by theory

High-throughput Screening

- Continue exploring mixed alkali borohydrides, other promising candidates guided by theory

Nanoengineering

- Explore possibilities to design alternative nanostructured metal hydrides to improve hydrogen storage properties