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SAND2007-4281P

On the Challenge to Synthesize New Metal Hydrides and Potential for High-Pressure Reversible Materials

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Invited Presentation at 'Hydrogen-Metal Systems'
Gordon Research Conference, Colby College, Waterville, ME
July 9, 2007

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Features of Complex Metal Hydrides

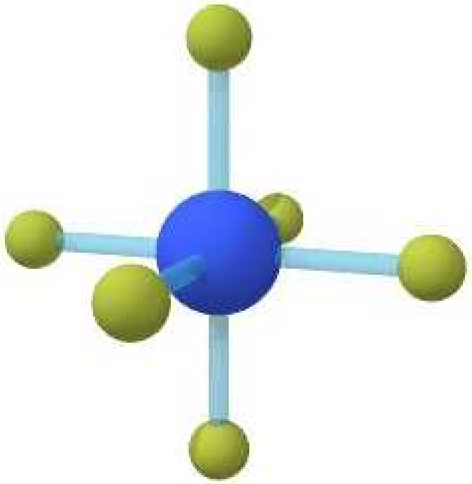
- A complex hydride consists of an anionic complex $[MH_x]^{z-}$ that is stabilized by a cation matrix consisting of one or more alkali or alkaline earth metals

Advantages:

- High-hydrogen content
- Properties can be tuned depending on the counter ion stabilizing the anionic M-H complex: $A_x[MH_y]$
- Some are light-weight: alanates, fluoride-related hydrides

Disadvantages:

- Too thermodynamically stable, or too unstable…
- Slow kinetics



Anionic complex $[MH_6]^{y-}$

To discover new materials, we must find the right cationic matrix that stabilizes a certain anionic complex which determines the features of the complex metal hydride

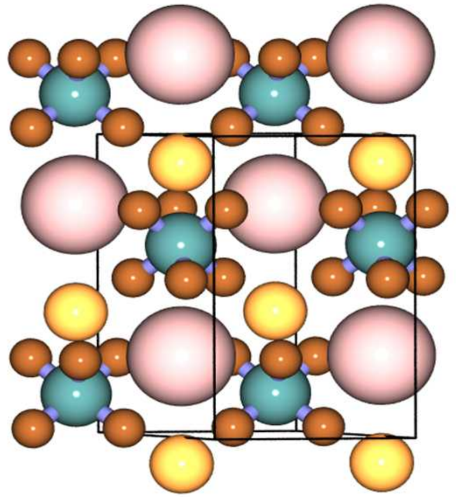
Known Anionic Complexes

VIB	VIIB		VIIIB		IB	IIB	IIIA
							^{5}**B** $[BH_4]^-$
							^{13}**Al** $[AlH_4]^-$ $[AlH_6]^{3-}$
^{24}**Cr** $[CrH_3]^{3-}$	^{25}**Mn** $[MnH_4]^{2-}$ $[MnH_6]^{5-}$	^{26}**Fe** $[FeH_6]^{4-}$	^{27}**Co** $[CoH_4]^{5-}$ $[CoH_5]^{4-}$	^{28}**Ni** $[NiH_4]^{4-}$	^{29}**Cu** $[CuH_4]^{3-}$	^{30}**Zn** $[ZnH_4]^{2-}$	^{31}**Ga** $[GaH_4]^-$
^{42}**Mo** 羊 羊	^{43}**Tc** $[TcH_9]^{2-}$	^{44}**Ru** $[Ru_2H_6]^{12-}$ $[RuH_4]^{4-}$ $[RuH_5]^{5-}$ $[RuH_6]^{4-}$ $[RuH_7]^{3-}$	^{45}**Rh** $[RhH_4]^{3-}$ $[RhH_5]^{4-}$ $[RhH_6]^{3-}$	^{46}**Pd** $[PdH_2]^{2-}$ $[PdH_3]^{3-}$ $[PdH_4]^{2-}$ $[PdH_4]^{4-}$	^{47}**Ag** 羊 羊	^{48}**Cd** $[CdH_4]^{2-}$	^{49}**In** 羊 羊
^{74}**W** 羊 羊	^{75}**Re** $[ReH_6]^{3-}$ $[ReH_6]^{5-}$ $[ReH_9]^{2-}$	^{76}**Os** $[OsH_6]^{4-}$ $[OsH_7]^{3-}$ $[OsH_8]^{2-}$	^{77}**Ir** $[IrH_3]^{6-}$ $[IrH_4]^{5-}$ $[IrH_5]^{4-}$ $[IrH_6]^{3-}$	^{78}**Pt** $[PtH_2]^{2-}$ $[PtH_4]^{2-}$ $[PtH_6]^{2-}$ $[Pt_2H_9]^{5-}$	^{79}**Au** 羊 羊	^{80}**Hg** 羊 羊	^{81}**Tl** 羊 羊

Screening for New Metal Hydrides at SNL

- Select potential high-capacity ternary system and find the cation matrix that stabilizes a certain anionic complex

- Theory guidance: Monte Carlo (MC) technique provides minimum energy structures for subsequent enthalpy estimates. (E. Majzoub)



MC-generated Structure

- Examples of potential structures:
  - A-Si-H; A = Li, Na, K, Mg to form $[SiH_x]^{y-}$
  - A-Ge-H; A = Li, Na, K, Mg to form $[GeH_x]^{y-}$
  - $AB(BH_4)_x$ (mixed borohydrides)

Solid-State Synthesis of Complex Metal Hydrides

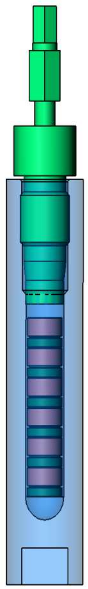
‘Hot-sintering’ under H_2-pressures

- **Metal + Binary Hydride + H_2 → Complex Hydride**
- Hydrogen pressure <100 bar in an autoclave
- Temperature <600°C
- Reaction time: several hours to several days
- Most known complex metal hydrides have been made by hot-sintering

The sintering technique is also used by groups at: U. Geneva (Switzerland), MPI (Germany), Stockholm University (Sweden), IFE (Norway), SRNL (USA), U. Tohoku, AIST (Japan)

High-pressure Sintering Technique for Discovering New Complex Metal Hydrides

Metal + Binary Hydride + H_2 → Complex Hydride
Boride + Binary Hydride + H_2 → Metal Borohydride



Established a synthesis route that combines high-energy milling (SPEX) followed by hot-sintering under high H_2-pressures (in-house station)

We can test six samples per experiment at a certain P, T and reaction time. Screening involves both searching for new materials and catalysts

Commercial autoclave with 6 steel crucibles

Normal Run:
<700bar H_2-pressure, <450ºC

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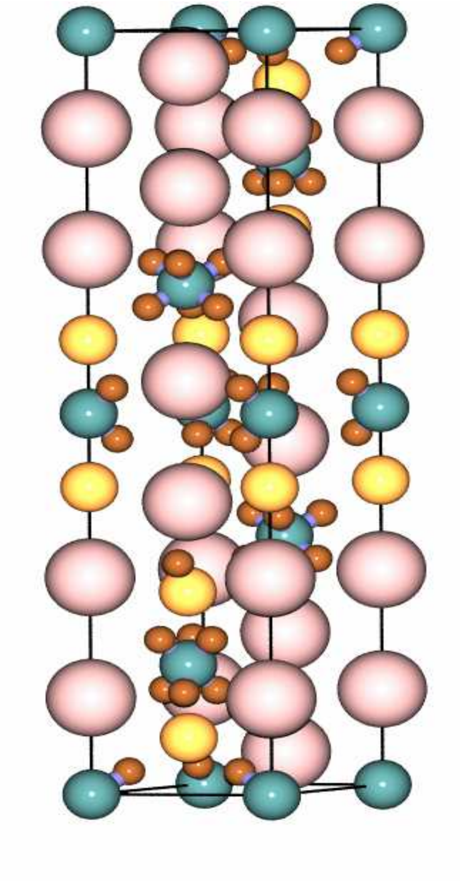
Synthesis and Characterization of K_2LiAlH_6



A New Bialkali Alanate

- We wanted to find an alanate with higher H-content and better sorption properties than sodium alanate ($NaAlH_4$)
- These bialkali alanate systems were investigated:

Potential for >6wt% Hydrogen

- **Li-K-Al-H (successful synthesis)**
- **Li-Mg-Al-H**
- **Li-Ca-Al-H**
- **Li-Ti-Al-H**
- **Mg-Ti-Al-H**

(Li-Mg-Al-H, Li-Ca-Al-H, Li-Ti-Al-H, Mg-Ti-Al-H:) No reaction observed

- Then, the synthesis route was optimized by mixing $LiAlH_4$+2KH and treating at 700 bar H_2-pressure and 320ºC for 1 day.

Other known bialkali alanates in the literature: Na_2LiAlH_6 and K_2NaAlH_6 and $LiMg(AlH_4)_3$

J. Huot, S. Boily, V. Guther, R. Schulz, J. Alloys Compd., 383 (1999) 304.
W. Brinks, B.C. Hauback, C.M. Jensen, R. Zidan, J. Alloys Comp., 392 (2005) 27.
J. Graetz, Y. Lee, J.J. Reilly, S. Park, T. Vogt, Phys. Rev. B, v.71, (2005) 184115.
M. Mamatha, B. Bogdanovic, M. Felderhoff, A. Pommerin, W. Schmidt, F. Schuth, C. Weidenthaler, J. Alloys Compd., 407 (2006) 78.

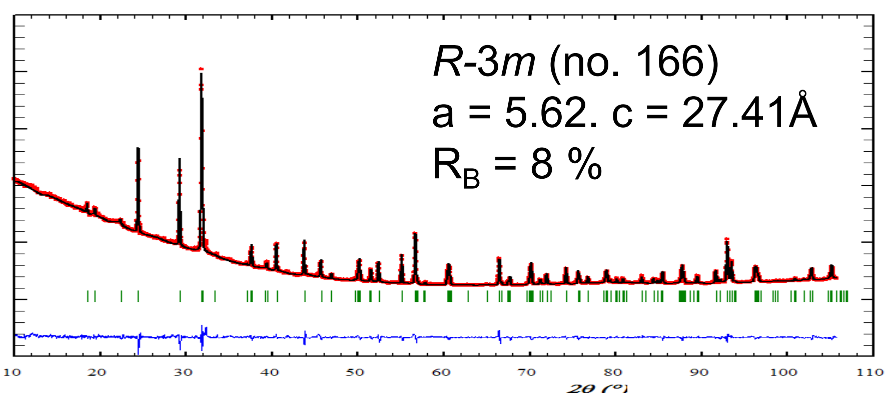
Characterization of K_2LiAlH_6

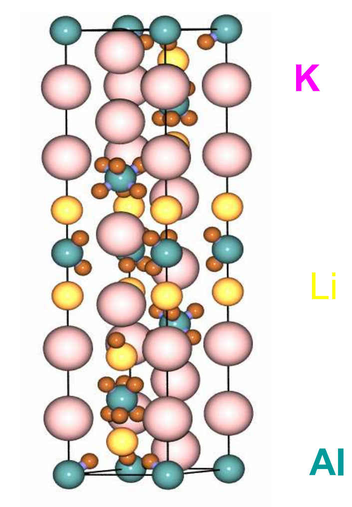
$LiAlH_4 + 2KH \rightarrow K_2LiAlH_6$ at 700 bar and 320°C

•<u>Hydrogen storage properties</u>:
Desorption >200ºC; Absorption >320°C and 100bar H_2
$K_2LiAlH_6 \leftrightarrow 2KH + LiH + Al + 3/2H_2$ (2.5 wt % theo.)
Slow kinetics

•K_2LiAlH_6 is isostructural with HT-K_2LiAlF_6
•Structure supported by *ab-initio* calculations

Plot from Rietveld refinement

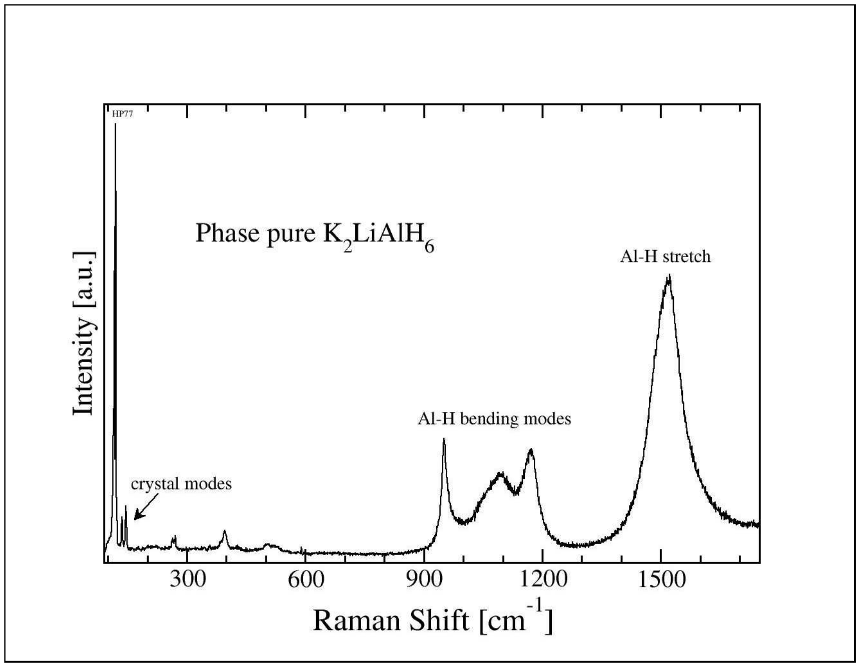


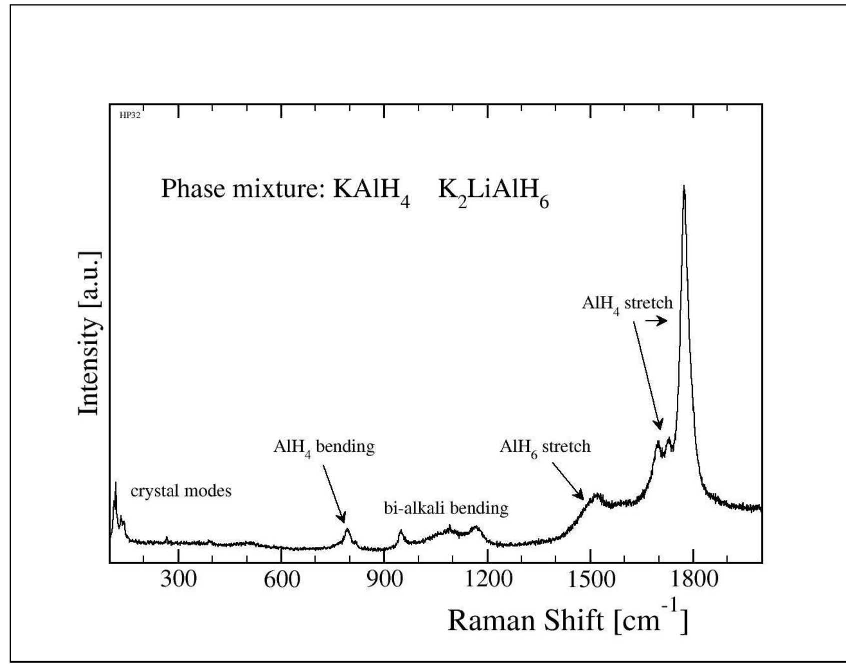


Note: Not the same phase as J. Graetz et al, Phys. Rev. B, v.71, (2005) 184115

Raman Spectrum of K_2LiAlH_6 and $KAlH_4$

The following tentative assignments are proposed based on comparisons with calculations and experimental data taken for the $NaAlH_4$ compound:





- Raman spectra of pure K_2LiAlH_6 showing the Al-H bending and stretching modes of the AlH_6^{3-} anion

- Raman spectra of a sample containing $KAlH_4$ and K_2LiAlH_6 showing the Al-H bending and stretching modes of AlH_4^- and AlH_6^{3-} anions

Eric Majzoub

Calculated Total Energies of K_2LiAlH_6

Structure Type	F.U./unit cell	VASP (eV/fu)	Symmetry	Space Group no.
HT-K_2LiAlF_6	6	-30.700	*R-3m*	166
Cs_2NaAlF_6	4	-30.700	*C2/m*	12
K_3MoF_6	4	-30.589	*Fm-3m*	225
Na_2LiAlF_6	2	-30.588	$P2_1/n$	14
Sr_2NiWO_6	2	-30.588	*I4/m*	87
LT-K_2LiAlF_6	4	-30.587	*Fm-3m*	225
Si_2LiAlO_6	4	-29.855	*C2/c*	14
Pb_2BiVO_6	4	-29.613	*Pnma*	62

Calculated total energies of K_2LiAlH_6 for several structure types taken from the ICSD database

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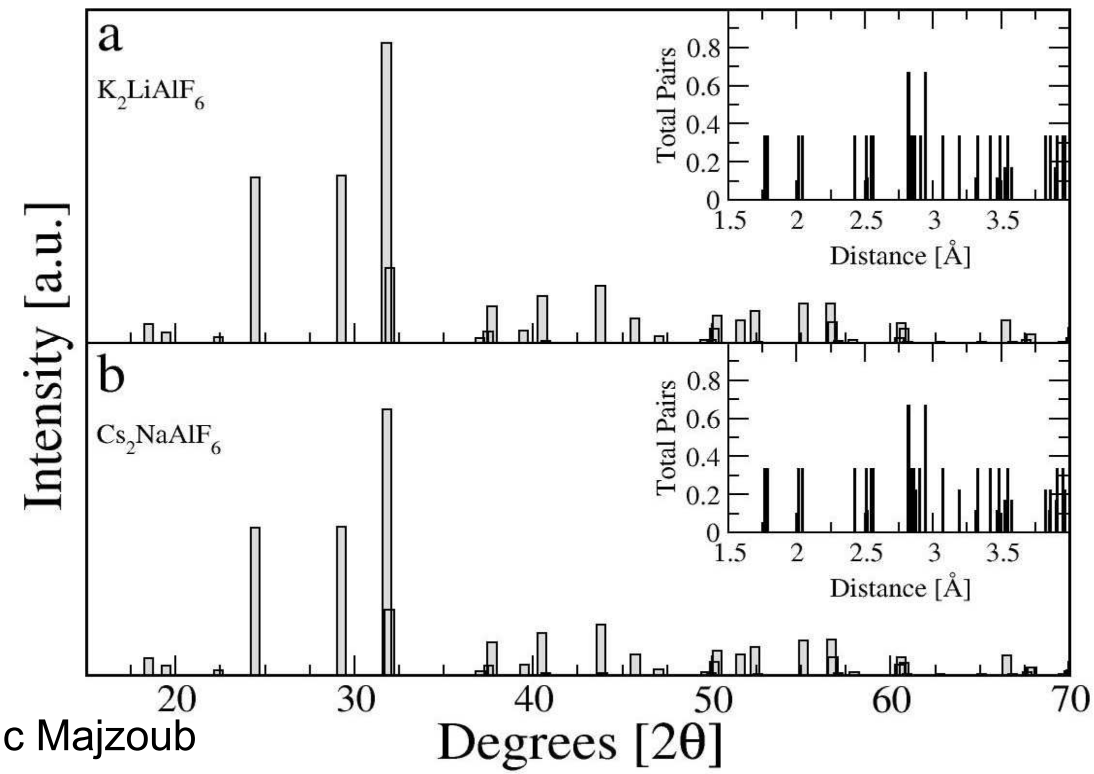
Calculated X-ray Diffraction Patterns



(a) HT-K_2LiAlF_6 structure spacegroup *R*-3*m*

(b) Cs_2NaAlF_6 structure spacegroup *C*2/*m*

Eric Majzoub

Diffraction patterns very similar…

thus,

The Cs_2NaAlF_6 structure type was used as an input model for Rietveld refinements. This resulted in higher R_B= 12%, thus validating the conclusion that the HT-K_2LiAlF_6 type-structure best describes the structure of K_2LiAlH_6

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No Cation Mixing in Bialkali K_2LiAlH_6

- Rietveld refinement indicates no mixing of different cations
- Ab-initio mixing calculations:
- Entropy of mixing energy (~ -45meV/fu) is much smaller than the increase in electronic energy (~ +300-700 meV/fu)
- Size difference between K^+, Li^+ cations is significant
- No mixing implies little or no thermodynamic “tunability”

Conclusions K_2LiAlH_6

- ✓ A bialkali alanate K_2LiAlH_6 was synthesized and characterized
- ✓ K_2LiAlH_6 is less stable than $KAlH_4$, but more stable than $NaAlH_4$
- ✓ *Ab-initio* total energy calculations were performed, including relaxations, of the Rietveld refined structure for comparison to database and other structures and further support the validity of the structure determination
- ✓ The calculated structure that agrees with the Rietveld refined structure has the lowest energy
- ✓ No mixing of cations…

E. Rönnebro, E. Majzoub, J. Phys. Chem. B., 110(51), (2006) 25686-25691

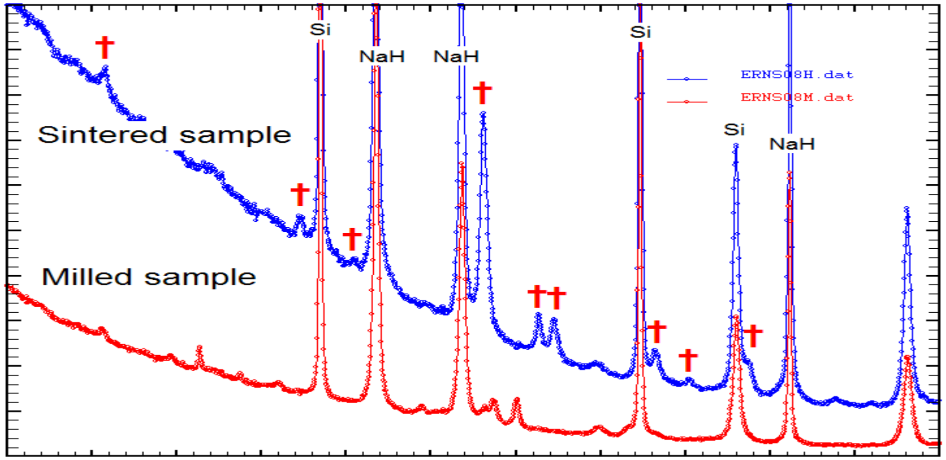
Screening for New Light-weight High-capacity Metal Hydrides

Can $[SiH_x]^{y-}$ exist in solid state stabilized by Li, Na, K, Mg or Ca?

$2NaH + Si \rightarrow$ [Na-Si-H] (high-pressure sintering)

- **Investigation of $[SiH_6]^{2-}$ stabilization by Li^+, Na^+ or Ca^{2+}**
- **XRD reveals new phases in Na-Si-H system**
  - **Hydrogen content was investigated by neutron spectroscopy and NMR, but showed very small H-content**
  - **Different phases appear depending on reaction conditions**

Collaborations with
NIST (NPD),
JPL&LLNL (NMR)
U. Utah (reactive milling)
HRL (milling)



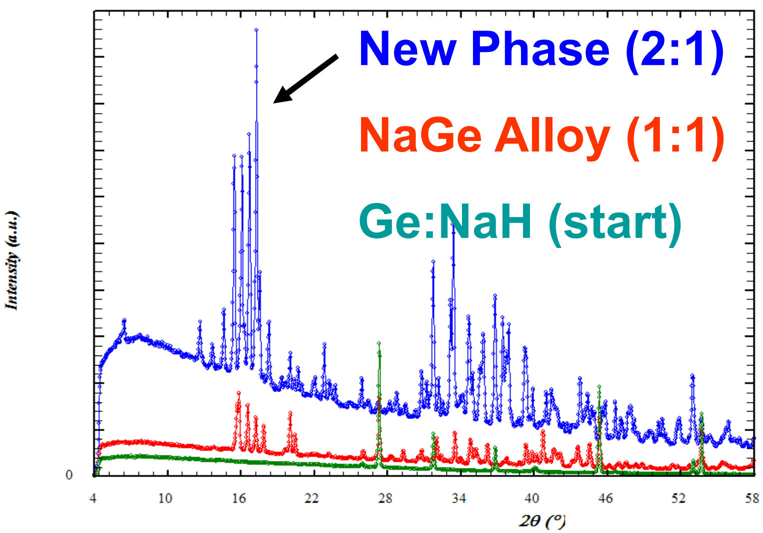
XRD pattern

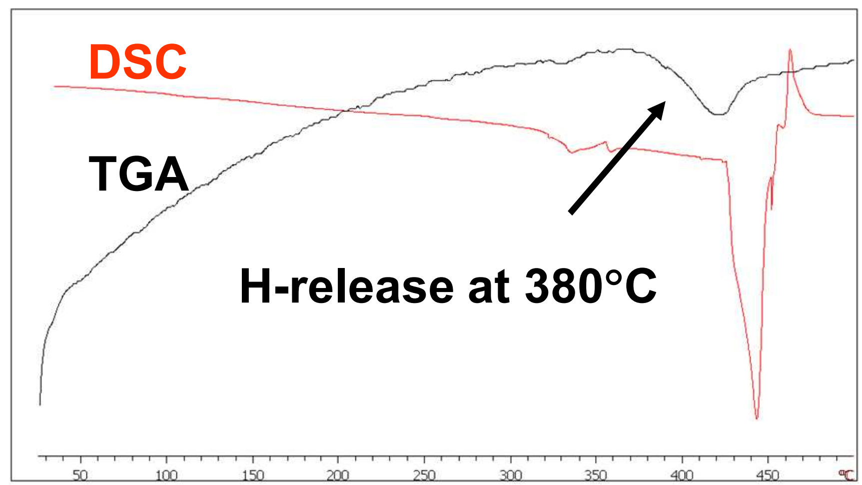
† = New phase

Can $[GeH_x]^{y-}$ exist in solid state stabilized by Li, Na, K, Mg or Ca?

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

New Na_2GeH_x compound





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 endothermic phase transition

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

Reversible Hydrogen Storage in Catalyzed Calcium Borohydride

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. %

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

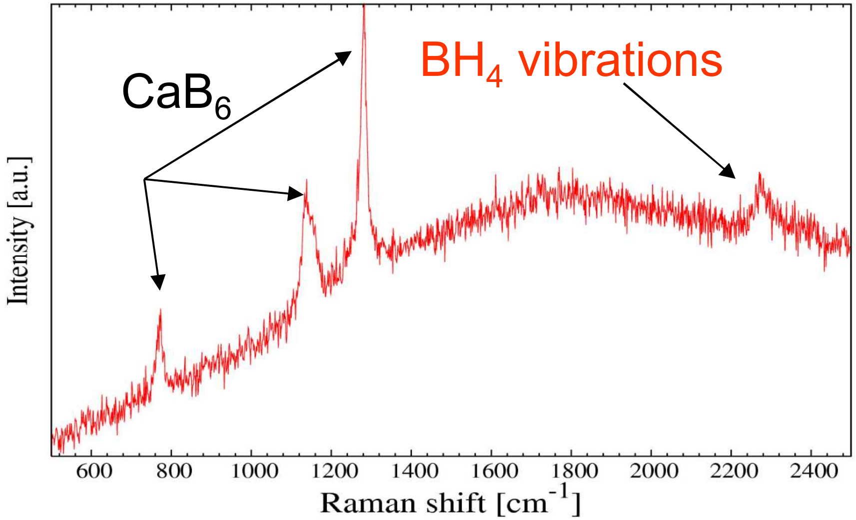
- By trying several additives, the product yield from HP-sintering was improved to ~ 60%, while improving kinetics (Patent filed)
- Identified the Ca-B-H compound as $Ca(BH_4)_2$ by thorough characterization teaming with our MHCoE partners and collaborators
- Prepared pure, crystalline $Ca(BH_4)_2$ from Aldrich $Ca(BH_4)_2 \cdot 2THF$ for PCT-desorption characterizations with different additives

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

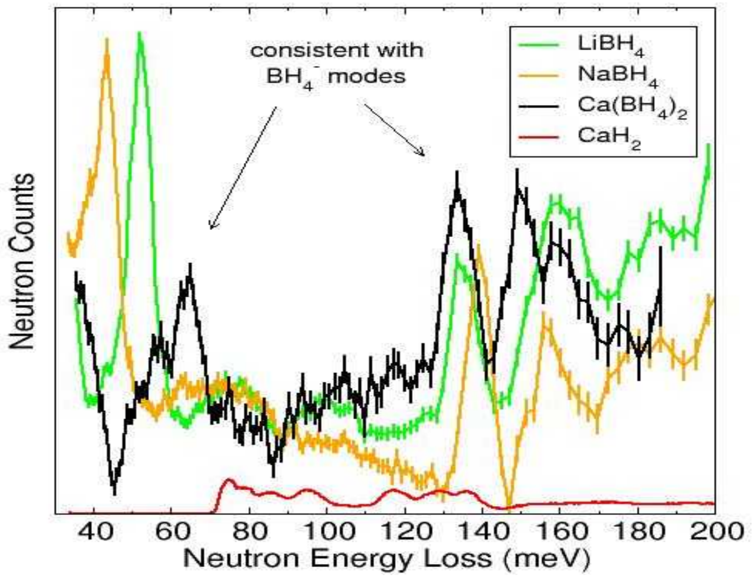
- $2LiBH_4 + CaCl_2 \rightarrow Ca(BH_4)_2 + 2LiCl$ (Nakamori, Orimo et al, J. Alloys Compd, in press)
- $MgB_2 + CaH_2 + 4H_2 \rightarrow Ca(BH_4)_2 + MgH_2$ » 8.3 wt% calc (Dornheim, Klassen et al, J. Alloys Compd, in press)

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*



Neutron Vibrational Spectra shows BH_4^- (T. Udovic, NIST)



Results:

- XRD (SNL, UNR) 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)

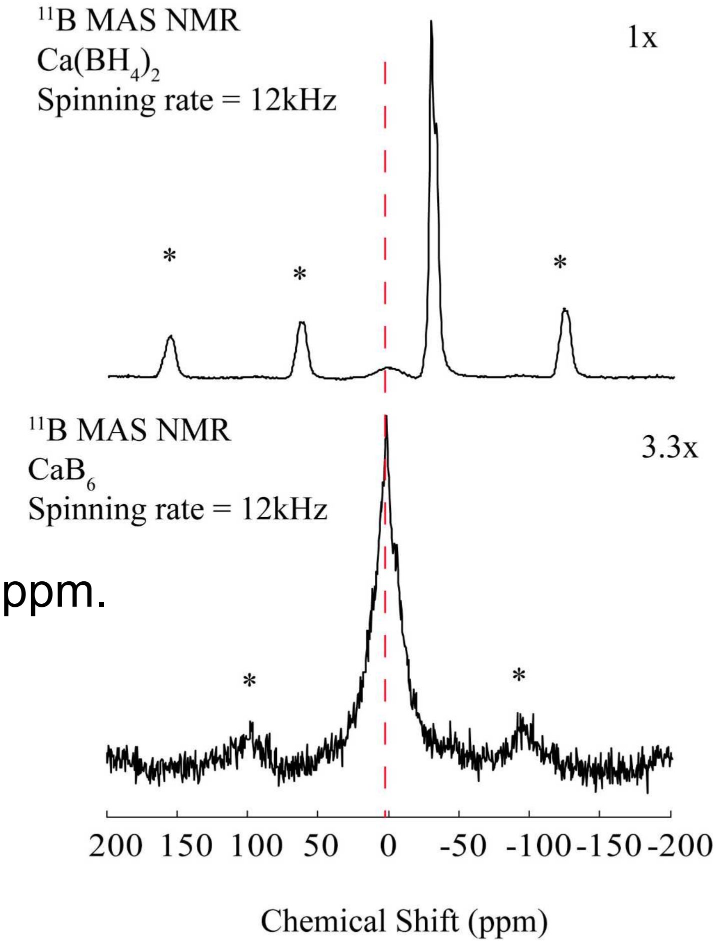
^{11}B Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) was performed on $Ca(BH_4)_2$ and CaB_6

The ^{11}B MAS NMR indicates at least 3 different boron sites in $Ca(BH_4)_2$:

1) at 2.3ppm, indicating CaB_6
2) at -29.7ppm
3) at -32.8ppm

The last two boron sites are unknown.

Both samples were referenced to H_3BO_3 at 19.8ppm.



Dr. Julie Herberg, LLNL: Dr. Robert Bowman, JPL

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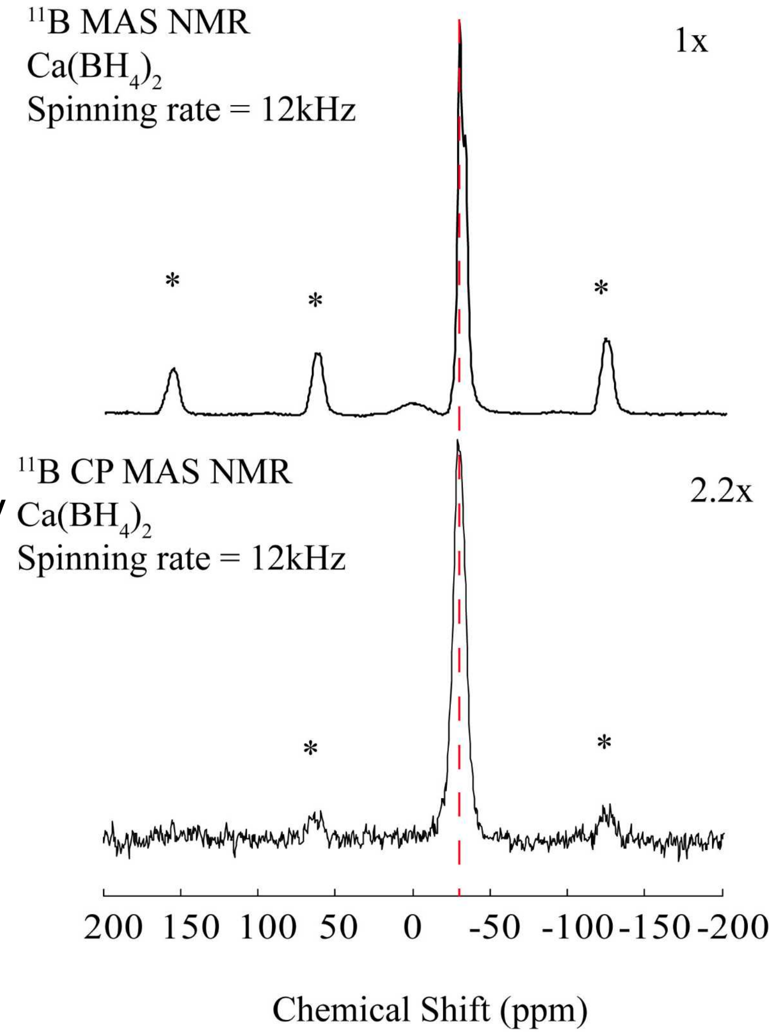
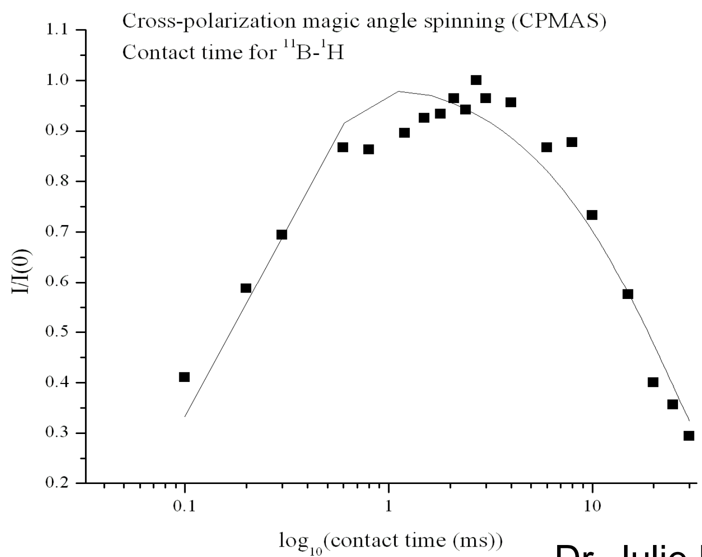
^{11}B and ^{11}B Cross-polarization (CP) Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) was performed on $Ca(BH_4)_2$

The ^{11}B CPMAS NMR indicates that the peak at -29.7ppm is associated with boron attached to hydrogen in $Ca(BH_4)_2$.

Varying the contact time between the ^{11}B and ^{1}H, further indicates that boron is attached to hydrogen in this material.

We are currently investigating this to further identify these unknown boron sites.



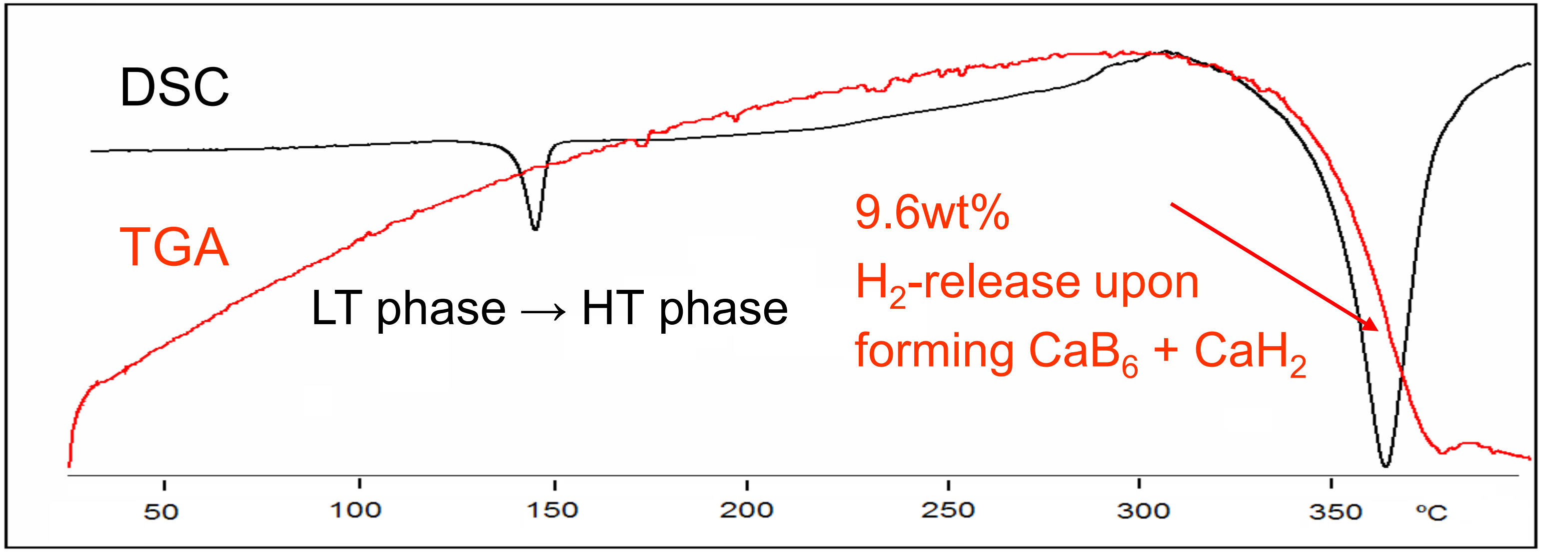


Center for National Security Applications of Magnetic Resonance

Dr. Julie Herberg, LLNL: Dr. Robert Bowman, JPL

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

In-situ XRD of Dehydrogenation Reaction

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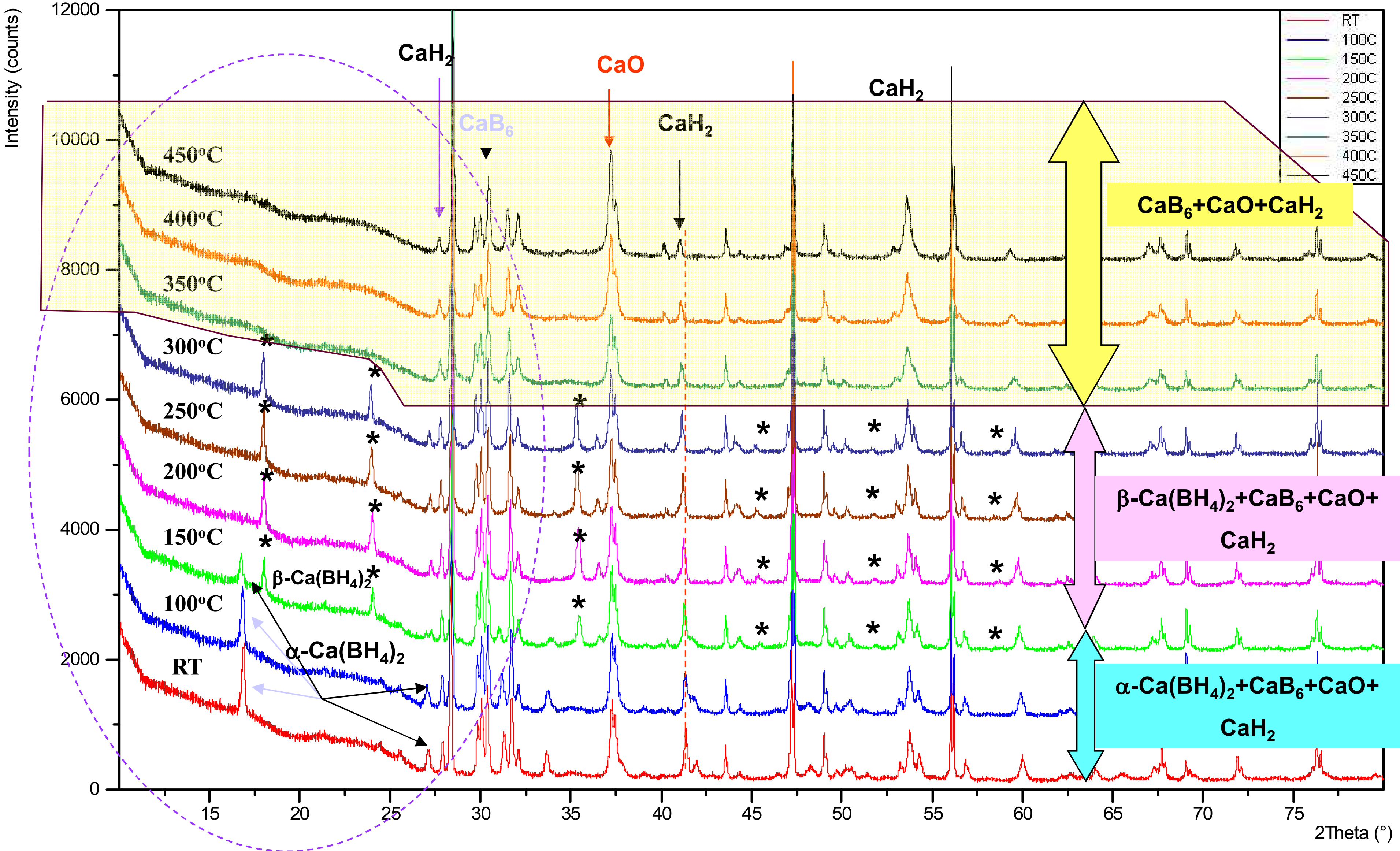
- ***Observed New β Ca(BH$_4$)$_2$***

By Wen-Ming Chien and Dhanesh Chandra



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$Ca(BH_4)_2$ Shows Reversibility

Dehydrogenation:

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

(9.6 wt. % H released)

Hydrogenation:

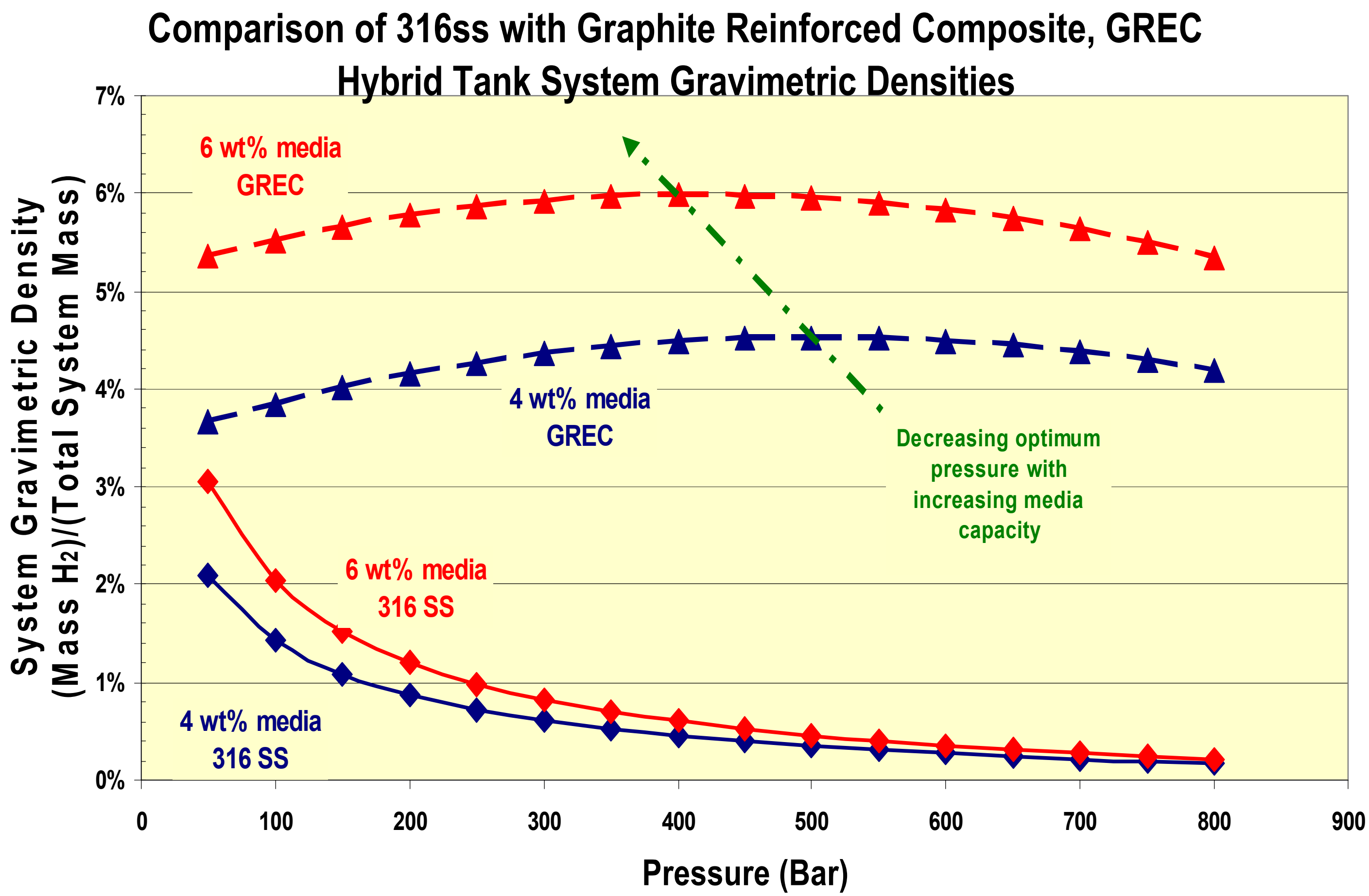
$$CaB_6 + 2CaH_2 \xrightarrow[390\ ^\circ C]{100\ bar\ H_2} 1\%\ Ca(BH_4)_2\ yield$$

However,

$$CaB_6 + 2CaH_2 \xrightarrow[400\ ^\circ C]{700\ bar\ H_2} 60\%\ Ca(BH_4)_2\ yield$$

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

High Pressure/ Metal Hydride Tank Designs



Don Anton, SRNL:

"…..with a composite tank operating at 400 bar, a reversible 6 wt. % media satisfies the DOE 2010 goal for System Gravimetric Density….."

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Future Work

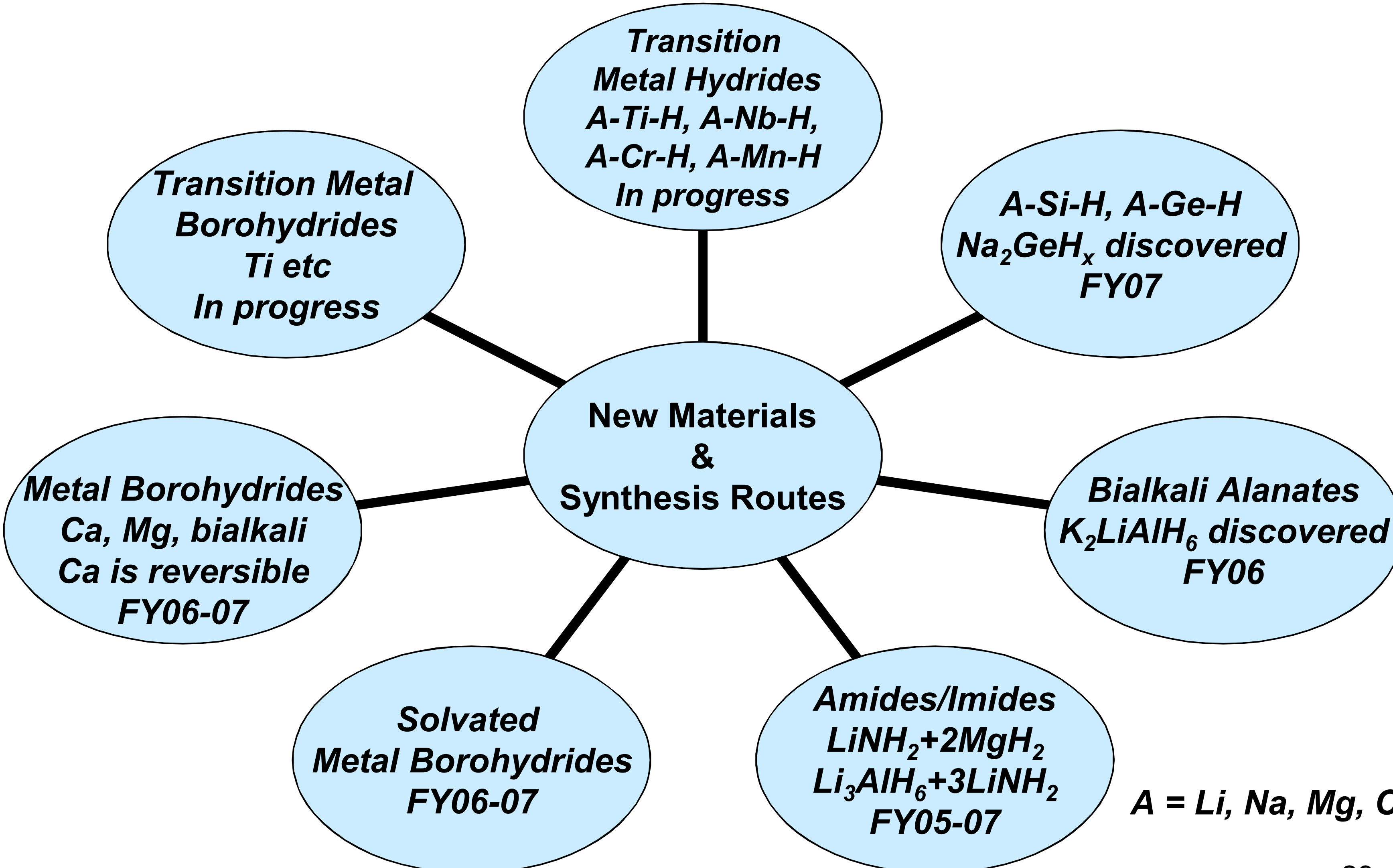
Calcium Borohydride

- 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

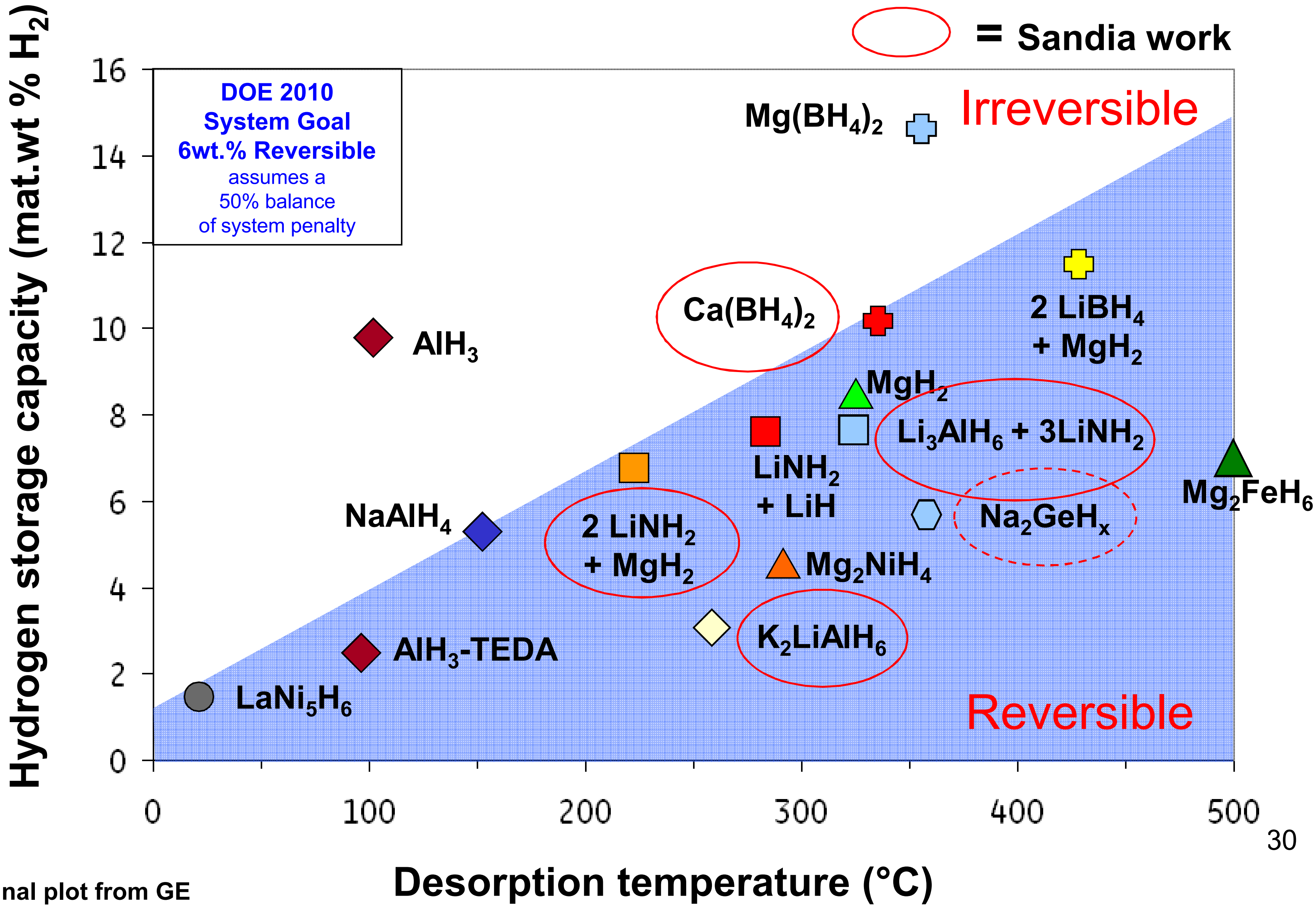
- Explore bialkali borohydrides guided by MC theory
- Teaming with our partners to explore reversibility of other metal borohydrides at our high-hydrogen pressure facility

Investigated Metal Hydride Systems FY05-FY07 at Sandia



A = Li, Na, Mg, Ca

Status Relative to DOE Targets



Original plot from GE

Path Forward

Theoretical Bialkali Borohydride Stability

Eric Majzoub

- 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)**

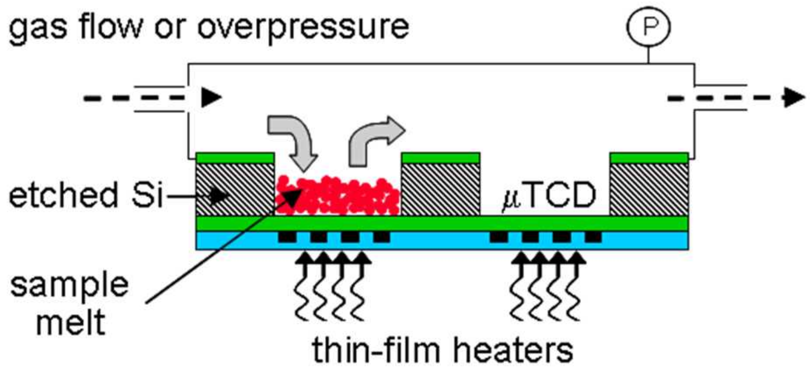
We have identified two potentially stable mixed cation borohydrides and will attempt synthesis

New Combinatorial Method for Rapid Screening of New Materials

Tony McDaniel

Motivation: A breakthrough material is needed….

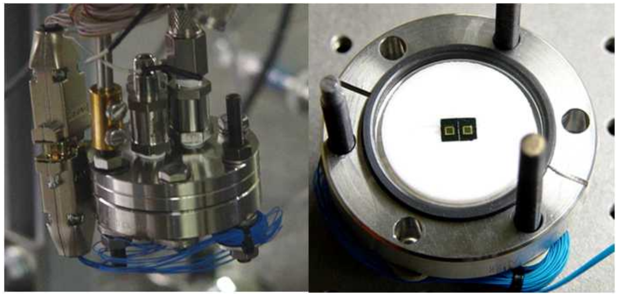
- Utilize arrays of micro-hotplates to synthesize and characterize materials
  - High-temperature and high-pressure processing of precursors
    - *800 °C and 2000 bar H_2*
  - Micro-scale in-situ diagnostics
    - *calorimetry and H_2 gas detection*
- Statistical methods to formulate and analyze the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



Prototype 130 bar H_2 fully instrumented system

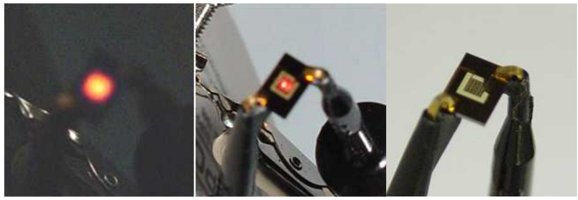
✓2 micro-hotplates
✓Calorimeter and gas composition diagnostics
- Proof Materials: MgH_2, $NaAlH_4$ (in progress)
- Target: Bialkali Borohydrides

internal chamber



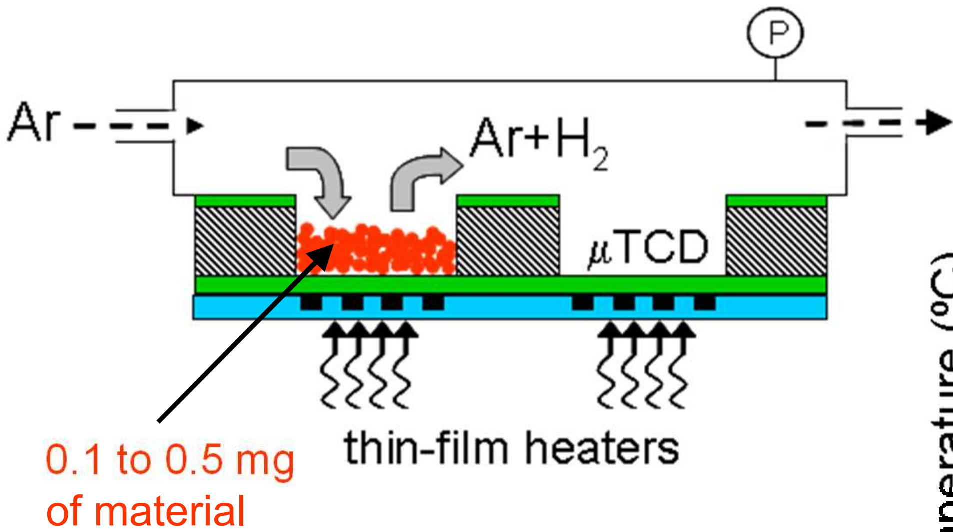
2 micro hot plates in 2.75” OD flange

hotplate in air at 1000 K



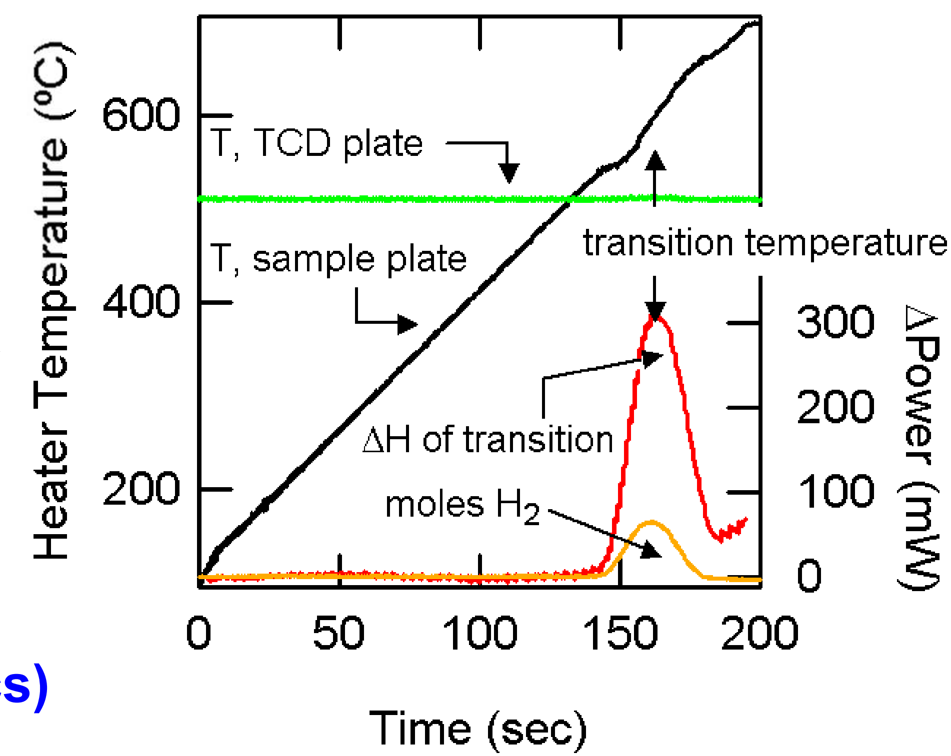
ΔH Desorption, H_2 Release from MH Detected With In-Situ Diagnostics

Sandia National Laboratories
Tony McDaniel



TCD = thermal conductivity detector (for H_2 detection)

$$MgH_2 \rightarrow Mg + H_2$$



✓ **Rapid thermal characterization with high sensitivity**
- **Transition temperature (kinetics)**
- **Enthalpy of transition**
- **H_2 capacity**

✓ **Enables a unique combinatorial approach (information rich)**

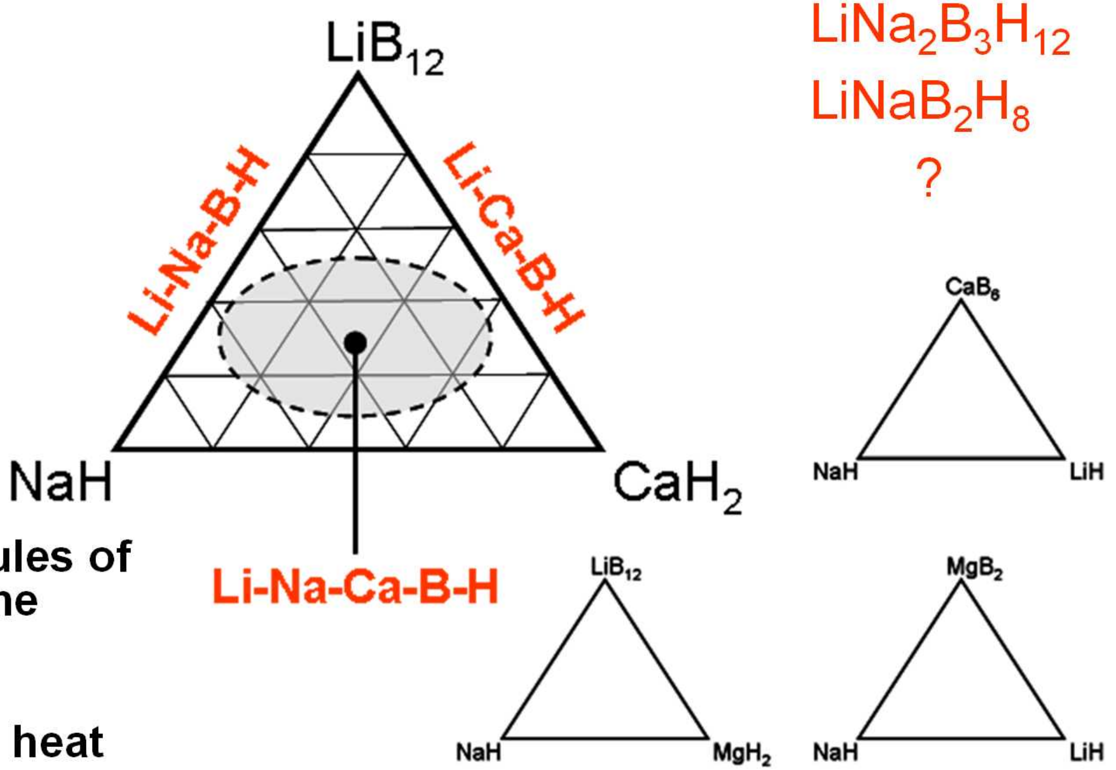
High-throughput Screening Guided By Theoretical Predictions

Tony McDaniel

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**

Summary

Alanates

- A new alanate, K_2LiAlH_6, was used to develop new discovery strategies
- Determined structure of K_2LiAlH_6 and investigated hydrogen sorption properties
- Ab-initio calculations verified the crystal structure

Ternary Silicon and Germanium Hydrides

- A new Na_2GeH_x compound found; H-release observed by TGA, characterization in progress

Borohydrides

- Demonstrated new solid state route to synthesize $Ca(BH_4)_2$. In-situ XRD, TGA&DSC showed phase transformations and 9.6wt% hydrogen release
- Catalyzed Calcium borohydride shows reversible H-storage

Future Work

Borohydrides

➢ Synthesize bialkali borohydrides and explore reversibility of (Ca, Mg, Sc, Ti, Al etc) borohydrides based on theoretical predictions

Synthesis of New Complex Anionic Materials

➢ Discover new complex anionic materials by high-throughput screening and sintering under high H_2-pressure and down-select the most promising materials with support from theoretical modeling

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