High-capacity Hydrogen Storage Systems via Mechanochemistry

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and Eric Majzoub (UMSL)

2017 Annual Merit Review

Project ID # ST119

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Overview

Timeline

- Start Date: July 1, 2015
  - Phase 1: September 30, 2016
  - Phase 2: October 1, 2016 - September 30, 2017
  - Phase 3: October 1, 2017 - September 30, 2018*
- End Date: June 30, 2018
- % Complete: 60

*Project continuation and direction determined annually by DOE

Barriers addressed

(A) System Weight and Volume
(B) System Cost
(O) Lack of Understanding of hydrogen Chemisorption

Budget

- Total Project budget: $1.225 M
  - Total Recipient Share: $0.025 M
  - Total Federal Share: $ 1.2 M
- Total funds received: $200K (FY15), $500K (FY16), $300K (FY17), $200K (FY18-plan)
- Total DOE Funds Spent (to date): $564,343K as of March 31, 2017
- Subcontract UMSL: $58K (per phase)

Partner(s)

• UMSL: Eric Majzoub (Computational effort)

UMSL

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Relevance/Objectives

Main Focus: Development of Novel High H-capacity Si-based borohydrides (Si-BH) and composites

Objectives: Development of low-cost, high-performance hydrogen storage materials based on:

1. Silicon-based complex borohydrides

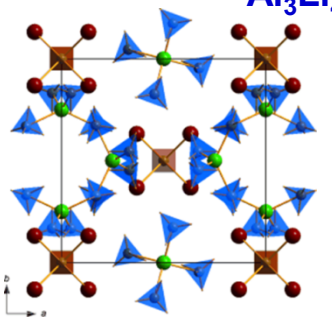
- Projected to have borderline thermodynamic stability.
- Stabilization strategies based on hypersalt/adduct formation; cation and anion engineering.

2. ***Borohydride/graphene composites***
(Discontinued as per PM guidance)

Relevance/Objectives

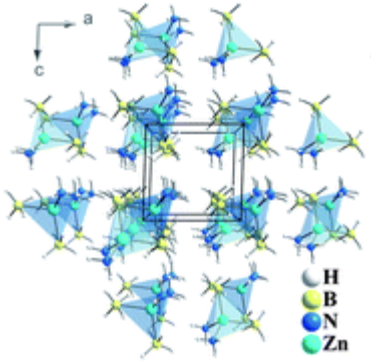
- Borohydrides have largest gravimetric density among all known metal hydrides: $LiBH_4$, $Mg(BH_4)_2$, $Al(BH_4)_3$,..
- Like nearly all other complex hydrides they suffer from poor kinetics and limited reversibility
- Structurally diverse: provide numerous opportunities for tuning
- May be stabilized by forming hypersalts and/or adducts
- No Si-based borohydrides reported in the past; Si and B are abundant and inexpensive

$Al_3Li_4(BH_4)_{13}$



Int. J. Hydr. En., 2013, **38**, 2790

$Zn(BH_4)_2 \cdot 2NH_3$



Energy Environ. Sci., 2012,**5**, 7590

Approach/Milestones

Task 1	*Screening, Synthesis and Characterization of Novel Si-BH via Hypersalt Stabilization (FY16)*	
QPM 1.1	Calculate stability of Si-BH hypersalts with alkali or alkaline earth cations	100%
QPM 1.2	Demonstrate Si-BH formation through metathesis reactions	100%
QPM 1.3	Computationally identify candidate Si-BH hypersalts for synthesis	100%
Task 2	*Graphene/hydride composite-based storage of metal hydrides (FY16)*	
QPM 1.4	Prepare graphene/hydride composites with $LiBH_4$ via mechanochemistry	100%
Go/No Go	Demonstrate that novel Si-BH hypersalts can be stabilized and have desorption temperatures lower than 200°C.	Go
Task 3	*Novel Si-BH via Hypersalt Stabilization (FY17)*	
QPM 2.1	Demonstrate reversibility of a Si-BH hypersalt candidate	100%
QPM 2.2	Demonstrate formation of a sulfur stabilized Si-BH in one other system e.g. (Na/K/)BH_4-SiS_2, $Mg(BH_4)_2$-SiS_2	80%
QPM 2.3	Demonstrate reversibility of a sulfur stabilized Si-BH	80%
Task 4	*Si-BH by high-pressure ball-milling (FY17)*	
QPM 4.4	Demonstrate Si-BH formation through ball-milling of Si and boron-containing compounds under high hydrogen pressure	In progress
Go/No Go	Demonstrate that Si-BH can achieve at least 50 % reversibility and reversible capacities of at least 2.5 wt.% below 200°C and 5 wt.% below 350°C	9/31/2017

Accomplishments: $LiBH_4 – SiBr_4$ system

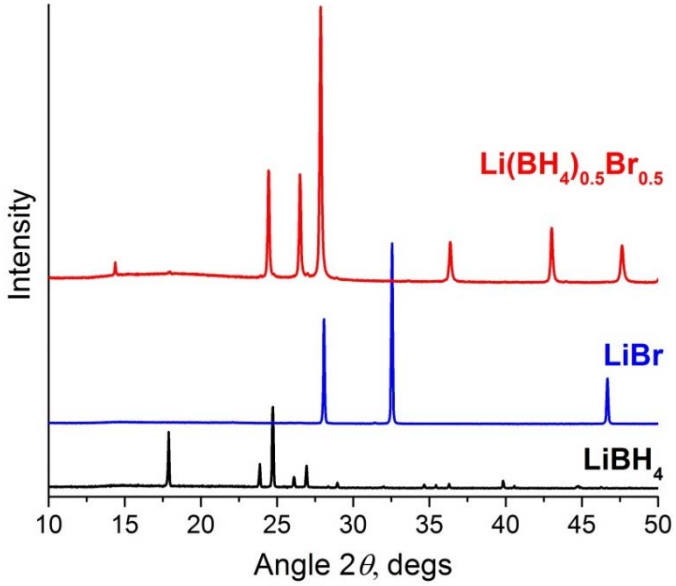
$$8LiBH_4(c) + SiBr_4(l) \rightarrow 8Li(BH_4)_{0.5}Br_{0.5}(c) + Si(BH_4)_4$$

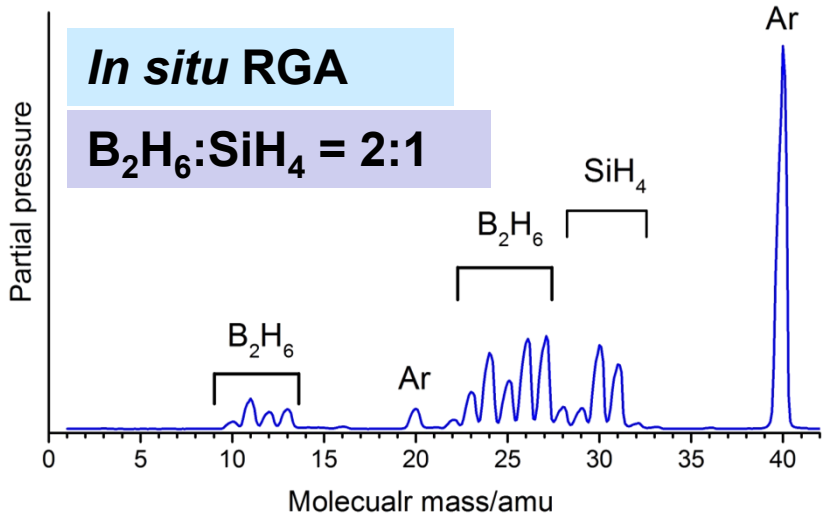
$$Si(BH_4)_4 \rightarrow 2B_2H_6(g) + SiH_4(g)$$

Rietveld-refined structure

$Li(BH_4)_{0.5}Br_{0.5}$ (SG $P6_3mc$)

a = 4.2007(4) Å; c = 6.7185(7) Å





MGCLP calculations of gas phase reaction energies at 300 K

Reaction	ΔH, kJ/mol	ΔE, kJ/mol	ΔS, J/mol·K
$SiH_4 + 2B_2H_6 \rightarrow Si(BH_4)_4$	-86.22	107.60	-287.41
$SiH_4 + 1B_2H_6 \rightarrow SiH_2(BH_4)_2$	-41.24	46.74	-137.49
$SiF_2H_2 + 1B_2H_6 \rightarrow SiF_2(BH_4)_2$	-46.90	36.29	-156.34
$SiCl_2H_2 + 1B_2H_6 \rightarrow SiCl_2(BH_4)_2$	-38.68	47.67	-128.96
$SiBr_2H_2 + 1B_2H_6 \rightarrow SiBr_2(BH_4)_2$	-39.82	48.53	-132.75

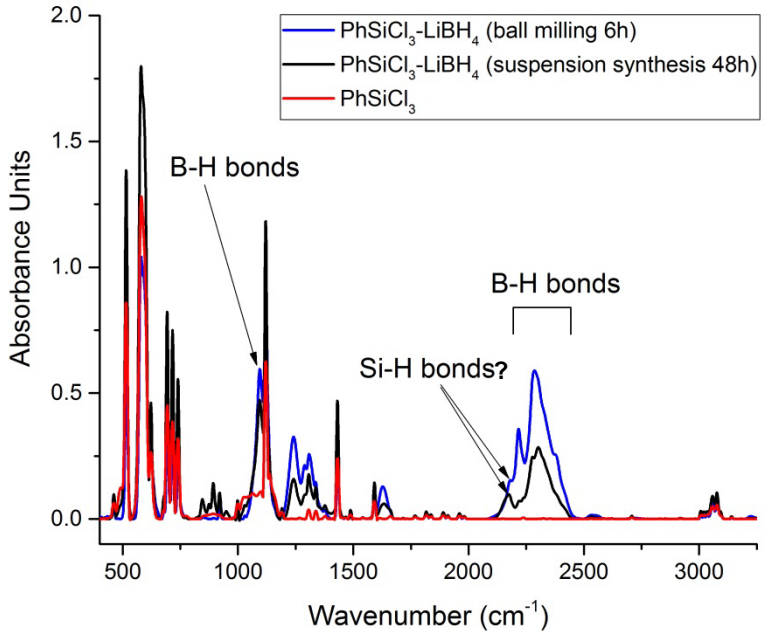
Halide substitutions tend to stabilize Si-BHs clusters in gas phase and may stabilize in solid

Accomplishments: *$LiBH_4$ – $PhSiCl_3$ system*

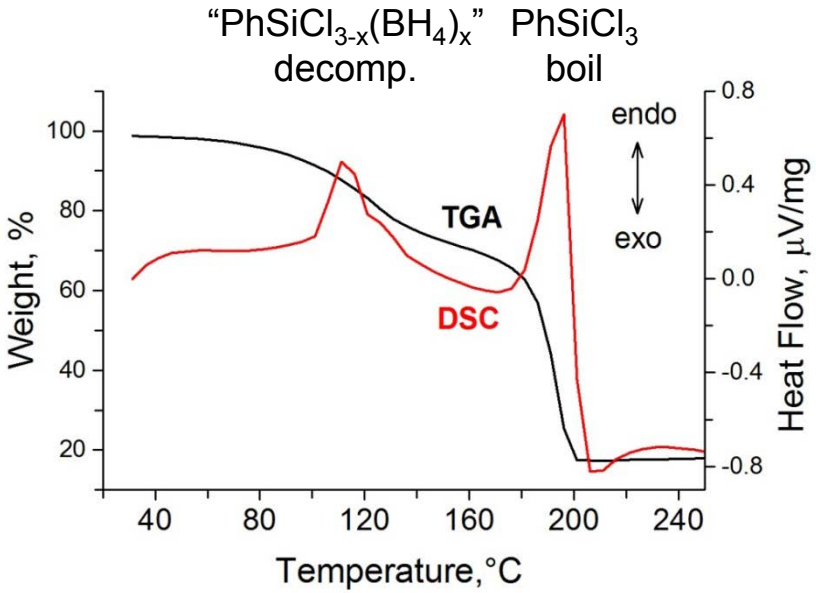
$xLiBH_4(c) + PhSiCl_3(l) \rightarrow xLiCl(c) + \text{“}PhSiCl_{3-x}(BH_4)_x\text{”}?(a)$

XRD: $LiCl+LiBH_4$+amorphous phase

FT-IR: BH_y ($y \leq 4$) group; Si-H bonds



DSC-TGA of the ball-milled sample



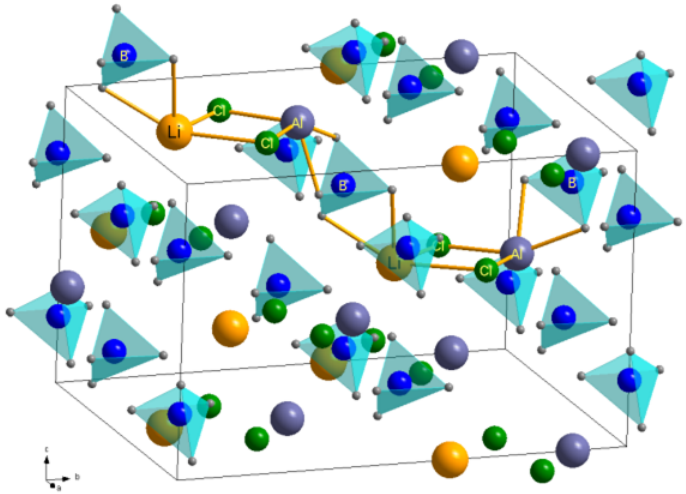
Charge delocalization effect of phenyl or substituted phenyl group may potentially stabilize Si-based borohydrides

Accomplishments: $LiBH_4 – AlCl_3$ system

Stabilization of a new phase

$$13LiBH_4 + 3AlCl_3 \rightarrow Li_4Al_3(BH_4)_{13} + 9LiCl$$

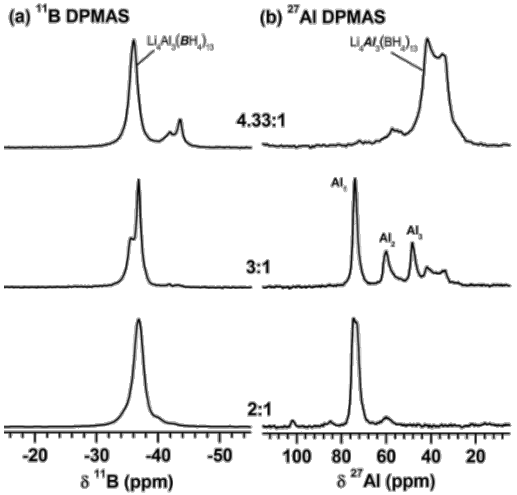
$$2LiBH_4 + AlCl_3 \rightarrow LiAl(BH_4)_2Cl_2 + LiCl$$



Rietveld-refined

SG: C2 *(#5)*;
a=8.4717(5) Å
b=11.6699(7) Å
c=7.5108(4) Å
β = 90.04(1)°

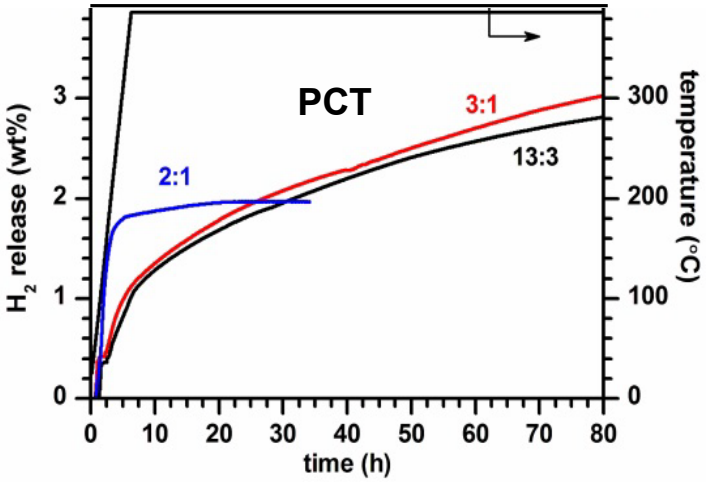
SSNMR



Structure solution based on combined XRD, NMR and DFT

RGA

$LiBH_4$:$AlCl_3$	H_2 (%)	B_2H_6 (%)
13:3	84.0	**16.0**
3:1	99.7	**0.3**
2:1	99.9	**Undetected**

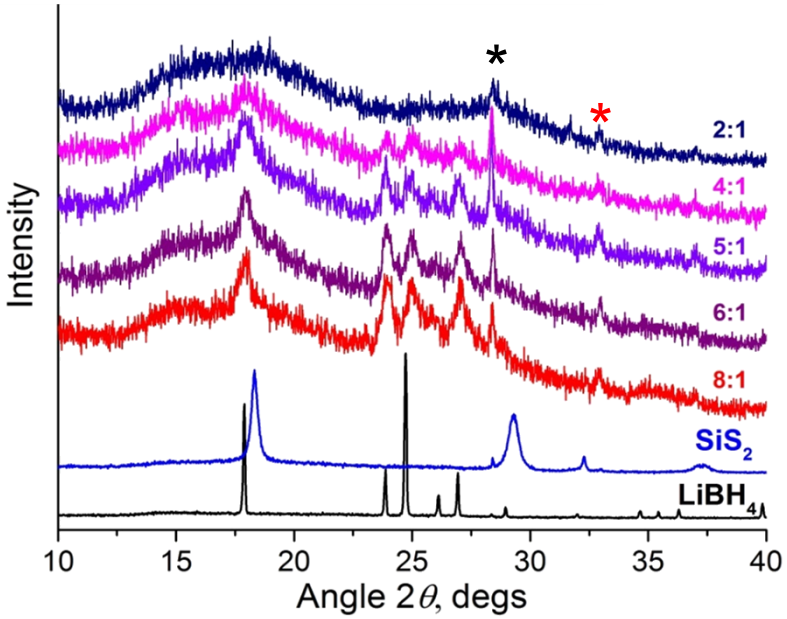


Significant reduction in B_2H_6 release is observed

Accomplishments: *$LiBH_4$ – SiS_2 system*

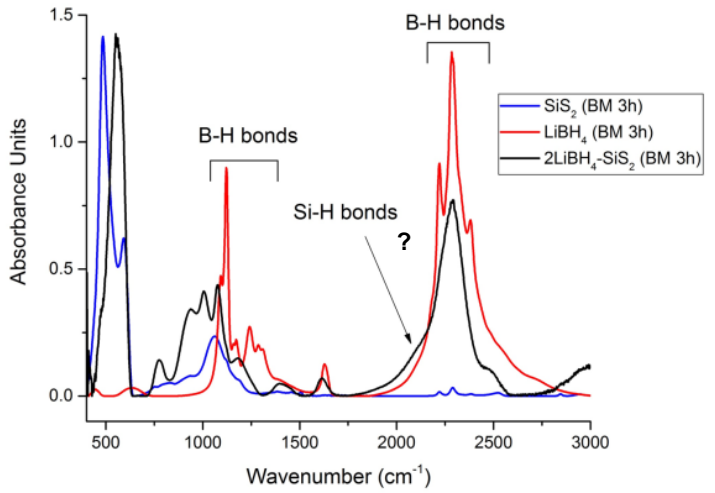
$2LiBH_4(c) + SiS_2(c) = \text{“}Li_2SiS_2(BH_4)_2\text{”}(a)$

2:1 molar mixture yields X-ray amorphous product: *No starting materials*.

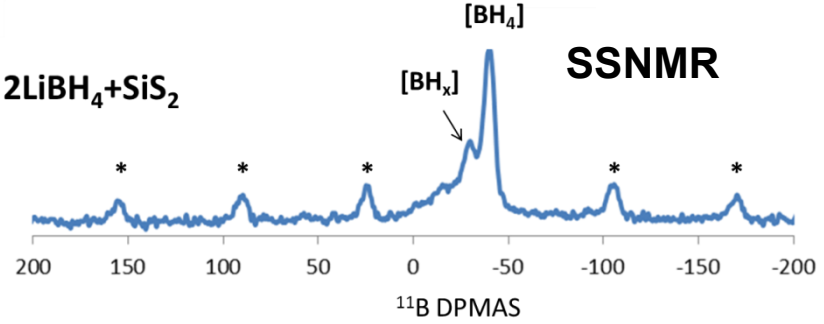


*Si and *FeS_2 impurities from SiS_2 precursor

FT-IR



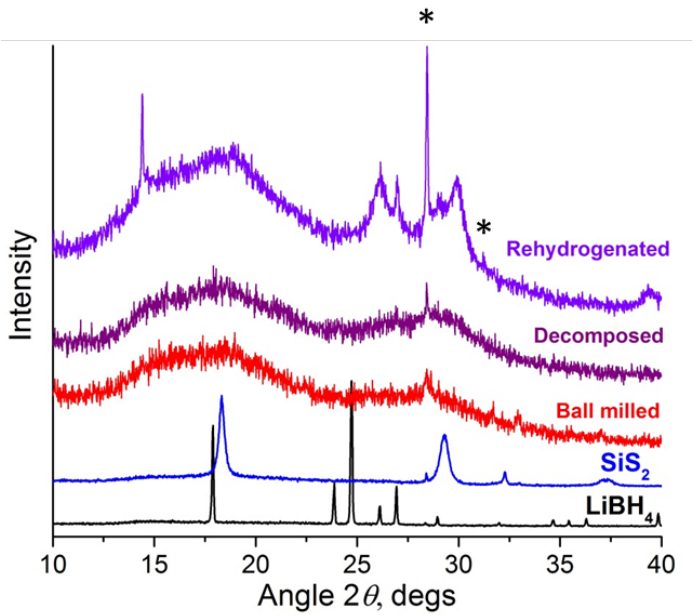
SSNMR



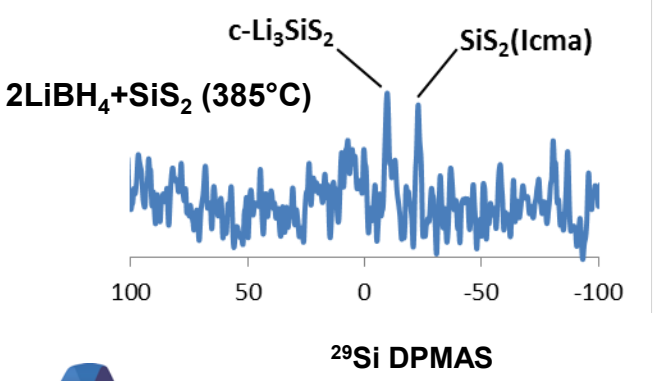
Formation of Si-BH with a nominal composition of “$Li_2SiS_2(BH_4)_2$”is likely

Accomplishments: *$LiBH_4$ – SiS_2 system*

Reversibility in "$Li_2SiS_2(BH_4)_2$"

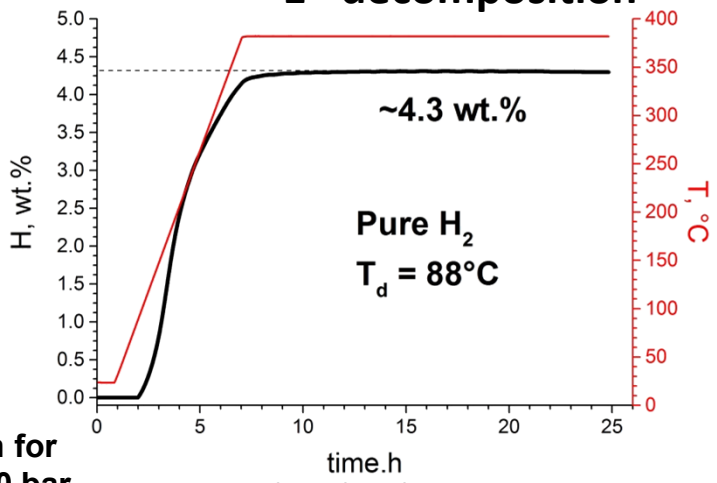


*impurities from SiS_2 precursor



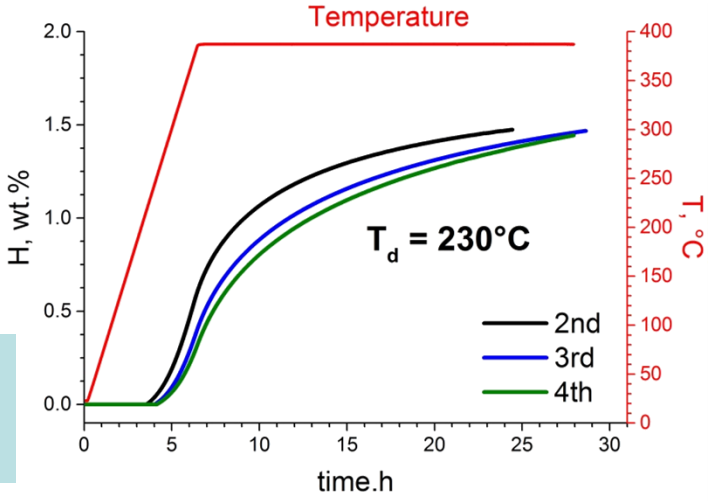
^{29}Si DPMAS

1st decomposition



Hydrogenation for 10 hours at 160 bar and 380°C

2nd, 3rd, 4th decomposition



Nearly 35 % reversibility

Accomplishments – *$LiBH_4$-SiS_2 system*

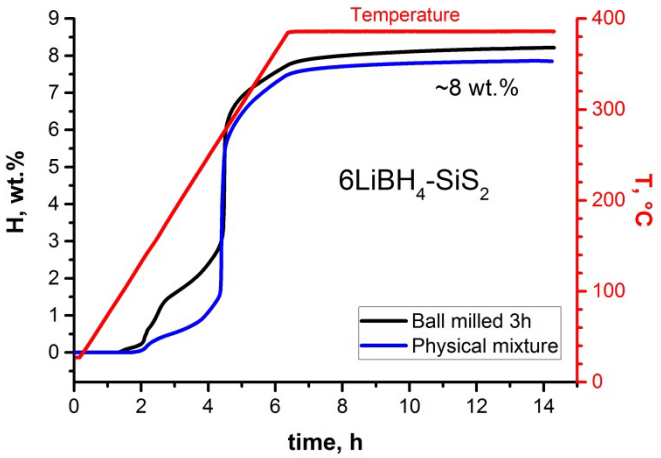
Desorption $xLiBH_4 – SiS_2$ (x= 2-8)

$LiBH_4$:SiS_2	Experim. H_2, wt. %	Theoretical H_2, wt.%	Products based on XRD
2:1	4.3	5.9	SiS_2, Li_2S
4:1	7.1	8.9	↓SiS_2, ↑Li_2S
5:1	7.5	9.9	↓(?)SiS_2, ↑Li_2S
6:1	8.2	10.7	↑Li_2S
8:1	6.2	11.9	$LiBH_4$, Li_2S

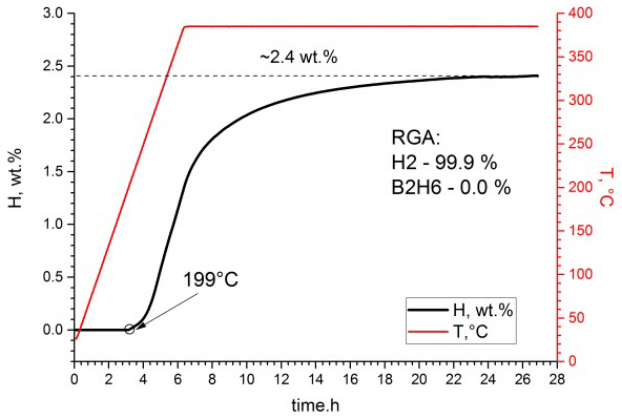
- Highest H_2 release observed in 6:1 ratio
- Nearly 30 % reversible capacity achieved

Cycling $6LiBH_4 – SiS_2$

1st desorption



Desorption: after 1st abs (ball milled sample)

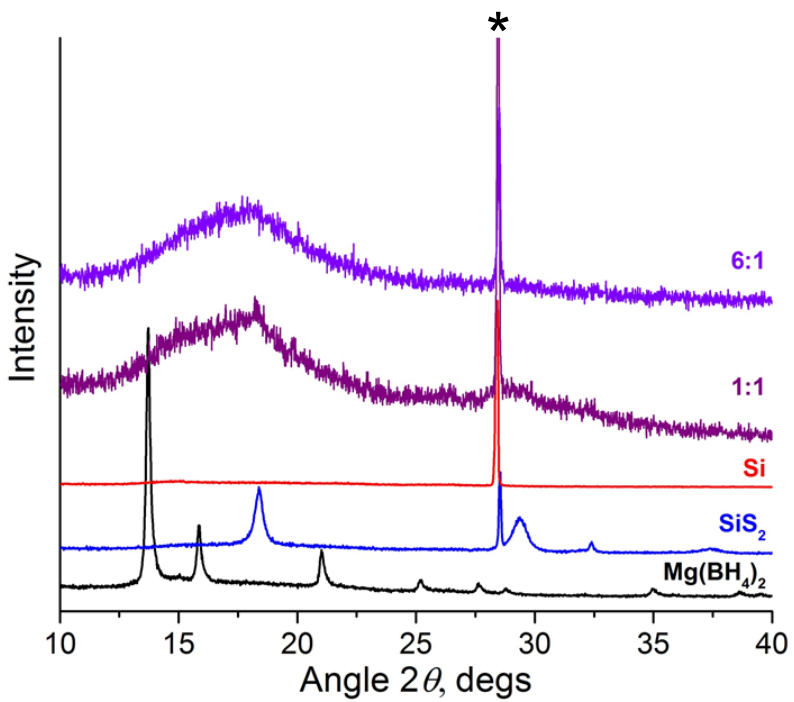


Hydrogenation for 10 hours at 160 bar and 380°C

Accomplishments: *$Mg(BH_4)_2$ – SiS_2 system*

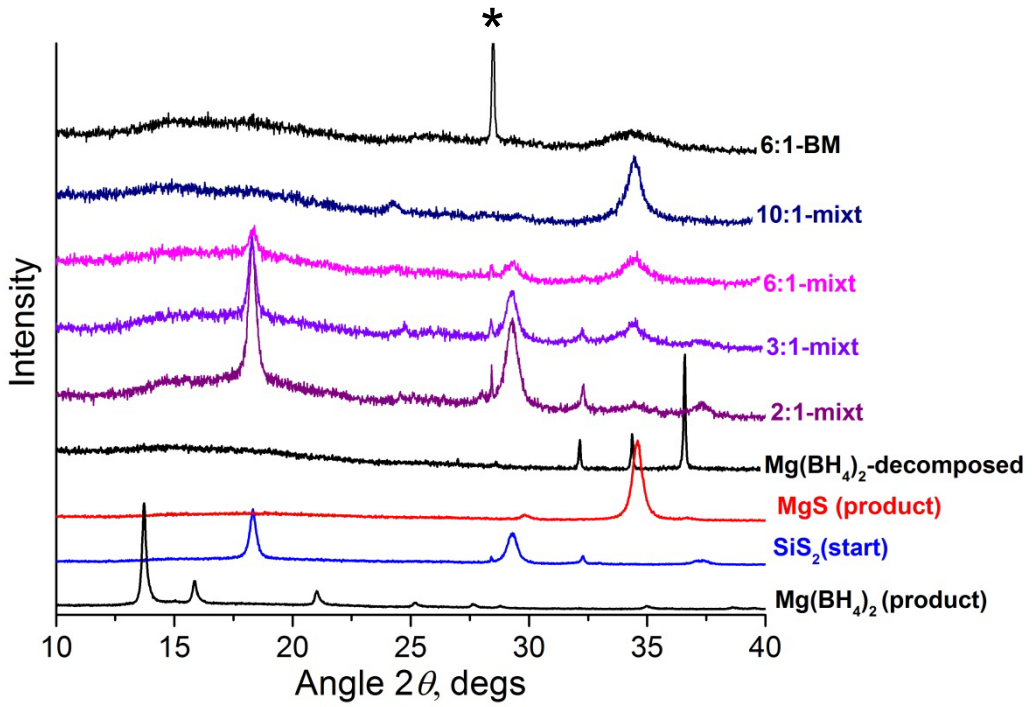
Ball milled $Mg(BH_4)_2$-SiS_2

Reaction proceeds, Amorphous product



* Si from precursor

Desorption of $Mg(BH_4)_2$-SiS_2

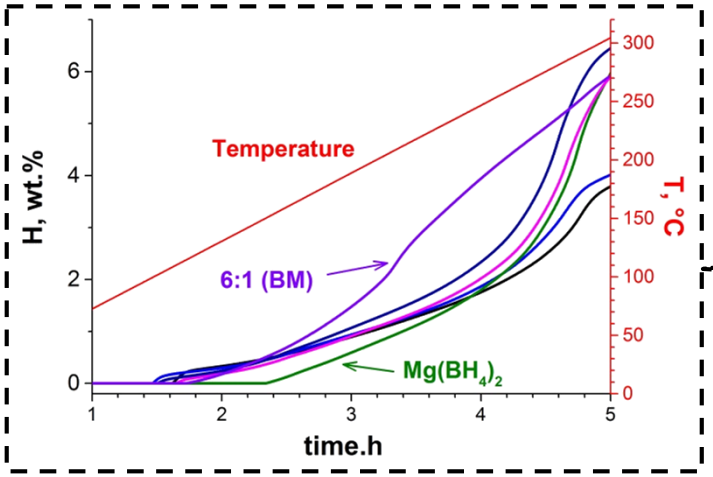


- SiS_2 remains after desorption of physical mixtures
- No SiS_2 after desorption of a milled sample

Formation of a mixed Mg and/or S stabilized Si-BH is likely

Accomplishments: $Mg(BH_4)_2 - SiS_2$ system

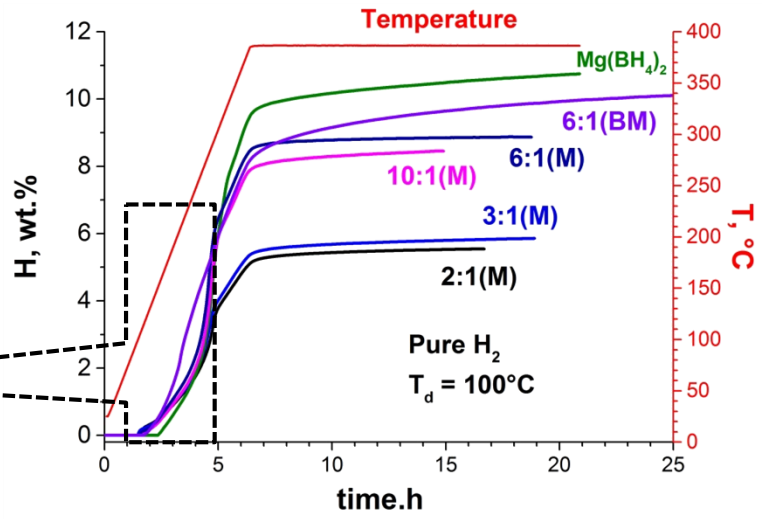
Reversibility in $xMg(BH_4)_2$-SiS_2



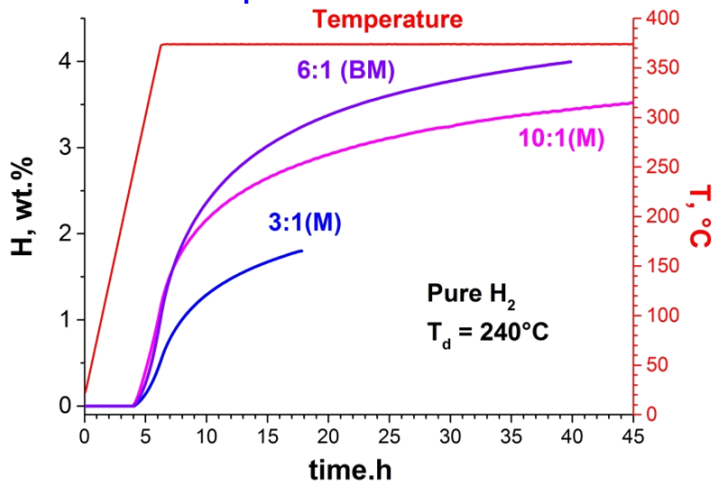
$6Mg(BH_4)_2$-SiS_2 systems shows improved kinetics and ca. 40 % reversible capacity

Potential to achieve phase 2 targets:
2.5 wt. % (200°C) and 5 wt. % (300°C)

Desorption: milled(BM) or mixed(M)



Desorption: after 1st abs



Hydrogenation for 10 hours at 160 bar and 380°C

Accomplishments: Summary of $MBH_4 – SiS_2$ systems

System, ratio	Theo. H_2 wt.%	1st decomposition			2nd decomposition		
		wt. % H_2	T_{ons}	% of total H_2	wt. % H_2	T_{ons}	% of initial H_2
$LiBH_4$-SiS_2							
2:1	5.9	4.3	88	73	1.5	230	30
4:1	8.9	7.1	113	81			
5:1	9.9	7.5	116	76			
6:1	10.7	**8.2**	**92**	**77**	**2.4**	**199**	**30**
8:1	11.9	6.2	96	52			
$LiBH_4$ (BM 3h)	18.2	2.9	276	16			
$NaBH_4$-SiS_2							
2:1	4.8	3.3	124	69	1	270	30
5:1	7.1	2.1	134	29.6			
6:1	7.5	2.4	159	32			
$Mg(BH_4)_2$-SiS_2							
2:1	8.0	5.6	101	70			
3:1	9.4	5.9	99	62.8	1.8	246	30
6:1	11.5	8.94	104	77.7			
6:1 (B.M.)	11.5	**10.12**	**117**	88	**4.0**	249	40
10:1	12.6	8.5	112	67.5	3.77	243	44
$Mg(BH_4)_2$ (pure)	14.8	10.7	150	72.3			

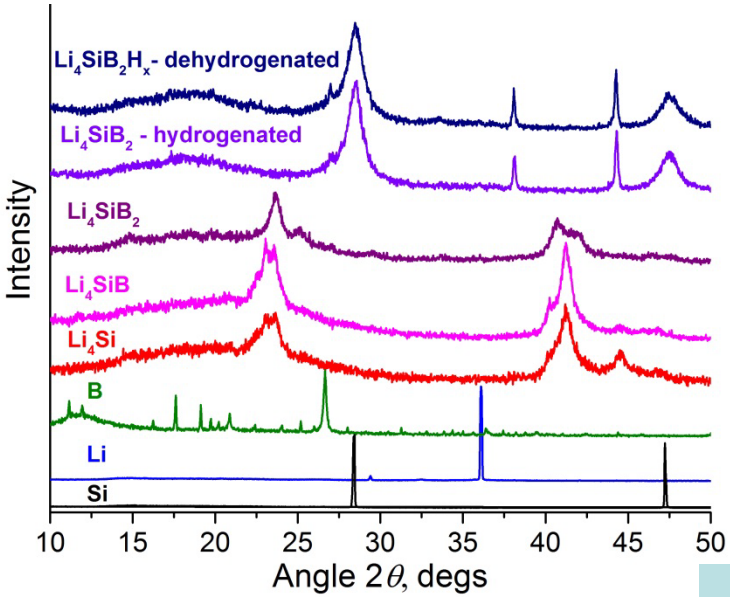
Accomplishments: *Li-Si-B-H system*

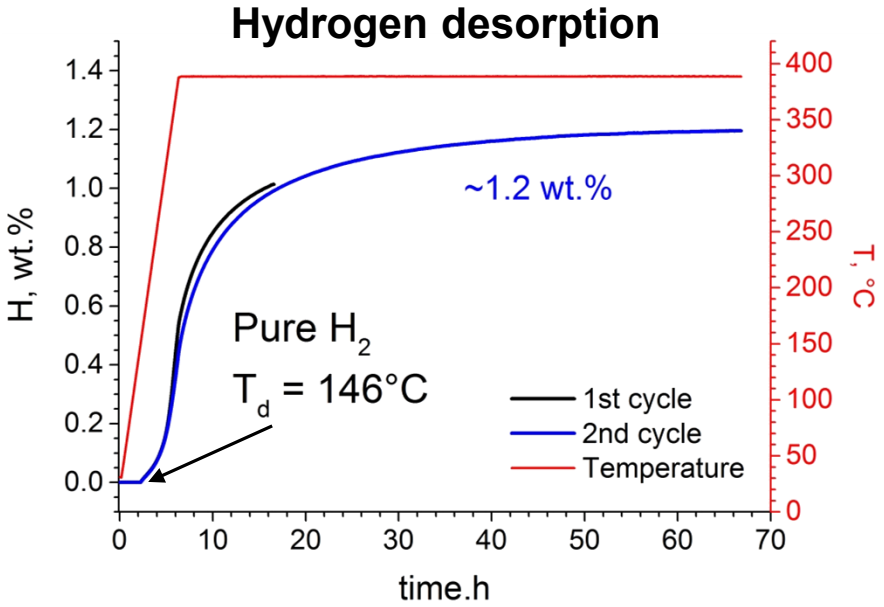
A potential for low formal Si-valence in Si-BHs

$$4Li + Si \xrightarrow{B.M.} \text{“}Li_4Si\text{”} \text{ (close to } Li_{15}Si_4)$$

$$4Li + Si + B_{(a)} \xrightarrow{B.M.} \text{“}Li_4SiB\text{”}$$

$$4Li + Si + 2B_{(a)} \xrightarrow{B.M.} \text{“}Li_4SiB_2\text{”}$$





Hydrogenation: 10 h at 160 bar and 380°C

- **~1.2 % reversible capacity**
- **Role of B to be explored**

4LiH/Si mixture releases 0.8 wt. % H_2 at 450°C (T_{ons}=270°C)
[J. Phys.Chem. B, 2004, 108, 13977]

Formation of a hydride containing both Si and B is likely. Good candidate for HP milling.

Future work: *Li-Si-B-H system*

Ternary Li-Si-B phase are barely known

"Li_4Si_2B", "Li_8Si_2B", etc. investigated as potential Li-electrodes

(A.F. Summels, J. Electrochem. Soc. 1978, *125*, 1632)

$LiSi_2B$, 10 GPa synthesis, Zintl phase

(M. Zeilinger et al., Angew. Chem. Intern. Ed. 2013, *52*, 5978)

Path forward:

$$xLi^0 + Si^0 + yB^0 \xrightarrow{BM} Li_xSiB_y$$

$$Li_xSiB_y \leftrightarrow Li_xSi(BH_n)_y \quad (\pm H_2)$$

Nanocrystalline materials

Milling under H_2 pressure

Ultra high H_2 pressure experiments – in collaboration with HyMARC

Summary

- Tasks 2.1-3. *Novel Silicon-based Borohydrides via Hypersalt Stabilization*
  - Cat/Si/B/H/Anion hypersalts can be prepared mechanochemically
  - Halide derivatives of $Si(BH_4)_4$ may be stabilized via high pressure application (based on MGCLP calculations, to be examined in collaboration with HyMARC)
  - Sulfide anion can stabilize silicon borohydrides in Li and Mg containing systems
  - T_d onsets of as-prepared hypersalts meet the DOE targets
  - Cycling of H_2 in MBH_4-SiS_2 systems (M=Li, Na, Mg) can reach 30-40 % of the initial hydrogen capacity
  - Observed composition controlled suppression of B_2H_6 $\rightarrow$ improved potential for reversibility
- Task 2.4. *High-Pressure Mechanochemistry*
  - "Li_4SiB_2" and "Li_xSiB_y" prepared mechanochemically may open a field toward low-valence-silicon Si-BHs

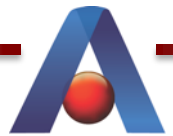
Remaining Challenges and Barriers

- Separation of as-synthesized Si-BHs from by-products
- Crystal structure determination due to amorphization upon synthesis
- Identifying Si-H bonds/interactions in a newly synthesized Si-BHs
- High H_2 pressure mechanochemistry activity reinstatement is slower than anticipated

Future plans

- Detailed study of mixed Si-BHs (X-, N- diffraction, FT-IR, NMR, DSC)
- Improve reversibility of hydrogen in promising systems
- Stabilization of derivatives of $Si(BH_4)_4$ by using high pressures and low temperatures
- Further study of $M(BH_4)_n$-SiS_2 (n=1, 2) systems for reversible hydrogen storage
- Hypersalt synthesis via ball milling at high hydrogen pressures using M-Si-B solids where M=Li, Na, Mg, Ca, Al
- Hypersalt synthesis at ultra high hydrogen pressures in collaboration with HyMARC using M-Si-B solids where M=Li, Na, Mg, Ca, Al

Backup Slides



Reviewers Comments

FY2016 Reviewers Comment	FY2016 Response to Comments
None of known borohydrides has been found to undergo reversible dehydrogenation due to the concurrent elimination of diborane upon thermal dehydrogenation.	Completely agree. We found that B_2H_6 emissions can be strongly suppressed by composition control (e.g. by introducing halide or sulfide anions).
Syntheses of lightly stabilized aluminum borohydrides has been achieved only through low-temperature "wet" chemistry approaches, not ball milling. Thus, mixed-metal borohydrides that undergo reversible dehydrogenation and the preparation of compounds with borderline stabilities through ball milling seems unlikely.	1. Unstable AlH_3 has been prepared in 100% yields by ball-milling. 2. We have at least two examples of Si-H bonds co-existing with $[BH_4]^-$ in solids prepared mechanochemically
The isolation of compounds with silicon in the +2 oxidation state seems unlikely. It would be good to see some literature precedent for Si^{2+} compounds.	Si^{2+} has been reported only in a gas phase. Higher relative stability of Si^{2+} compared to Si^{4+} is PEGS projection for Si-BHs. Formally low Si valence may be feasible by starting from Si^0, as in "Li_4SiB_n", n≥ 2.
This project does not employ the techniques that have become standard in the structural characterization of borohydrides: IR, multinuclear NMR and structure determinations derived from Rietveld analysis of PXD data.	Rietveld was work in progress then, now done. Two structures have been solved and fully refined. SSNMR, liquid NMR and FTIR are now routinely applied.
DOE reviewers, and the project investigators should review the literature and work funded by DOE's Office of BES and accomplished by SRNL and VCU. They have made both Si and Al hypersalts.	We are fully aware of work on hypersalts published by SRNL and VCU. While the Al hypersalts are well characterized, we found no examples with Si in the structures.
The weight changes presented do not represent a progression toward DOE goals.	$LiBH_4/Mg(BH_4)_2$-SiS_2 systems release 8.2/10 wt.% H_2, and if reversible, will meet the 2020 targets. We explore their reversibility.
The conclusion of no B_2H_6 formation is not justifiable given the experimental protocol	Agree. We are only referring to suppression of B_2H_6 release based on comparing its *relative* concentrations seen under similar conditions.
The inclusion of this project within HyMARC should be a vast improvement.	Agree. HyMARC's high pressure reactor will significantly benefit this program. We are initiating the dialog.
The borohydride/graphene composite work could be deleted to allow more time on the main Si borohydride mechanochemistry effort	Done. After a discussion with the Program Manager this work has been discontinued. Resources reallocated to synthesis of Si-BHs

Approach - Synthesis and Characterization; Subtasks 2.1–2.4

1. Synthesis:

- Mechanochemistry (both at cryogenic and RT)

2. Characterization:

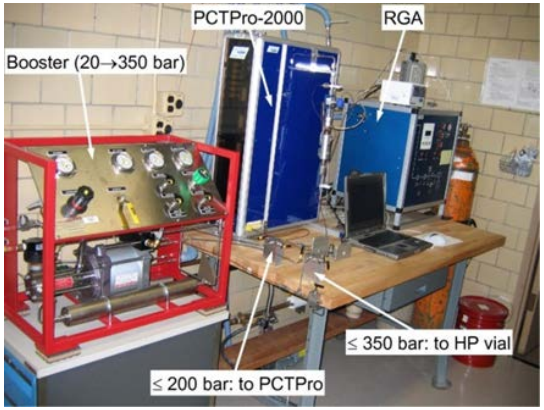
- Powder X-ray diffraction

- Gas sorption analysis - PCTPro-2000 integrated with gas analyzer.

-1D and 2D Solid-state NMR of spin-$^{1}/_{2}$ (^{1}H, ^{29}Si) and quadrupolar (^{7}Li, ^{11}B, ^{23}Na) nuclei, including highly sensitive DNP SSNMR

- Fourier transform infrared spectroscopy (FT-IR)

- Thermogravimetric analysis combined with differential scanning calorimetry (TGA-DSC).



Approach - Theory and Computation Subtasks 1.4, 3.3: PEGS+DFT Hypersalt Stability Screening

Computational Methods:

- Crystal structure candidates generated using the prototype electrostatic ground states (**PEGS**) method [PRB, 77, 104115 (2008)]
- Thermodynamic properties and decomposition pathways predicted using multi-gas canonical linear programming (**MGCLP**) [J. Phys. Chem. C., 118, 14759 (2014)]
- Density functional theory (**DFT**) using the VASP code

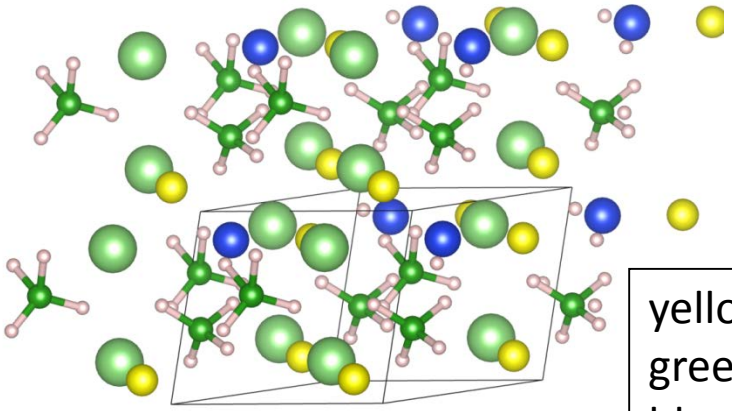
Accomplishments: *$LiBH_4$ – SiS_2 system*

$2LiBH_4 + SiS_2 = Li_2SiS_2(BH_4)_2$

Theo. Capacity 6.2 wt.% H_2

$$Li_2SiS_2(BH_4)_2 \rightarrow 2B + Li_2S + \tfrac{1}{2}\,Si + \tfrac{1}{2}\,SiS_2 + 4H_2$$

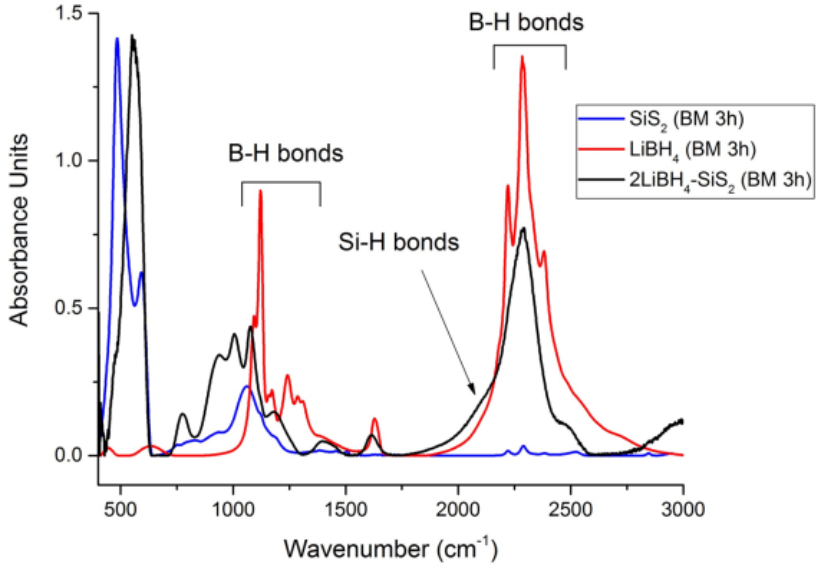
- **ΔH = 32 kJ/mol H_2**
- **T_c = -33 °C**



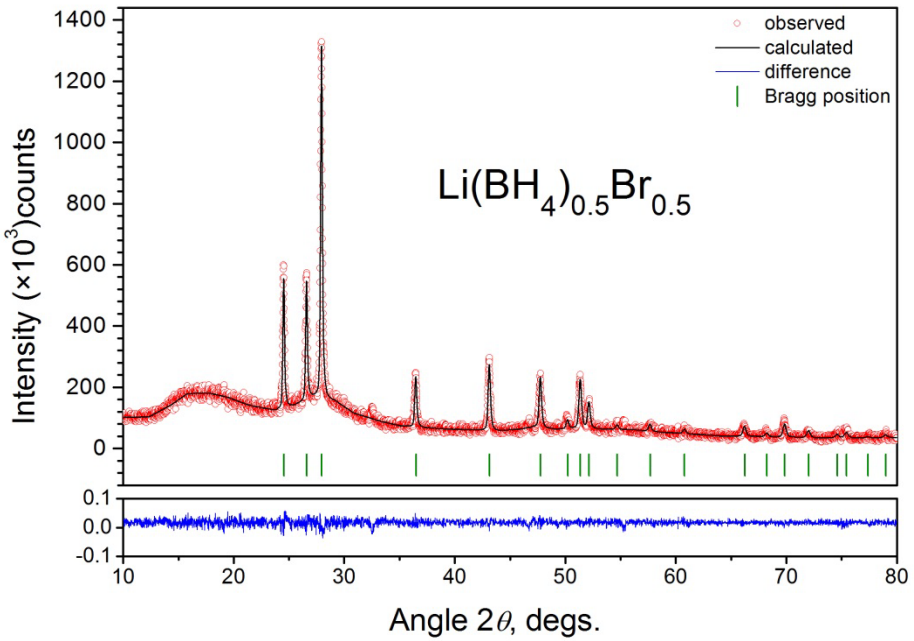
PEGS

yellow=S
green=Li
blue=Si

FT-IR spectra



Accomplishments: $LiBH_4 – SiBr_4$ system



Rietveld refinement of the $Li(BH_4)_{0.5}Br_{0.5}$ structure

Phase data	
Formula unit	$Li(BH_4)_{0.5}Br_{0.5}$
Crystal system	hexagonal
Space group	$P6_3mc$ (186)
Cell parameters	a=4.2007(4) Å
	c=6.7185(7) Å
Pearson's code	hP12
R_p, R_{wp}	7.15%; 9.51 %

Atomic parameters

Atom	Wyck.	S.O.F.	x/a	y/b	z/c	U [Å^2]
Li	2b	1	1/3	2/3	0	0.089(2)
B	2b	0.51(2)	1/3	2/3	0.599(3)	0.066(2)
Br	2b	0.49(2)	1/3	2/3	0.599(3)	0.066(2)
H1	2b	0.51(2)	1/3	2/3	0.417(3)	0.085(2)
H2	6c	0.51 (2)	0.130(18)	0.261(18)	0.670(3)	0.085(2)

Accomplishments: $LiBH_4 – AlCl_3$ system

Atomic parameters						
Atom	Wyck.	S.O.F.	x/a	y/b	z/c	U [Å²]
Al1	2a	1	0	0.8645(2)	0	0.0777(7)
Al2	2b	1	0	0.3640(2)	1/2	0.0777(7)
Li1	2b	1	0	0.0915(2)	1/2	0.0777(7)
Li2	2a	1	0	0.5914(2)	0	0.0777(7)
Cl1	4c	1	0.6802(2)	0.2438(2)	-0.0064(2)	0.0777(7)
Cl2	4c	1	0.7892(2)	0.2430(2)	0.4620(2)	0.0777(7)
B1	4c	1	-0.0011(2)	0.4774(2)	0.7180(2)	0.0777(7)
H1	4c	1	-0.1006(2)	0.3988(2)	0.7014(2)	0.0777(7)
H2	4c	1	0.5436(2)	0.0667(2)	0.2514(2)	0.0777(7)
H3	4c	1	0.0745(2)	0.4516(2)	0.8494(2)	0.0777(7)
H4	4c	1	0.8730(2)	0.4831(2)	0.3755(2)	0.0777(7)
B2	4c	1	0.4590(2)	0.4784(2)	0.7516(2)	0.0777(7)
H5	4c	1	0.5562(2)	0.3979(2)	0.7606(2)	0.0777(7)
H6	4c	1	-0.0671(2)	0.0663(2)	0.2178(2)	0.0777(7)
H7	4c	1	0.3773(2)	0.4557(2)	0.6237(2)	0.0777(7)
H8	4c	1	0.1007(2)	-0.0157(2)	0.0869(2)	0.0777(7)

Rietveld refinement of the $LiAl(BH_4)_2Cl_2$ structure

Phase data	
Formula unit	$LiAl(BH_4)_2Cl_2$
Crystal system	monoclinic
Space group	C2 (5)
Cell parameters	*a*=8.4717(5) Å *b*=11.6699(6) Å *c*=7.5108(4) Å β = 90.04(1)°
Pearson code	mC56
R_p, R_{wp}	5.36%; 7.55 %