

Boron-Based Hydrogen Storage: Ternary Borides and Beyond

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Timeline

- Project start date: 08/01/2014
- Project end date: 01/31/2016

Budget

- Total project budget: \$562.5K
 - Total federal share: \$500K
 - Total recipient share: \$62.5K
 - Total DOE funds spent*: \$195.3K

* as of 3/31/15

Technical Barriers

- A. System weight and volume
- C. Efficiency
- E. Charging and discharge rates

Partners

- HRL Laboratories (*lead, boranes*)
- Sandia National Laboratories (*subcontractor, ternary borides*)
- University of Missouri, St. Louis (*subcontractor, theory*)

Objectives and Outcome

Previous work (*MHCoE et al.*) identified boron-based storage materials as very attractive given their versatility and high capacities (> 10 wt%), although the cycling rates were poor (*multiple phases, kinetically limited*)

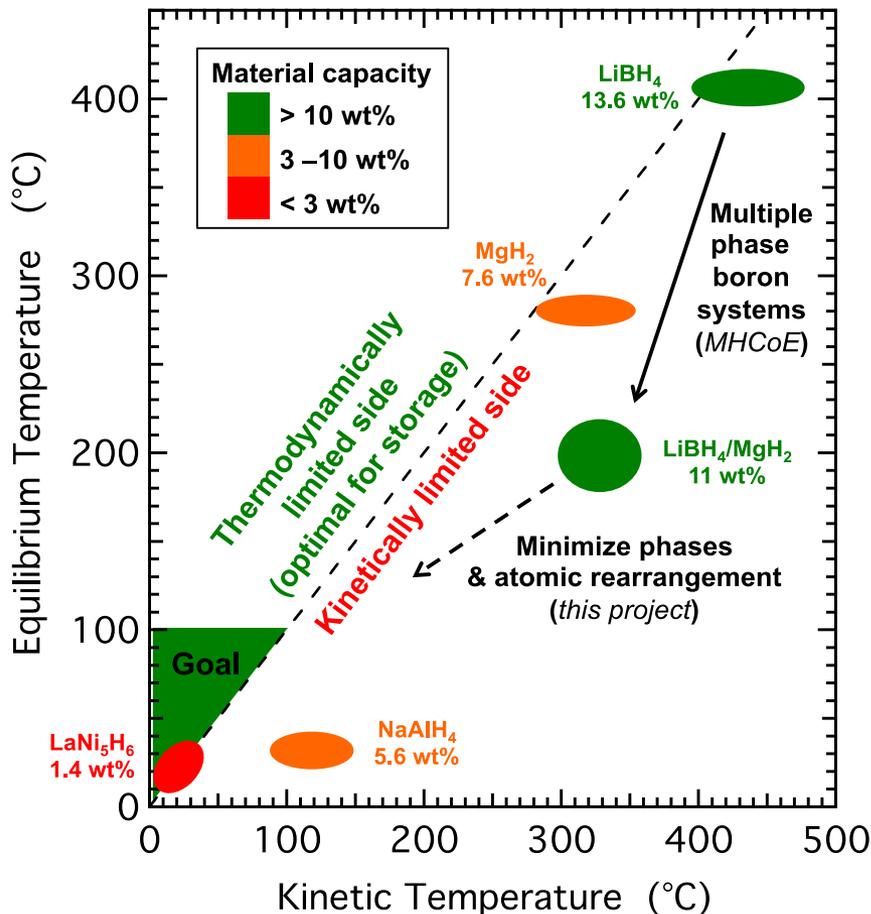
Objectives

Improve kinetics by:

- 1) eliminating multi-phase kinetic barriers (*ternary borides/mixed-metal borohydrides that maintain single phases during cycling*)
- 2) minimizing B-atom rearrangement (*“lithiated boranes”: boranes that cycle while preserving the B-B framework*)

Expected outcome

An experimental and computational assessment of ternary borides and lithiated boranes to meet the DOE targets for onboard hydrogen storage



Synergetic Experimental & Computational Effort

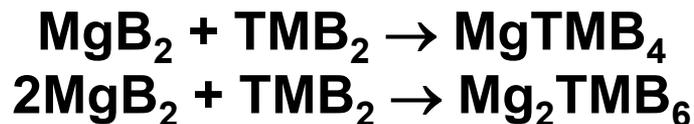
- Begin from both dehydrogenated and hydrogenated states
- Use computations (*PEGS and DFT*) to guide material choices
- Ternary borides:
 - synthesize Mg + (V, Cr, Mn, Fe, Co) borides using mechano-chemistry
 - synthesize mixed-metal borohydrides by solution or solid-state reactions
 - evaluate hydrogen cycling behavior (*Sieverts measurements*)
- Lithiated boranes:
 - survey candidate boranes (*molecular to extended frameworks*)
 - synthesize borane/LiH composites by mechanical milling
 - evaluate for B-H/B-Li exchange hydrogen cycling (*Sieverts measurements*)

Milestones completed (*Sept 2014 to March 2015*)

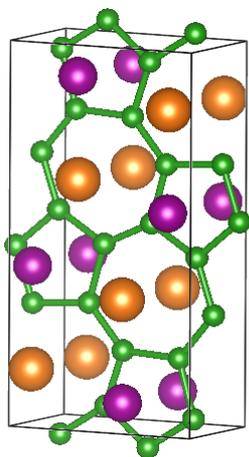
- Computational assessment of the stability and hydrogen cycling energetics of Mg/TM ternary borides and borohydrides
- Synthesis of Mg/Mn ternary borides (*theoretically capable of 11 wt% H₂ uptake*)
- Computations of model B-H/B-Li exchange energetics
- Survey of borane substrates for lithiation (*with > 9 wt% H₂*)

Formation Energy of Ternary Borides

DFT ($T = 0\text{ K}$) using known experimental structures as prototypes



TM-substituted experimental
structures

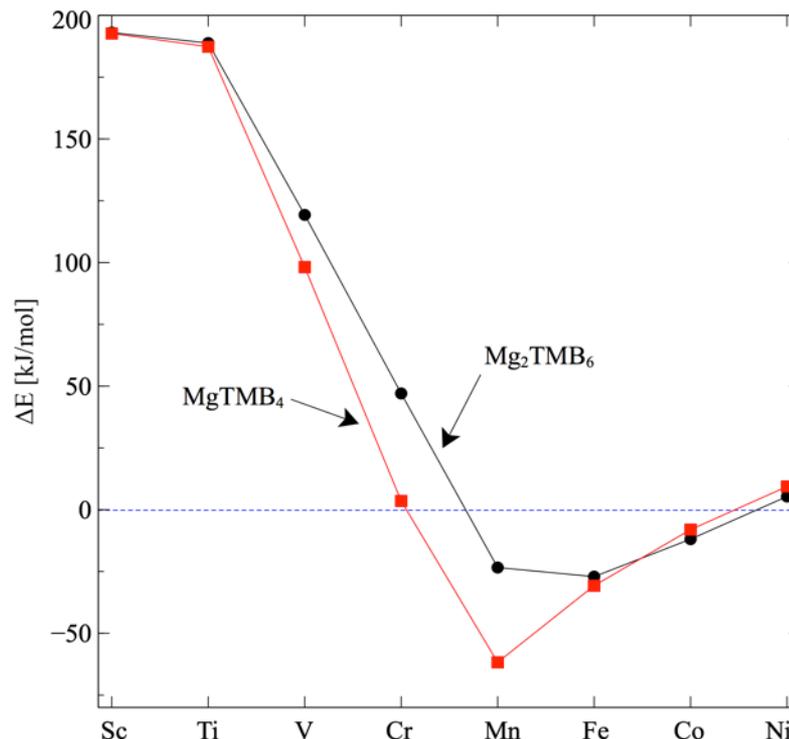


MgTMB_4

Example:

CeCrB_4
 NiScB_4

Pbam
prototypes



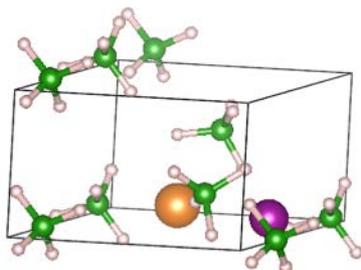
- TM = Mn, Fe, and Co predicted to be favorably stable ($\Delta E < 0\text{ kJ/mol}$)
- TM = Sc, Ti, and V likely unstable with respect to the starting borides
- TM = Cr and Ni are borderline.

Dehydrogenation of Mg/TM Borohydrides

- PEGS borohydride structures ($T = 0$ K)
- Pbam ternary borides (*TM-sub. exp. structures*)
- $E(\text{H}_2) = -630$ kJ/mol

PEGS calculations for
 $\text{MgTM}(\text{BH}_4)_4 \rightarrow \text{MgTMB}_4 + 8\text{H}_2$

Mg:TM

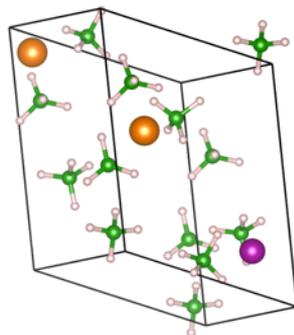
 $\text{MgTM}(\text{BH}_4)_4$ 

TM	$\text{MgTM}(\text{BH}_4)_4$ [kJ/mol]	MgTMB_4 [kJ/mol]	dE [kJ/mol- H_2]
Mn	-8585.5	-3720.9	-25.14
Fe	-8579.7	-3632.7	-14.79
Co	-8431.2	-3510.4	-18.06

1:1

PEGS calculations for

$\text{Mg}_2\text{TM}(\text{BH}_4)_6 \rightarrow \text{Mg}_2\text{TMB}_6 + 12\text{H}_2$

 $\text{Mg}_2\text{TM}(\text{BH}_4)_6$ 

TM	$\text{Mg}_2\text{TM}(\text{BH}_4)_6$ [kJ/mol]	Mg_2TMB_6 [kJ/mol]	dE [kJ/mol- H_2]
Mn	-12760.4	-5159.4	+0.21
Fe	-12704.1	-5105.1	-0.05
Co	-12557.6	-4989.7	-2.66

2:1

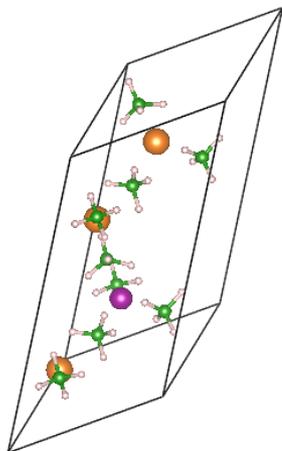
- Predicted dehydrogenation enthalpies are unfavorably exothermic (*negative*) or only slightly endothermic (*positive*)

Dehydrogenation of $\text{Mg}_3\text{Mn}(\text{BH}_4)_8$

PEGS calculations for



3:1



$\text{Mg}_3\text{Mn}(\text{BH}_4)_8$ [kJ/mol]	Mg_2MnB_6 [kJ/mol]	MgB_2 [kJ/mol]	dE [kJ/mol- H_2]
-16891.6	-5158.5	-1475.4	+7.73

$$E(\text{H}_2) = -630 \text{ kJ/mol}$$

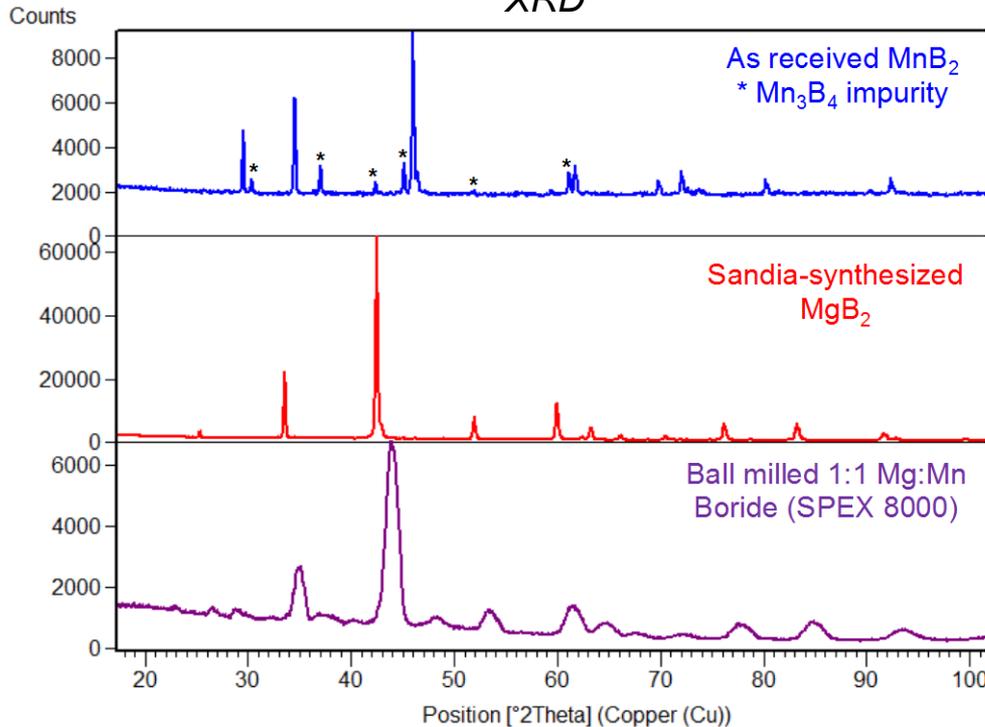
- Predicted enthalpy is favorably positive
- Larger Mg:TM ratios tend toward more positive enthalpies
- However, dehydrogenated state is not single phase (Mg_3MnB_8 is predicted to be unstable and decompose into $\text{Mg}_2\text{MnB}_6 + \text{MgB}_2$)
- Considering higher Mg:Mn ratios and Ca analogs that may provide stable ternary borides



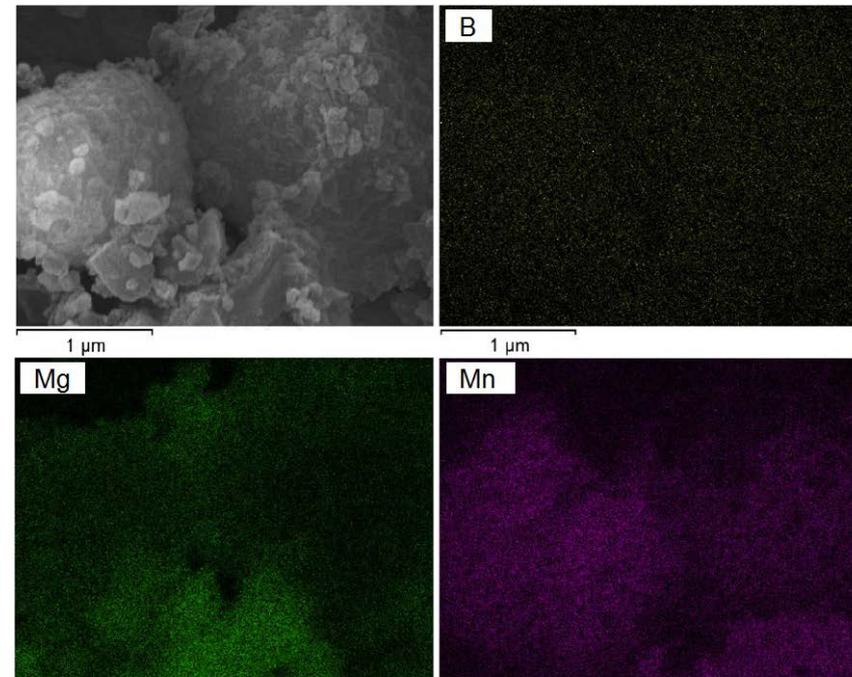
Synthesis of Mg/Mn Ternary Borides

Mechano-chemical reaction (*SPEX 8000 mill, 16 hr*)
 $x\text{MgB}_2 + (1-x)\text{MnB}_2 \rightarrow \text{Mg}_x\text{Mn}_{1-x}\text{B}_2$ ($x = 0.5, 0.75$ and 0.9)

XRD



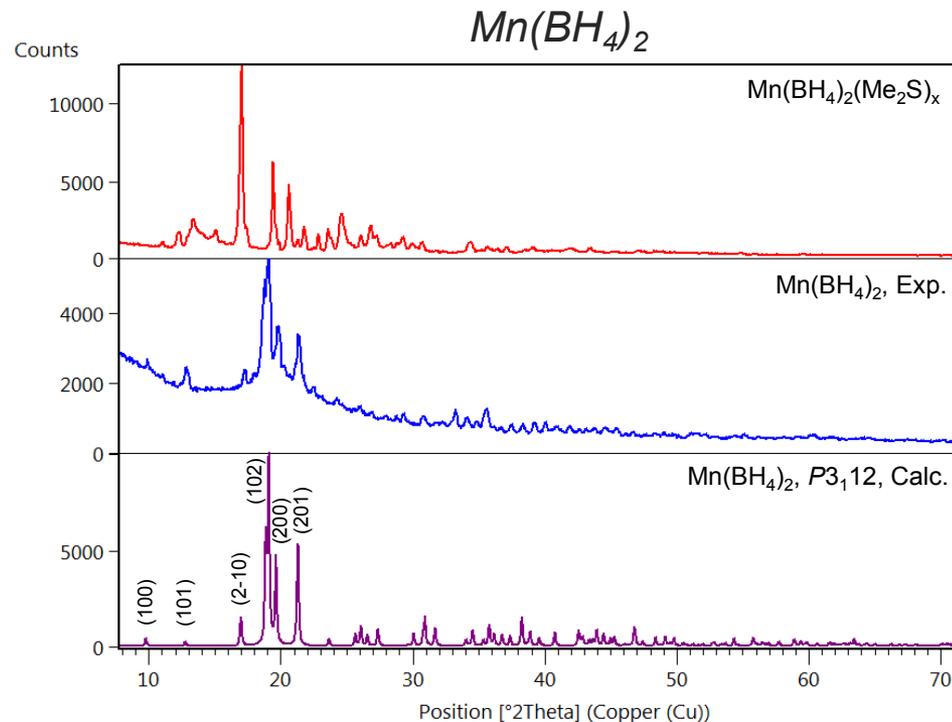
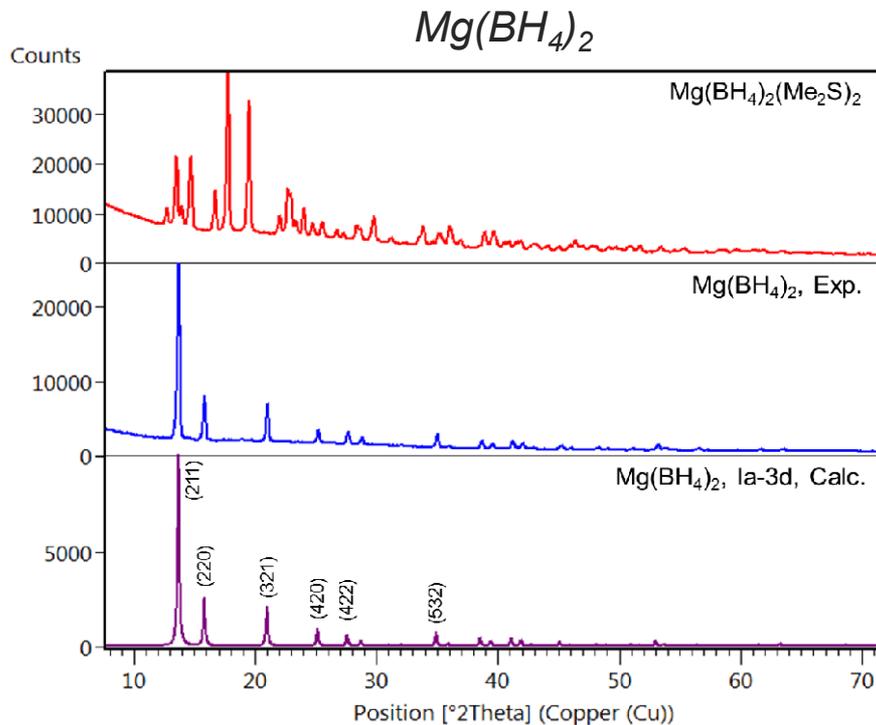
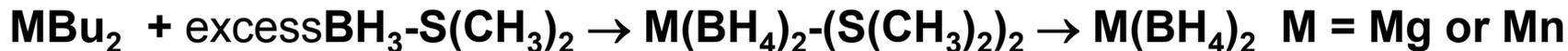
EDX



- XRD data shows successful synthesis of single-phase ternary Mg/Mn boride
- EDX confirms homogeneous atom distribution (*at ~ 100 nm resolution*)
- Evaluate for hydrogenation (*preliminary measurement shows ~ 1.2 wt% uptake*)

Synthesis of $\text{Mg}(\text{BH}_4)_2$ and $\text{Mn}(\text{BH}_4)_2$

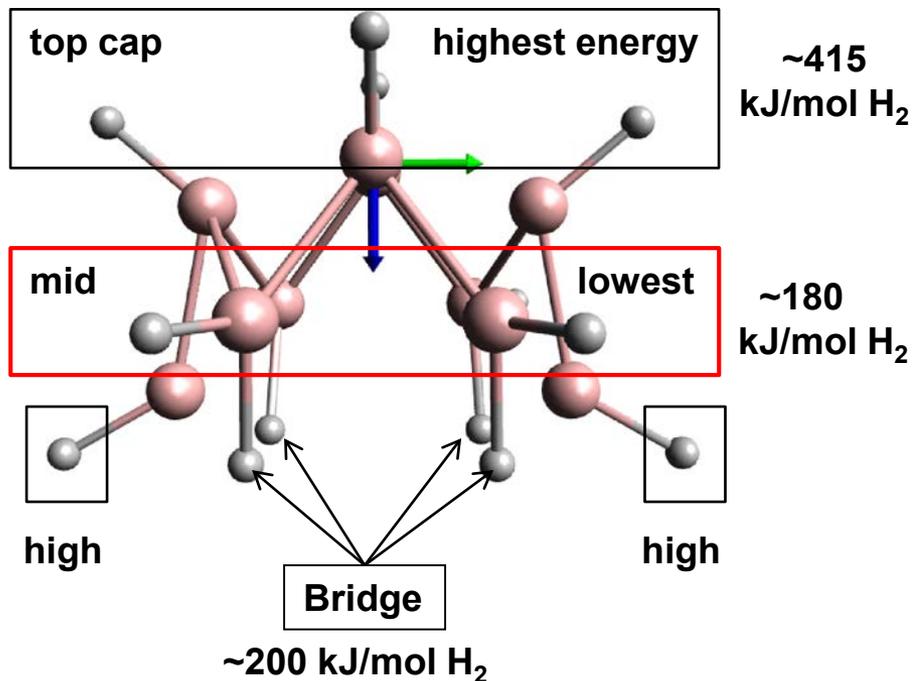
Solution phase reaction (*heptane/toluene*)



- XRD confirms successful preparation of phase pure $\text{Mg}(\text{BH}_4)_2$ and $\text{Mn}(\text{BH}_4)_2$
- A new synthetic route to manganese borohydride
- These are starting materials to make Mg/Mn mixed-metal borohydride via solid-state and solution synthesis routes

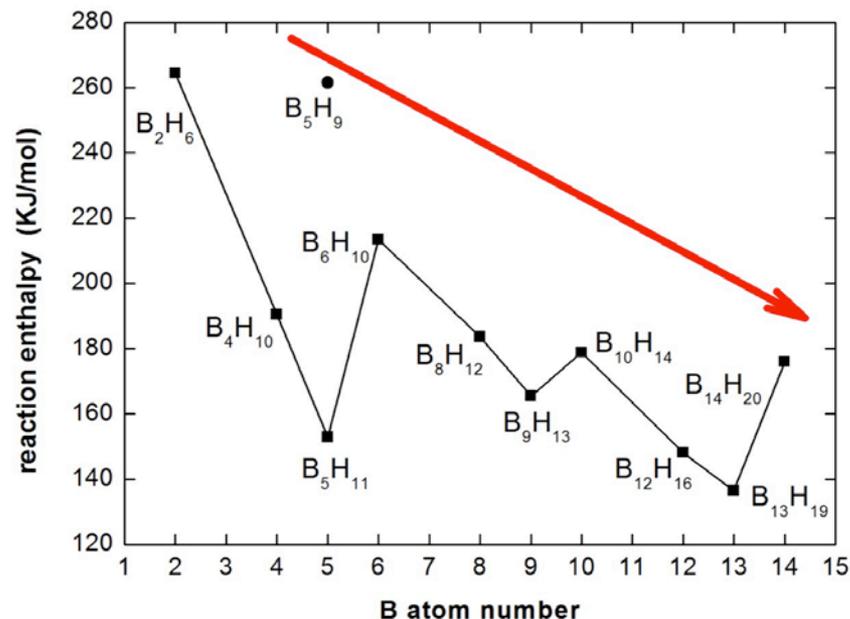
B-H/Li-H Exchange Energetics

Single Li exchange into decaborane



- **Lowest energy sites are non-bridging hydrogen on BH_2** (bridge sites are 2nd lowest)
- **However, “exchange” occurs with large structure deformation** (Li moves over open faces)

Lowest energy single Li exchange into increasing boron frameworks

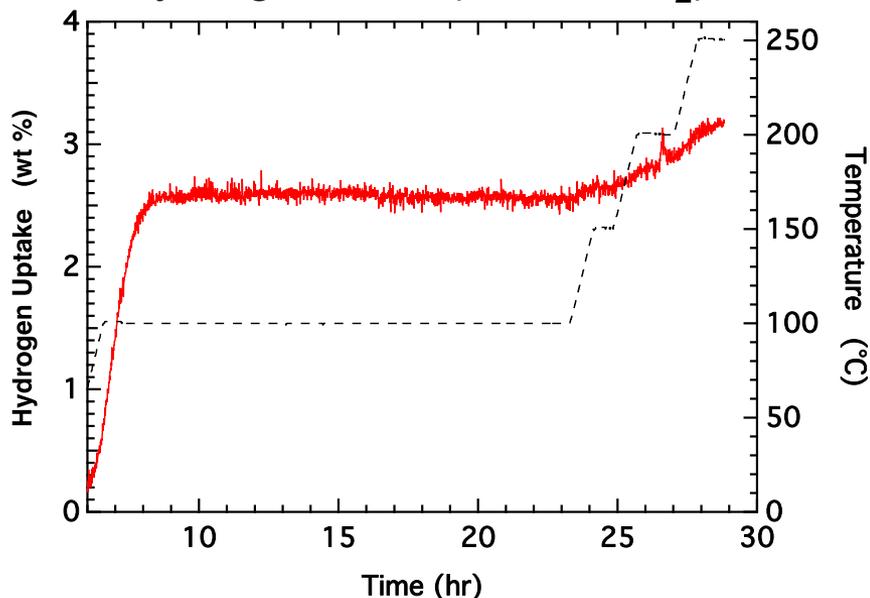


- **Predicted enthalpies are large**
- **However, energy decreases with size of the boron framework**

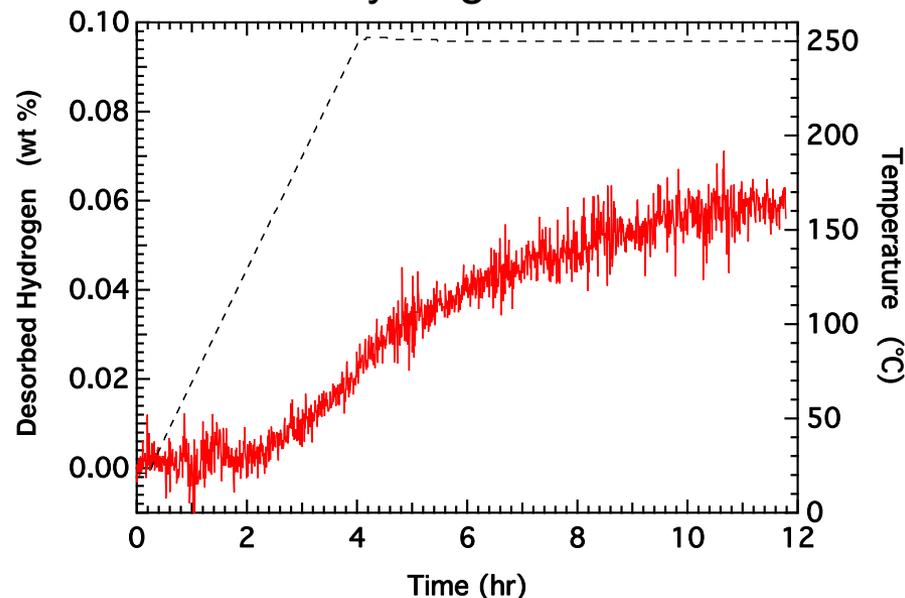
Hydrogenation of Li_7B_6 Alloy Substrate

Li_7B_6 synthesized by direct reaction of B kneaded with Li metal foil
 (450°C, 48 hr, sealed steel vessel)

Hydrogenation (100 bar H_2)



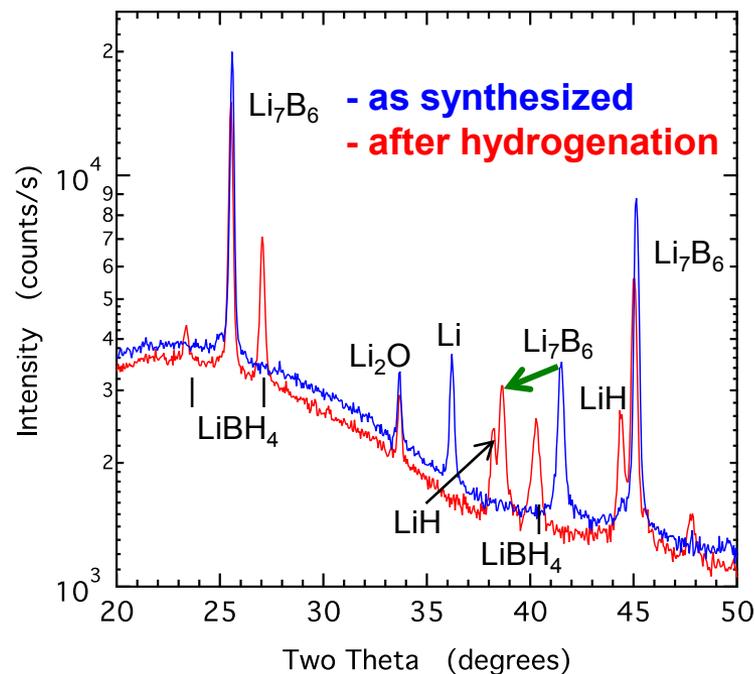
Dehydrogenation



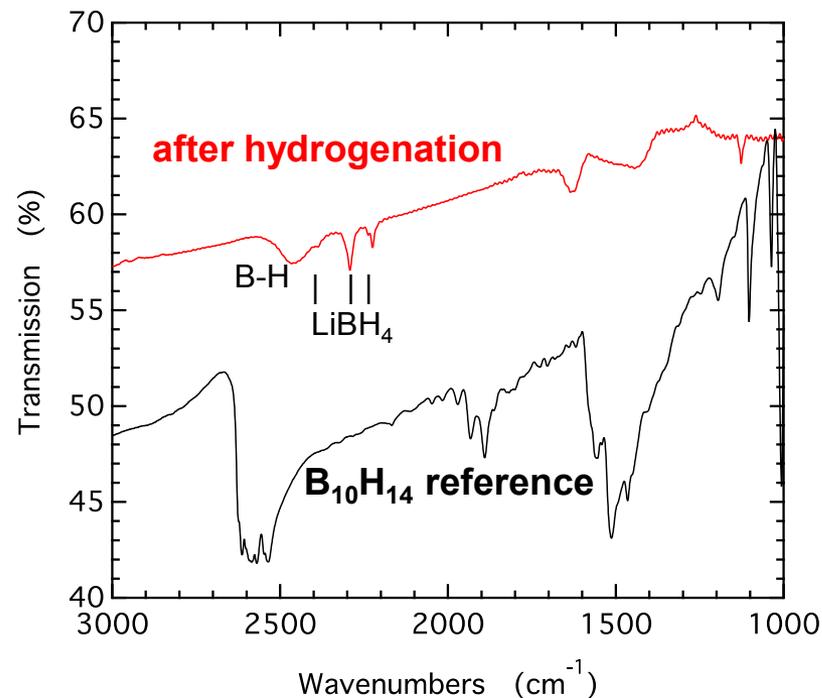
- Significant (2.6 wt%) low temperature (100°C) hydrogenation observed
- Could be due to unreacted Li metal, however
- XRD (next slide) gives starting composition of $0.9\text{Li}_7\text{B}_6 + 0.08\text{Li} + 0.02\text{Li}_2\text{O}$
- This predicts only 0.08 wt% H_2 uptake from unreacted Li
- Much greater observed uptake suggests additional reaction (see next slide)
- However, no significant dehydrogenation up to 250°C

Characterization of Li_7B_6 Alloy Reaction

XRD



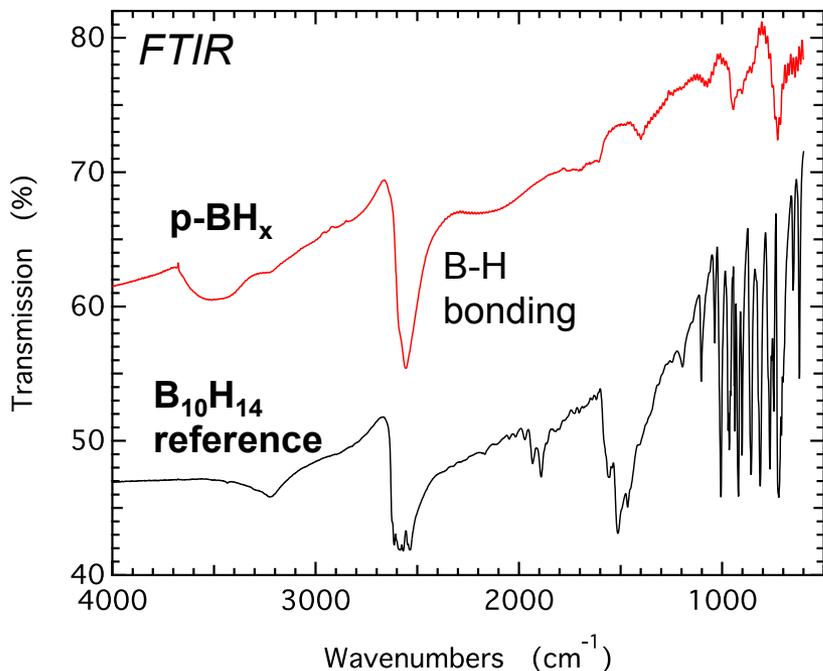
IR



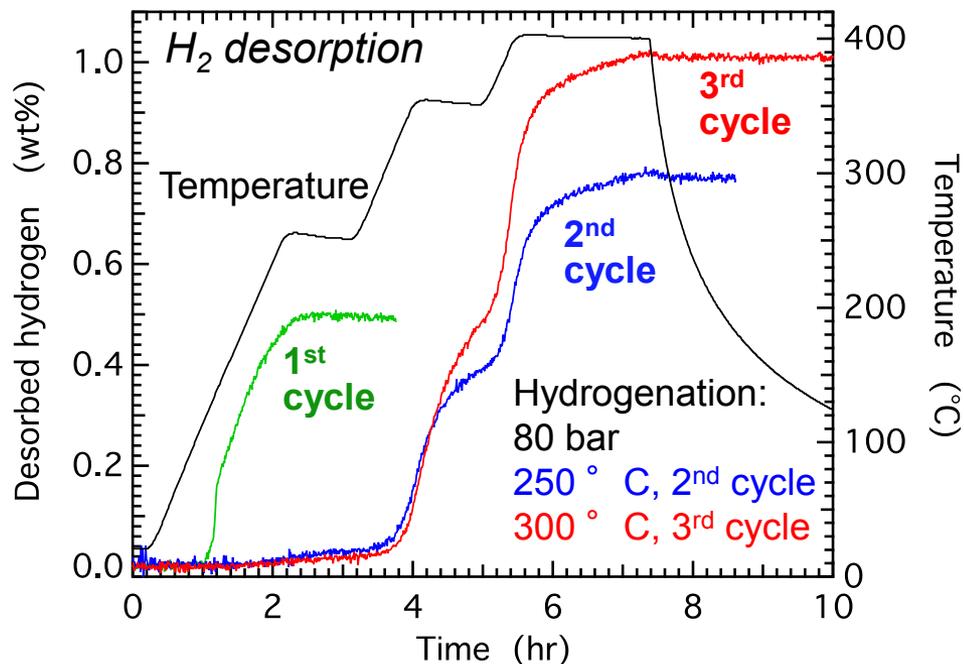
- XRD and IR results indicate formation of LiBH_4 upon hydrogenation
- IR shows additional B-H bonding not associated with LiBH_4
- Shift in XRD peak (*green arrow*) suggests H-intercalated Li boride
- This possible new phase is supported by our calculations of Li_8B_7 and $\text{Li}_9\text{B}_7\text{H}$

Polymeric Borane Substrate

Polymerized $B_{10}H_{14}$ ($p-BH_x$)
(250 ° C, 48 hr sealed steel vessel)



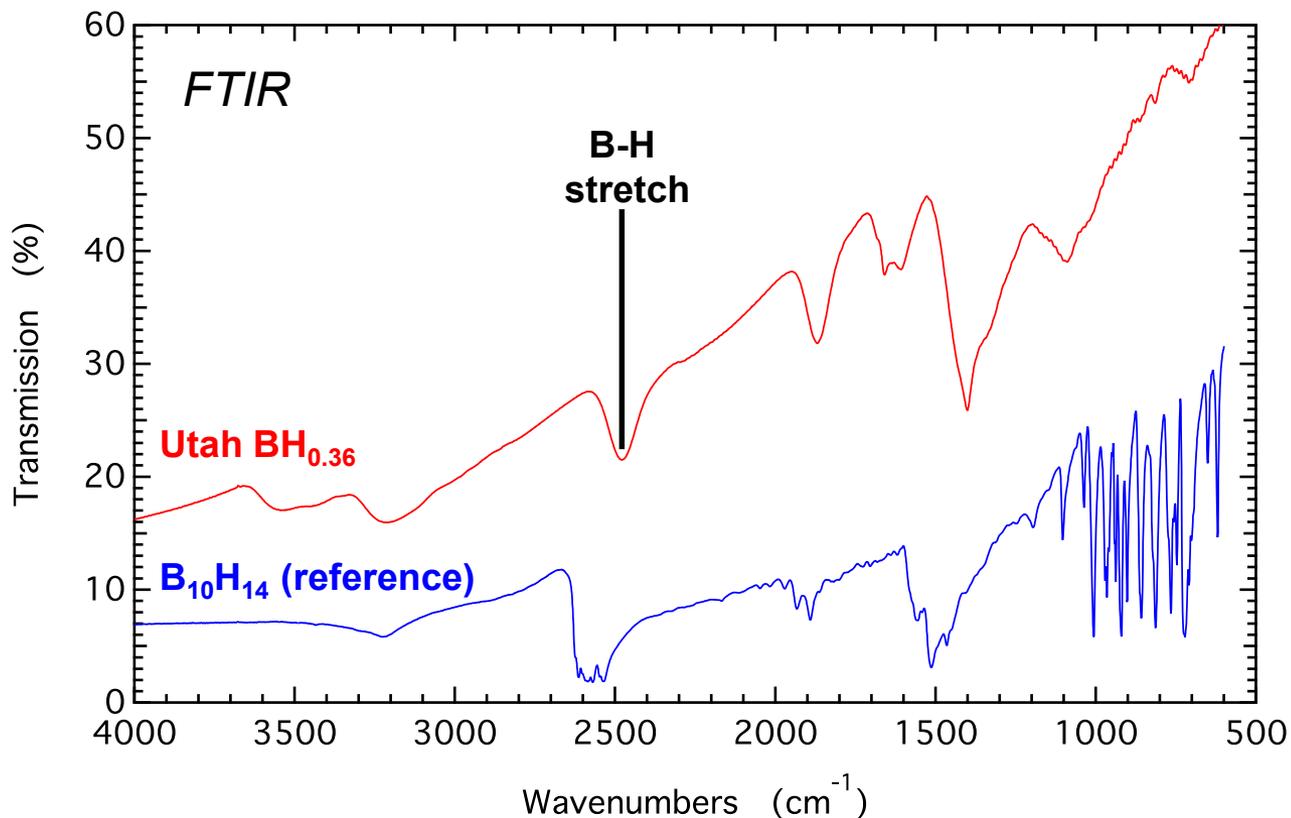
Hydrogen cycling
 $p-BH_x + LiH$ (milled 20 hr)



- $p-BH_x$ avoids sublimation of molecular substrates (eg, $B_{10}H_{14}$ and $C_2B_{10}H_{12}$)
- Significant B-H bonding retained ($x = 0.64 \pm 0.02$ by PGAA conducted at NIST)
- So far, ~ 1 wt% cyclable H_2 (maximum = 7.7 wt% for $x = 0.64$)
- Optimize polymerization for lithiation reaction (capacity and kinetics)

Hydrogenated Boron Nanoparticle Substrate

$\text{BH}_{0.36}$ nanoparticles (prepared by high energy milling of B in H_2)
obtain from Prof. Scott Anderson (U Utah)



- Result confirms similar FTIR characterization performed at Utah
- Mill with LiH for lithiation reaction

Project partners

- **HRL** (*prime, experimental effort focused on lithiated boranes*)
- **Sandia National Laboratories** (*subcontractor, experimental effort focused on ternary borides*)
- **University of Missouri, St. Louis** (*subcontractor, theory/computation effort to predict energetics of lithiated boranes and ternary borides*)

Formally, all partners contribute to all tasks

External collaborations

- **University of Utah, Prof. Scott Anderson** (*provided BH_x nanoparticles*)
- **NIST, Terry Udovic** (*PGAA, neutron vibrational spectroscopy*)

Future Work

- **Ternary borides:**
 - Characterize hydrogenation/dehydrogenation behavior of Mg/Mn borides
 - Synthesize Mg/Mn mixed-metal borohydride and characterize the dehydrogenation/rehydrogenation behavior
 - Prepare Fe and Co-based ternary boride and borohydride materials
- **Lithiated boranes:**
 - Optimize polymerized borane for cycling kinetics and capacity
 - Consider doping (eg, C, N, O) to lower enthalpy (*use input from computations*)
 - Perform LiH exchange reaction with $\text{BH}_{0.36}$ nanoparticles
 - Consider including a catalyst (*materials contain no transition metals*)
- **Theory/computation:**
 - Energies for multiple Li exchanges, C-substituted boranes, and extended borane structures
 - Critical temperatures for solubility of Mn and Zn in MgB_2
 - Stability of CaTMB_4 and Ca_2TMB_6
 - Stability using PEGS structures of $\text{CaTM}(\text{BH}_4)_4$ and $\text{Ca}_2\text{TM}(\text{BH}_4)_6$

Summary

- **Ternary borides:**
 - Successfully synthesized Mg/Mn (1:1, 3:1, and 9:1) ternary borides
 - Synthesized phase pure Mg and Mn borohydrides (*using a common scheme amenable for mixed-metals*)
- **Lithiated boranes:**
 - Synthesized Li_7B_6 alloy and demonstrated slight hydrogenation (*possibly forming a new phase*)
 - Polymerized decaborane and demonstrated 1 wt% reversible hydrogen cycling by reaction with LiH
- **Theory/computation:**
 - Predicted favorable ternary borides for Mg-TM, TM = Mn, Fe, and Co
 - Predicted stability of $\text{Mg}_n\text{Mn}_m(\text{BH}_4)_{2(n+m)}$ increases with Mg:Mn ratio
 - Both 1:1 and 2:1 borohydrides dehydrogenate exothermically. The 3:1 composition is predicted to dehydrogenate and phase separate with an endothermic enthalpy of about 7 kJ/mol H_2
 - Predicted Li/H exchange energy for small ($n < 20$) borane clusters is positive but too large ($> 100 \text{ kJ/mol-H}_2$), although it decreases with cluster size

Technical Back-Up Slides (3)

Lithiated Boranes: $B_nH_x + yLiH \leftrightarrow B_nH_{x-y}Li_y + yH_2$

- Idea is to preserve B-B bonding framework (*avoid B-B bond rearrangement*), although, formally there are still two phases (BH_x and LiH) with interface
- Would be a new type of hydrogen storage reaction
 - could be considered a B-H/Li-H metathesis reaction
 - some analogy to LiH/hydrocarbon polymer reaction (DOI: 10.1221/cm500042c)
- Large range of possible borane substrate classes:
 - Molecular ($B_{10}H_{14}$, $C_2B_{10}H_{12}$)
 - Polymeric ($B_{18}H_{22}$ or larger BH_x)
 - Nanoparticle ($B_{80}H_{60}$, from U. Utah)
 - Alloy (Li_7B_6 , dehydrogenated state)

Li-B Alloy

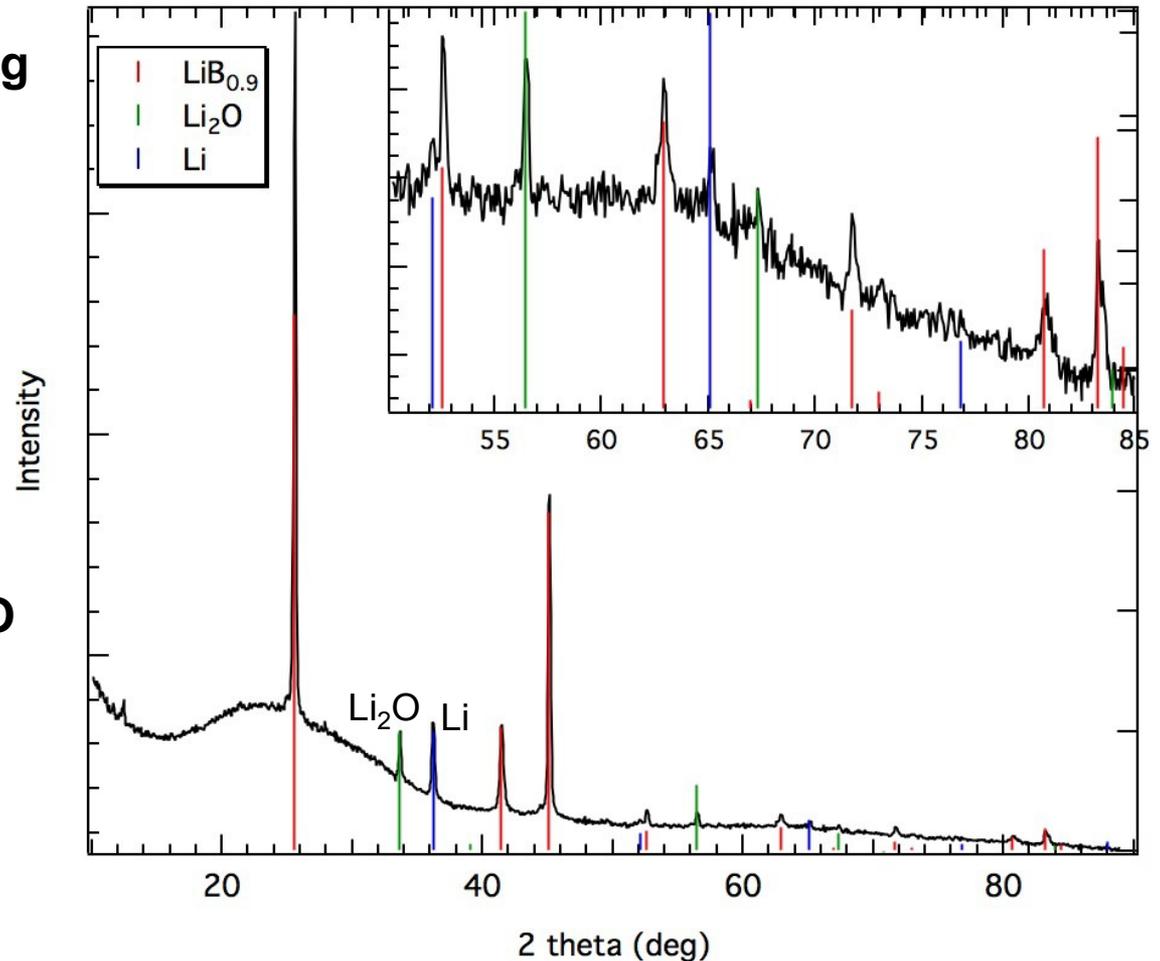
- **Synthesis of Li_7B_6 alloy:** (*Angew. Chem. Int. Ed.* 2000, 39, 2349-2353)

- 8Li + 6B (*in glove box, mixed/kneaded*)
- started with 2 g
- sealed in 1/2" OD SS tubing

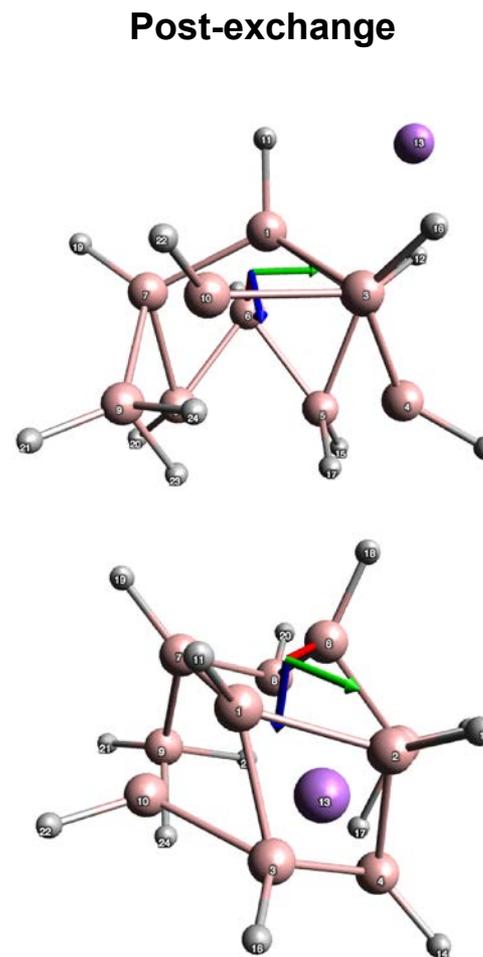
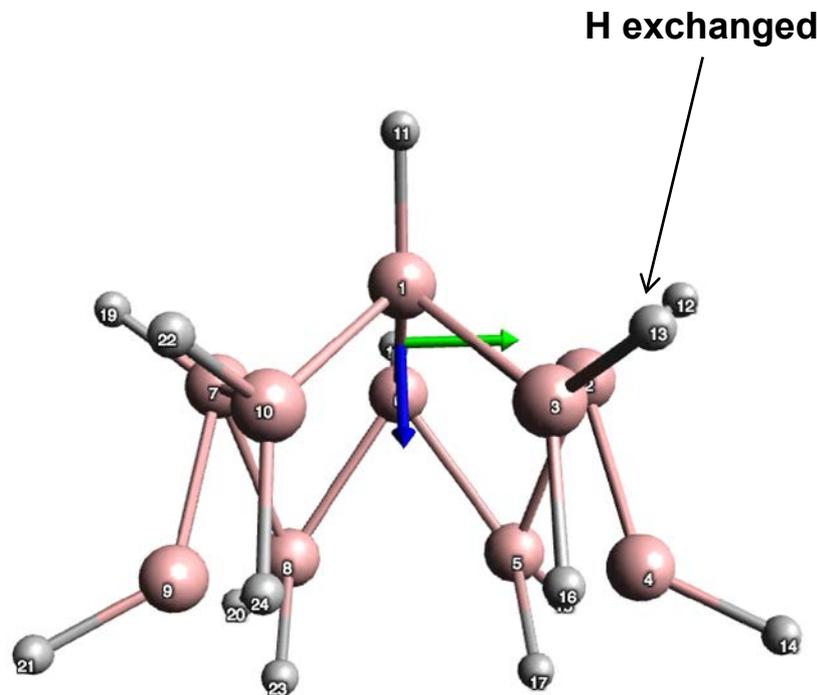


- 48 h at 450°C (*in air*)
- recovered 0.8 g
- Predominate phase is $\text{LiB}_{0.9}$ with unreacted Li metal and impurity Li_2O

- This sample will be treated in hydrogen



Large Deformations in Decaborane Configuration Upon 1st Li Exchange



- **Caveat: gas phase calculations**
- **Li prefers open face locations**
- **Large boron cage structure deformation**
- **B-H coordination may change**