



Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

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Caltech
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Project ID # ST072

Overview

Timeline

- Project start date:
October 1, 2004
- Project end date:
December 31, 2010
Percent complete: 90%

Budget

- Total project funding
DOE share \$1M (5 yrs)
Contractor share \$250k (5 yrs)
- Funding for FY07
DOE share \$200k
Contractor share \$50k
- Funding for FY08
DOE share \$200k
Contractor share \$50k

Barriers

- (B) Weight and volume of on board hydrogen storage systems
- (M) Reversibility of high capacity solid state storage materials
- (N) Kinetics (fueling/refueling times) associated with current solid state storage materials

Partners

Interactions/ collaborations:

John Vajo, HRL Laboratories
Vitalie Stavila, Sandia Natl. Lab.
Karl Johnson, Univ. Pittsburgh
David Sholl, Georgia Inst. Tech.
J.C. Zhao, GE/Ohio State Univ.
Terry Udovic, NIST
Joseph Reiter, JPL
Craig Jensen, U. Hawaii

Relevance

- To assess whether thermodynamically tractable reactions based on hydride destabilization, that should be reversible but appear not to be, are kinetically limited.
- To enable short hydrogenation times associated with refueling, that will require short solid-state and gas-solid diffusion path lengths.
- To address the problems associated with large, light-metal-hydride enthalpies (hydrogen fueling/refueling temperatures) and develop strategies to address thermodynamic issues surrounding the use of these materials through hydride destabilization. Systems of interest determined through “computational screening” by MHCoe partner members.
- To understand issues related to grain growth and surface/interface energies, which are vital in order to understand the kinetics of hydrogenation/dehydrogenation reactions.

Approach

- Ball milling of destabilization candidates and gravimetric dehydrogenation and hydrogenation evaluation of thermodynamically appropriate systems, using Sieverts apparatus systems at Caltech and at JPL.
- Analysis of borohydride reaction pathway intermediates, like closo-boranes to see if these structures can be destabilized.
- DFT calculations of specific hydride destabilization formation enthalpies and reaction enthalpies.
- X-ray diffraction for determining reaction product phases.
- NMR analysis (at the Caltech Solid State NMR facility) to determine bonding and phase formation in systems that lack long range crystallographic order.
- Transmission electron microscopy (at the Caltech Kavli Nanoscience Institute and the Material Science TEM facilities) and energy filtered imaging to determine microstructural evolution and phase inhomogeneities in scaffold based systems.

Technical accomplishments: Investigation of $2\text{LiBH}_4\text{-MgH}_2$ under H_2 back pressure via NMR

Background:

- Inconsistencies in determining closo-dodecaborane ($\text{MB}_{12}\text{H}_{12}$) formation. $\text{B}_{12}\text{H}_{12}$ appeared to be ubiquitous in metal borohydride reactions^{1,2} and scaffold experiments of LiBH_4 ³.
- But original destabilization system, $2\text{LiBH}_4\text{-MgH}_2$, showed reversibility (no NMR of $\text{B}_{12}\text{H}_{12}$) while it has been assumed that $\text{B}_{12}\text{H}_{12}$ intermediates are stable.
- Several studies⁴⁻⁵ showed the importance of H_2 back pressure to avoid direct decomposition of LiBH_4 , the case where the hydrogen capacity drops as the discharge/charge cycle goes due to the interference from the stable $\text{MB}_{12}\text{H}_{12}$.
- Uncertainty as to whether $\text{B}_{12}\text{H}_{12}$ suppressed in presence of high (4 bar) backpressure or whether $\text{B}_{12}\text{H}_{12}$ phase destabilized during cycling.
- Our recent work indicated that closo-borane extremely stable, so
- Case revisited to assess phase formation at high and moderate (1.5 bar) backpressure to probe limits of that show that modest back-pressure inadequate to suppress $\text{B}_{12}\text{H}_{12}$ formation.

¹“Experimental studies on intermediate compound of LiBH_4 ,” S. Orimo and Y. Nakamori, N. Ohba, K. Miwa, M. Aoki, and S. Towata, A. Züttel, *Appl. Phys. Lett.* 89, 021920(2006).

²“NMR Confirmation for Formation of $[\text{B}_{12}\text{H}_{12}]^{2-}$ Complexes during Hydrogen Desorption from Metal Borohydrides,” S.-J. Hwang, R. C. Bowman, Jr. J. W. Reiter, J. Rijssenbeek, G. L. Soloveichik, J.-C. Zhao, H. Kabbour and C. C. Ahn, *J. Phys. Chem. C Lett.* 112, 3164-3169 (2008).

³“Enhanced Hydrogen Storage Kinetics of LiBH_4 in Nanoporous Carbon Scaffolds, A. F. Gross, J. J. Vajo,” S. L. Van Atta, and G. L. Olson, *J. Phys. Chem. C* (2008), 112, 5651-5657

⁴“Reversible Storage of Hydrogen in Destabilized LiBH_4 ” J. J. Vajo, S. Skeith and F. Mertens, *J. Phys. Chem. B*, Vol. 109, No. 9 (2005).

⁵Pinkerton, et al. *JPC C*, 2007, 111, 12881.

Technical accomplishments: Can $B_{12}H_{12}$ be destabilized?

Reaction 6 from V. Ozolins, E. H. Majzoub and C. Wolverton, JACS (2008) shown in table below suggests destabilization route: $(6^*) Li_2B_{12}H_{12} + 6MgH_2 \rightarrow 6MgB_2 + 2LiH + 11H_2$ but NMR indicates that **no** MgB_2 formed and that all dehydrogenation from initial MgH_2

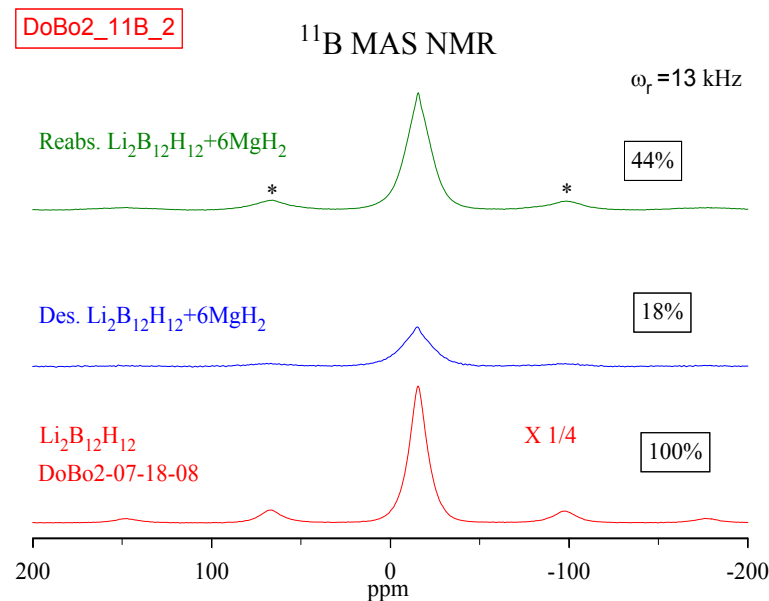
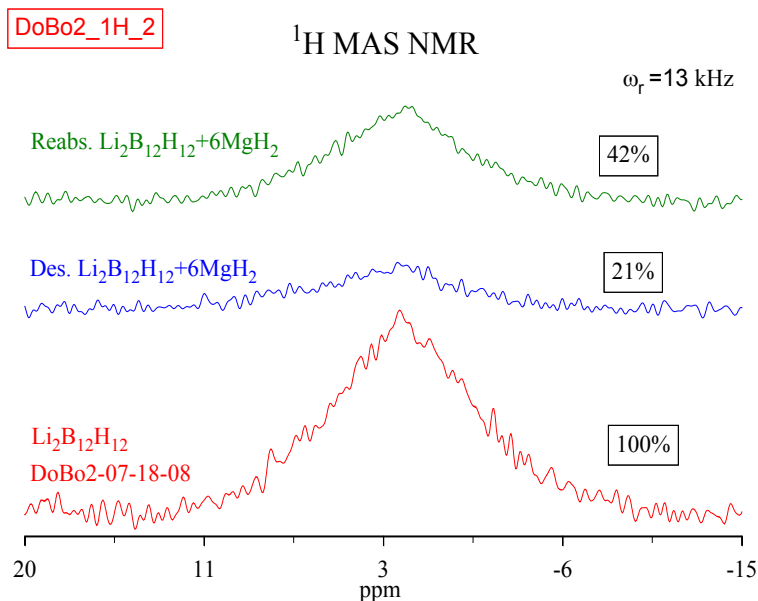
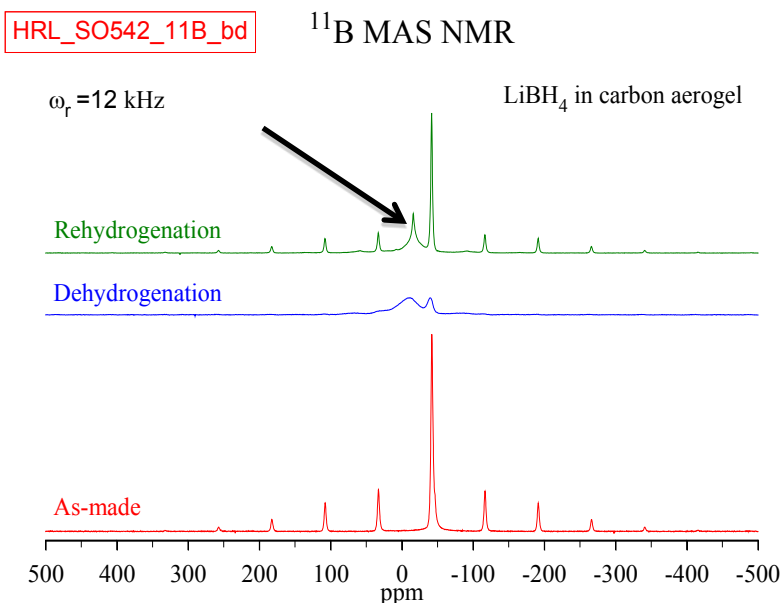


Table 2. Predicted Decomposition Reactions for Borohydrides^a

	reaction	wt % (kg H_2 /kg)	vol density (g H_2 /l)	ΔH^0 K	ΔH^{300} K	ΔS^{300} K	T_c ($^{\circ}C$)
Destabilized Reactions with $X_nB_{12}H_{12}$ Compounds							
(4)	$Li_2B_{12}H_{12} + 2CaH_2 \rightarrow 2CaB_6 + 2LiH + 7H_2$	5.9	67	43.1	51.1	128.2	123
(5)	$Li_2B_{12}H_{12} + 6Mg \rightarrow 6MgB_2 + 2LiH + 5H_2$	3.3	40	53.4	60.2	112.0	259
(6*)	$Li_2B_{12}H_{12} + 6MgH_2 \rightarrow 6MgB_2 + 2LiH + 11H_2$	7.1	53	52.4	60.1	123.3	215
(7)	$MgB_{12}H_{12} + 5MgH_2 \rightarrow 6MgB_2 + 11H_2$	7.5	86	42.1	50.0	123.9	128
(8)	$CaB_{12}H_{12} + CaH_2 \rightarrow 2CaB_6 + 7H_2$	6.3	85	38.6	47.0	130.7	86
(9)	$CaB_{12}H_{12} + 3MgH_2 \rightarrow 3MgB_2 + CaB_6 + 9H_2$	7.0	91	45.2	53.2	126.7	144

Technical accomplishments: Can $B_{12}H_{12}$ be destabilized? cont'd

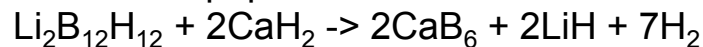
Given the apparent ubiquity of $B_{12}H_{12}$ formation as shown below for example in the work that describes the improved kinetics of $LiBH_4$ in a carbon scaffold as shown from our analysis below, some effort was expended in probing for evidence that this phase might be destabilized.



Characteristic -12 ppm peak from $Li_2B_{12}H_{12}$ shown from scaffold dehydrogenated $LiBH_4$ from "Enhanced Hydrogen Storage Kinetics of $LiBH_4$ in Nanoporous Carbon Scaffolds, A. F. Gross, J. J. Vajo," S. L. Van Atta, and G. L. Olson, J. Phys. Chem. C (2008), 112, 5651-5657

An assessment of other reactions suggested in the paper by Ozolins, et al were run in order to probe for destabilization reactions, were not successful in destabilizing the $B_{12}H_{12}$ phase.

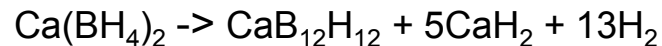
Reaction 4 in that paper:



was run in both directions at $400^\circ C$, no hydrogen was released.

Reaction 8, $CaB_{12}H_{12} + CaH_2 \rightarrow 2CaB_6 + 7H_2$ was run from right to left at >90 bar pressure with no hydrogen uptake that could be measured. We note however that V. Stavila of Sandia National Lab. was able to run this reaction but temperatures of $>450^\circ C$ were required.

In addition, reaction 14 from that paper:



was run from right to left with no hydrogen uptake that could be measured.

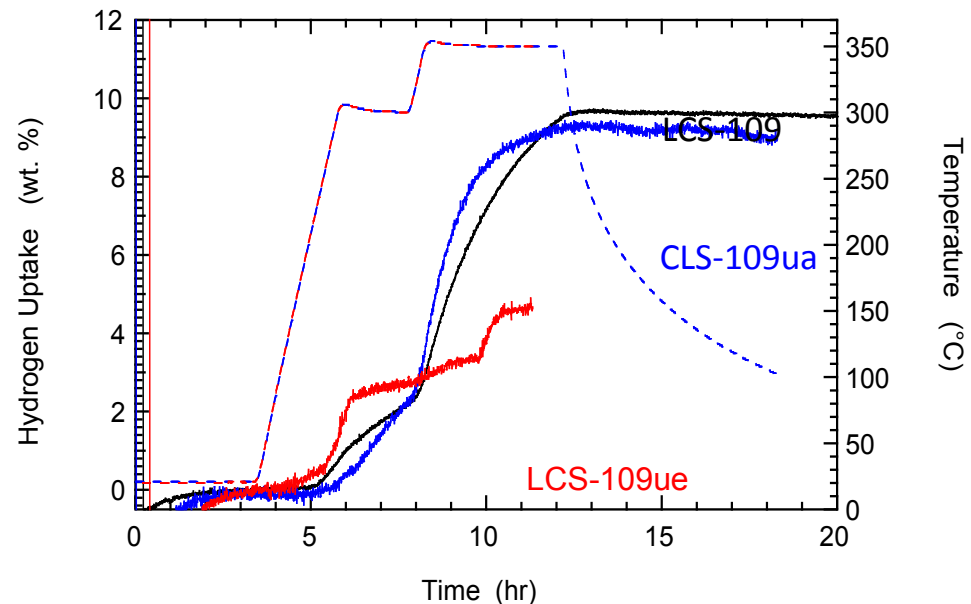
Reaction 15, $3Ca(BH_4)_2 \rightarrow CaB_6 + 2CaH_2 + 10H_2$ was run in both directions and partial reversibility was seen when the reaction is run from left to right (60%) but no reaction was seen in going from right to left.

Technical accomplishments: Investigation of initial $2\text{LiBH}_4\text{-MgH}_2$ reaction under H_2 back pressure via NMR

6 samples analyzed via NMR for this work:

1. LCS-109: The as-prepared $2\text{LiH} + \text{MgB}_2$ mixture after milling for 1 hr.
2. LCS-109ua: Half of the as-prepared sample LCS-109 after the first hydrogenation.
3. LCS-109ub: The same sample after dehydrogenation into **4 bar** H_2 .
4. LCS-109uc: The rehydrogenation of LCS-109ub after it had been dehydrogenated in 4 bar H_2 .
5. LCS-109ud: The other half of sample LCS-109ua after dehydrogenation into vacuum.
6. LCS-109ue. After rehydrogenation of LCS-109ud.

Figure at right shows temperature ramp (dotted trace) and uptake plots for samples into 4 bar hydrogen backpressure or into vacuum.



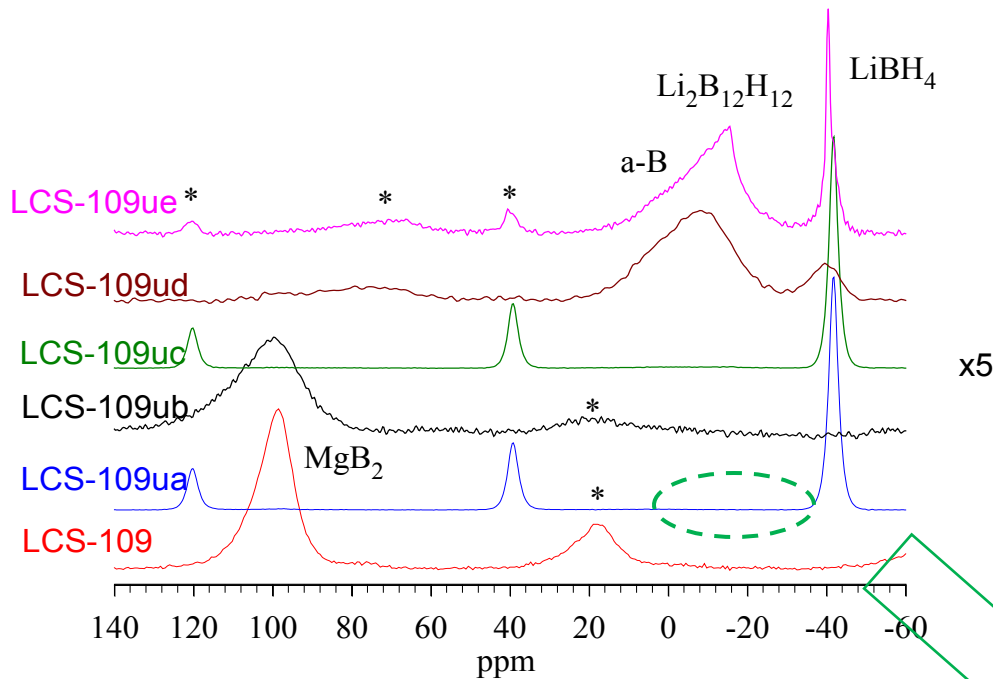
Technical accomplishments: Investigation of $2\text{LiBH}_4\text{-MgH}_2$ under H_2 back pressure via NMR (cont'd)

HRL09_LCS109_11B

^{11}B MAS NMR

$\omega_r = 13$ kHz

Phases identified and quantified by NMR



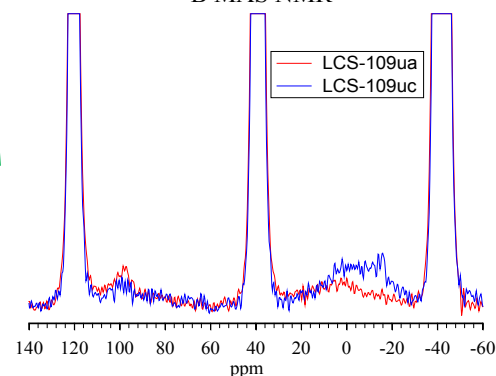
Sample	MgB_2	LiBH_4	a-B	$\text{B}_{12}\text{H}_{12}$ related
LCS-109	0.98			
LCS-109a	0.01	0.96	0.02	<0.01
LCS-109b	0.95			0.05
LCS-109c	0.01	0.94	0.02	0.03
LCS-109d	0.04	0.14	0.29	0.53
LCS-109e	0.02	0.23	0.18	0.58

x5

HRL09_LCS109_11B_1

$\omega_r = 13$ kHz

^{11}B MAS NMR

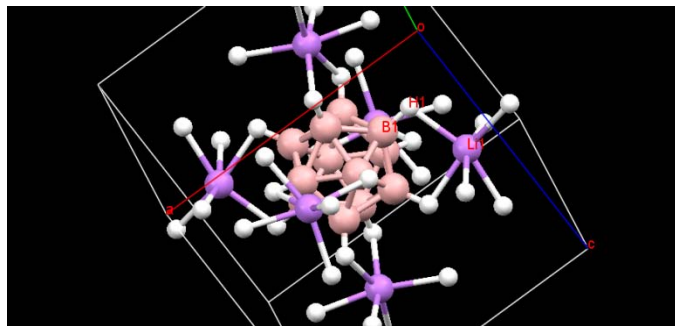


Negligible amount of intermediate formed

- NMR shows intermediate formation due to direct decomposition of LiBH_4 is directly responsible for the degraded performance of the hydrogen storage system.
- 4 bar H_2 back pressure suppress the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ formation.
- Alternative reaction route for $\text{M}(\text{BH}_4)_n$ alone without MH_2 has not been fully studied. H_2 back pressure study might be helpful.

Technical accomplishments: NMR Investigation of dodecaborates ($MB_{12}H_{12}$, $M=Li, Mg, Ca$)

To better assess the physicochemical property of metal dodecaborates ($MB_{12}H_{12}$, $M=Li, K, Ca, Mg$, etc), during desorption of metal borohydrides, the dynamics was probed by static variable-temperature NMR spectroscopy.



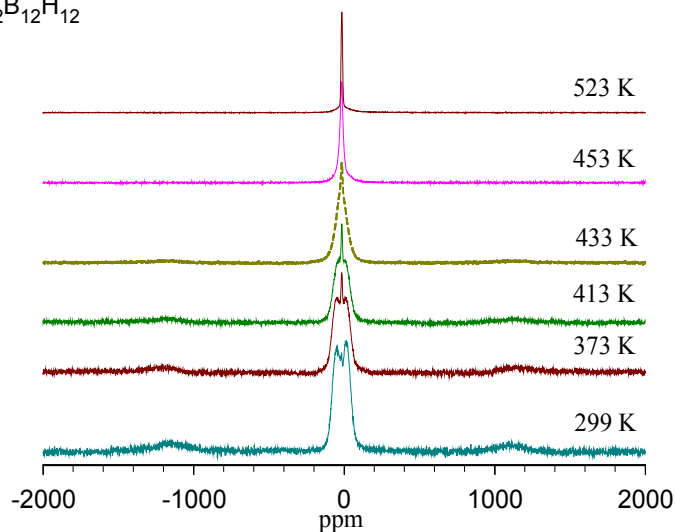
Crystal structure of $Li_2B_{12}H_{12}$ ¹

- ^{11}B ($I=3/2$, quadrupole) static lineshape a sensitive measure of molecular jumping motion.²
- Disappearance of powder pattern of satellite transition (peaks ± 1100 ppm) and narrowing of central transition (~ 0 ppm) seen as T increases.
- Depending on cation size and crystal structure, dynamic activation energy varies widely (note difference between Li and K seen for first time).

LiDoBo_VT_11B

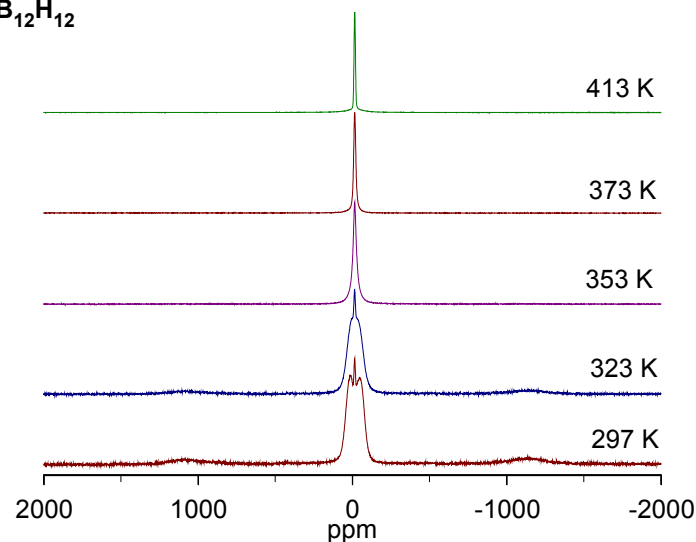
^{11}B Static NMR

$Li_2B_{12}H_{12}$



^{11}B Static NMR

$K_2B_{12}H_{12}$



¹Her, J.-H. et al. *Inorg. Chem.* **2008**, *47*, 9757.

²Tiritiris, I. et al. *Appl. Magn. Reson.* **2007**, *32*, 459.

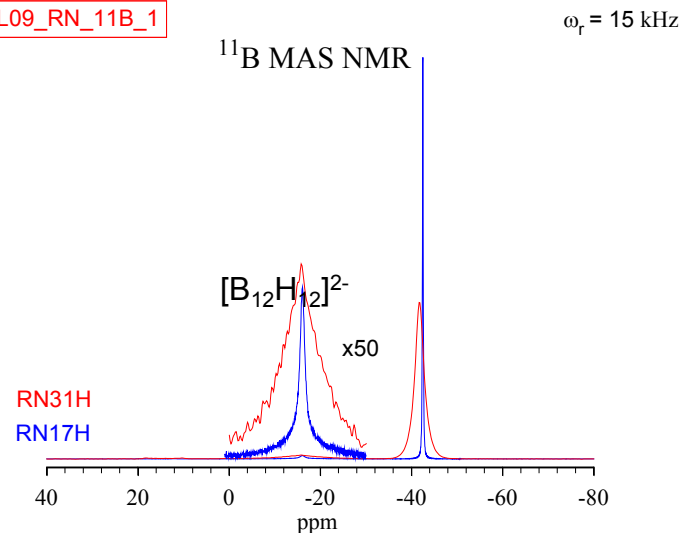
Technical accomplishments: Destabilization of dodecaborates ($\text{MB}_{12}\text{H}_{12}$, $\text{M}=\text{Li}, \text{Na}, \text{K}$)

- In collaboration with Sandia National Laboratory (V. Stavila) conversion of $\text{MB}_{12}\text{H}_{12}$ to $\text{M}(\text{BH}_4)_n$ via high pressure evaluated. As noted earlier, our previous attempts at lower pressure (H_2 pressure up to 90 bar) of $\text{MB}_{12}\text{H}_{12} + \text{MH}_n$ reactions unsuccessful despite estimated low thermodynamic barrier¹



- SNL performed reactions using high H_2 (930 bar) pressure at $T > 550^\circ\text{C}$ after high-energy ball milling over 1 hour. ^{11}B MAS NMR analysis shows formation of $\text{M}(\text{BH}_4)_n$ in significant fraction (see Table for the ratio between the reactant and product). Destabilization of the closo-borane phase possible but conditions required for this are extreme.

SNL09_RN_11B_1



Formation of $\text{M}(\text{BH}_4)_n$ quantified by NMR

Reaction	Conditions	$\text{M}_2\text{B}_{12}\text{H}_{12}$	MBH_4
$\text{Na}_2\text{B}_{12}\text{H}_{12} + 10\text{NaH}$	500°C , 793 bar H_2 , 72 h	9.3	89.6
$\text{Li}_2\text{B}_{12}\text{H}_{12} + 10\text{LiH}$	500°C , 931 bar H_2 , 72 h	9.1	89.6
$\text{K}_2\text{B}_{12}\text{H}_{12} + 10\text{KH}$	500°C , 931 bar H_2 , 72 h	7.8	92.2

¹V. Ozolins, E. H. Majzoub and C. Wolverton, JACS (2008)

Summary

- Previously believed that $B_{12}H_{12}$ formation a universal problem in destabilization reactions with borohydrides that would lead to irreversible hydrogenation/dehydrogenation reactions.
- Destabilization reactions of the closo-boranes suggested by theory not achievable under normal experimental conditions.
- Conditions of high pressure and temperature (performed at Sandia National Laboratory) show that borohydride phase can be reformed.
- Closo-borane formation can be minimized by dehydrogenation into modest (4 bar) back pressure whereas dehydrogenation into vacuum or 1.5 bar pressure results in dodeca-borane formation.