Lightweight Borohydrides for Hydrogen Storage

DOE Hydrogen Program

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– A Member of the DOE Metal Hydride Center of Excellence –

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Project ID:
STP_42_Zhao

Program Overview

Timeline

- Project start date: FY2008
- Project end date: FY2011
- Percent complete: 30%

Barriers

- Right heat of formation (J)
- Absorption / desorption kinetics (E)
- Reversibility for borohydrides (D, P)

Budget

- Total Project Funding: *$2.8M*
  - DOE Share: $2.2M
  - OSU Share: $0.6M
- Funding Received for FY08

  $523K (DOE), $130K (OSU-Cost)
- Funding for FY09 (estimate): $670K

Partners/Collaborations

- Members of DOE MHCoE
- Collaborations with ORNL, JPL, Caltech, U. Pitt, SNL, Univ. Nevada, and U. Utah.

Objectives & Relevance

Overall	Discover and develop a high capacity (> 6 wt.%) lightweight hydride capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.
FY08	• Study the desorption mechanism and explore ways to make $Mg(BH_4)_2$ reversible, especially by synthesizing and studying the stability of $MgB_{12}H_{12}$; • Study an aluminoborane compound AlB_4H_{11} for suitability for hydrogen storage; • Explore new hydride materials.
FY09	• Study $Mg(BH_4)_2$, $Mg(B_3H_8)_2$, and $MgB_{12}H_{12}$ and their amine complexes for hydrogen storage; • Synthesize and characterize new boro-amine hydride materials.

This project is directly exploring materials to meet the DOE 2010 hydrogen storage targets for onboard vehicular applications.

Approach

- Explore two classes of materials: $Mg(BH_4)_2$-based materials and aluminoborane compounds such as AlB_4H_{11} and their amine complexes;
- Study the crystal structures and the decomposition mechanisms using multiple techniques such as interrupted PCT tests, NMR, IR, DSC, and residual gas analysis;
- Develop reversibility strategy from detailed mechanistic understanding of the complex desorption processes (such understanding is crucial for reversibility of all borohydrides);
- Synthesize new hydrides and complexes in collaboration with ORNL, JPL, Caltech, Sandia, and NIST.

Go / No-Go Decision Point for Synthesis of Anhydrous $MgB_{12}H_{12}$:

December 2009.

Go / No-Go Decision Point for Aluminoborane Compounds:

March 2010: > 80% reversibility at < 300ºC, 150 bars of H_2.

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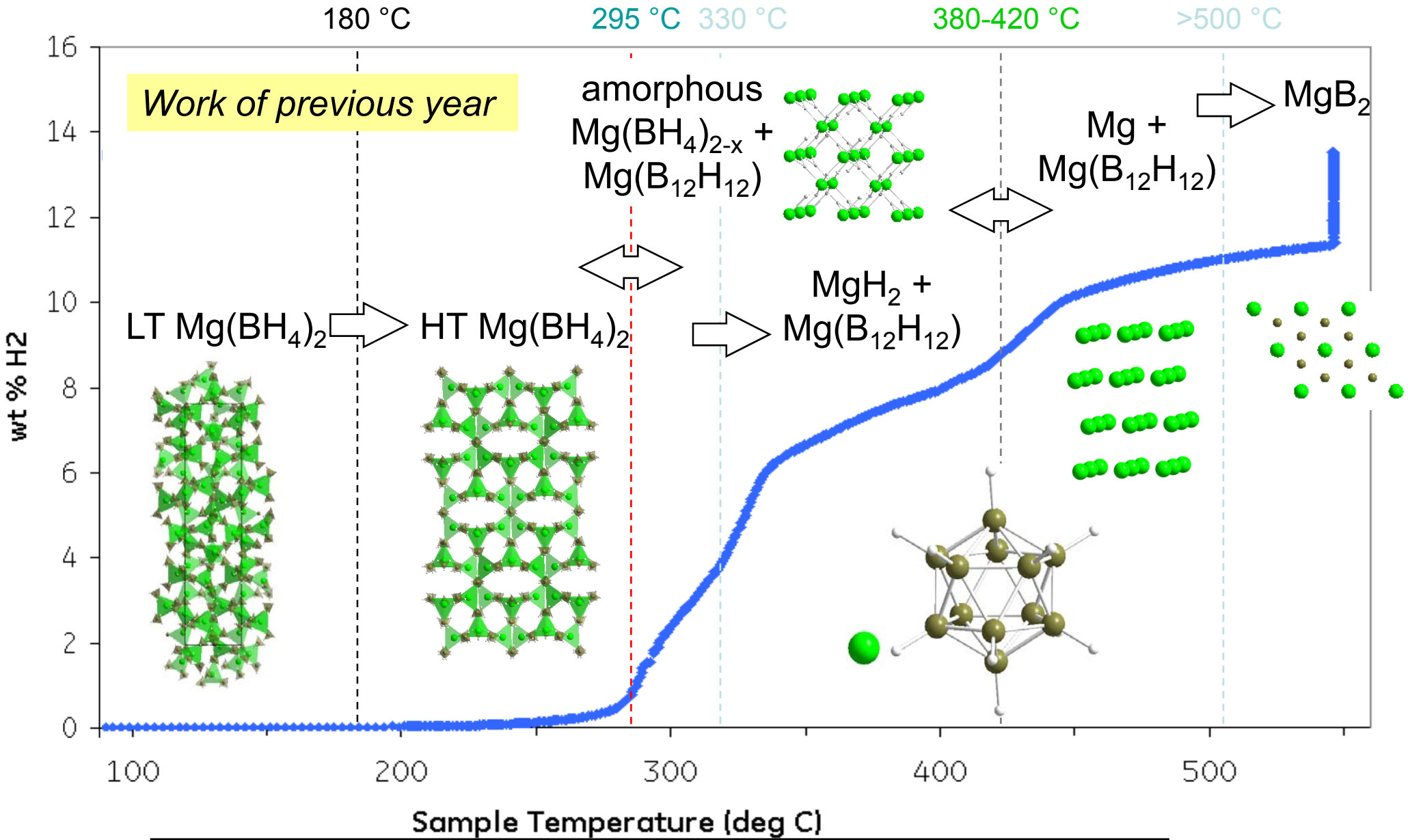
$Mg(BH_4)_2$ Desorption



Understanding the $MgB_{12}H_{12}$ intermediate phase is critical for improving the reversibility of $Mg(BH_4)_2$.

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Technical Accomplishments

$MgB_{12}H_{12}$ Synthesis and Characterization

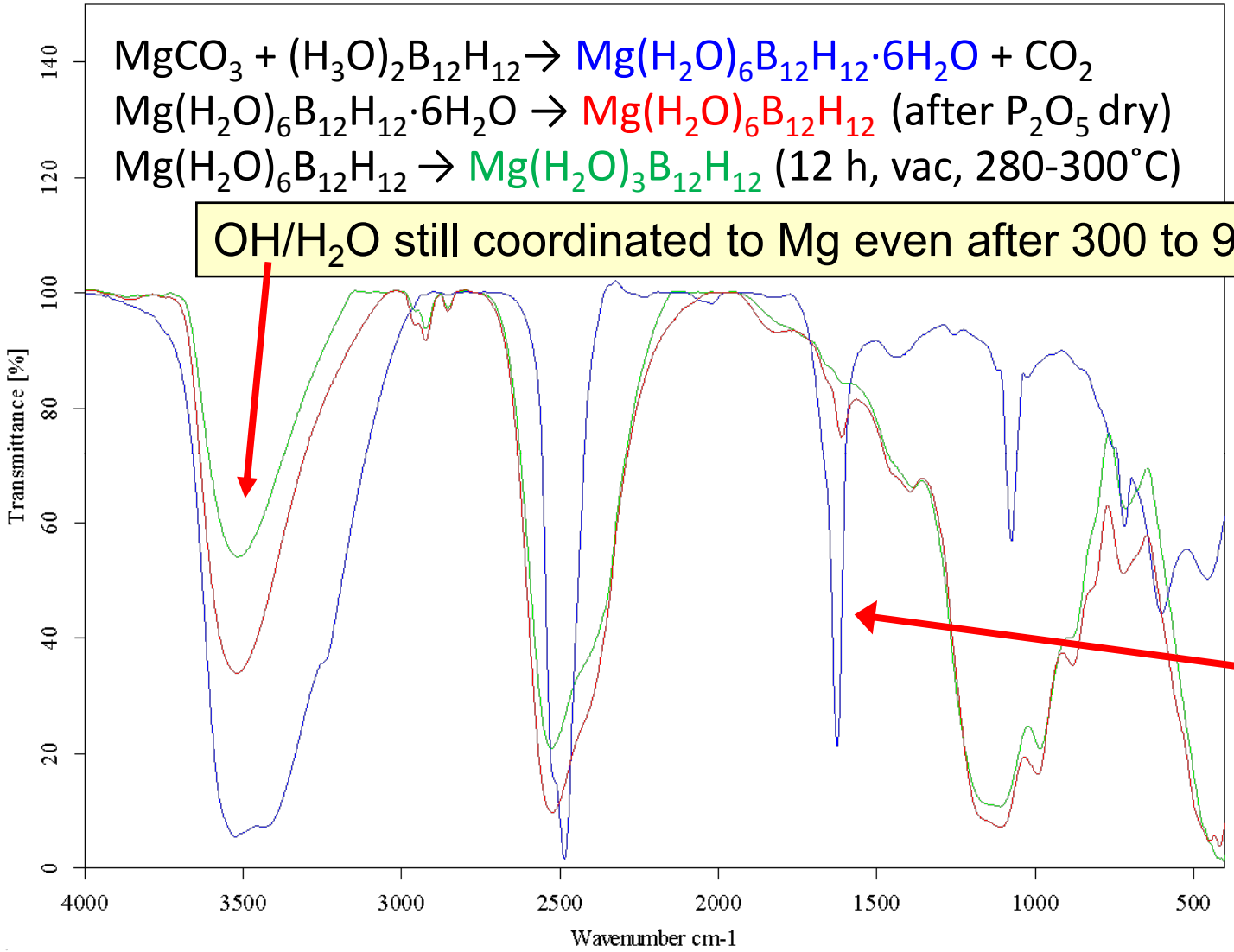
$MgCO_3 + (H_3O)_2B_{12}H_{12} \rightarrow Mg(H_2O)_6B_{12}H_{12}\cdot 6H_2O + CO_2$

$Mg(H_2O)_6B_{12}H_{12}\cdot 6H_2O \rightarrow Mg(H_2O)_6B_{12}H_{12}$ (after P_2O_5 dry)

$Mg(H_2O)_6B_{12}H_{12} \rightarrow Mg(H_2O)_3B_{12}H_{12}$ (12 h, vac, 280-300˚C)

Sandia also did similar synthesis

OH/H_2O still coordinated to Mg even after 300 to 900˚C exposure



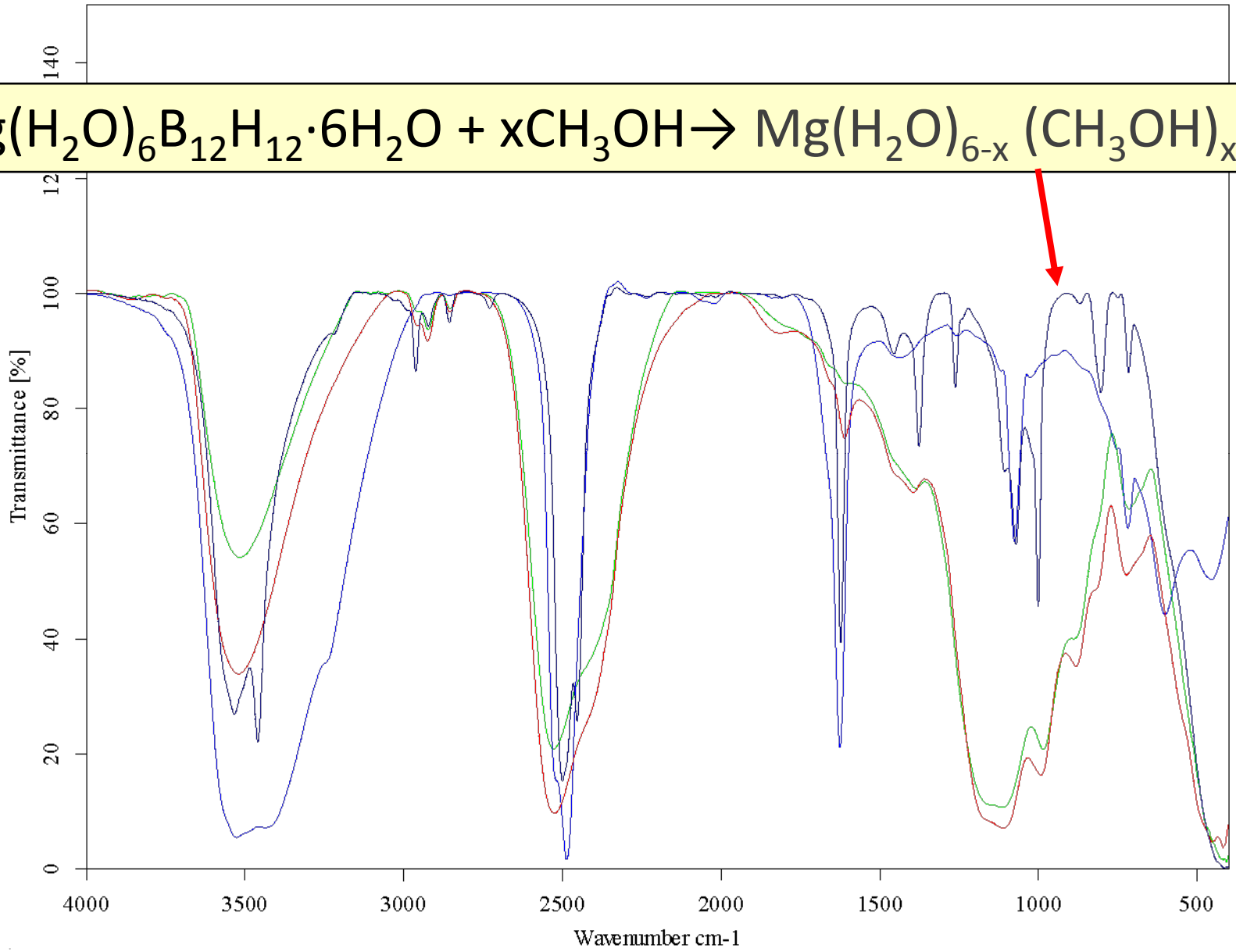
6 loosely attached (zeolitic) H_2O were removed by drying

Literature claim of anhydrous $MgB_{12}H_{12}$ was found to be incorrect

Z. Anorg. Allg. Chem. **2004**, 630, *541*.

$MgB_{12}H_{12}$ Synthesis and Characterization

$$Mg(H_2O)_6B_{12}H_{12}\cdot 6H_2O + xCH_3OH \rightarrow Mg(H_2O)_{6-x}(CH_3OH)_xB_{12}H_{12}$$

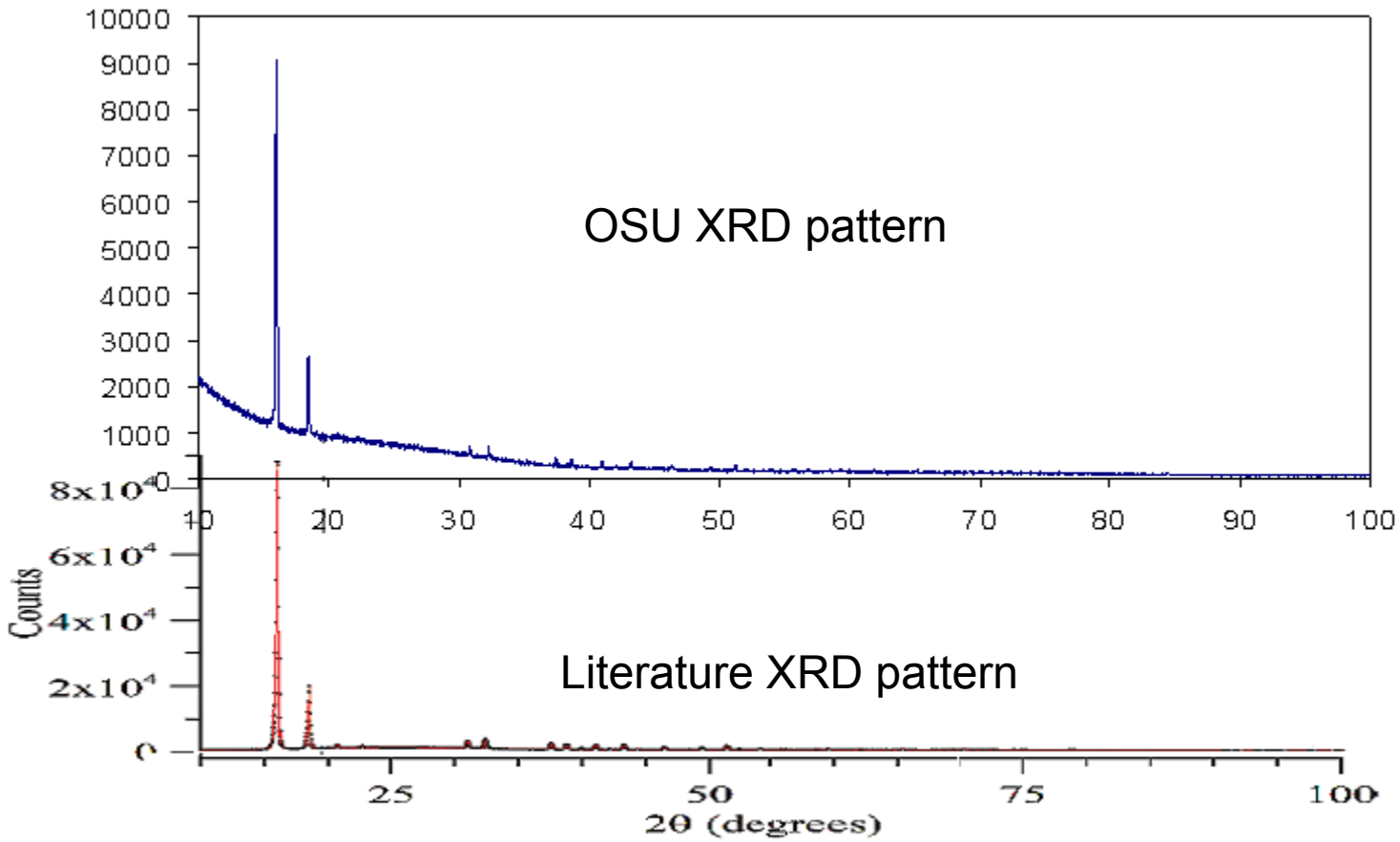


- CH_3OH cannot totally replace H_2O to make anhydrous $MgB_{12}H_{12}$.
- Several other methods to make pure, anhydrous $MgB_{12}H_{12}$ are still being explored.

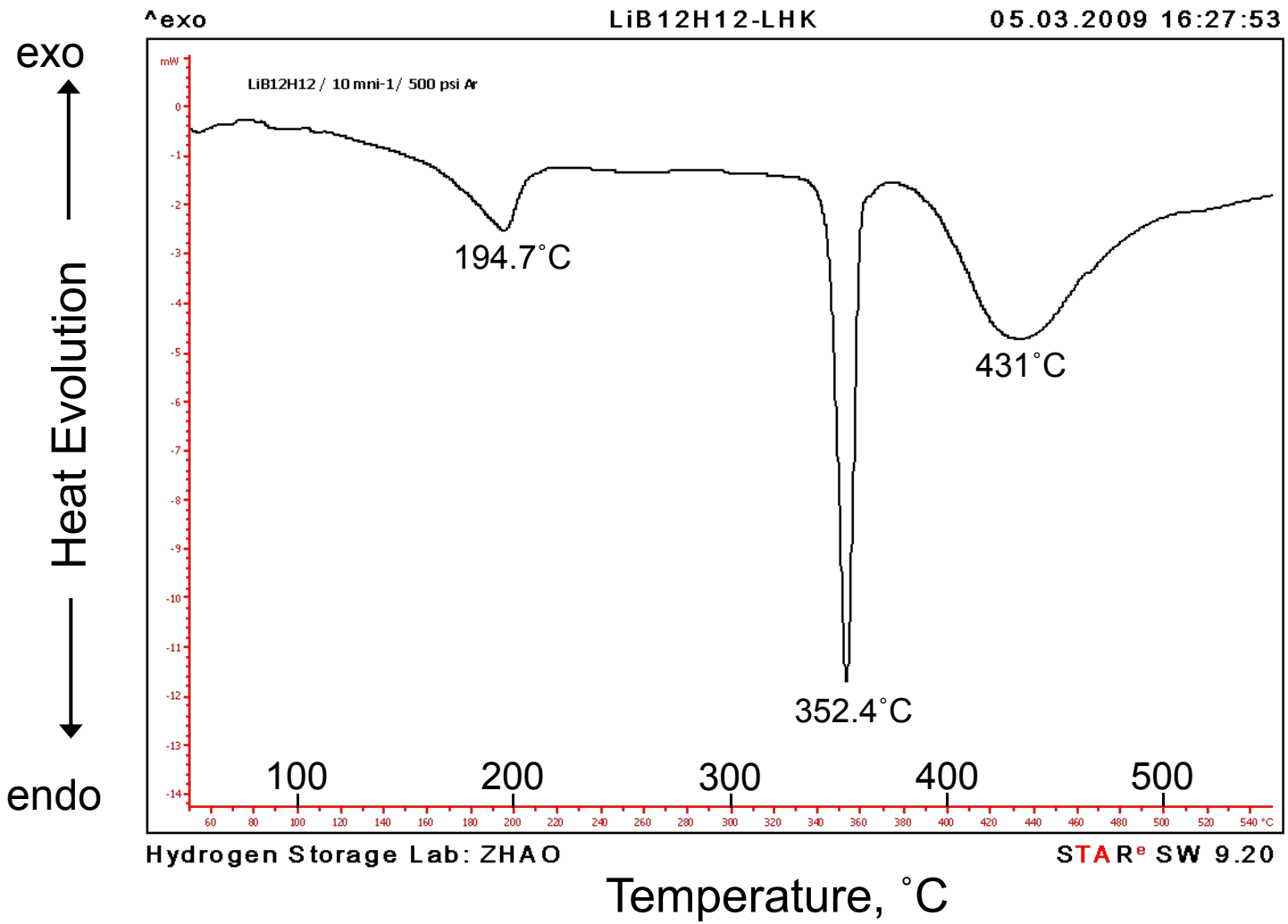
$Li_2B_{12}H_{12}$ Synthesis and Characterization

- Several different methods have been tried to make anhydrous $MgB_{12}H_{12}$, but so far none of them is successful.
- In the process of exploring these methods, we made $Li_2B_{12}H_{12}$ and are providing the material to HRL for encapsulation into aerogels.

$B_{12}H_{12}$ salt $\xrightarrow[\text{Acidic ion exchange resin}]{\text{Cation exchange}}$ $(H_3O)_2[B_{12}H_{12}]$ $\xrightarrow[\text{LiOH}]{\text{neutralization}}$ $Li_2(H_2O)_7[B_{12}H_{12}]$ $\xrightarrow{\text{heating}}$ $Li_2B_{12}H_{12}$



$Li_2B_{12}H_{12}$ Synthesis and Characterization



DSC of $Li_2B_{12}H_{12}$ showing its stability

Technical Accomplishments

Understanding $Mg(BH_4)_2(NH_3)_2$ desorption

- High resolution NMR (MAS, CPMAS, MQMAS) was employed to compare the desorption products of $Mg(BH_4)_2$, $Mg(BH_4)_2(NH_3)_2$, and $Mg(BH_4)_2(NH_3)_2 + nLiBH_4$ (n = 1,2).
- Disordered BN is identified as initial desorption product of $Mg(BH_4)_2(NH_3)_2$.
- $[B_{12}H_{12}]^{2-}$ anion is the primary intermediate species during desorption of $LiBH_4$, $Mg(BH_4)_2$, and $Mg(BH_4)_2(NH_3)_2 + nLiBH_4$ (n = 1,2).
- A manuscript is in the process for submission for publication.

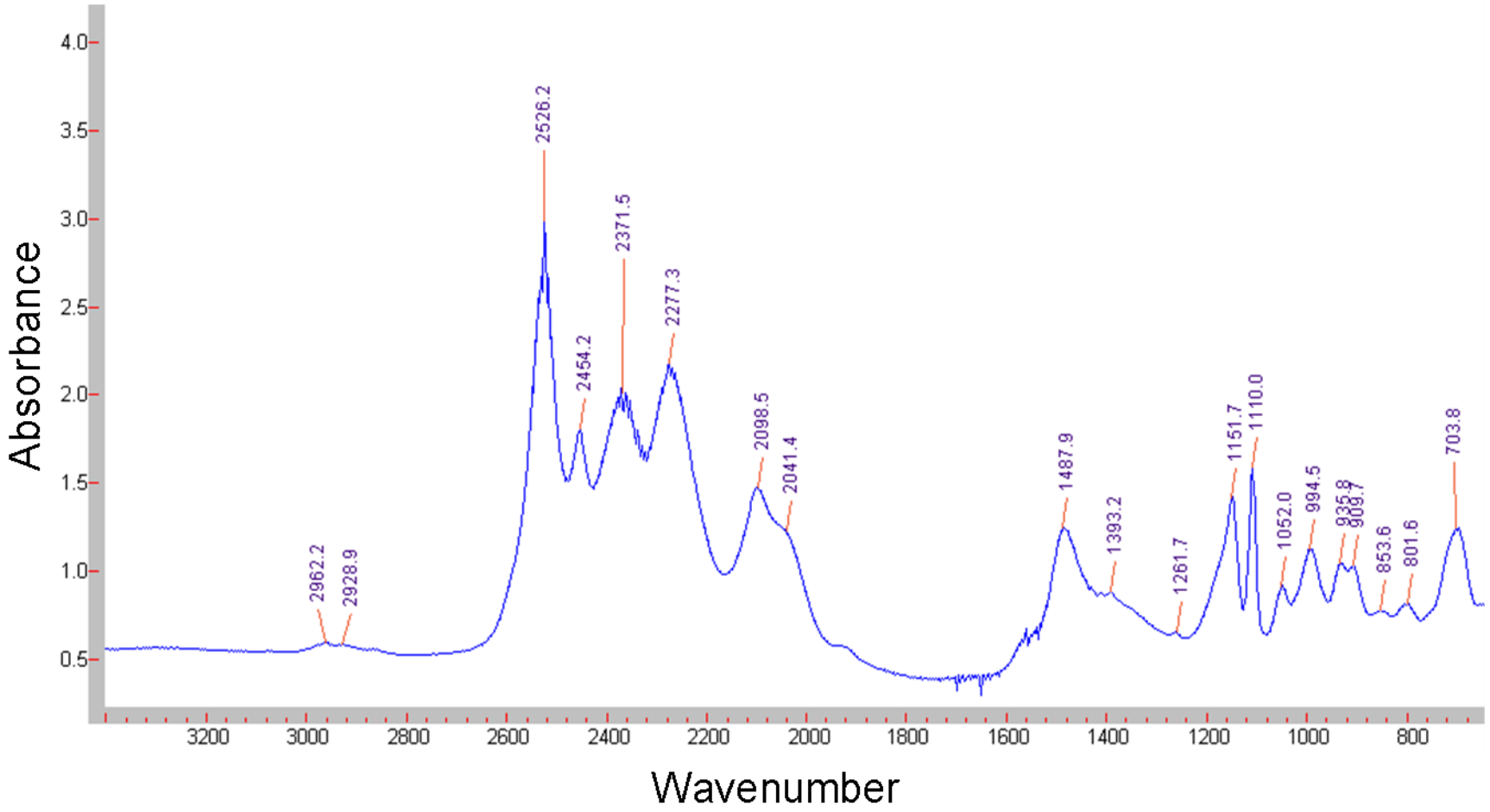
Technical Accomplishments

Aluminoborane compounds: AlB_4H_{11}, AlB_5H_{12}, AlB_6H_{13}, ……

- Himpsl and Bond synthesized them in 1981.
- ORNL synthesized AlB_4H_{11} for the first time since 1981
- Preliminary analyses performed at ORNL, JPL, and Caltech
- High wt.% hydrogen (13.5%, 12.9% & 12.4%)
- Attractive desorption temperature (100 to 125˚C).
- Small amounts of B_2H_6 formation (<1%) observed by us
- Early indication of partial reversibility observed for the 1st time.

First Synthesized AlB_4H_{11} since 1981

$$2\ Al(BH_4)_3 + B_2H_6 \leftrightarrow 2\ AlB_4H_{11} + 4H_2$$



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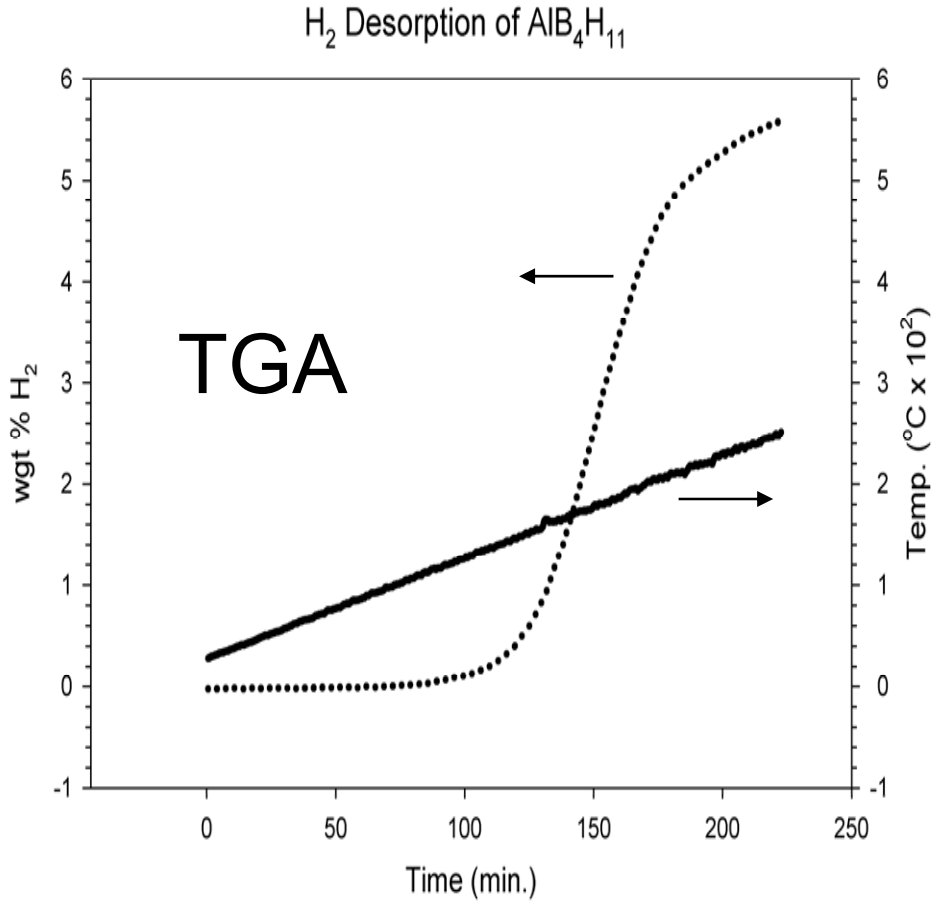
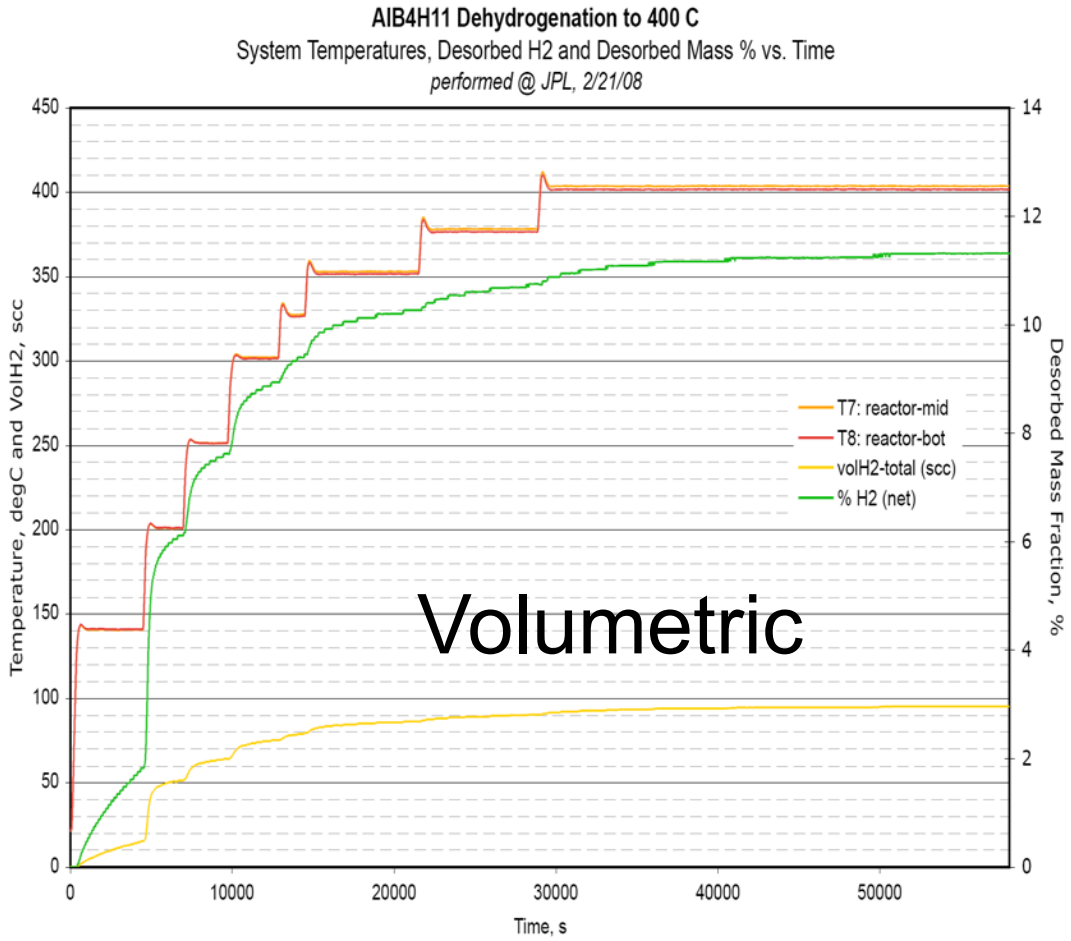
AlB_4H_{11}





- Attractive low desorption temperature
- High wt.% hydrogen

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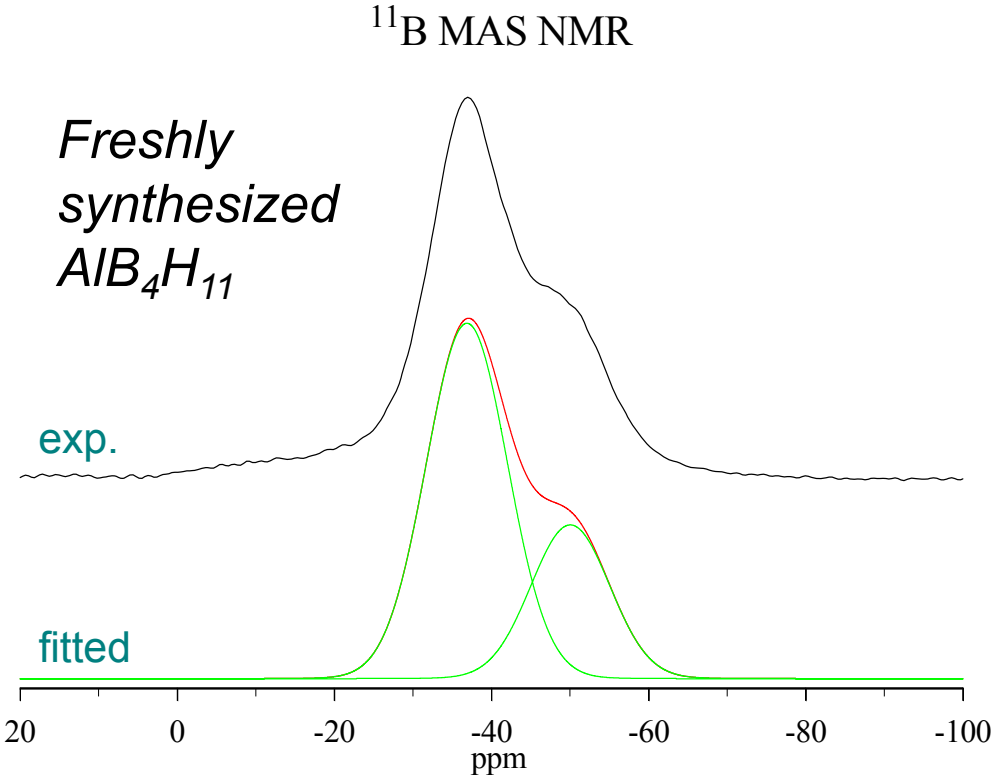
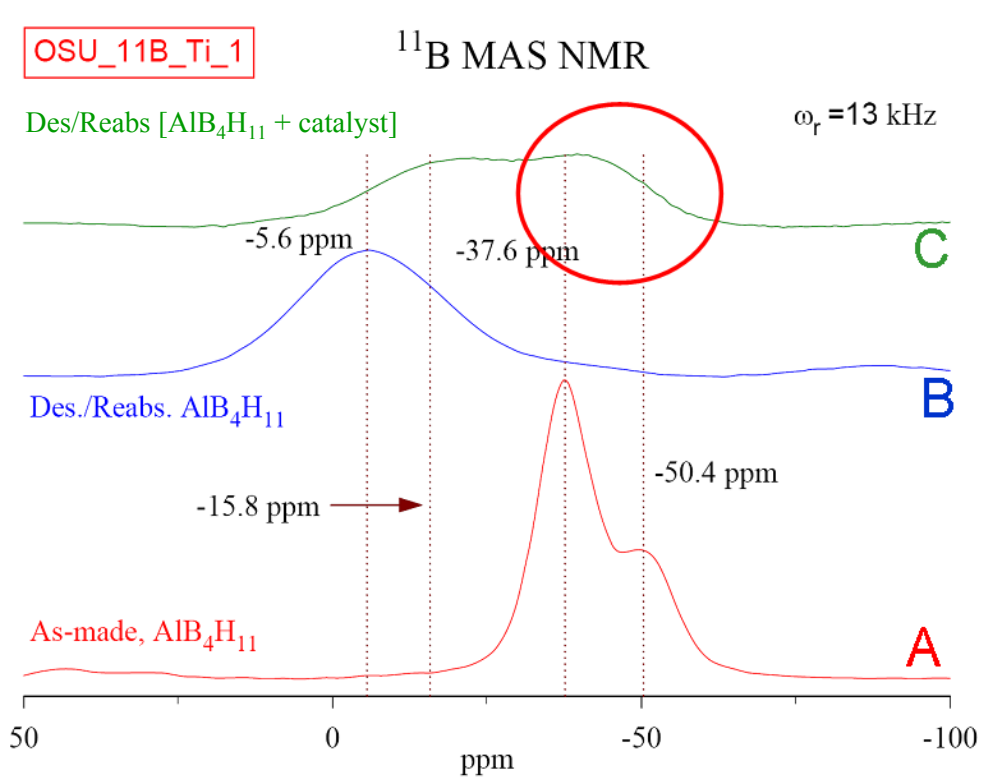
AlB_4H_{11}

Partial reversibility observed for the first time at mild conditions: 200ºC, 90 bar H_2, 5 hours





Two different boron environments – structure still unknown (amorphous)

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Future Work

FY09

- Continue to synthesize single-phase $MB_{12}H_{12}$ phase for mechanism, stability and structure study (M = Li, Mg, and Ca)
- Synthesize and characterize amine and alumino complexes of borohydrides, especially $XMg(BH_4)_2(NH_3)_2$, and $Mg(AlH_4)(BH_4)$
- Characterize desorption products of AlB_4H_{11}
- Explore catalytic effects on reversibility of AlB_4H_{11}.
- Synthesize $M(B_3H_8)_2$ and $MB_{10}H_{10}$, and other hydrides.

FY10

- Explore new classes of materials in collaboration with ORNL, Sandia, U. Utah, and JPL/Caltech
- Continue mechanistic and catalyst screening work for improving reversibility

Collaborations

- We have established extremely effective collaborations among several members of the MHCoE partners. For instance, ORNL synthesized AlB_4B_{11} at the request of OSU/GE. The samples are then analyzed at ORNL, JPL and Caltech for hydrogen desorption and structures (via NMR).
- OSU synthesized $Mg(BH_4)_2$ and $Li_2B_{12}H_{12}$ and provided the materials to UTRC and HRL for nano-framework encapsulations.
- A new subgroup on borohydride-amine complexes was formed to coordinate the research on this class of materials with J.-C. Zhao as the group lead.
- Sandia provided $Cs_2B_{12}H_{12}$ to OSU for initial synthesis trials of $MgB_{12}H_{12}$.
- $MgB_{12}H_{12}$ (hydrous) was then sent to NIST and Caltech for analysis in addition to OSU analysis using NMR and DSC.

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Summary

- We tried to synthesize $MgB_{12}H_{12}$ in order to study the stability of this very important intermediate phase formed during $Mg(BH_4)_2$ decomposition. We found that the literature claim of anhydrous $MgB_{12}H_{12}$ was incorrect. We subsequently tried several different methods, but are still not able make the anhydrous product. Work in progress.
- In collaboration with ORNL, JPL, and Caltech, we studied a "new" class of hydrides – aluminoborane compounds for hydrogen storage. These compounds such as AlB_4H_{11} have low desorption temperatures, high wt.% hydrogen, low amounts of diborane, and at least partial reversibility at mild conditions (200ºC, 90 bar H_2). We consider these compounds attractive candidates.

Summary (continued)

- We re-synthesized $Mg(BH_4)_2(NH_3)_2$ using both a solvent process and a solvent-free process (developed at ORNL) and are in the process of studying its decomposition and rehydriding processes and mechanism. We have gained much better understanding of its desorption process via high-resolution NMR studies.
- In addition to synthesize and characterize $MgB_{12}H_{12}$, $Mg(BH_4)_2(NH_3)_2$, $XMg(BH_4)_2(NH_3)_2$, $Mg(AlH_4)(BH_4)$, AlB_4H_{11}, we are also making good progress in synthesizing $Mg(B_3H_8)_2$, $MgB_{10}H_{10}$, and other borohydrides and their amine complexes.
- We synthesized $Li_2B_{12}H_{12}$ and are in the process of providing the material to MHCoE partners for encapsulation into aerogels and other studies.