Lightweight Metal Hydrides for Hydrogen Storage

DOE Award #: DE-FC3605GO15062

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The Ohio State University

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Project ID #: ST032

Program Overview

Timeline

- Project start date: FY2008
- Project end date: FY2011
- Percent complete: 75%

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 FY09
  $650K (DOE), $163K (OSU-Cost)
- Funding for FY10: $700K

Partners/Collaborations

- Members of DOE MHCoE
- Collaborations with ORNL, JPL, Caltech, UTRC, SNL, Univ. of Nevada, and Univ. of Utah, Univ. of Washington, Ford, NIST.

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Objectives & Relevance

Overall	Discover and develop a high capacity (> 6 wt.%) lightweight hydride capable of meeting or exceeding the 2015 DOE/FreedomCAR targets.
FY09	• Study $Mg(BH_4)_2$, especially by synthesizing & studying the stability of $MgB_{12}H_{12}$ (anhydrous compound not obtained); • Study aluminoborane compounds AlB_4H_{11}, AlB_5H_{12} and AlB_6H_{13} for suitability for hydrogen storage.
FY10	• Study the absorption & desorption kinetics with and without catalysts to improve the reversibility of AlB_4H_{11},and other aluminoborane compounds; • Study their structures and kinetic mechanisms.

This project is directly exploring materials to meet the DOE 2015 hydrogen storage targets

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Approach

- Study aluminoborane compounds such as AlB_4H_{11} for hydrogen storage;
- 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*:**

Passed the Go/No-Go decision with a Go in March 2010

Technical Accomplishments:
Upfront summary

- **AlB_4H_{11}** (13.5 wt.% H):
  - 13.5wt.% H, low desorption T.
  - Studied using TGA, PCT, XRD, NMR, IR, DSC, TPD-MS.
  - 2.5%H re-absorption at mild conditions.
- **A New Aluminoborane Synthesized**:
  - Light yellow solid.
  - Characterization in progress.
- **AlB_5H_{12} & AlB_6H_{13}**:
  - Synthesis in progress – starting compounds hard to scale up.
  - All reported to have low desorption T.
  - Excellent flexibility in structures.

AlB_4H_{11} showed reversibility at mild conditions.

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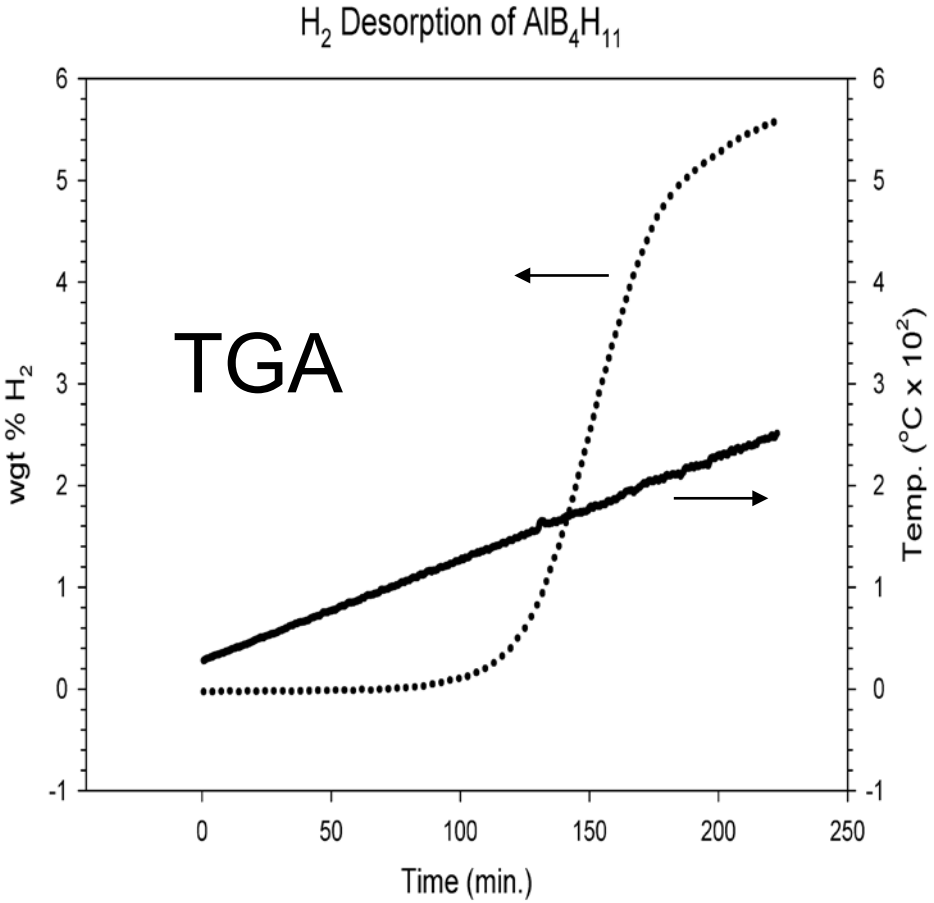
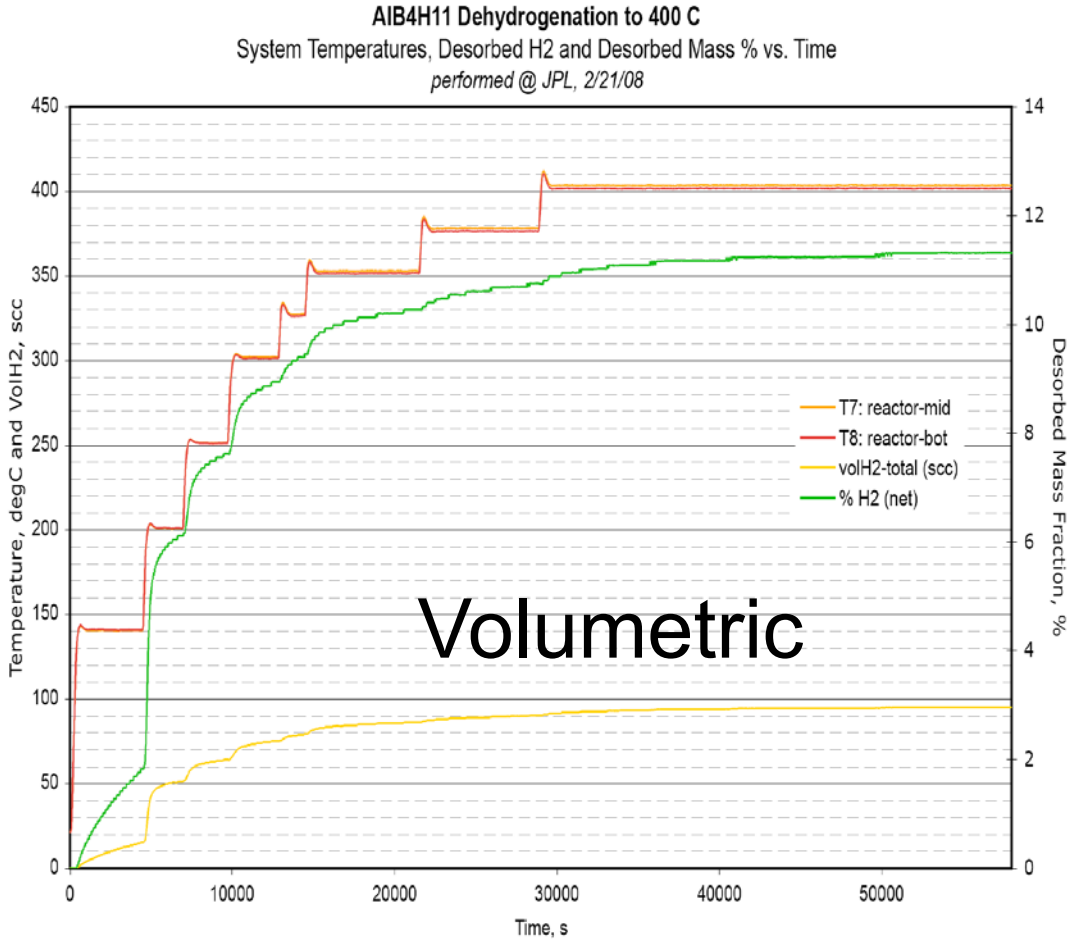
AlB_4H_{11} – Synthesis and Desorption

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



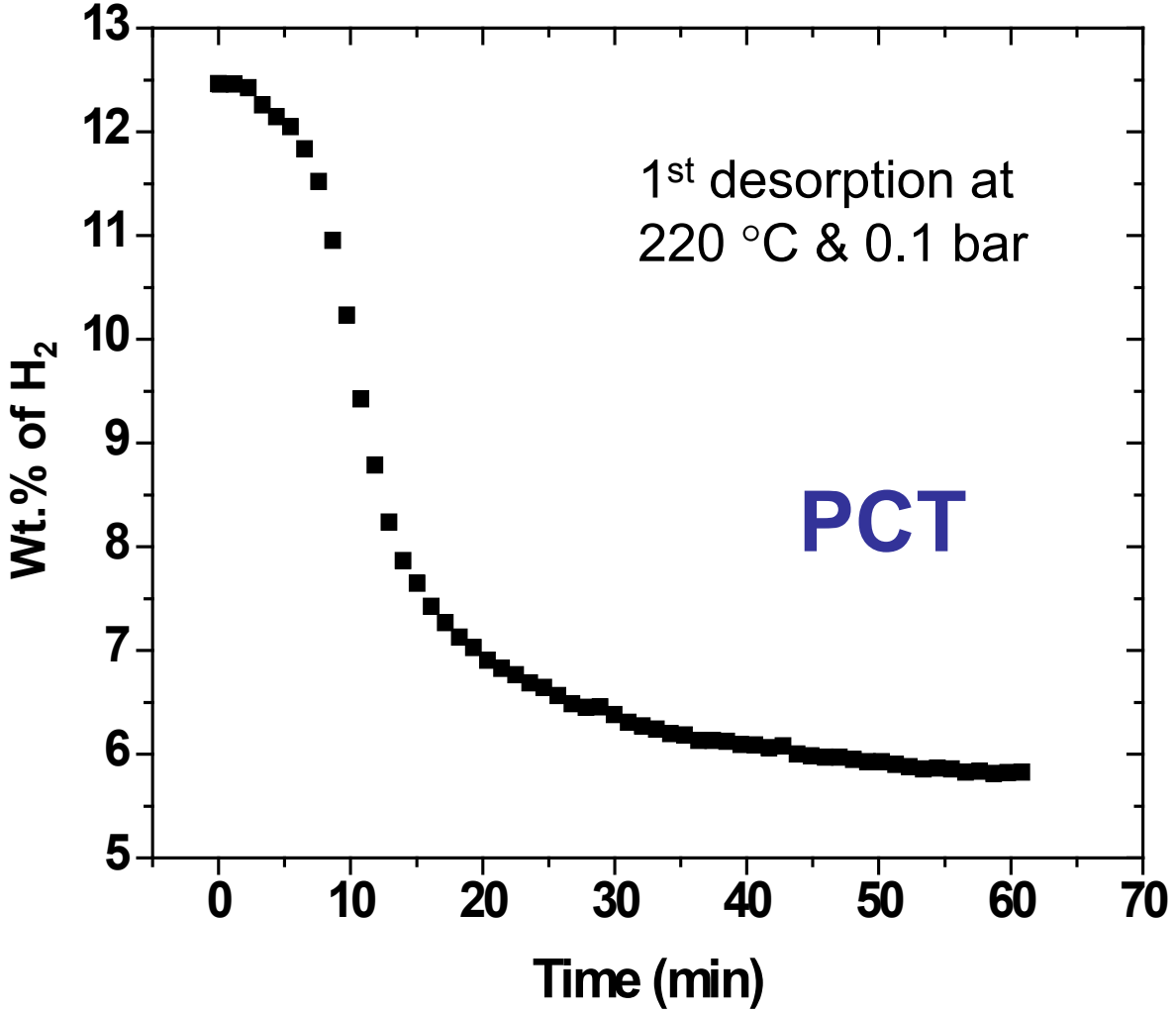


- Attractive low desorption temperature
- High wt.% hydrogen

Zhao, Knight, Brown, Kim, Hwang, Reiter, Bowman, Zan, Kulleck

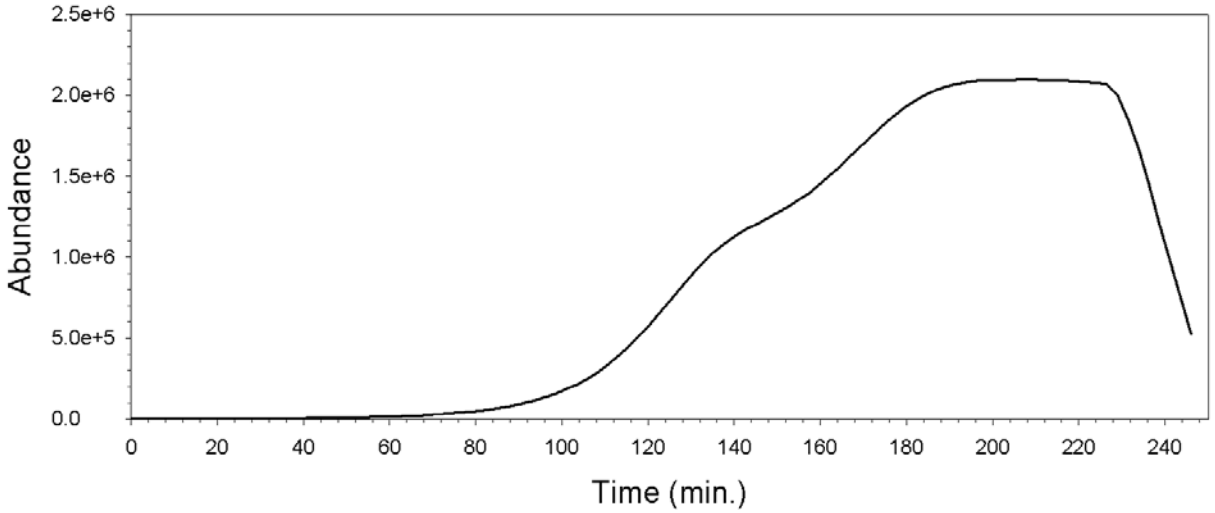
AlB_4H_{11} – Dehydrogenation properties

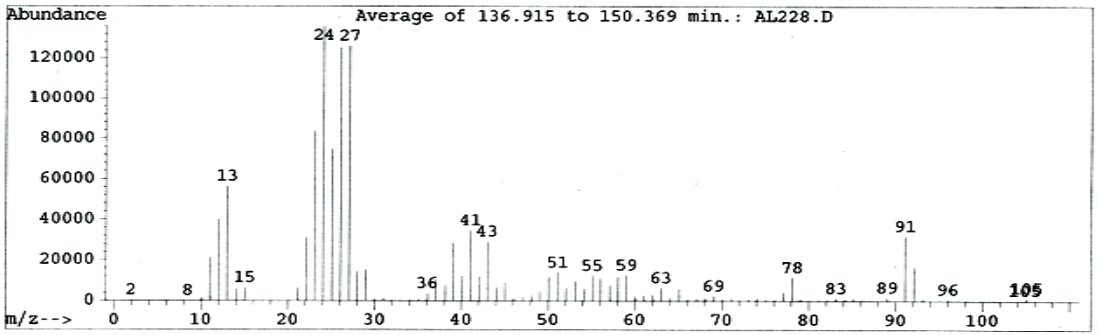
AlB_4H_{11} mixed with $TiCl_3$ by manual grinding in mortar and pestle for 10 min



PCT measurement showed 6.5 wt.%H release at 220 ºC

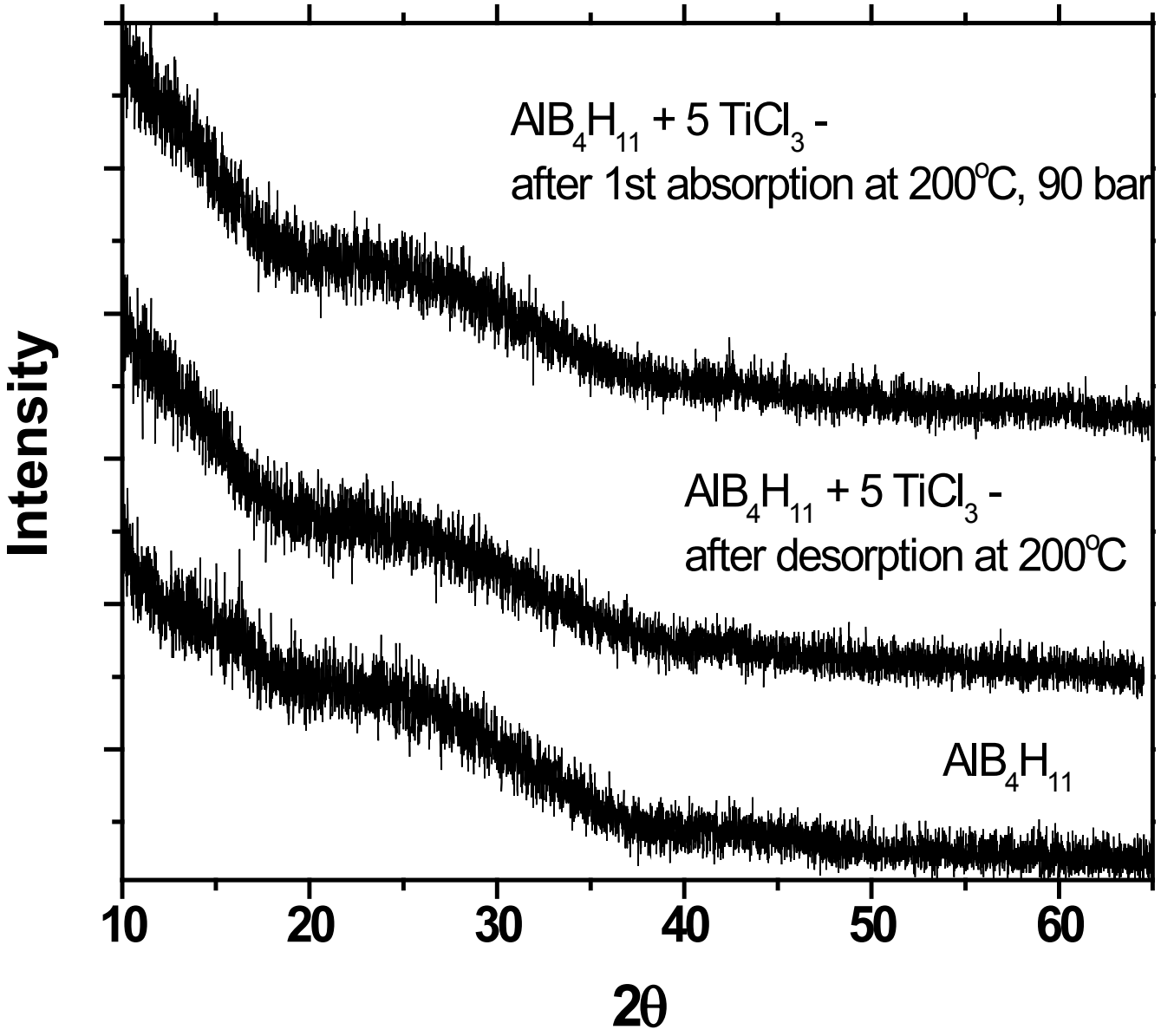
AlB_4H_{11} – TPD-MS





- Hydrogen is the predominant gas desorbed
- Some B_2H_6 formation: ~1% of gas

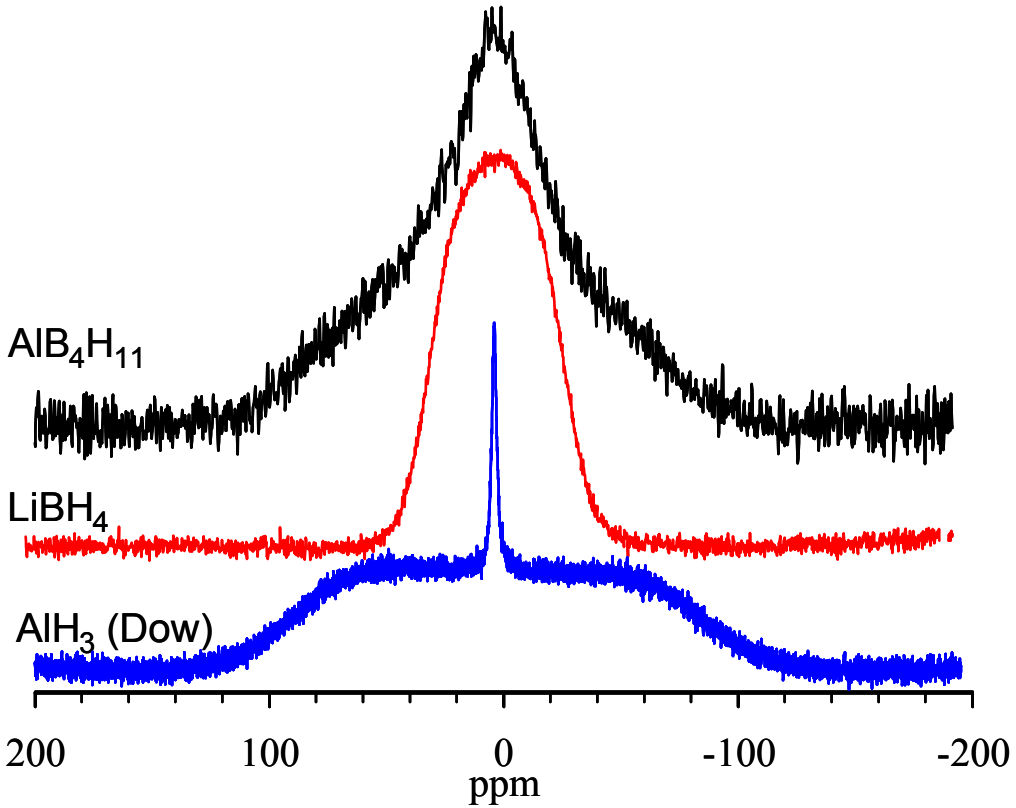
AlB_4H_{11} – XRD



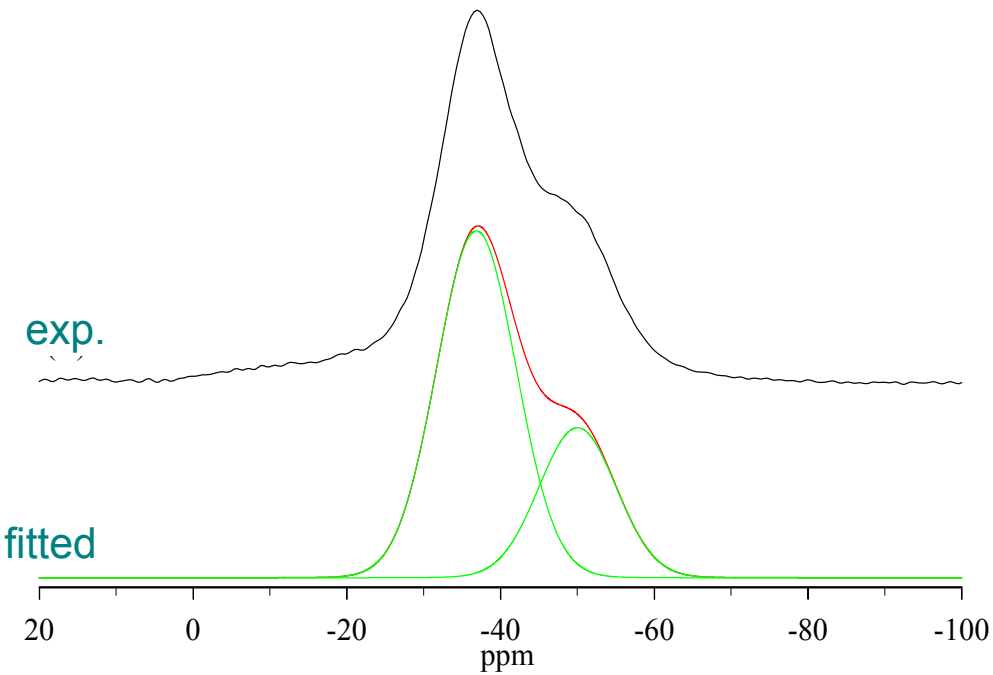
- Amorphous white solid – before and after desorption
- Didn't form borides that would be hard to reverse

AlB_4H_{11} – NMR

^{1}H static NMR spectra



^{11}B MAS NMR



- The structure of AlB_4H_{11} is still unknown – amorphous.
- Seems forming a polymer
- Have two boron environments based on NMR.

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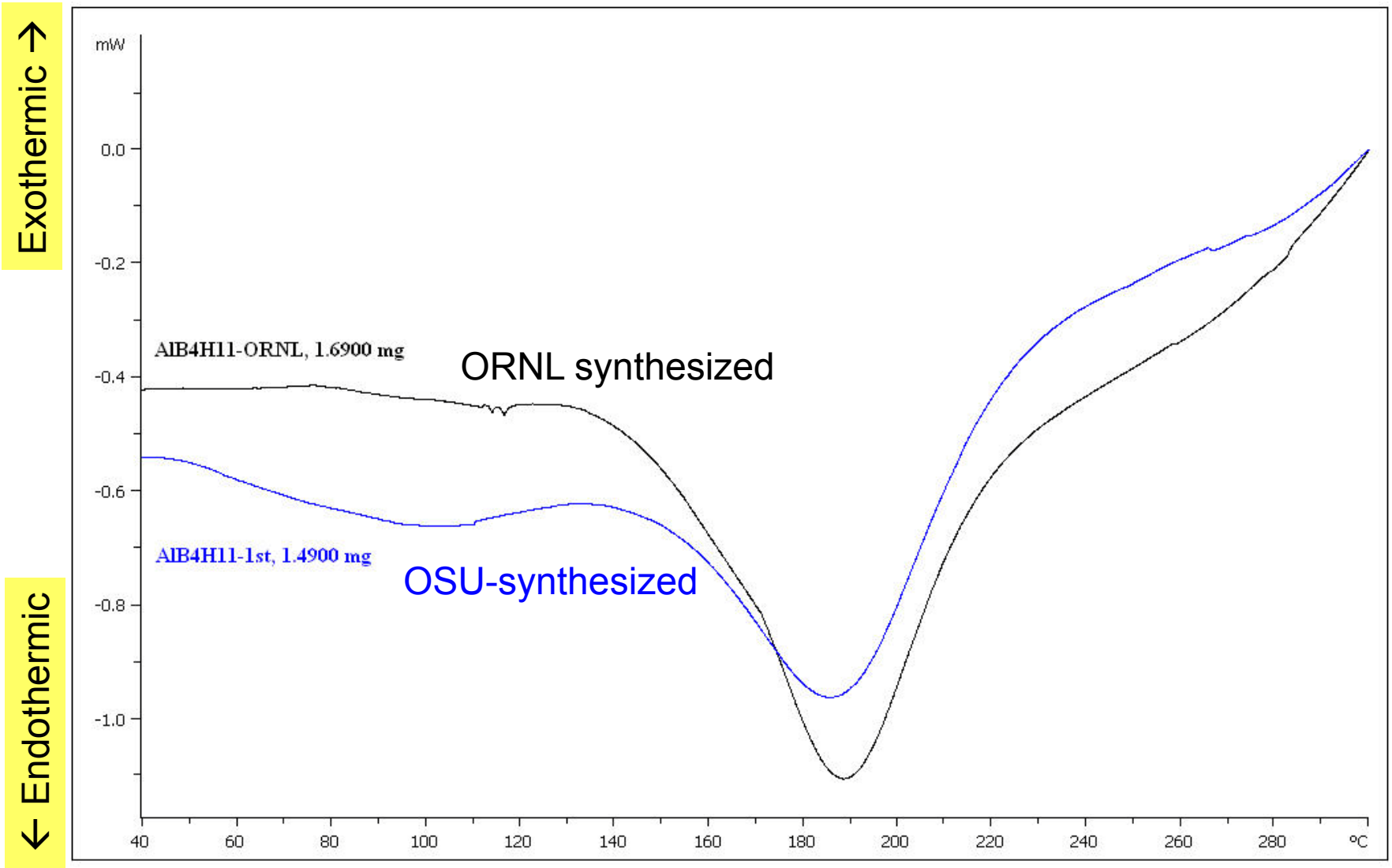
AlB_4H_{11} - DSC



Good news: endothermic desorption – thermodynamically reversible

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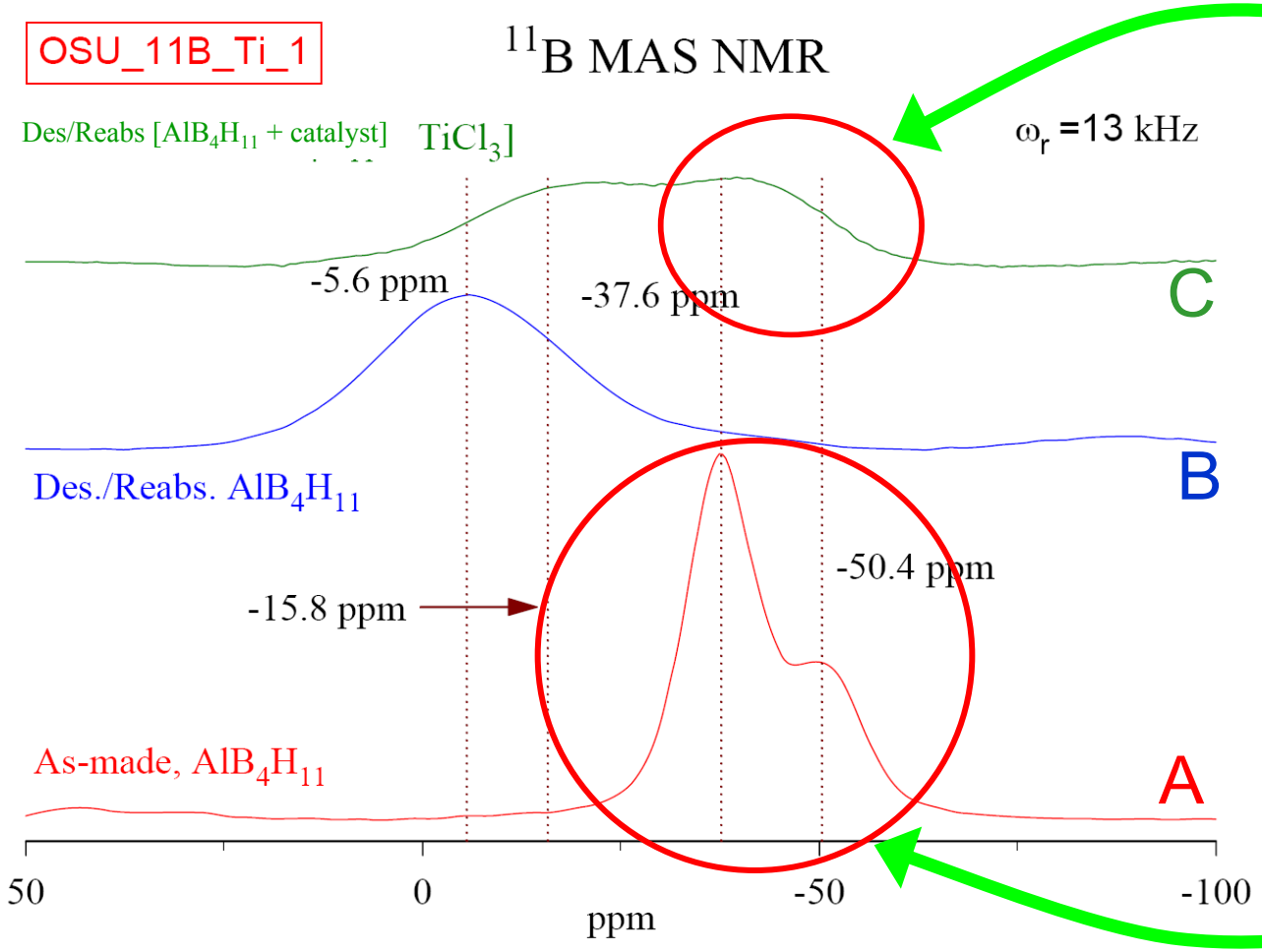
AlB_4H_{11} – Reversibility



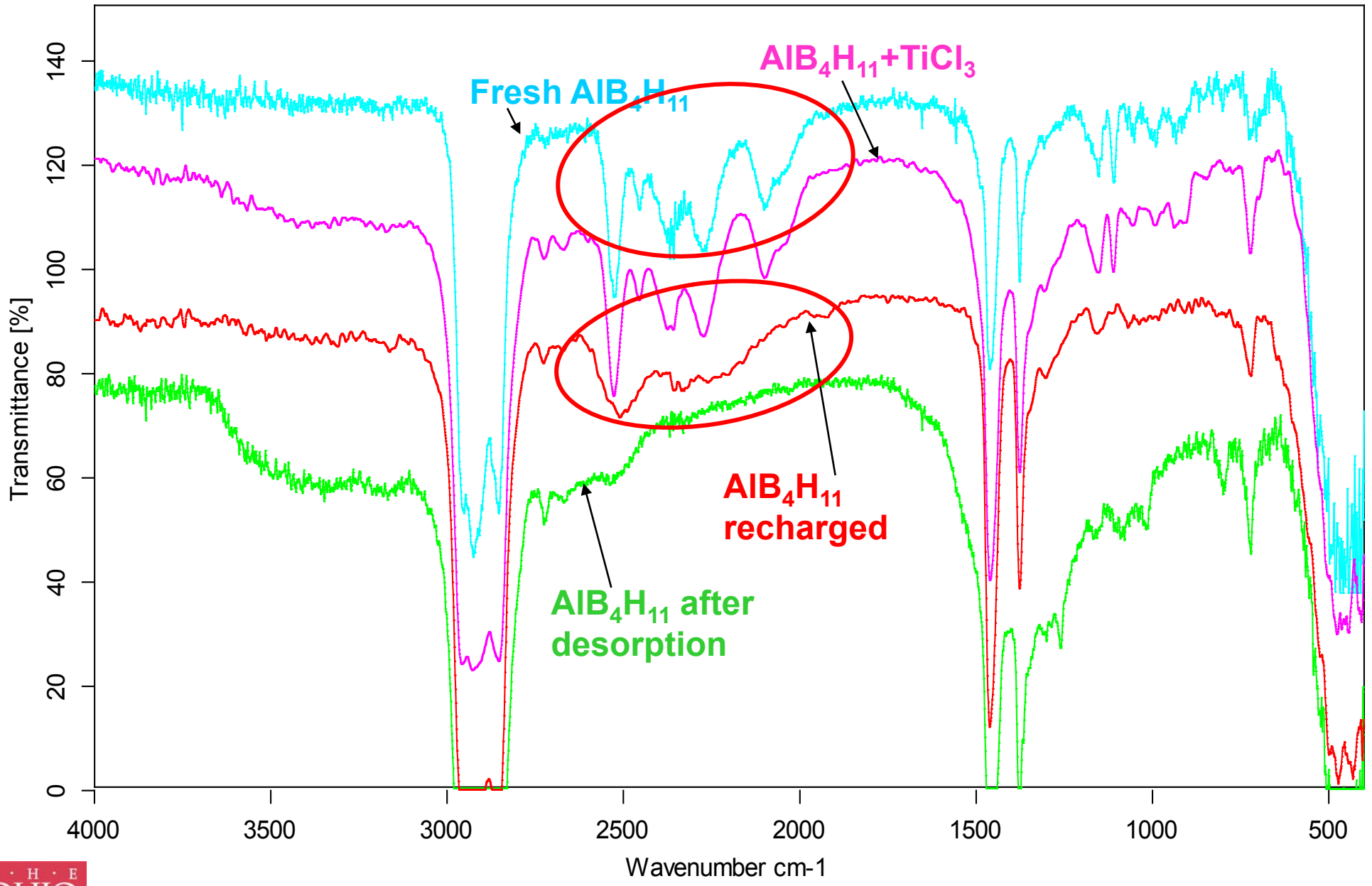
Signals associated with AlB_4H_{11} reappeared after hydrogen charging

Reversibility observed for at mild conditions: 200ºC, 90 bar H_2, 5 hr.

Zhao, Knight, Brown, Kim, Hwang, Reiter, Bowman, Zan, Kulleck

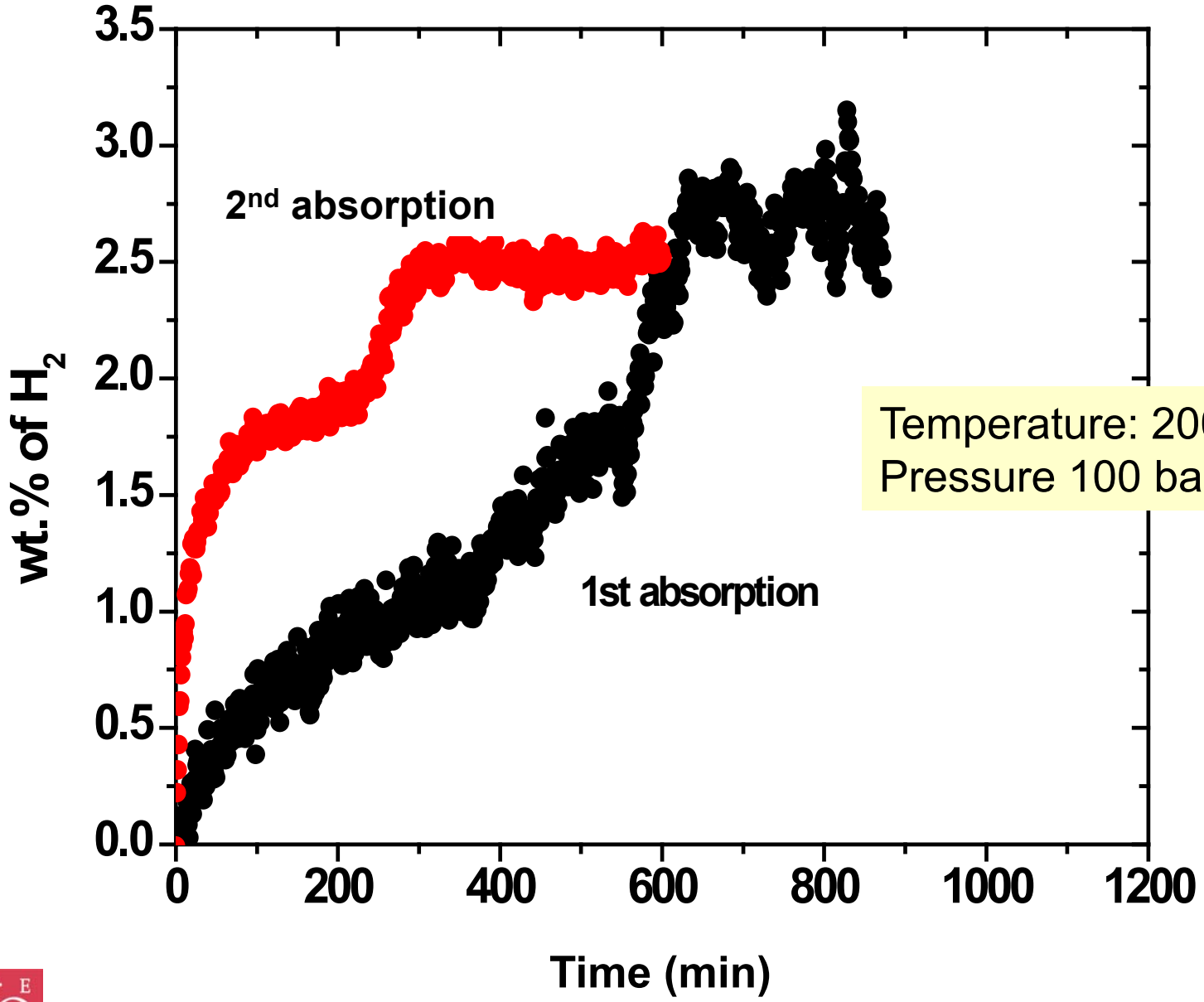
AlB_4H_{11} – Reversibility

IR



Characteristic peaks re-appeared after H_2 charging

AlB_4H_{11} – Reversibility



PCT

Temperature: 200 °C
Pressure 100 bar (1st), 97 bar (2nd)

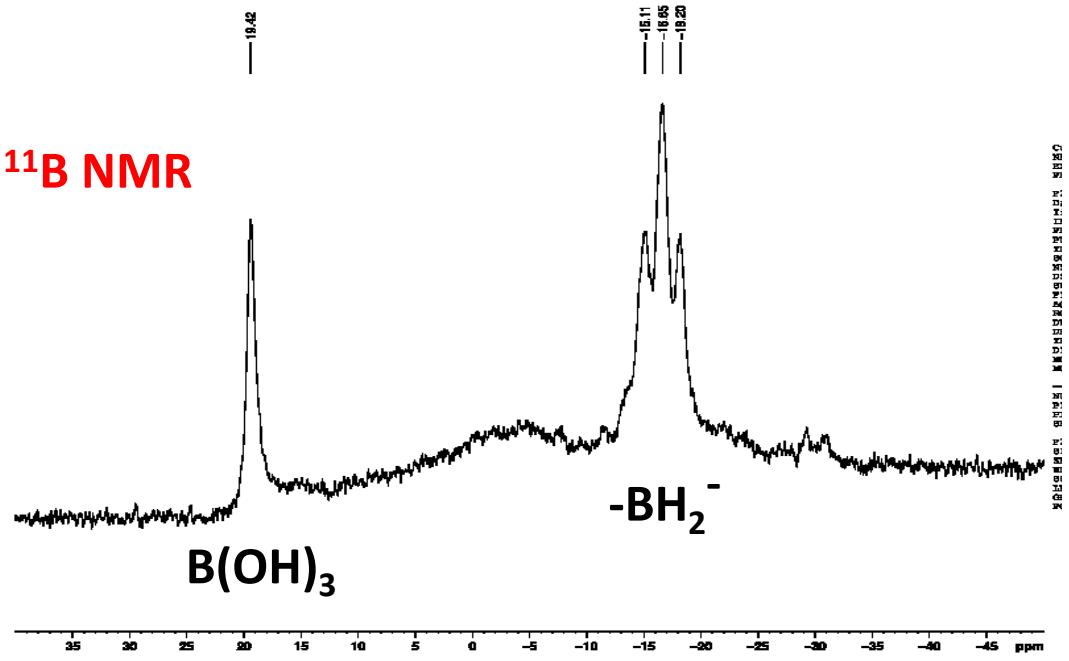
PCT measurements showed clear re-absorption of H_2.

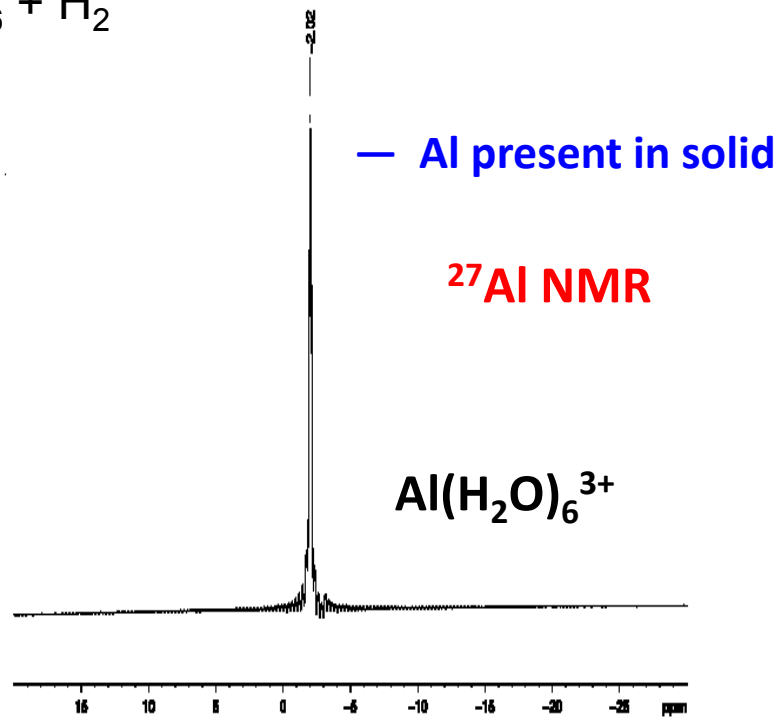
Synthesis of a New Aluminoborane

$$2\,B_{10}H_{14} + Al(BH_4)_3 \xrightarrow[100\ ^\circ C]{C_6H_6} \textbf{Light yellow solid}$$

For solution NMR:

Light yellow solid + 3 $HCl/H_2O \rightarrow B(OH)_3 + Cl_3Al(H_2O)_6 + H_2$





- A new aluminoborane compound synthesized.
- Both Al and B in the solid and the formula unknown at this point.
- Structure and property study in progress.

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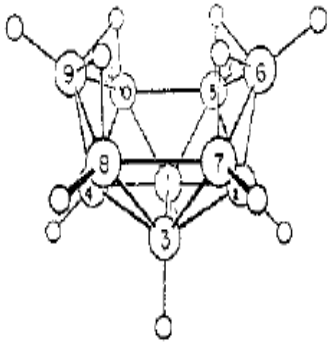
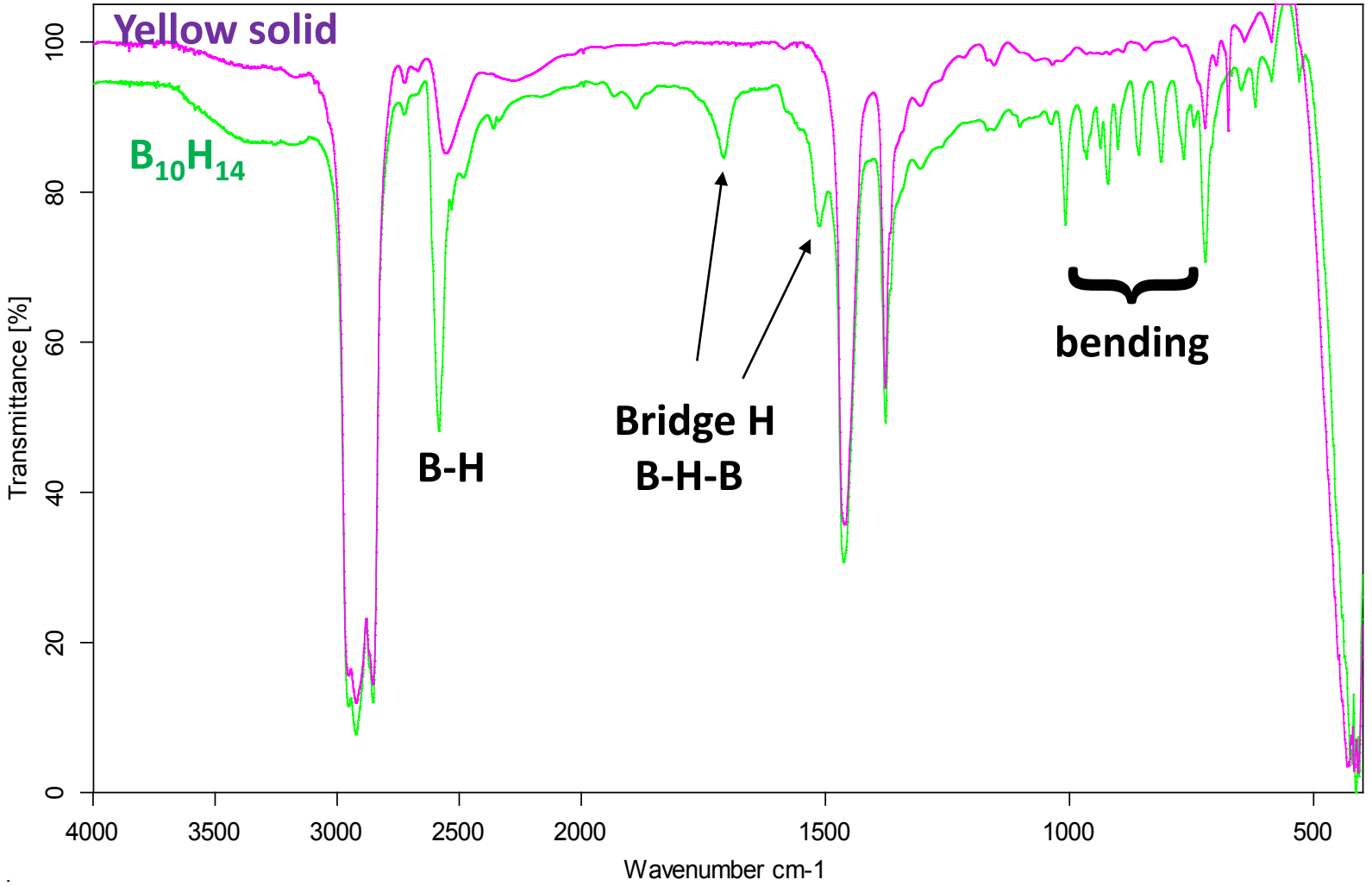
A New Aluminoborane

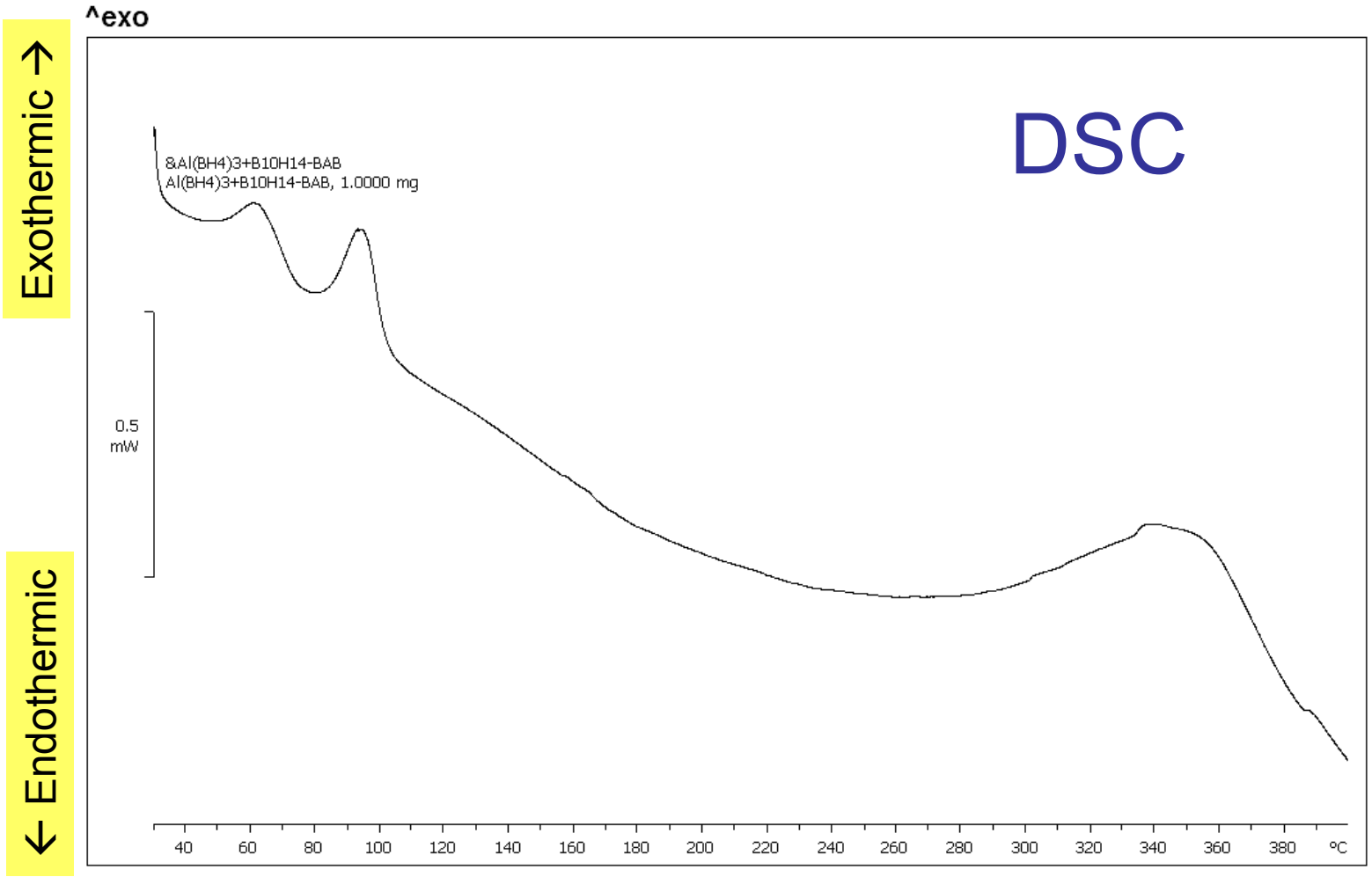


$B_{10}H_{14}$



- The bending vibration peaks and the bridge hydrogen peaks (B-H-B) of $B_{10}H_{14}$ disappear after reaction.
- B-H stretching peak of product shifted to lower wavenumber by ~ 50 cm^{-1}.
- Investigation of the solid by solid state NMR & elemental analysis underway.

A New Aluminoborane



- DSC shows complicated behavior.
- Other characterization in progress, especially related to reversibility.

Other Aluminoborane Compounds: AlB_4H_{11}, AlB_5H_{12}, AlB_6H_{13}

$$2\ Al(BH_4)_3 + B_2H_6 \xrightarrow[\text{Benzene, 18 h}]{100^oC} 2\ \mathbf{AlB_4H_{11}} + 4\ H_2$$

$$Al(BH_4)_3 + B_5H_9 \xrightarrow[\text{Benzene, 45 h}]{80^oC} \mathbf{AlB_5H_{12}} + B_2H_6 + H_2 + \text{decomposition products}$$

$$Al(BH_4)_3 + 2\ B_4H_{10} \xrightarrow[\text{Benzene, 67 h}]{25^oC} (BH_4)Al(B_3H_8)_2 + 2\ B_2H_6$$

$$(BH_4)Al(B_3H_8)_2 \xrightarrow[\text{Benzene, 27 h}]{100^oC} \mathbf{AlB_6H_{13}} + \tfrac{1}{2}\ B_2H_6 + 2\ H_2$$

- Synthesis & characterization of AlB_5H_{12} & AlB_6H_{13} in progress
- It took a while to scale up the synthesis of starting B_5H_9 and B_4H_{10}.
- All the aluminoboranes reportedly have low desorption T.
- Good flexibility in forming various aluminoboranes.

Himpsl & Bond: JACS, 103, 1098-1102 (1981).

Summary

- Synthesized gram quantities of AlB_4H_{11} at OSU.
- Performed characterizations using TGA, PCT, XRD, NMR, IR, DSC, TPD-MS.
- Amorphous structure with polymerization (Neutron study in progress at NIST).
- Low desorption temperature (starts ~120ºC), high wt.% H_2 with small amounts of B_2H_6 (~1 vol.% gas).
- DSC shows endothermic desorption: thermodynamically reversible.
- Clearly demonstrated reversibility using PCT, IR and NMR.
- Synthesized a new aluminoborane by reacting $Al(BH_4)_3$ with $B_{10}H_{14}$.
- Syntheses of other aluminoboranes in progress – good progress made in synthesis of starting materials: B_4H_{10} & B_5H_9.

It is remarkable for a compound containing only Al and B to absorb hydrogen at mild conditions (≤ 100 bar H_2, ≤ 220ºC).

Technical Accomplishments:
Summary #2 (additional slides)

- **$(NH_4)_2B_{12}H_{12}$** (11.2 wt.% H):
  - Synthesized at the request of Ford.
  - Structure, NMR and IR confirmed.
  - Endothermic desorption – possible for reversibility.
  - Sandia STMBS analysis showed ~ 1 mol.% NH_3 in H_2.
- **$(NH_4)_2B_{10}H_{10}$** (11.7 wt.% H):
  - Less stable than $(NH_4)_2B_{12}H_{12}$ – lower desorption T.
  - Sandia STMBS analysis showed ~ 3.3 mol.% NH_3 in H_2.
  - Showed 1.7 wt.% H re-absorption during H_2-charging
- **Attempt to synthesize $MgB_{12}H_{12}$**:
  - This intermediate important to $Mg(BH_4)_2$ reversibility.
  - Literature claim of anhydrous $MgB_{12}H_{12}$ synthesis is wrong.
  - Mechanism studied in detail and published.

Future Work

FY10

- Perform more kinetic study and catalytic screening to reduce the desorption temperature and improve reversibility of aluminoborane compounds.
- Compare the properties and structures of aluminoboranes and study their hydrogenation and dehydrogenation mechanisms.
- Complete the study of properties and reversibility of $(NH_4)_2B_{12}H_{12}$ and $(NH_4)_2B_{10}H_{10}$.

FY11

- Continue to improve reversibility of aluminoborane compounds by in-depth study of their structures, properties and hydrogen absorption and desorption mechanisms.
- Apply the knowledge/understanding to further synthesis.
- Provide property data to system-level engineering team.

Collaborations

- ORNL synthesized AlB_4B_{11} at the request of GE/OSU. The samples are then analyzed at ORNL, JPL and Caltech for hydrogen desorption and structures (via NMR). The synthesis expertise was then transferred to OSU. OSU is synthesizing other aluminoborane compounds AlB_5B_{12} and AlB_6B_{13}.
- AlB_4H_{11} synthesized at OSU was sent to NIST for neutron and TEM analysis.
- $Mg(BH_4)_2$ and $Li_2B_{12}H_{12}$ synthesized at OSU was provided to UTRC and HRL for nano-framework encapsulations.
- $Mg(BH_4)_2$ synthesized at OSU was sent to University of Washington for solid state NMR analysis and to NIST for TEM analysis.
- Collaboration established with University of Utah for reversibility study of $Mg(BH_4)_2$.
- Several compounds synthesized at OSU were sent to Sandia for analysis using STMBS (simultaneous thermogravimetric modulated beam mass spectrometry).
- $(NH_4)_2B_{12}H_{12}$ synthesized at OSU was sent to Ford for further study.

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