

# Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Materials & The Development of Efficient Amine- Borane Regeneration Cycles

(part of the DOE Chemical Hydrogen Storage  
Center of Excellence)



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Project ID #  
ST 11

# Overview

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## Timeline

- Project Start Date: FY05
- Project End Date: FY09
- Percent complete: 70%

## Budget

- Total project funding for Phase I (05-08)
  - DOE Total \$813,924
  - Contractor share \$203,481
- Funding for FY07
  - \$320K (DOE) \$80K (cost share)
- Funding for FY08
  - \$146K (DOE) \$36.5K (cost share)

## Barriers

- Cost
- System weight and volume
- Regeneration Processes

## Direct Collaborators

- Participant in the DOE Chemical Hydrogen Storage Center of Excellence
- LANL, PNNL, U. Alabama, and Rohm and Haas Company

# Objectives

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## Regeneration

- Provide new materials, compounds and support for chemical regeneration of amine-boranes or boron amides from B-X (X= halide or oxide) compounds. (revised task)
- To develop a method of regenerating amine-boranes from spent fuel with use of a metal formate/hydride cyclable system.
- To develop light element hydride nanomaterials for spent chemical hydride regeneration such as ammonia-borane “AB” regeneration.

## Release

- Enhancement of hydrogen release for chemical hydrides such as ammonia-borane “AB” with light element hydride nanoparticles.
  - Produce light element hydride nanoparticles in a low cost, high yield method.

# Timeline

| Task   | Year 1 | Year 2 | Year 3  | Year 4 | Year 5 |
|--|--------|--------|---------|--------|--------|
| <b>Task 1&amp; 2:</b> Nanoparticle and Main Group Compounds Synthesis<br>Synthesis of SiH and Si(NH <sub>2</sub> ), SiH and Si(NH <sub>2</sub> ). Characterization of Si <sub>1-x</sub> M <sub>x</sub> H and Si <sub>1-x</sub> M <sub>x</sub> NH <sub>2</sub> composition and reactivity . | →      |        | ⛔ No Go |        |        |
| <b>New 06/07: Task 2:</b> Regeneration of E–H Materials (E = B, Al, Si, Zn, Ge, or Sn) Synthesis of compounds with E–H, E–NH <sub>2</sub> , E–OC(O)H groups. Characterization of compounds and regeneration under mild conditions.   |        | →      |         |        |        |
|  |        | →      |         |        |        |
| <b>Task 3:</b> Characterization and Testing<br>Test reactivity, thermolysis, and regeneration of various alloys and main group compounds.  | →      |        |         |        |        |
| <b>Task 4:</b> Demonstrate the potential for hydride terminated nanoparticles to egenerate spent chemical hydrides such as ammonia borane.   |        |        | →       |        |        |
| <b>Task 5:</b> Demonstrate the effect of nanoparticle addition to the kinetics of of hydrogen release.   |        |        | →       |        |        |
| <b>Task 6:</b> Investigation of other main group element formates for ejection of carbon dioxide with formation of element hydrides.   |        |        | →       |        |        |
| <b>Task 7:</b> Evaluate stability, cyclability, and reaction chemistry of main group hydride species.  |        |        | →       |        |        |


**New/revised**

# Plan & Approach

Regeneration: Use main group formate small molecules or hydride nanomaterials as low cost reagents to convert B–O or B–X in one step to B–H.

Main group formate compounds

- Synthesize main group formates. Investigate their interconversion under mild reaction conditions with the object of creating a simple chemical cycle to regenerate B–H bonds in Ammonia-Borane.

Light element hydride nanomaterials

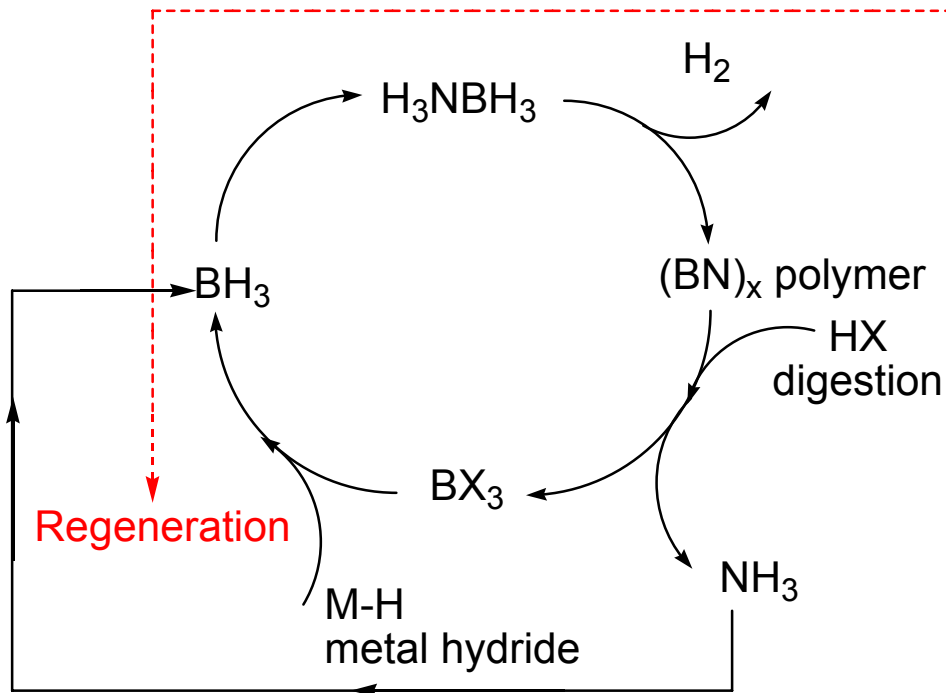
- Synthesize light element hydride nanomaterials like Si–H, Si<sub>1-x</sub>C<sub>x</sub>–H,
- Si<sub>1-x</sub>Al<sub>x</sub>–H, and react with B(OR)<sub>3</sub> and BX<sub>3</sub> and follow reaction by NMR.

Release: Nanoparticles provide an inexpensive additive that can effect the release of hydrogen from AB by providing a weakly coordinating Lewis acid platform.

–Enhancement of release kinetics with additional of light element metal hydride nanomaterials

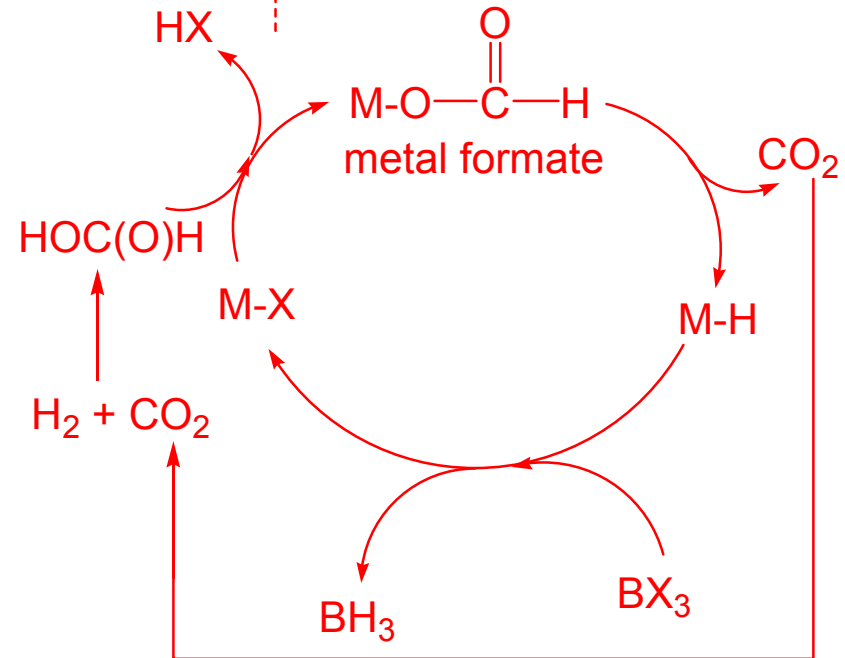
–Elimination of foaming problem related to hydrogen release of ammonia borane

# Relevance to Overall Regeneration Cycle



X = halogen or oxo group

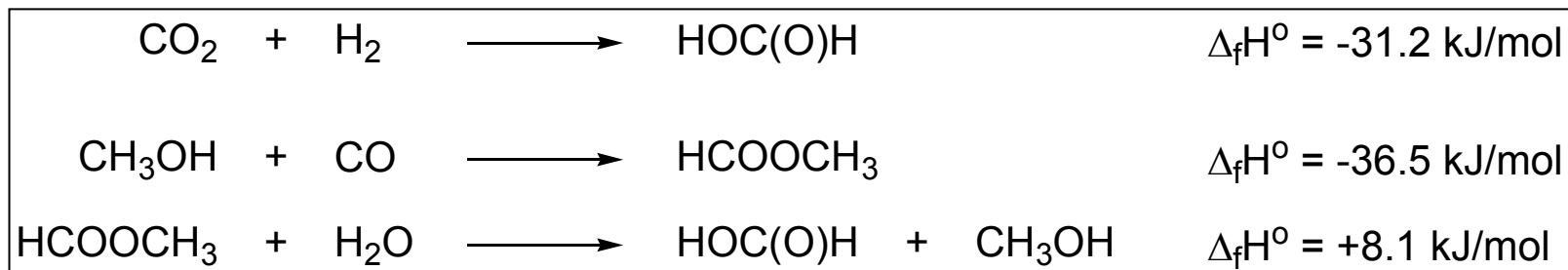
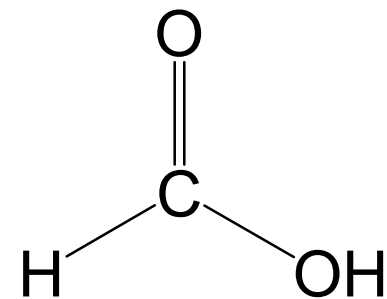
Simplified LANL Cycle for H<sub>2</sub> Storage



Simplified UC Davis  
Formate/Hydride Regeneration  
Cycle

# Formic Acid

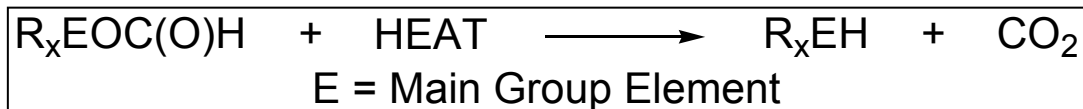
- Formic acid is produced as a by-product in the manufacture of acetic acid.
  - The acid can also be produced through reactions with carbon dioxide and hydrogen gas.
  - The more common method involves combining methanol and carbon monoxide in the presence of a strong base, followed by hydrolysis to produce the acid.



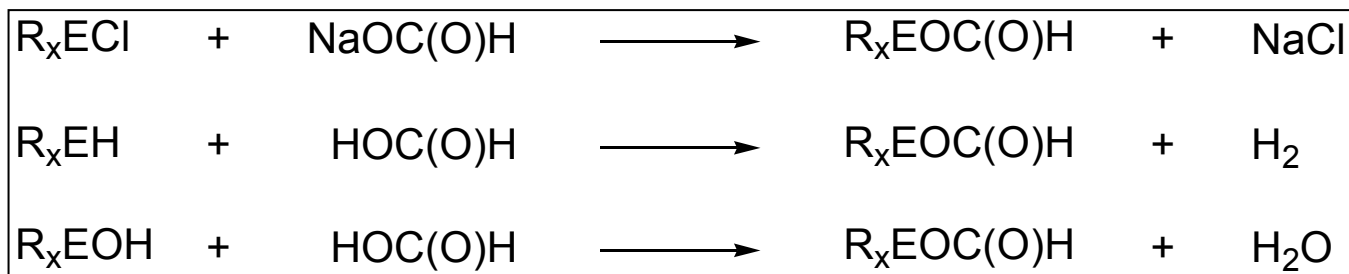
*From Standard Enthalpies of formation at 298.15 K  
CRC Handbook of Chemistry and Physics, 1995*

# Objective - Approach to Metal Hydrides

- Our approach to metal hydride synthesis is by the conversion of metal formates through loss of carbon dioxide under mild (< 200 °C) thermolysis conditions.



- There are a variety of synthetic strategies available for the generation of element-formate compounds. The choice of reaction conditions depends on the main group element and the organic substituents and can be guided by computational investigations.
- The Center has chosen to start with commercially available, cheap hydrides and formic acid was deemed a reasonable starting point





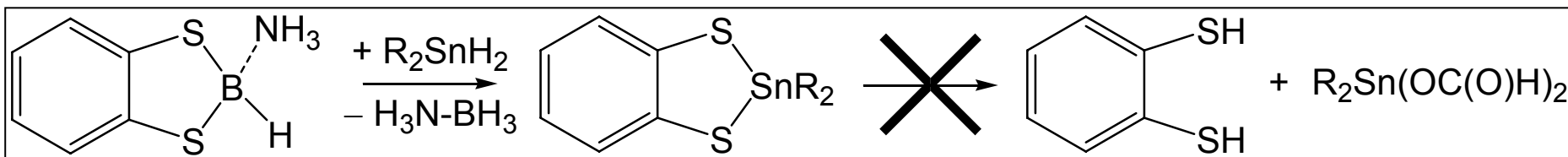
# Summary of Accomplishments - Regeneration

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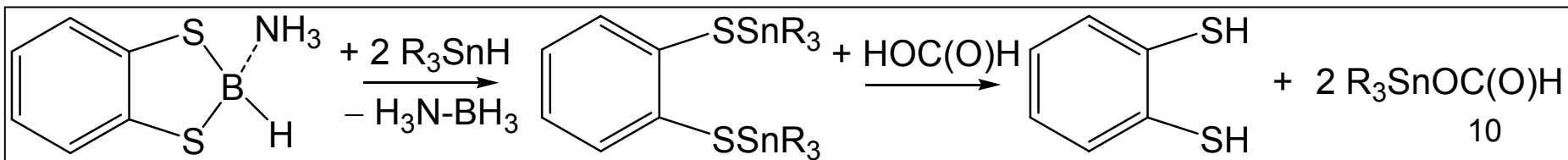
- Confirmation that boron formates eject CO rather than CO<sub>2</sub> (as predicted by calculations – Camaioni, PNNL) .
- Confirmation that a dialkyltin diformate, gave neither CO nor CO<sub>2</sub> ejection (resulting from polymeric solid-state structure).
- Developed and demonstrated a generic route to tin monoformate synthesis.
- Synthesis and characterization of monomeric and one-dimensional tin formates.
- Si-H nanoparticles for regeneration of B-H from B-Cl and B-O: Preliminary results (NMR) show the production of ammonia-borane (AB) by simple one pot method.

## Switch to Tin Monoformate Reagents

- In the LANL cycle, the tin hydride is added to a boron dithiolate to regenerate AB and give a tin dithiolate.

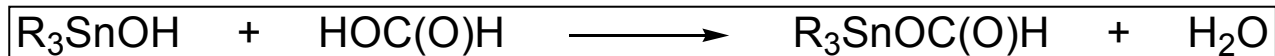


- Computational calculations (Dixon, Alabama) suggest that the conversion of this tin species to the diformate by formic acid (concurrently regenerating the dithiol used in digestion) to be very energetically expensive.
- As a result of these calculations, we have switched our focus to tin monoformates.
  - Two equivalents will be used and the resulting tin-sulfur compound will be easier to convert to the formate.

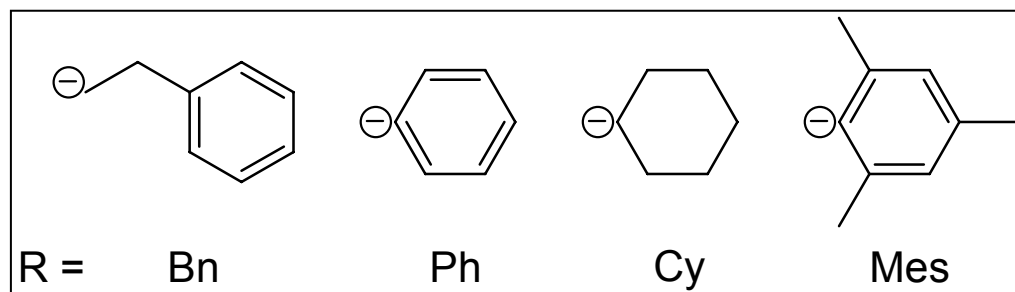


# Progress Towards Tin Monoformates

- Tin formates are most readily accessible by conversion of tin hydroxides and are stable to air and moisture.



- This versatile synthetic method allows for a wide range of organic substituents.
  - The variety of substituents allows tuning of the reactivity of the tin formate to facilitate carbon dioxide release to generate metal hydrides.

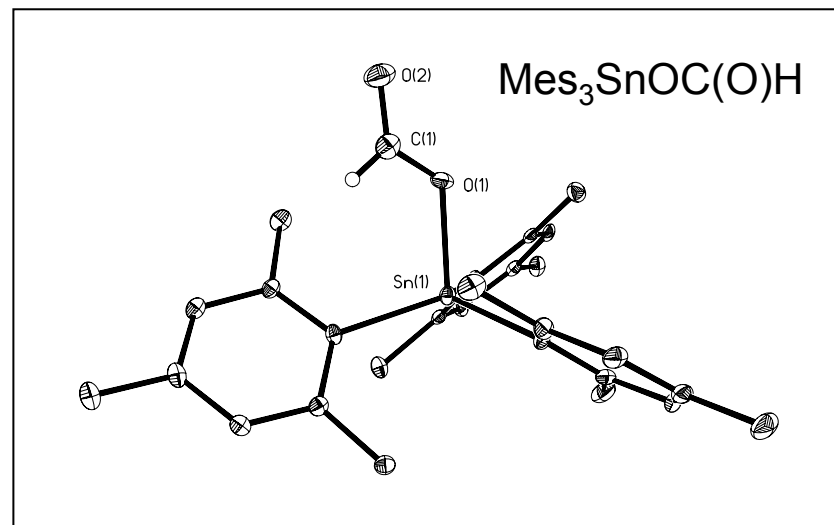


<sup>1</sup>Molloy *et al.*, *J. Chem. Soc., Dalton Trans.*, **1987**, 101.

<sup>2</sup>Xu *et al.*, *Huaxue Xuebao*, **1992**, 50, 508.

# Successful Synthesis of a Monomeric Tin Formate

- We have synthesized a monomeric tin formate, characterized by X-ray diffraction and NMR spectroscopy:
  - Sn-O = 2.072 Å (ave.)
  - $^{119}\text{Sn}$  NMR  $\delta$  = -118.0 ppm
  - $^1\text{H}$  NMR  $\delta$  = 8.22 ppm
  - $^{13}\text{C}$  NMR  $\delta$  = 164.4 ppm



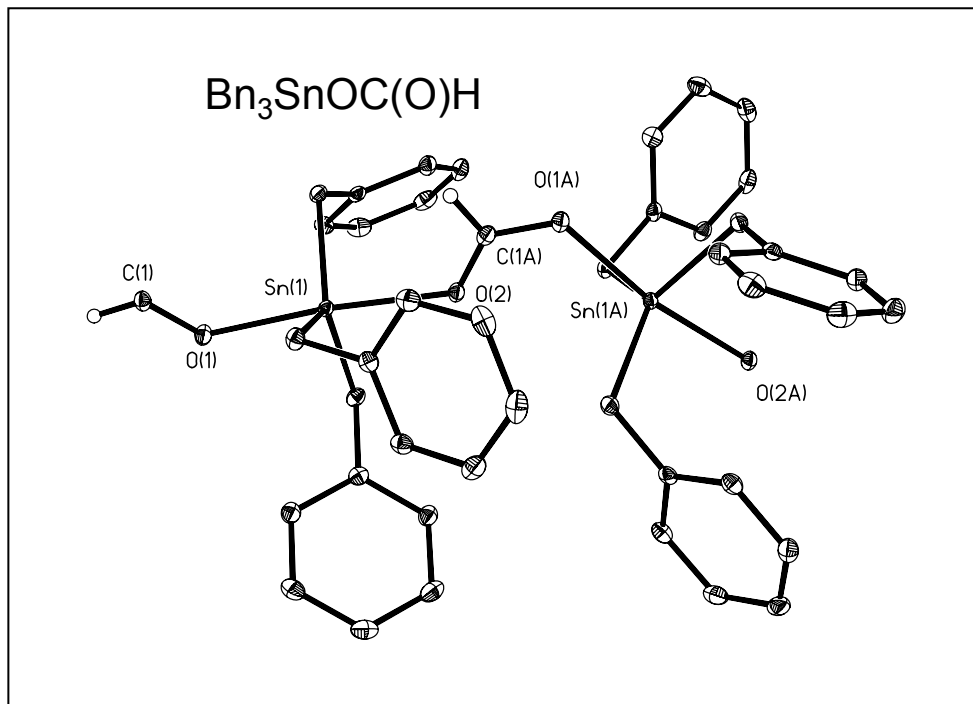
- Preliminary attempts at CO<sub>2</sub> ejection have lead to either no detectable reaction or decomposition. We are continuing to vary the reaction conditions, however the substituents around tin may be too bulky and are preventing CO<sub>2</sub> release.

# Synthesis of $\text{Bn}_3\text{SnOC(O)H}$

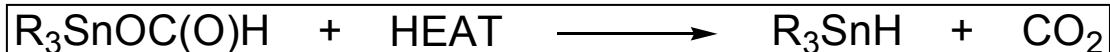
- Using the same synthetic approach, we have synthesized  $\text{Bn}_3\text{SnOC(O)H}$ , which adopts a chain-like polymer in the solid-state.

This species is a promising candidate for monomeric tin formates in solution.

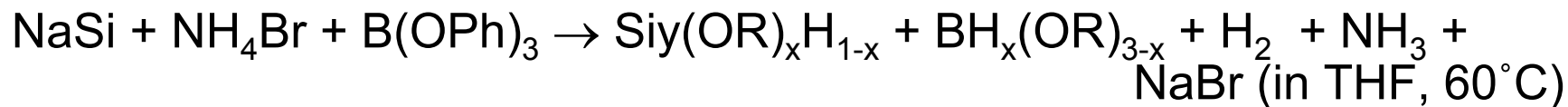
–  $\text{Sn-O} = 2.265 \text{ \AA}$  (ave.)



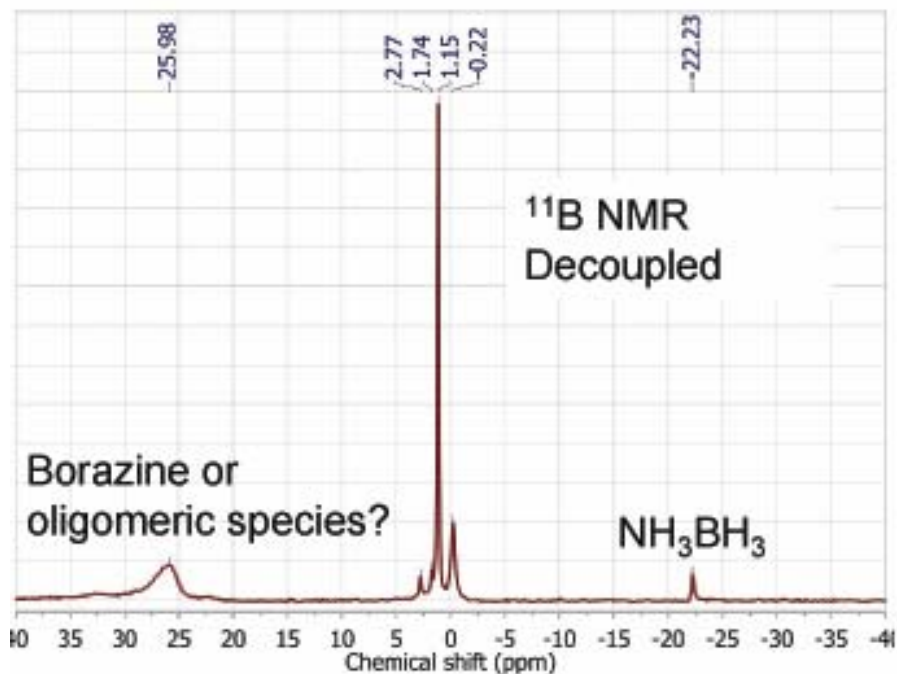
- Studies are currently underway examining thermolysis reactions of this tin formate as well other derivatives to determine the optimal conditions and substituents for maximum hydride formation efficiency.



# Preliminary Work on Regeneration Demonstrates B-H Bond Formation



- Hydrogen capped Si NP can be prepared and used in situ to generate BH bonds (reaction above).
- NMR spectroscopy indicates that ammonia borane (AB) can be formed in this reaction along with other BH species (~0 ppm).
- Systematic investigation of optimal reaction conditions for B-(OR) transformation to B-H are underway.



# Future Directions - Regeneration

- Continue varying the substituents on tin formates to determine optimal conditions for hydride formation under thermolysis conditions.
- Conversion of tin thiolates to formates.
  - Choice of thiolate based on results from LANL from their spent fuel digestion steps.
- Investigate the conversion of gallium formates to hydrides as an alternate source of metal hydrides.
- Investigation of other routes to Main Group formates that do not involve formic acid:
  - Hydrogenolysis of singlet diradical compounds
  - Direct addition of hydrogen to E-X bonds
- Use  $\text{Si}_x\text{E}_{1-x}\text{-H}$  nanoparticles (E = B, C, Al and x= 10, 20%) for regeneration of B-H from B-Cl and B-O using both solid state (ball mill) and solution methods.

# Summary of Accomplishments - Release

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- Light element hydride nanomaterials to affect hydrogen release kinetics: Preliminary results show elimination of foam problem associated with release, lowering of the release temperature, smaller enthalpy for the first release of H<sub>2</sub> from AB.
- No Go for further development of Si and Si alloy nanoparticles as hydrogen storage materials (wt % ~4 , release temperature ~ 250°C).
- No Go for further investigation of light element framework structures (clathrates) as current wt % is too low and not enough promise for significant hydrogen uptake.\*

\*(If one assumes that at least 4 H<sub>2</sub> molecules will fill the large cages and 2 H<sub>2</sub> molecules in the small cages, the expected composition would be H<sub>128</sub>Si<sub>136</sub> or approximately 3.5 wt% hydrogen).



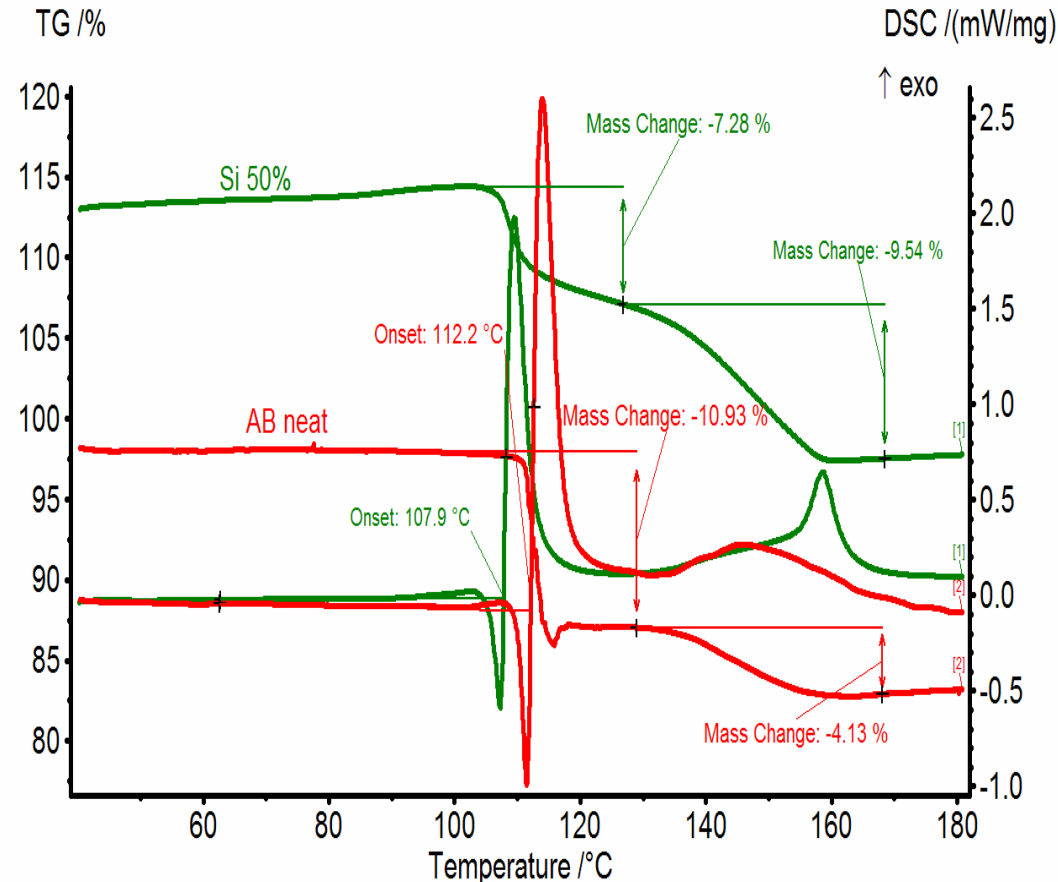
# Enhancement of H<sub>2</sub> Release by Light element hydride Nanomaterials to Ammonia Borane (AB)

TG/DSC

AB

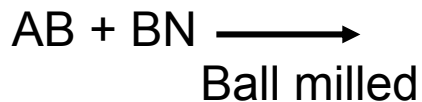
(1:1) Si)-H: AB

- The weight loss starts at lower temperatures and it is less exothermic for the AB+Si)-H NP mixtures
- The 50 % Si)-H NP mixture eliminates foaming while the 10% C doped Si)-H NPs minimize foaming (not shown).
- 50 wt% Si)-H reduces the initial mass loss from ~11 % (AB) to 7 % and second step shows slightly higher mass loss ~ 4 % (AB) to ~9 wt %.



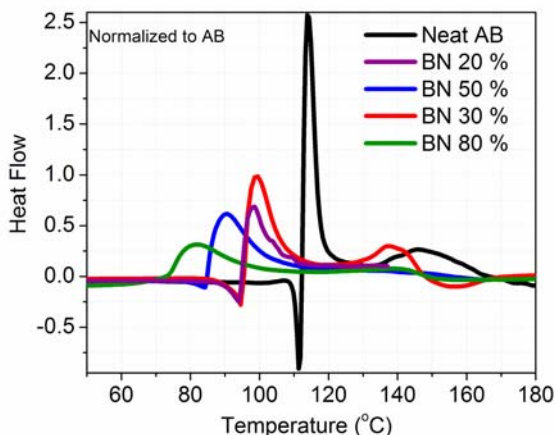
# Enhancement of H<sub>2</sub> Release from Ammonia Borane (AB) by addition of BN along with elimination of foaming problem: Preliminary Results

BN as a possible additive?

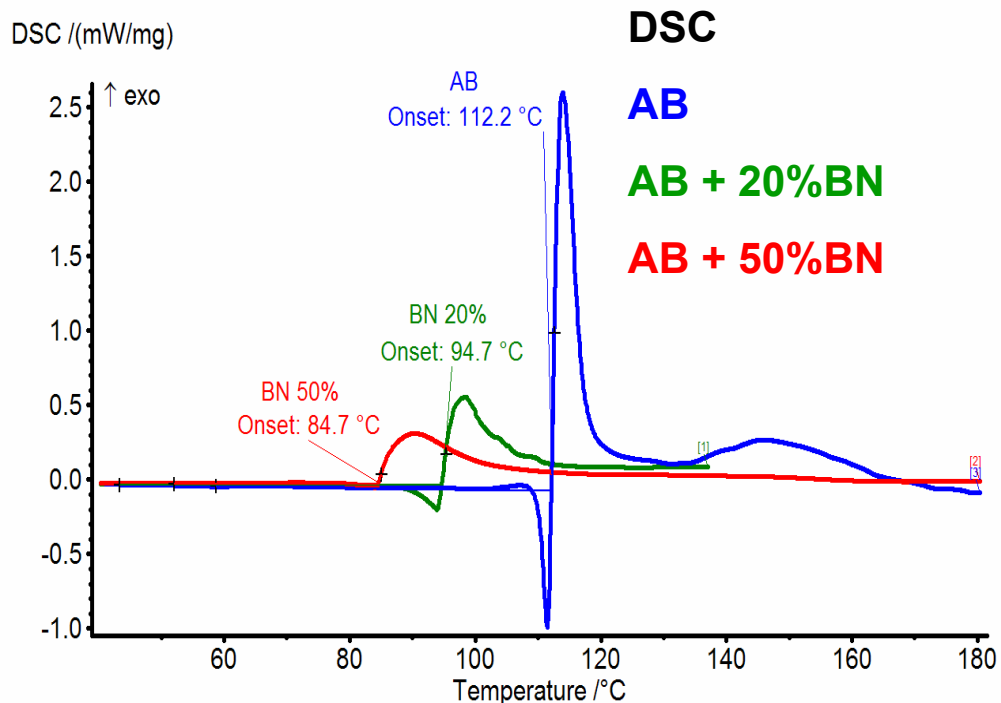


Addition of BN

- reduces T of H<sub>2</sub> desorption
- Less exothermic reaction
- Decreases borazine by-product (measured by TG/MS)\*



Normalized enthalpies



## Future Directions - Release

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- Develop a method of M-H recycling via hydrogenolysis as an alternative to the metal formate/hydride approach.
- Further optimization of light element nanoparticles (such as BN) to reduce foam and to affect the hydrogen release kinetics without adding contamination, additional weight, and regeneration issues.
- Investigate the rate of H<sub>2</sub> release with addition of nanoparticles.
- Investigate the number of equivalence that can be obtained with addition of light element nanoparticles.
- Regenerate the Si<sub>x</sub>E<sub>1-x</sub>)–X (X = Cl, O) nanoparticles to Si<sub>x</sub>E<sub>1-x</sub>)–H.

# Project Summary

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- **Relevance:** Spent chemical hydride and ammonia borane (AB) regeneration.
- **Approach:** Synthesis and characterization of novel nanomaterials and the synthesis of metal hydrides for efficient ammonia borane (AB) regeneration.
- **Technical Accomplishments and Progress:** (**Regeneration**) Elimination of boron formates as a potential hydride precursor, synthesis of a tin monoformate for conversion to the hydride. Preliminary results for nanoparticles show the regeneration of B-H bonds from a  $B(OR)_3$  model system. (**Release**) Preliminary results show that nanoparticle additives reduce the temperature and release of  $H_2$  from AB while eliminating the foam problem.
- **Technology Transfer/Collaborations:** Active partnership with LANL, PNNL, Rohm & Hass, U. Alabama, U. Penn, presentations, publications, and patent applications.
- **Proposed Future Research:** Test nanoparticles for possible regeneration ability and effect on hydrogen release effects of ammonia borane. Testing of tin monoformates for  $CO_2$  release and investigation of other synthetic routes to suitable metal hydrides.

# Collaborations

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- **LANL:** Synthesis of metal hydrides for cost effective regeneration. Provide support for metal hydride recycle to overall regeneration scheme.
- **PNNL:** Characterization of nanomaterials, theoretical calculations of regeneration cycle energetics. Support for kinetics and release of ammonia borane (AB).
- **U. Alabama:** theoretical calculations of hydrogen storage cycles, application of nanomaterials to regeneration and release.
- **SiGNa:** scale-up and commercial source of NaSi.

# Acknowledgements

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## **Nanomaterials:**

Doinita Neiner  
Julia Wang

Tom Autrey (PNNL)  
Don Camaioni (PNNL)

Alex Navrotsky (UCD): XRD  
Ping Yu (UCD): MAS NMR

Michael Lefenfeld SiGNa

## **Small Molecules:**

Bobby Ellis  
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Audra Betzer  
Zhongliang Zhu

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Fran Stephens (LANL)  
John Gordon (LANL)  
Ben Davis (LANL)  
Jerry Potter (PNNL)  
Michael Mock (PNNL)