

IV.A.1c Lightweight Metal Hydrides for Hydrogen Storage

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Objectives

- Develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.
- Synthesize and study aluminoborane compounds and other lightweight, high-capacity boron hydrides for hydrogen storage.
- Perform detailed characterization of the decomposition mechanisms, desorbed gaseous species and structures of the synthesized compounds.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan:

- (D) Durability/Operability
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (E) Charging/Discharging Rates
- (J) Thermal Management

Technical Targets

This project is conducting fundamental studies of the decomposition mechanism of $\text{Mg}(\text{BH}_4)_2$. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$3-7/gasoline gallon equivalent (gge) at the pump
- Specific energy: 1.5 kWh/kg (4.5 wt% H_2)
- Energy density: 0.9 kWh/L (0.028 kg/L)

Accomplishments

- Synthesized gram quantities of $\text{AlB}_4\text{H}_{11}$; studied it using differential scanning calorimetry (DSC), pressure-composition-temperature (PCT), X-ray diffraction (XRD), and nuclear magnetic resonance (NMR); and demonstrated rehydrogenation at mild conditions (this compound is one of the very few boron-containing hydrides that are reversible at mild conditions).
- Spent considerable amount of effort to develop a process to synthesize $\text{AlB}_6\text{H}_{15}$ and performed preliminary study of this compound.
- Synthesized new aluminoboranes by reacting decaborane ($\text{B}_{10}\text{H}_{14}$) with $\text{Al}(\text{BH}_4)_3$ at different ratios; thus demonstrated good compositional flexibility of aluminoborane compounds.
- Synthesized and studied several boron cage compounds such as $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ and $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ for hydrogen storage in collaboration with Sandia National Laboratories (SNL).
- Developed a convenient and safe method for synthesizing ammonium octahydrotriborate ($\text{NH}_4\text{B}_3\text{H}_8$) which has a very high H content (20 wt%); further study is in progress.
- Developed a new method to synthesize aminodiborane ($\text{NH}_2\text{B}_2\text{H}_5$) – a very reactive reagent that can be used to synthesize many other compounds for hydrogen storage; from aminodiborane, we synthesized an inorganic butane analogue $\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_3$ which was predicted to be an intermediate during the decomposition of NH_3BH_3 ; thus its properties will be important for the NH_3BH_3 research.



Introduction

The DOE defines on-board hydrogen storage for mobile vehicles as a “Grand Challenge”. It is one of

the biggest hurdles to the implementation of hydrogen-powered vehicles. Metal hydrides have the advantages of the highest volumetric density, relatively low working pressure, and reasonable working temperature range. The disadvantage of current reversible hydrides is a significant weight penalty. Metal borohydrides have among the highest gravimetric hydrogen storage capacities with the potential to meet the DOE gravimetric density targets and to offset the system weight penalties. However, desorption temperature, reversibility and diborane formation during desorption are challenging issues for these materials. This project attempts to develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.

Approach

- Explore aluminoborane compounds such as $\text{AlB}_4\text{H}_{11}$ and other high-capacity, lightweight boron hydrides.
- Study the crystal structures and the decomposition mechanisms using multiple techniques such as interrupted PCT tests, NMR, infrared (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 Oak Ridge National Laboratory (ORNL), SNL, and National Institute of Standards and Technology (NIST).

Results

Aluminoboranes $\text{AlB}_4\text{H}_{11}$, $\text{AlB}_5\text{H}_{12}$ and $\text{AlB}_6\text{H}_{13}$ were reported by Himpsl and Bond in 1981 [1], but these compounds have eluded the attention of the worldwide hydrogen storage research community for more than a quarter of a century. They have very attractive properties for hydrogen storage: high hydrogen capacity (i.e., 13.5, 12.9, and 12.4 wt% H, respectively) and attractive hydrogen desorption temperature (i.e., $\text{AlB}_4\text{H}_{11}$ decomposes at $\sim 125^\circ\text{C}$). In collaboration with ORNL, the Jet Propulsion Laboratory (JPL) and the California Institute of Technology (Caltech), we synthesized and studied $\text{AlB}_4\text{H}_{11}$ for hydrogen storage. $\text{AlB}_4\text{H}_{11}$ is an amorphous white solid that starts to release hydrogen around 125°C as demonstrated by both thermogravimetric analysis (TGA) and PCT tests. Mass spectroscopy analysis showed relatively clean desorption with a small amount of diborane (<1 mole%) [2]. A TiCl_3 catalyzed $\text{AlB}_4\text{H}_{11}$ desorbed 6.5 wt% H when it was heated to 220°C under 0.1 bar hydrogen pressure during a PCT test. The desorbed residue remained as amorphous. Re-hydrogenation was performed at

200°C , 100 bar hydrogen for the first run and 97 bar of hydrogen for the second run. About 2.5% hydrogen was re-absorbed each time based on the hydrogen pressure drop during the re-hydrogenation PCT tests (Figure 1). The observed reversibility (hydrogen absorption) during PCT tests was further confirmed by both IR and NMR analysis which both showed that signals associated with $\text{AlB}_4\text{H}_{11}$ re-appeared after the re-hydrogenation runs. The results clearly show that $\text{AlB}_4\text{H}_{11}$ is one of the very few boron-containing materials which show reversibility at mild conditions. DSC measurements also show that $\text{AlB}_4\text{H}_{11}$ dehydrogenates around 125°C with a broad endothermic peak, thus it is thermodynamically reversible (Figure 2). All these results together clearly show that is a very attractive candidate for reversible hydrogen storage. The key is to increase the reversibility weight% and improve both hydrogenation and rehydrogenation kinetics.

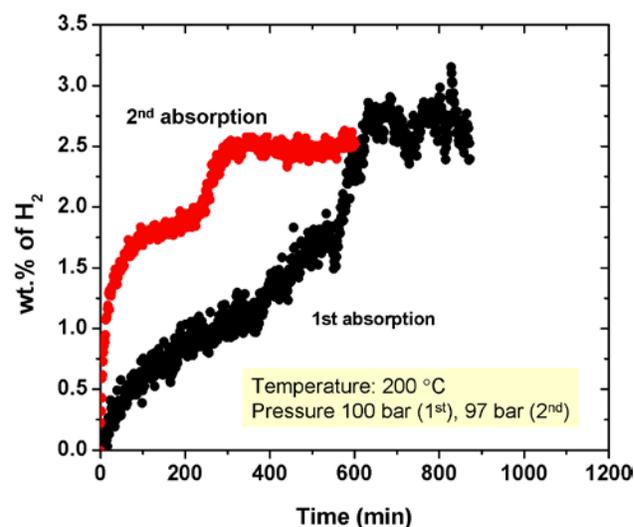


FIGURE 1. Rehydrogenation runs for $\text{AlB}_4\text{H}_{11}$ showing reversibility (hydrogen absorption) at mild conditions.

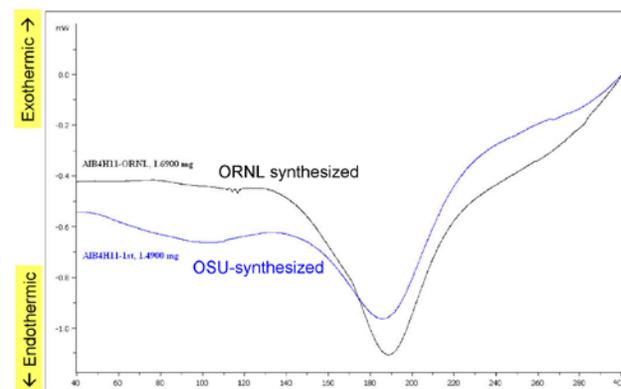


FIGURE 2. DSC curve of $\text{AlB}_4\text{H}_{11}$ showing endothermic desorption which is essential for reversibility.

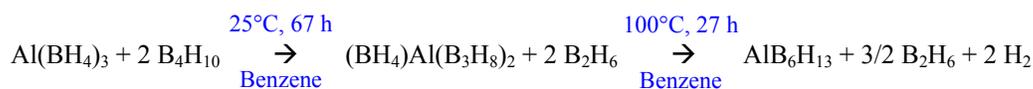
Based on the $\text{AlB}_4\text{H}_{11}$ synthesis experience, we explored the syntheses of other aluminoborane compounds such as $\text{AlB}_5\text{H}_{12}$ and $\text{AlB}_6\text{H}_{13}$ at OSU. Their syntheses require the both B_3H_9 and B_4H_{10} as the starting materials – both are tedious to make. Tetraborane (B_4H_{10}) was prepared by a solid-liquid reaction of KB_3H_8 with BCl_3 at -78°C for 90 min followed by stirring at room temperature for 20 min according to the procedure reported by Hill et al. [3]. KB_3H_8 was prepared by the reduction of BH_3 tetrahydrofuran (THF) with K-Hg amalgam. KB_3H_8 was washed with CH_2Cl_2 several times and recrystallized from THF solvent to remove all the impurities. A number of trials showed that it is very difficult to obtain pure B_4H_{10} by this method. Inconsistent stirring (due to the high viscosity) was the main issue in this reaction which never proceeded to the completion. Apparatus and special methods were designed and reaction conditions were optimized to try to obtain pure tetraborane; but a small amount of BCl_3 impurity was always found in the end product. Since the boiling points of BCl_3 and B_4H_{10} are very close, it's very hard to separate them. The BCl_3 impurity affects the synthesis of $\text{AlB}_6\text{H}_{13}$ considerably by reacting with $\text{Al}(\text{BH}_4)_3$ to produce $-\text{BHCl}_2$ species. Hence this procedure cannot be used to synthesize pure B_4H_{10} . Another method involved a reaction between $[\text{N}(\text{n-But})_4][\text{B}_3\text{H}_8]$ and liquid BBr_3 at 0°C for 1h. This is an efficient method as it was easy to separate tetraborane from other products and the yield was 60%. KB_3H_8 was converted to a corresponding tetrabutyl ammonium compound by reacting with tetrabutyl ammonium bromide in THF. The tetraborane was then reacted with $\text{Al}(\text{BH}_4)_3$ in a benzene solution that was stirred for 67 h. The solution was then turned to a viscous liquid which was further heated to 100°C for 27 h to obtain an insoluble pale yellow color solid. Solvent was evaporated under dynamic vacuum for overnight to obtain $\text{AlB}_6\text{H}_{13}$. The product was characterized by XRD, IR and DSC. The XRD pattern revealed that it was an amorphous material (polymeric) similar to the literature result. The IR spectrum and DSC profiles closely resemble to those of $\text{AlB}_4\text{H}_{11}$. Detailed analysis is in progress.

OSU (Prof. Sheldon Shore) has some decaborane ($\text{B}_{10}\text{H}_{14}$) (probably the only source in the world). We explored its reaction with $\text{Al}(\text{BH}_4)_3$ to see whether the aluminoborane compounds can be extended beyond the Himpsl-Bond compounds ($\text{AlB}_4\text{H}_{11}$, $\text{AlB}_5\text{H}_{12}$ and $\text{AlB}_6\text{H}_{13}$). Decaborane has four bridging hydrogens compared to two for diborane. Reaction of $\text{Al}(\text{BH}_4)_3$ with decaborane ($\text{B}_{10}\text{H}_{14}$) was tried in 1:2, 2:1 and 4:1 mole ratios respectively. The 1:2 reaction gave a yellow

solid but the 2:1 and 4:1 gave pale yellow solids with high yields (>80%). To confirm that the solids contain both Al and boron species, the solids were hydrolyzed and solution ^{11}B NMR and ^{27}Al NMR indicated the elemental presence. Elemental analysis of the product of the first reaction indicated that the Al:B ratio is 1:8 and there is 40% of carbon incorporated in the solid, which comes from the benzene solvent (^1H -MAS NMR indicated a peak at 7 ppm corresponding to benzene-type species). IR analysis indicated that the bridge hydrogens of the decaborane disappeared completely and a broad B-H peak emerged. ^{11}B MAS NMR of the solid showed a broad peak from 20 to -45 ppm that is centered at -15 ppm. ^{27}Al MAS NMR shows two Al peaks at 80 and 35 ppm. As the amount of $\text{Al}(\text{BH}_4)_3$ increased, more IR peaks corresponding to those observed in $\text{AlB}_4\text{H}_{11}$ become more evident in the 2:1 and 4:1 ratio reactions. Elemental analysis and solid state NMR characterization of the solids obtained from the 2:1 and 4:1 reactions are underway. Our results show that this family of aluminoborane compounds has a broad chemistry base and all of them form amorphous solids, which is very encouraging news.

The boron-cage compound $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ contains 11 wt% hydrogen and it is a crystalline compound. TGA measurements show that its desorption started $\sim 190^\circ\text{C}$ and $\sim 9\%$ weight loss was observed up to 400°C . PCT study showed a desorption of 8 wt% H at 400°C which is in reasonable agreement with the TGA result. Simultaneous thermogravimetric modulated beam mass spectrometer (STMBMS) analysis performed at SNL showed a small amount of ammonia release at temperatures between $\sim 200^\circ\text{C}$ and 280°C while H_2 release was observed from $\sim 200^\circ\text{C}$ all the way up to $1,000^\circ\text{C}$. No diborane was observed during the STMBMS analysis. STMBMS results show that the ratio of hydrogen to ammonia gas depends on the orifice size and the percentage of hydrogen in the gas mixture increases with the orifice size. At 35 mm orifice confinement, the ammonia in the desorbed H_2 gas from $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ was 3.3 mole% (Figure 3). Rehydrogenation of 1.8 wt% was observed at a mild condition (240°C and 93 bar hydrogen pressure) even without any catalyst. The ammonia formation needs to be addressed. The reversibility at mild conditions is very attractive, but the total amount of hydrogen released before the cage collapsing is relatively low.

$(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ is another boron-cage compound we studied for potential hydrogen storage. STMBMS analysis also showed a small amount of ammonia release at temperatures between $\sim 200^\circ\text{C}$ and 360°C . Its behavior is very similar to that of $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$. STMBMS



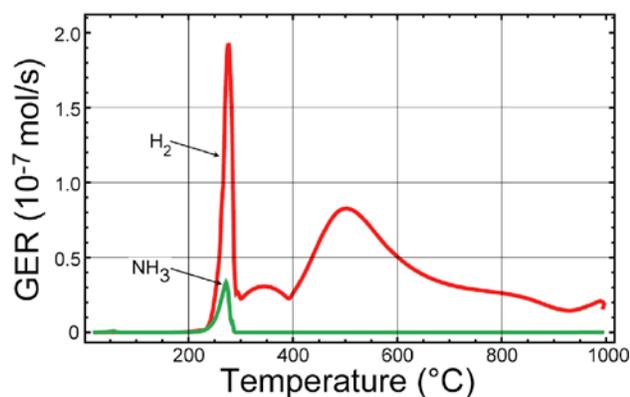


FIGURE 3. STMBMS gas evolution rate of $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ showing hydrogen release in two steps and small amount of ammonia release associated with the first step.

analysis showed both hydrogen and ammonia release at 200-365°C and pure H_2 at higher temperatures (Figure 4). No diborane was observed. Again the ratio of hydrogen to ammonia gas depends on the orifice size and the percentage of hydrogen in the gas mixture increases with the orifice size. At 35 mm orifice confinement, the ammonia in the desorbed H_2 gas from $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ was 0.9 mole%. The DSC curve (Figure 5) clearly shows endothermic desorption for the first step which can potentially be reversible based on thermodynamics. Similar to $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$, the ammonia formation needs to be addressed and the total amount of hydrogen released before the cage collapsing is relatively low.

Non-cage boron compounds such as $\text{M}_x\text{B}_3\text{H}_8$ may be less stable and easier for dehydrogenation and rehydrogenation. To explore this class of compound, we have developed a safe and convenient method for the synthesis of the starting material, NaB_3H_8 (Figure 6). Using this compound, we have also developed a convenient and safe method for the synthesis of ammonium octahydrotriborate ($\text{NH}_4\text{B}_3\text{H}_8$) which has an very high H content (20 wt%). We were able to identify its crystal structure for the first time for both NaB_3H_8 and $\text{NH}_4\text{B}_3\text{H}_8$. More characterization is in progress. These compounds can potentially serve as both metal hydrides and chemical hydrides.

To synthesize more boron-containing lightweight hydrides for hydrogen storage, we need to synthesize starting materials such as B_5H_9 , B_4H_{10} , and NaB_3H_8 . One of the very active chemical reagents is aminodiborane ($\text{NH}_2\text{B}_2\text{H}_5$) that can be used to synthesize many compounds. It was first found serendipitously and then prepared through a tedious procedure using diborane gas at -130°C with a low yield in 1,938 [4,5]. Except for its structure determination, no further studies of its reactions or properties have been reported in the past 70 years, mostly due to its

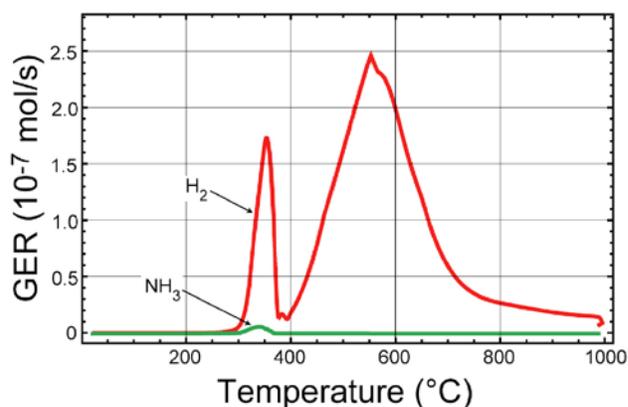


FIGURE 4. STMBMS gas evolution rate of $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ showing hydrogen release in two steps and small amount of ammonia release associated with the first step.

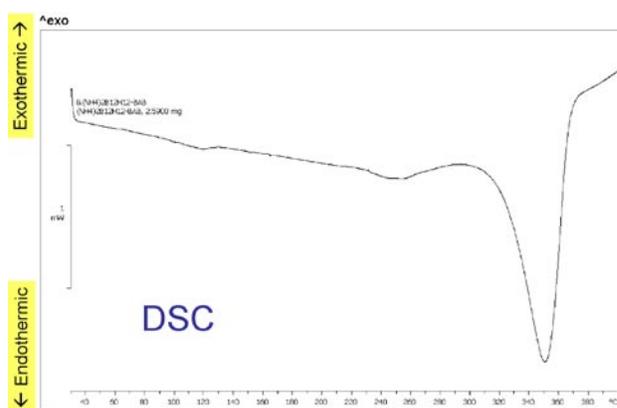


FIGURE 5. DSC curve of $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$ showing endothermic desorption which is essential for reversibility.

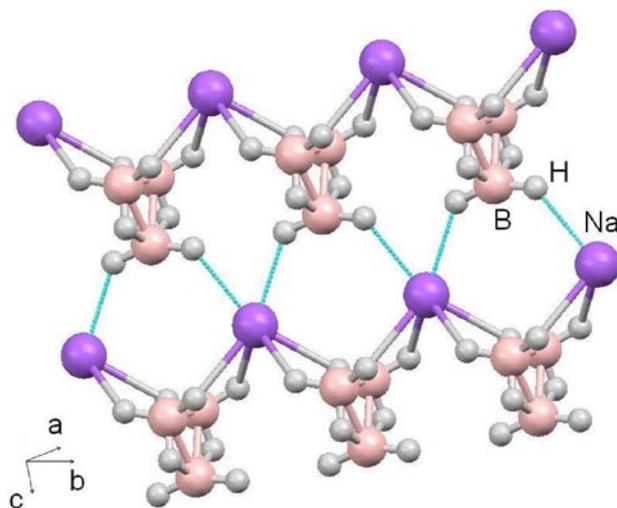


FIGURE 6. Crystal Structure of Unsolvated NaB_3H_8 (Na: violet, B: pink, H: grey)

unavailability. We recently developed a practical synthesis of aminodiborane using a new ambient temperature, catalyst-free reaction between ammonia borane and tetrahydrofuran borane [6]. The facile synthesis of aminodiborane will make this long-sought active chemical reagent readily available for both inorganic and organic syntheses. From aminodiborane, we synthesized an inorganic butane analogue $\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_3$, which is a potential hydrogen storage material with 16.9 wt% hydrogen. It has been predicted as an intermediate during thermal decomposition of NH_3BH_3 [7,8]. Thus, its properties are relevant to NH_3BH_3 studies as well as hydrogen storage research. This compound is a white solid at room temperature with a melting point of 62°C. Further study of its properties is in progress.

Conclusions and Future Directions

The OSU hydrogen storage materials research team has synthesized and tested several new compounds for hydrogen storage. This was made possible by the availability of several vacuum wet-chemistry synthesis lines in Prof. Sheldon Shore's laboratory, a group of dedicated researchers, the unique boron chemistry expertise and inorganic chemistry expertise in the group (especially single crystal structure identification expertise and NMR and IR expertise), and a dedicated hydride testing facility established in Dr. J.-C. Zhao's laboratory. Close collaboration with ORNL, JPL, Caltech, and NIST made possible effective synthesis and characterization of these compounds.

The materials we are synthesizing and studying include $\text{AlB}_4\text{H}_{11}$, $\text{AlB}_6\text{H}_{13}$, $(\text{NH}_4)_2\text{B}_{12}\text{H}_{12}$, $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$, NaB_5H_8 , $\text{NH}_4\text{B}_3\text{H}_8$, $\text{NH}_2\text{B}_2\text{H}_5$, $\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_3$, and new aluminoborane compounds made with $\text{B}_{10}\text{H}_{14}$. A few of these compounds showed endothermic desorption at low temperatures, thus they are good candidates for further study as potential reversible hydrogen storage materials. We have observed reversibility at mild conditions for $\text{AlB}_4\text{H}_{11}$ which is very remarkable for a compound containing only Al, B and H.

We will perform more detailed study of these compounds for hydrogen storage in collaboration with ORNL, JPL/Caltech, Sandia, and NIST. Several compounds have been sent to ORNL, NIST, Sandia, and Ford for various analyses and testing. We will focus on more promising candidates as the properties of these compounds are tested.

Special Recognitions & Awards/Patents Issued

1. Named by the National Academy of Engineering (NAE) as one of thirty outstanding young engineers from U.S. with thirty outstanding engineers from China to participate at the 1st China-America Frontiers of Engineering Symposium

at Beijing and Changsha, October 17-21, 2009. <http://www.nae.edu/File.aspx?id=16468>.

FY 2010 Publications/Presentations

1. X. Chen, J.-C. Zhao, and S.G. Shore, "Facile Synthesis of Aminodiborane and Inorganic Butane Analogue $\text{NH}_3\text{BH}_2\text{NH}_2\text{BH}_3$," *Journal of American Chemical Society (Communication)*, Published online July 20, 2010: <http://pubs.acs.org/doi/abs/10.1021/ja104938v>
2. H.K. Lingam, X. Chen, T. Yisgedu, Z. Huang, J.-C. Zhao, and S.G. Shore, "Redetermination of Di- μ -hydrido-hexahydrido-tetrakis(tetrahydrofuran)-dialuminium(III) magnesium(II)," *Acta Crystallographica E*, E66, m575 (2010).
3. Z. Huang, J. Gallucci, X. Chen, T. Yisgedu, H.K. Lingam, S.G. Shore, and J.-C. Zhao, " $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 7\text{NH}_3$: A New Ammine Complex for Ammonia Storage or Indirect Hydrogen Storage," *Journal of Materials Chemistry*, vol. 20, pp. 2743-2745 (2010).
4. X. Chen, H.K. Lingam, Z. Huang, T. Yisgedu, J.-C. Zhao, S.G. Shore, "Thermal Decomposition Behavior of Hydrated Magnesium Dodecahydrododecaborates," *Journal of Physical Chemistry Letters*, vol. 1, pp. 201-204 (2010).
5. T.B. Yisgedu, X. Chen, H.K. Lingam, Z. Huang, E.A. Meyers, S.G. Shore, and J.-C. Zhao, "Intermolecular Dihydrogen and Hydrogen Bonding Interactions in Ammonium Closo-decahydro-decaborate Sesquihydrate," *Acta Crystallographica C*, vol. 66, pp. m1-m3 (2010).
6. "Borohydrides, Aluminoboranes and Boron-Cage Compounds for Hydrogen Storage", J.-C. Zhao*, X. Chen, Z. Huang, H.K. Lingam, T. Yisgedu, B. Billet, and S.G. Shore, (Keynote lecture and session chair), First International Conference on Materials for Energy, Karlsruhe, Germany, July 4-8, 2010.
7. "Lightweight Metal Hydrides for Hydrogen Storage", J.-C. Zhao*, X. Chen, Z. Huang, H.K. Lingam, T. Yisgedu, B. Billet, and S.G. Shore, (Oral presentation) U.S. Department of Energy Annual Merit Review, Washington, D.C., June 7-11, 2010.
8. "Lightweight Metal Hydrides for Hydrogen Storage", J.-C. Zhao*, X. Chen, Z. Huang, H.K. Lingam, T. Yisgedu, B. Billet, and S.G. Shore, (Oral presentation) International Energy Agency (IEA) Task 22 Hydrogen Storage Experts' Meeting, Furnace Creek Inn, Death Valley, CA, April 10-15, 2010.
9. "Characterization Studies of Boron-Containing Compounds for Hydrogen Storage Applications", R.C. Bowman, Jr.*, G.M. Brown, D.A. Knight, J.-C. Zhao, J. Reiter, and J. Zan, (Invited talk) Materials Challenges in Alternative & Renewable Energy Sources 2010 Conference, Cocoa Beach, FL, February 21-24, 2010.
10. "Hydrogen Storage Materials", J.-C. Zhao*, (Invited talk) Central South University, Changsha, China, October 23, 2009.

11. "Lightweight Metal Hydrides for Hydrogen Storage", J.-C. Zhao*, X. Chen, Z. Huang, H.K. Lingam, T. Yisgedu, B. Billet, J. Hoy, and S.G. Shore, (Oral presentation) US Department of Energy Hydrogen Storage Tech Team Meeting, USCAR, Southfield, MI, September 17th, 2009.

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