



Complex metal hydrides for reversible hydrogen storage

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Hydrogen as a fuel



Biomass

**Hydro
Wind
Solar**



Nuclear

Oil



Coal

**Natural
Gas**

- 👍 *Hydrogen gas has almost three times energy content of gasoline (120 MJ/kg vs. 44 MJ/kg)*
- 👍 *H₂ Fuel Cells reach >80% efficiency in combined heat and power generation and >50% in electrical*

→ **Hydrogen** →

- 👎 *No natural source of hydrogen; difficult/expensive to produce*
- 👎 *Low density of H₂ gas and liquid => low volumetric energy content*
- 👎 *Volumetric compression and storage is problematic*



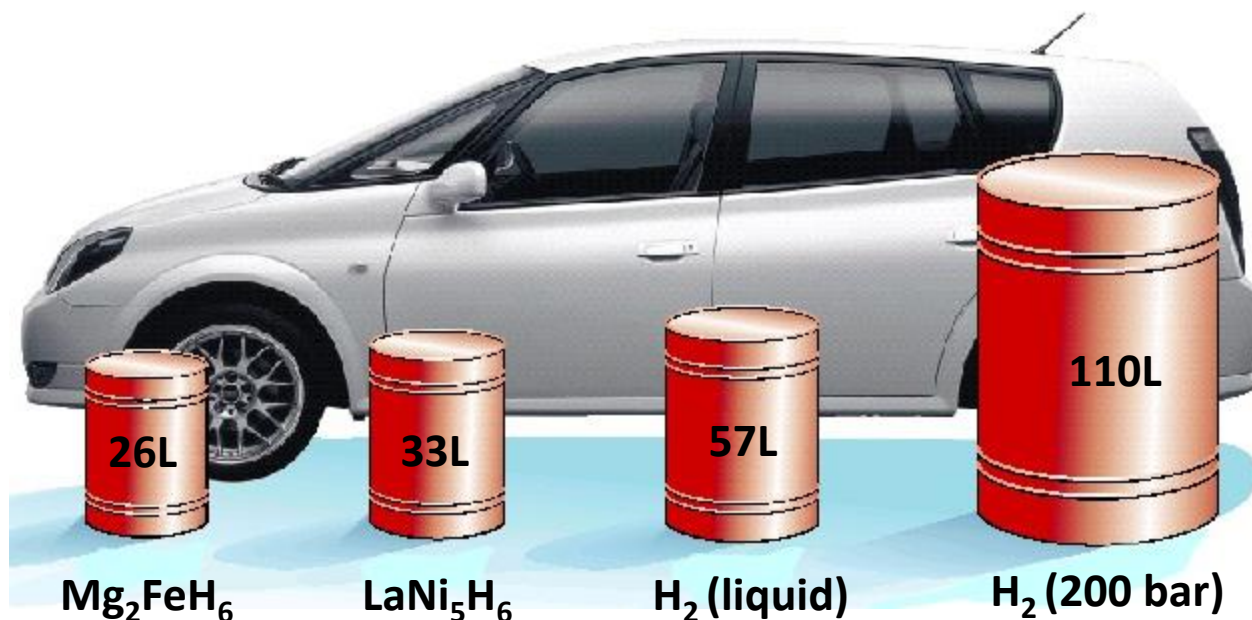
Courtesy of UTC Fuel Cells

📖 Solid-state hydrogen storage, Ed. G. Walker, 2008.

Hydrogen for transportation

Metal hydrides represent a class of materials with volumetric densities higher than gaseous or liquid hydrogen.

Volume Comparisons for 4 kg Vehicular H₂ Storage

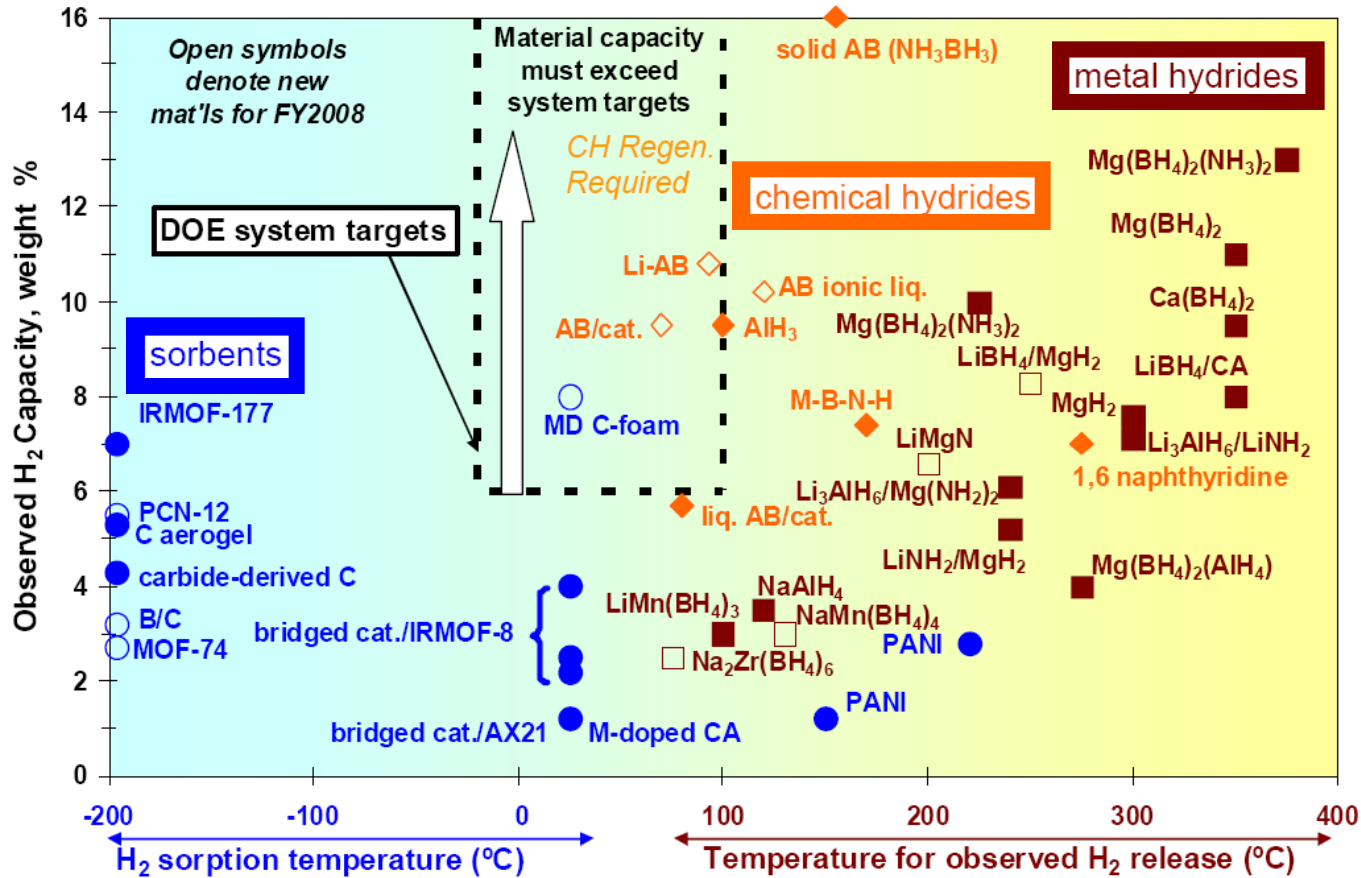


📖 Schlapbach & Züttel, *Nature*, 2001, 296.

Complex metal hydrides

N. Stetson & G. Sandrock (DOE)

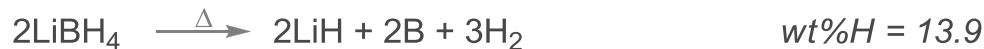
Material Capacity vs. Temperature




Borohydrides for hydrogen storage

Metal borohydrides represent a class of materials with high gravimetric and volumetric hydrogen densities.

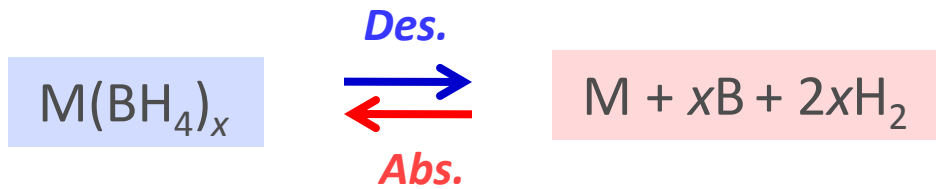
	Density (g/cm ³)	Hydrogen density (kg/m ³)	Hydrogen density (mass%)	Heat of formation, ΔH , (kJ/mol)	Melting / Decomposition* T, °C
LiBH ₄	0.66	122.1	18.5	-194	278
NaBH ₄	1.07	114.5	10.7	-191	505
Mg(BH ₄) ₂	0.78	147.4	14.9	-226	295*
Ca(BH ₄) ₂	1.07	124.1	11.6	-302	310*
Al(BH ₄) ₃	0.79 (liq.)	133.5	16.9	-131	-64
Zr(BH ₄) ₄	1.18	126.2	10.7	-398	29*



 Y. Nakamori, S. Orimo, *Borohydrides as hydrogen storage materials*, in “Solid-state hydrogen storage”, Ed. G. Walker, **2008**.

 S. Orimo, Y. Nakamori, J.R. Eliseo, A. Züttel, C.M. Jensen, *Chem. Rev.*, **2007**, 107, 4111.

Reversible borohydrides



Selected examples:



Züttel *et al. Scr. Mater.*, **2007**, 56, 823

Orimo *et al. J. Alloys. Comp.* **2005**, 404-406, 427

Soloveichik *et al. Int. J. Hydrogen Energy*, **2009**, 34, 916

Severa *et al. Chem. Commun.* **2010**, 46, 421

Kim *et al. Scr. Mater.*, **2008**, 58, 481

Rönnebro, Majzoub. *J. Phys. Chem. C.* **2007**, 111, 12045

high dehydrogenation temperatures

high pressure required for rehydrogenation

Problems & Challenges

contamination of H₂ gas with boron hydrides

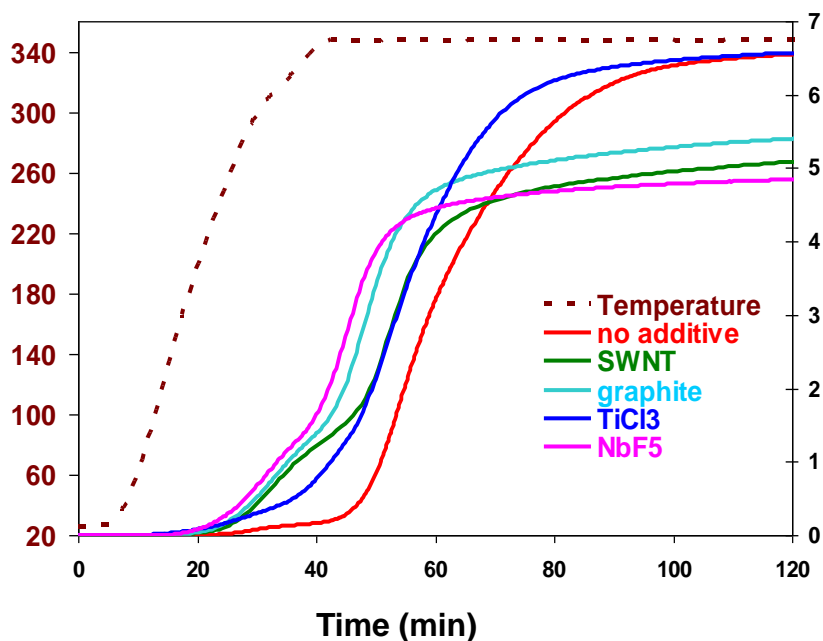
loss of capacity upon cycling

stable intermediates
([B₁₂H₁₂]²⁻, etc.)

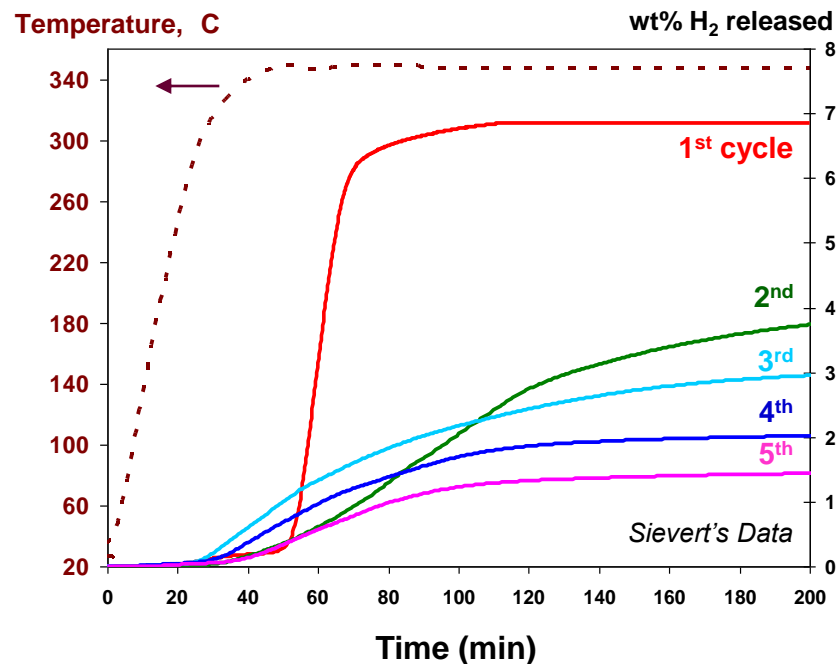
Hydrogen release from $\text{Ca}(\text{BH}_4)_2$

with Ewa Rönnebro and Mutlu Kartin (Sandia)

Additive Effect on $\text{Ca}(\text{BH}_4)_2$ Desorption



Life-cycle of $\text{Ca}(\text{BH}_4)_2$ with 4wt% PdCl_2 Additive

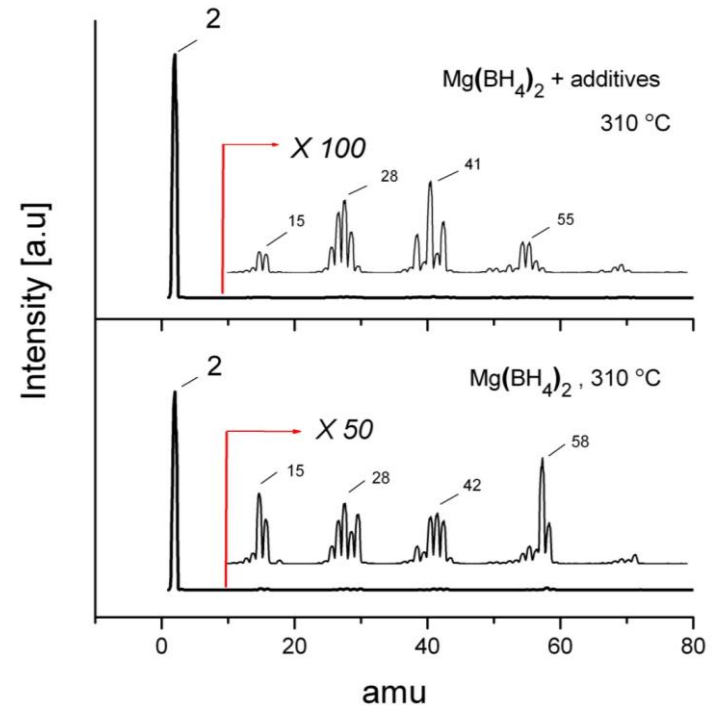
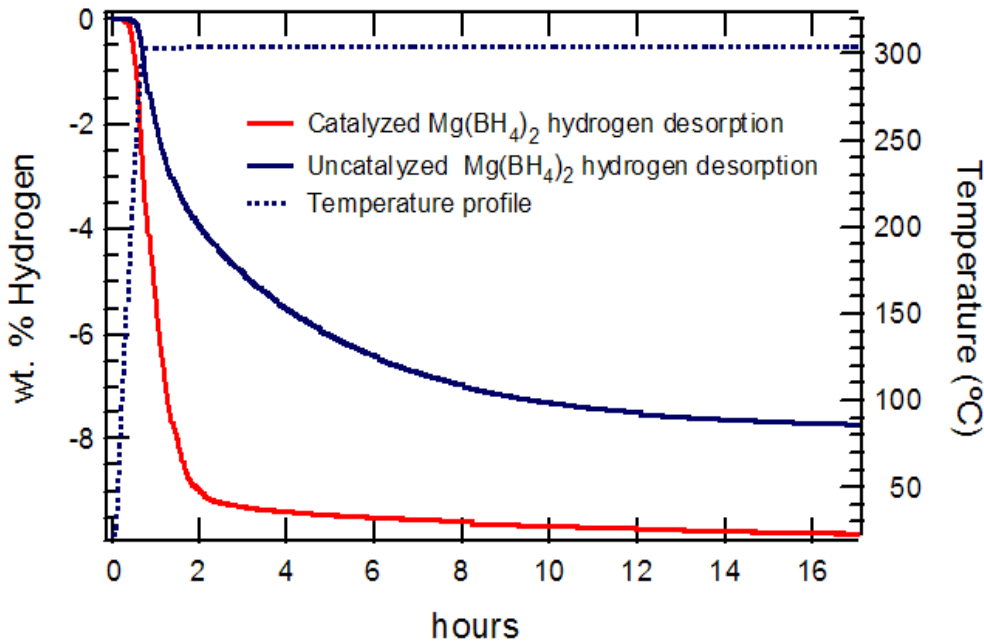



Results:

- Additives have a significant effect on H_2 release from $\text{Ca}(\text{BH}_4)_2$
- Significant capacity loss observed upon cycling

Hydrogen release from $\text{Mg}(\text{BH}_4)_2$

Desorption of $\text{Mg}(\text{BH}_4)_2$ ball-milled with 5mol % TiF_3 and 5mol% ScCl_3

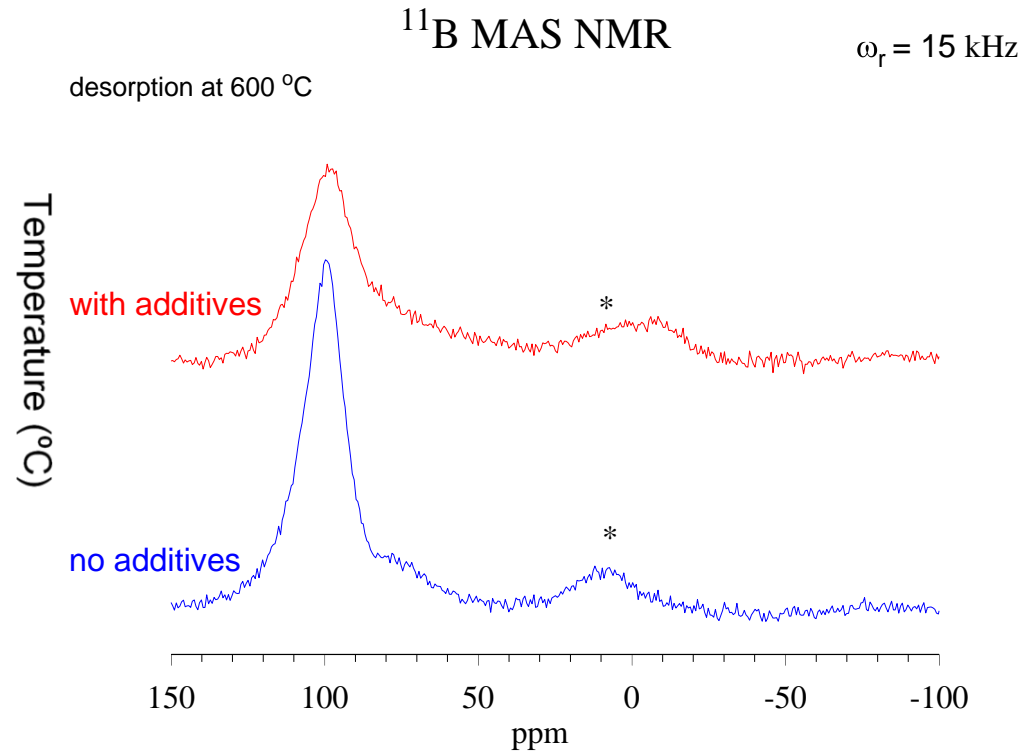
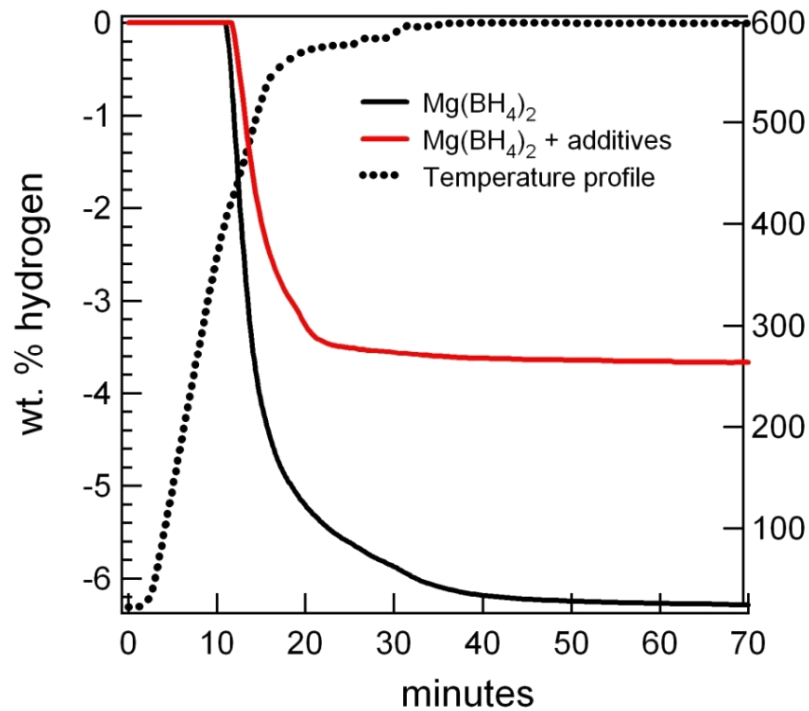


 R. Newhouse, V. Stavila, S. Hwang, L. Klebanoff, J.Z. Zhang *J. Phys. Chem. C* **2010**, 114, 5224.

- Significant improvement in hydrogen desorption of $\text{Mg}(\text{BH}_4)_2$ was observed in the presence of the $\text{TiF}_3/\text{ScCl}_3$ additive

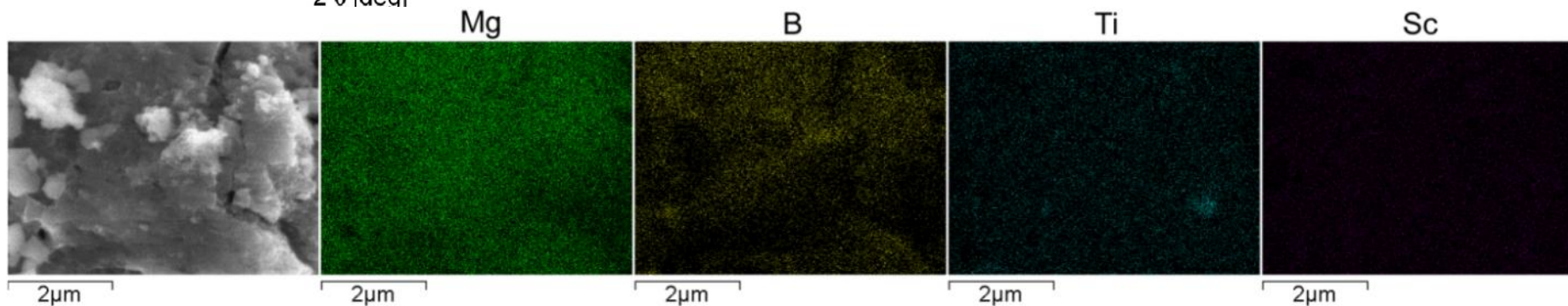
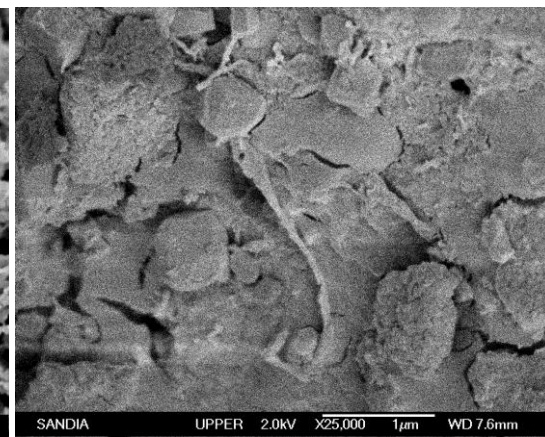
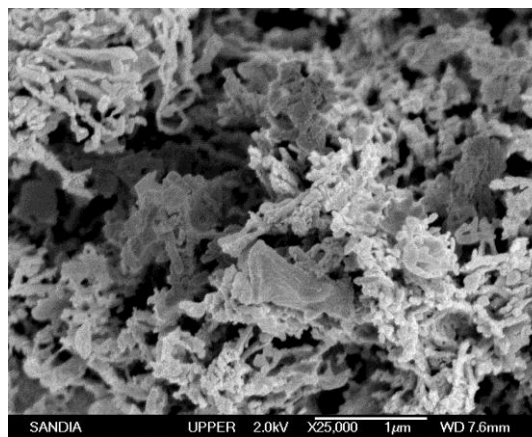
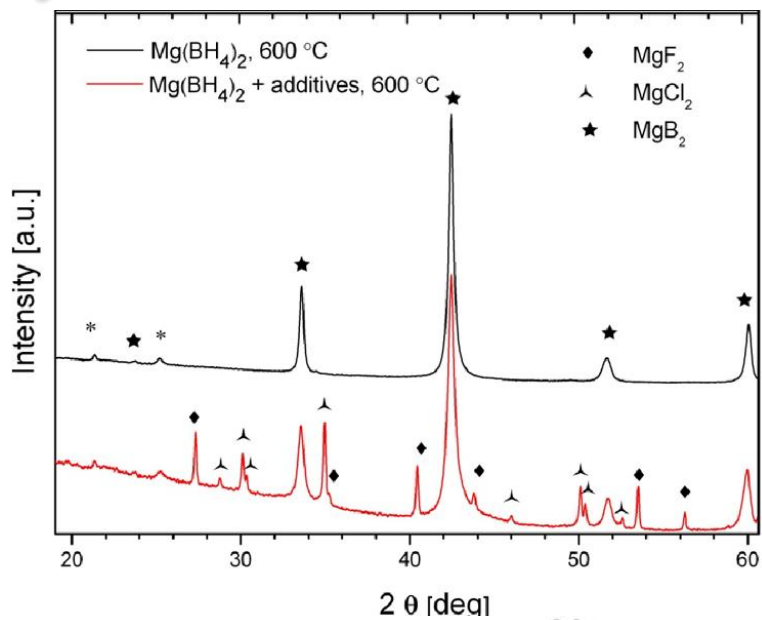
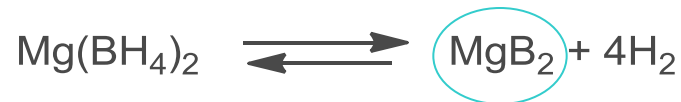
Hydrogen release from $\text{Mg}(\text{BH}_4)_2$

Desorption of $\text{Mg}(\text{BH}_4)_2$ ball-milled with 5mol % TiF_3 and 5mol% ScCl_3



- Up to 14 wt% H_2 released upon heating to 600 °C
- At 90 MPa and 390 °C rehydrogenation of 49% for the sample with additives and 66% for the un-doped sample with additives was observed

Hydrogen release from $\text{Mg}(\text{BH}_4)_2$

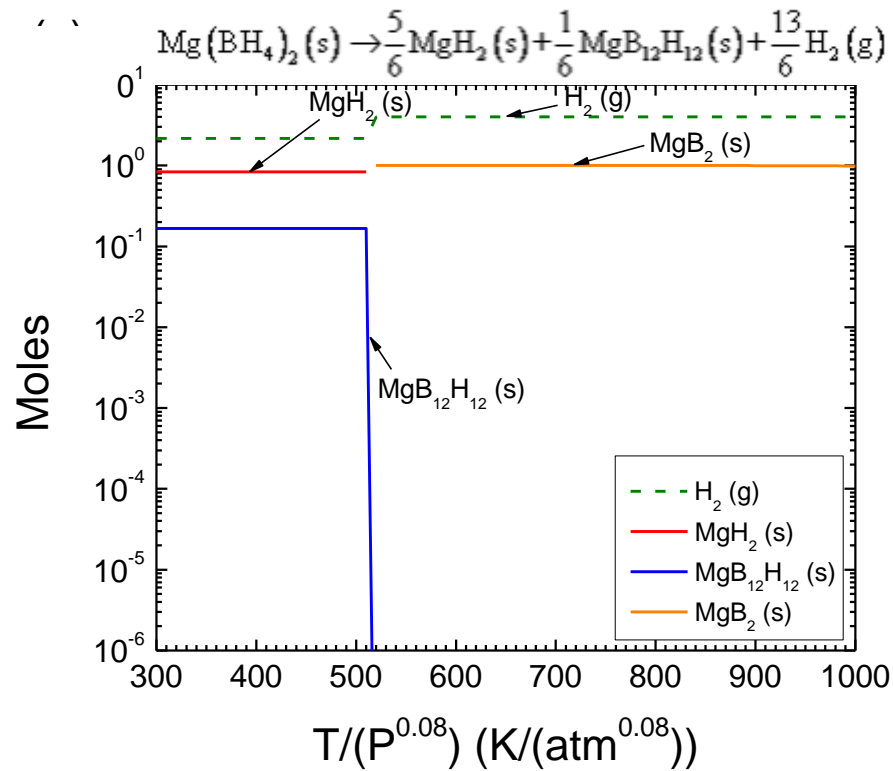
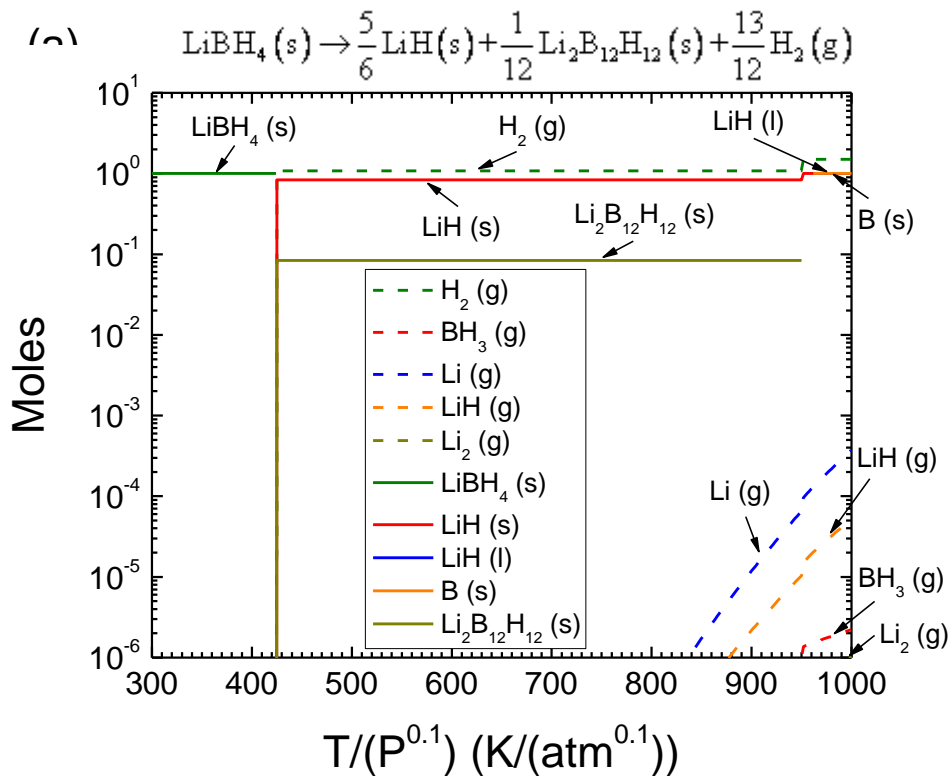


MgB_2 almost exclusively formed upon heating up to 600 °C

Additives distributed relatively uniformly throughout the boride sample

Modeling Complex Equilibria

In collaboration with M.D. Allendorf (Sandia) and Prof. Sholl's group (Georgia Tech)
 DFT (enthalpy, entropy, heat capacity) and FactSage (thermochemical calculations)



📖 K.C. Kim, M.D. Allendorf, V. Stavila, D.S. Sholl, *Phys. Chem. Chem. Phys.* **2010**, (in press)

[B₁₂H₁₂]²⁻ species: theory and experiment

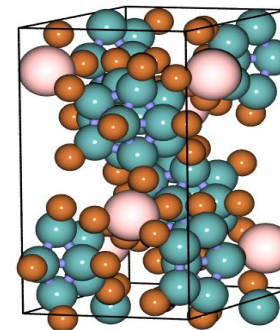
- Evidence of diborane and *closo*-polyborate cluster formation during borohydride desorption reactions prompted further analysis of [B₁₂H₁₂]²⁻ salts

The Prototype Electrostatic Ground State (PEGS) technique was used for structure determination and ΔH estimates

Calculations were performed by Prof. E. Majzoub (University of Missouri, St. Louis)

Predicted Structure

C2/c
Ca[B₁₂H₁₂]



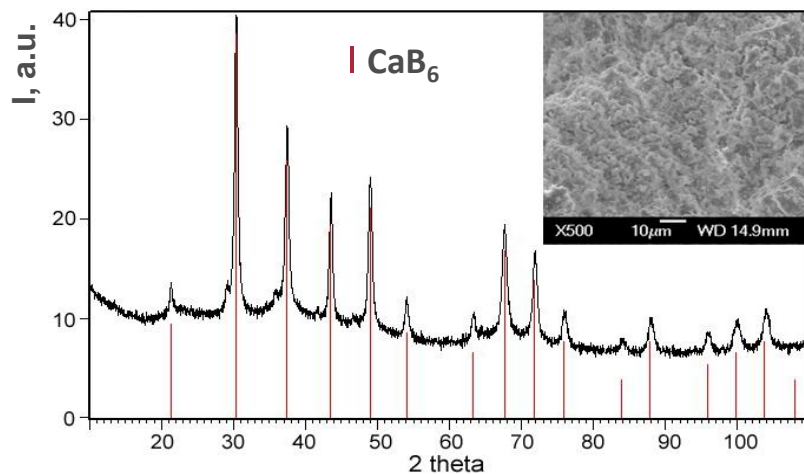
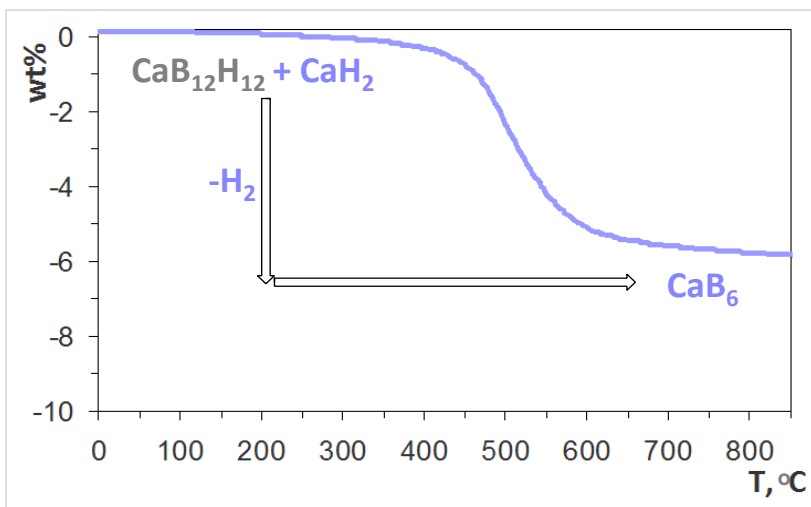
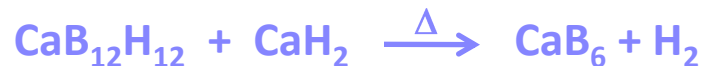
Several hydrogen storage reactions predicted to display favorable thermodynamics were explored, based on the first-principle calculations reported by *Ozolins et al.*

Ozolins, Majzoub, Wolverton. *J. Am. Chem. Soc.* **2009**, *131*, 230-237.

Borohydride reactions:

Predicted Reactions		Theoretical wt% H ₂	ΔH^{300K} kJ/mol H ₂	T _c (C)	Experimental Data: wt% H ₂ (350 °C)
5Mg(BH ₄) ₂ + 2LiBH ₄	Li ₂ B ₁₂ H ₁₂ + 5MgH ₂ + 13H ₂	8.4	24.4	-29	6.0
5Mg(BH ₄) ₂ + Ca(BH ₄) ₂	CaB ₁₂ H ₁₂ + 5MgH ₂ + 13H ₂	7.7	25.7	-18	4.4
5Ca(BH ₄) ₂ + 2LiBH ₄	Li ₂ B ₁₂ H ₁₂ + 5CaH ₂ + 13H ₂	6.7	37.9	83	5.2

$[B_{12}H_{12}]^{2-}$ Destabilization



- The presence of CaH_2 decreases the temperature required to form CaB_6 by $\approx 200\text{ }^\circ\text{C}$; the magnitude of the destabilizing effect is similar to the one observed in metal borohydrides.

Are $[B_{12}H_{12}]^{2-}$ species reversible ?

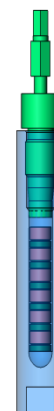
The predicted enthalpies of the $LiBH_4$, $Mg(BH_4)_2$ and $Ca(BH_4)_2$ dehydrogenation reactions to form $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$ suggest that the reverse processes are feasible.



 Ozolins, Majzoub, Wolverton, *J. Am. Chem. Soc.*, **2009**, *131*, 230.

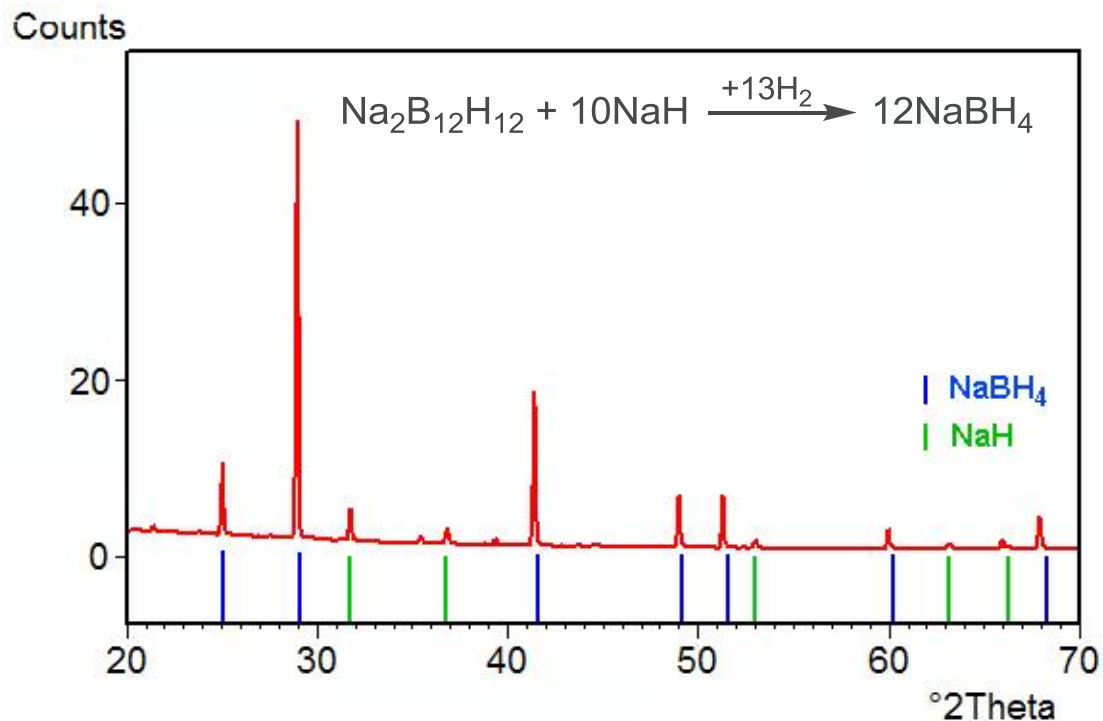
'Hot-sintering' under high H_2 -pressure

- $MB_{12}H_{12} + \text{Metal hydride} + H_2$
- High-energy ball milling for 60 to 180 min $\leq 100 \text{ MPa } H_2$
- Hydrogen pressure $\leq 100 \text{ MPa}$ in a high-temperature reactor $\leq 550 \text{ C}$
- Temperature $\leq 550 \text{ C}$
- Reaction time: several hours to several days



➤ Under these conditions individual metal borohydrides display at least partial reversibility!

Rehydrogenation of $[\text{B}_{12}\text{H}_{12}]^{2-}$ salts



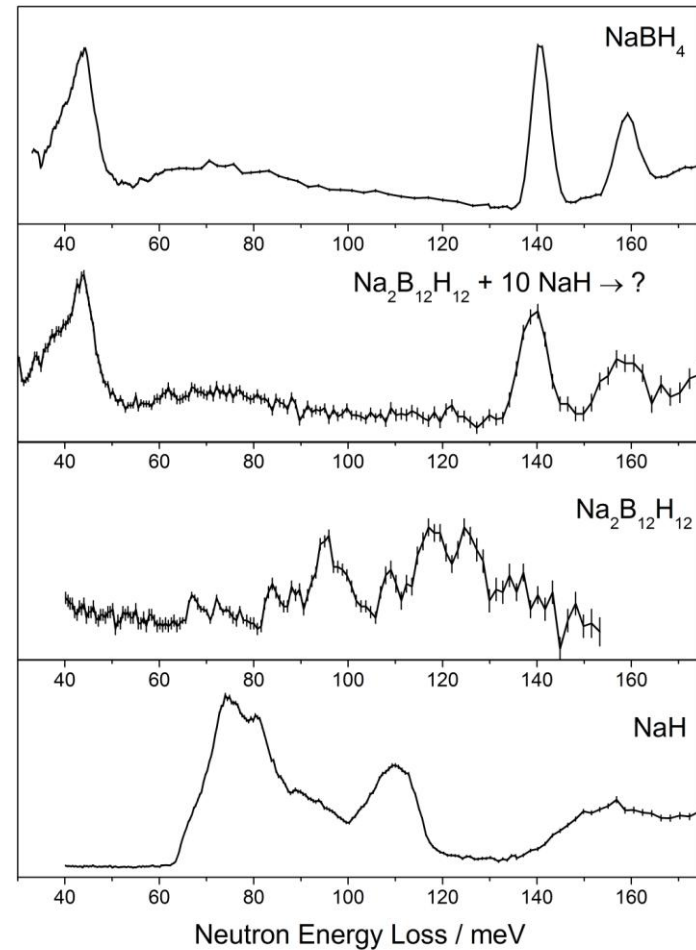
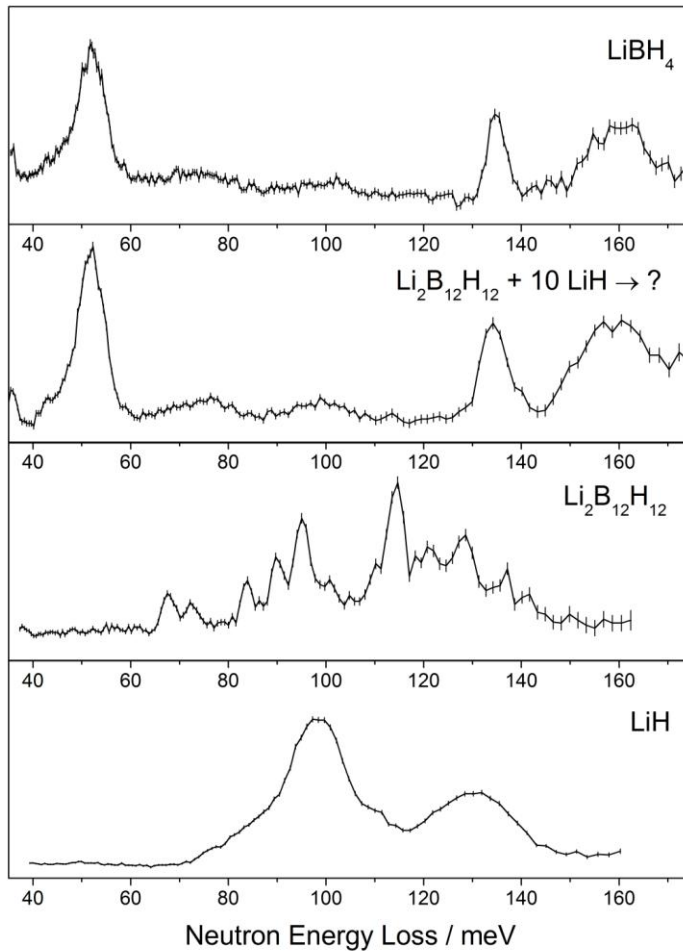
Results:

- $\text{CaB}_{12}\text{H}_{12} + 5\text{CaH}_2$ – no borohydride formation up to 500 °C and 90 MPa H_2
- $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ – partial hydrogenation to LiBH_4 and NaBH_4 at 500 °C and 90 MPa H_2

- $\text{CaB}_{12}\text{H}_{12}$ is not susceptible to rehydrogenation reactions;
- Rehydrogenation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ occurs in almost quantitative yield at high temperatures and hydrogen pressures.

Neutron Vibrational Spectroscopy

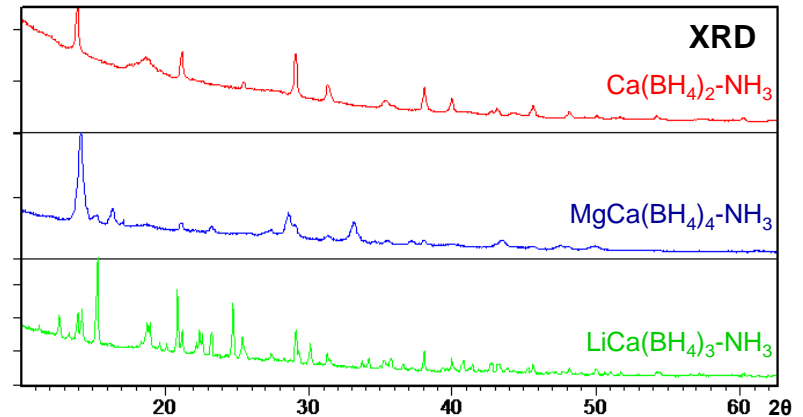
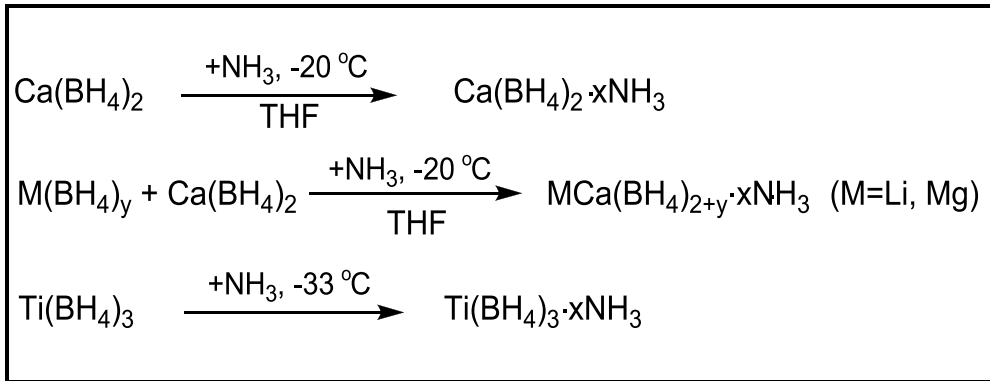
Work done in collaboration with Dr. T. Udovic (NIST)



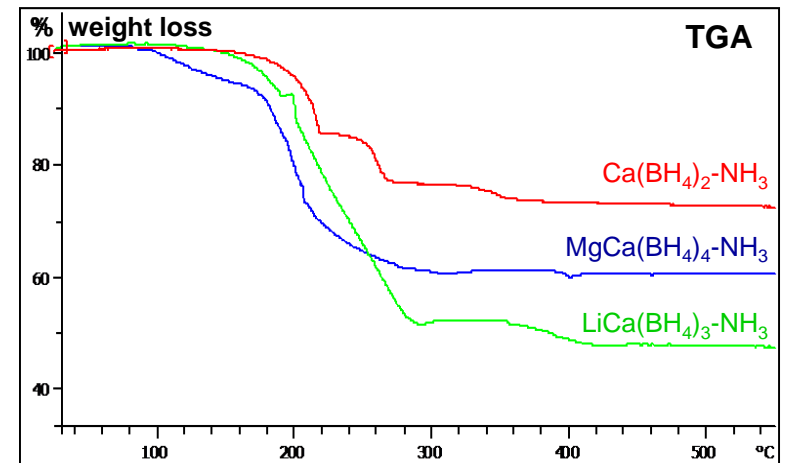
- NVS data suggest significant conversion of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ into LiBH_4 and NaBH_4

Borohydride-ammonia materials

Motivation: The presence of both 'hydridic' and 'protic' hydrogen atoms



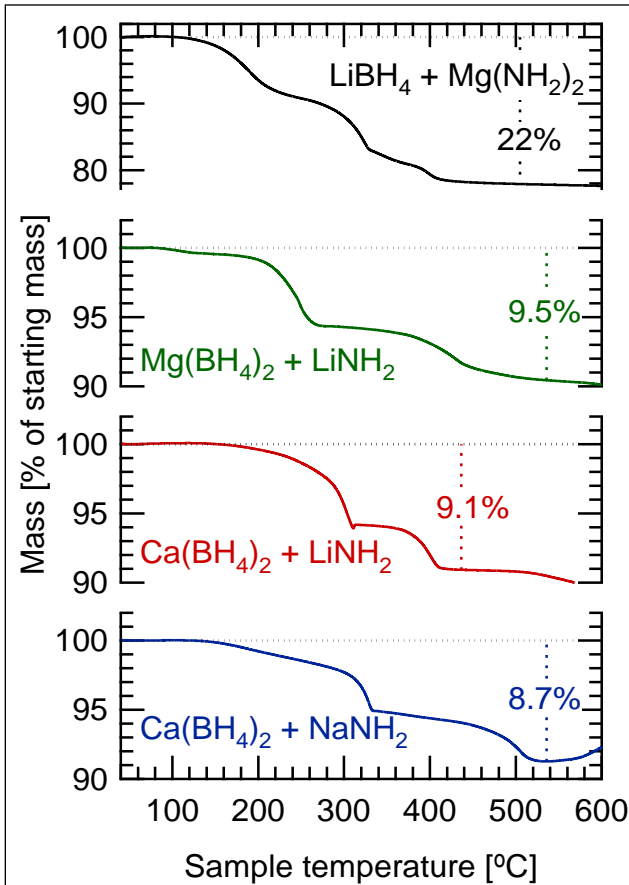
- The BH₄-NH₃ compounds display increased air- and moisture stability compared to the initial borohydrides
- Ca(BH₄)₂·NH₃, MgCa(BH₄)₄·NH₃ and LiCa(BH₄)₃·NH₃ adducts release significant amounts of NH₃ upon heating, confirmed by gas phase analysis
- New systems based on transition metals (e.g. Ti(III) and Mn(II)) are currently under investigation



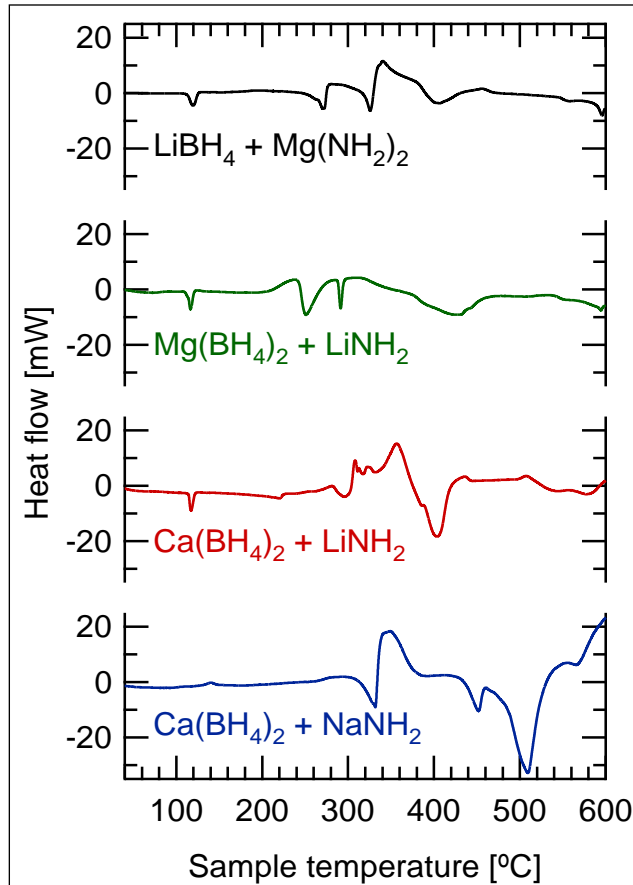
Borohydride-amide materials



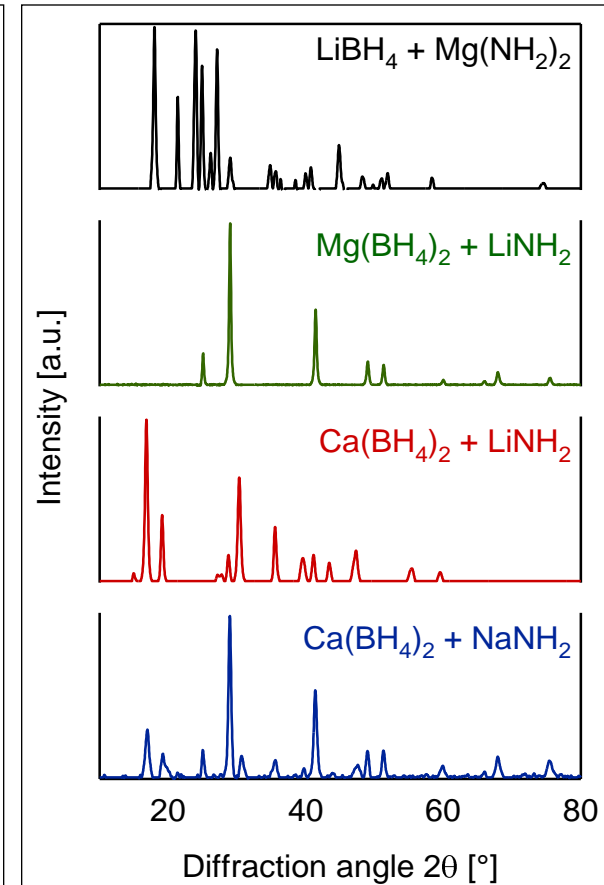
TGA



DSC



XRD



- Mixed borohydride-amide materials release hydrogen at low temperatures
- Problems include poor reversibility and contamination of H₂ with NH₃

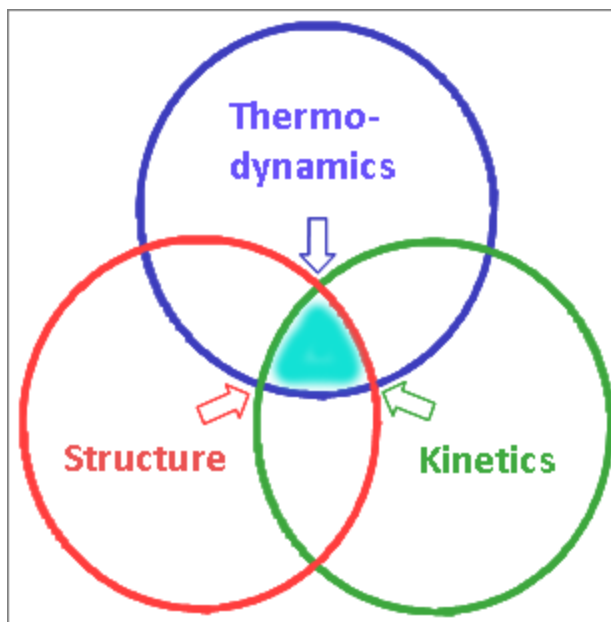
Path to improved reversibility

Approaches to new complex metal hydrides with improved hydrogen storage characteristics:

- *Selection of appropriate destabilizing agents to tune the stability of the intermediate species and render them susceptible to dehydrogenation and rehydrogenation reactions.*
- *Partial substitution of alkali or alkaline-earth cations with more electronegative cations (e.g. transition metals) to achieve a more efficient electron delocalization and decrease stability.*

- Prediction and evaluation of new materials using computational tools.
- Synthesis and testing of promising predicted materials.
- Identification of intermediate compounds formed during dehydrogenation / rehydrogenation.
- Optimization of the cycling characteristics using destabilizing approaches and catalysis.

Criteria: Gravimetric and volumetric densities, equilibrium pressure and temperature, fast dehydrogenation and rehydrogenation reactions





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