SAND2009-5225C

Alkali and alkaline–earth dodecahydro–*closo*–dodecaborates and their relevance to hydrogen storage

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METAL HYDRIDE CENTER OF EXCELLENCE

238th ACS National Meeting, Washington DC, August 19, 2009

Sandia National Laboratories

Metal borohydrides for hydrogen storage

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

	Density (*g/cm³*)	Hydrogen density (*kg/m³*)	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	?	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*

$$2LiBH_4 \xrightarrow{\Delta} 2LiH + 2B + 3H_2 \qquad wt\%H = 13.9$$

$$3Ca(BH_4)_2 \xrightarrow{\Delta} 2CaH_2 + CaB_6 + 10H_2 \qquad wt\%H = 11.6$$

$$Mg(BH_4)_2 \longrightarrow MgB_2 + 4H_2 \qquad wt\%H = 14.9$$

- 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 metal borohydrides

The most challenging aspect of hydrogen storage in metal borohydrides is achieving *reversibility* under practical conditions.

$$M(BH_4)_x \xrightleftharpoons[\text{Abs.}]{\text{Des.}} M + xB + 2xH_2$$

Selected examples:

$$2LiBH_4 \rightleftarrows 2LiH + 2B + 3H_2$$

Züttel *et al. Scr. Mater.*, **2007**, *56*, 823
Orimo *et al. J. Alloys. Comp*. **2005**, *404-406*, 427

$$Mg(BH_4)_2 \rightleftarrows MgB_2 + 4H_2$$

Soloveichik *et al. Int. J. Hydrogen Energy*, **2009**, *34*, 916
Li *et al. Acta Mater*. **2008**, *56*, 1342

$$3Ca(BH_4)_2 \rightleftarrows 2CaH_2 + CaB_6 + 10H_2$$

Kim *et al. Scr. Mater*., **2008**, *58*, 481
Rönnebro, Majzoub. *J. Phys. Chem*. C. 2007, 111, 12045

Several problems need to be addressed for the successful application of metal borohydrides as hydrogen storage media, including (*i*) *high dehydrogenation temperatures*, (*ii*) *high* H_2 *pressure for rehydrogenation*, (*iii*) *contamination of* H_2 *gas with boron hydrides* (*iv*) *limited reversibility.*

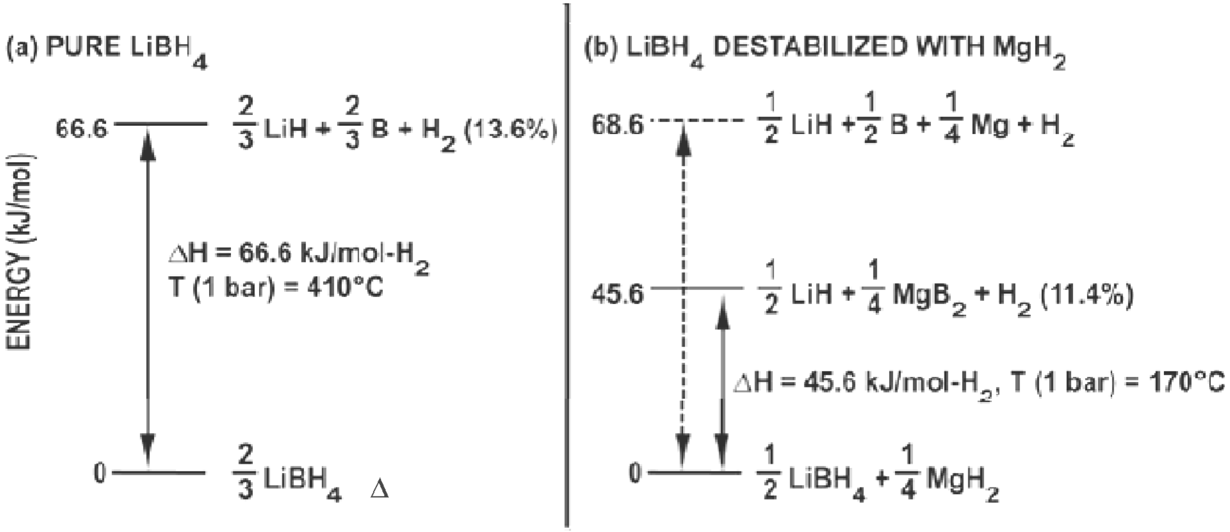
Destabilized borohydride systems

Equilibrium pressure $\mathbf{P_{eq}}$ and operating temperature **T** of a hydride material are set by the enthalpy **ΔH** of hydride formation:

$lnP_{eq} = \Delta H/RT - \Delta S/R$ *van't Hoff equation*

(a) $2LiBH_4 \xrightarrow{\Delta} 2LiH + 2B + 3H_2$

(b) $2LiBH_4 + MgH_2 \longrightarrow 2LiH + MgB_2 + 4H_2$

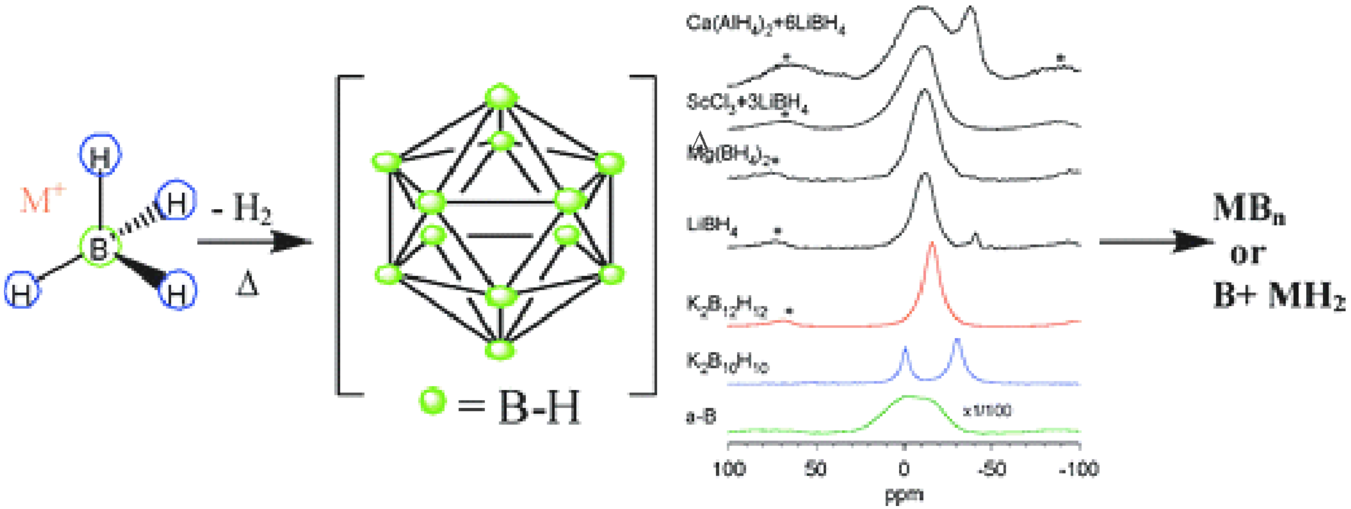


- MgB_2 formation decreases dehydrogenation enthalpy and lowers T_{1barH2} by 240 °C

Vajo, Skeith, Mertens, *J. Phys. Chem. B,* **2005**, *109*, 3719.

$[B_{12}H_{12}]^{2-}$ species detected among the products of decomposition of metal borohydrides

- Metal dodecahydro-*closo*-dodecaborate species were detected among the decomposition products of Li, Sc, Mg borohydrides.



$$12LiBH_4 \xrightarrow{\Delta} Li_2B_{12}H_{12} + 10LiH + 13H_2$$

$$6Mg(BH_4)_2 \longrightarrow MgB_{12}H_{12} + 5MgH_2 + 13H_2$$

📖 Hwang *et al.*, *J. Phys. Chem. C*, **2008,** *112,* 3164.

📖 Ohba *et al.*, *Phys. Rev. B*, **2006**, *74*, 075110.

📖 Orimo *et al.*, *Appl. Phys. Lett.*, **2006**, *89*, 021920

📖 Li *et al.*, *Nanotechnology*, **2009**, *20*, 204013.

$[B_{12}H_{12}]^{2-}$ compounds: theory and experiment

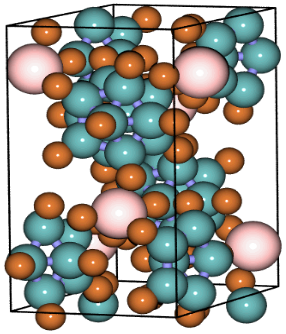
- Evidence of diborane and *closo*-polyborate cluster formation during borohydride desorption reactions prompted further analysis of $[B_{12}H_{12}]^{2-}$ salts

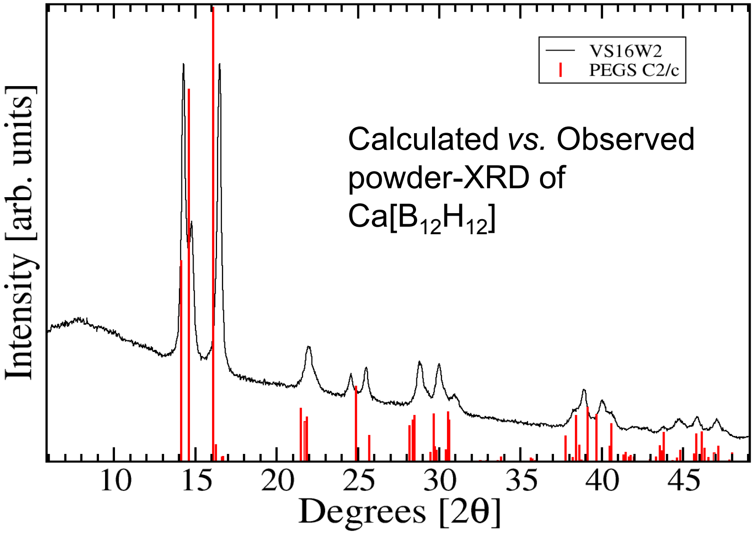
The Prototype Electrostatic Ground State (PEGS) technique was used for structure determination and ΔH estimates

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

Predicted Structure

C2/c
$Ca[B_{12}H_{12}]$

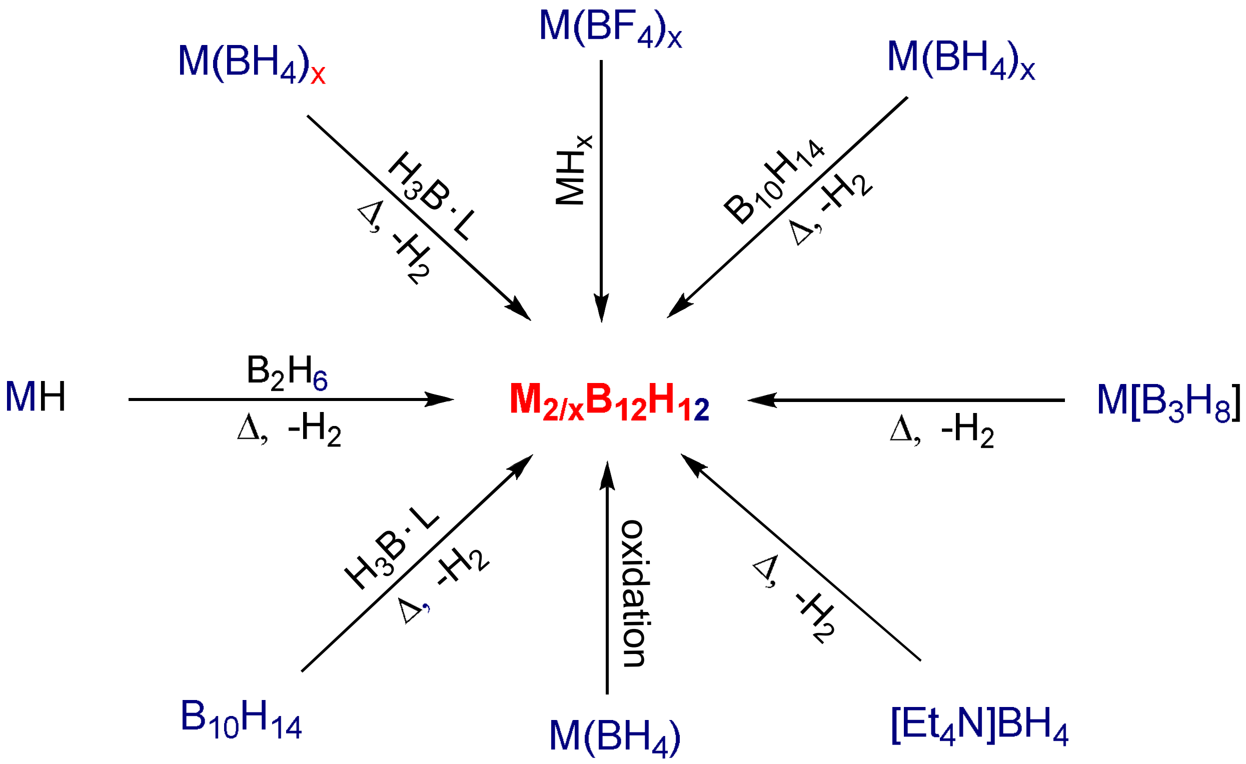




Calculated *vs.* Observed powder-XRD of $Ca[B_{12}H_{12}]$

Compound	PEGS Structures	SNL/NIST Data
$Li_2[B_{12}H_{12}]$	*C2/m* (#12)	*Pa*-3
$Na_2[B_{12}H_{12}]$	*P2₁/n* (#14)	*P2₁/n*
$Ca[B_{12}H_{12}]$	*C2/c* (#15)	*C2/c*
$Mg[B_{12}H_{12}]$	*C2/m* (#12)	Amorphous
$Sc_2[B_{12}H_{12}]_3$	*Cm* (#8)	Amorphous

Synthesis of [*closo*–$B_{12}H_{12}$]$^{2-}$ compounds



$M(BH_4)_x$

$M(BF_4)_x$

$M(BH_4)_x$

$H_3B\cdot L$

Δ, $-H_2$

MH_x

$B_{10}H_{14}$

Δ, $-H_2$

MH

B_2H_6

Δ, $-H_2$

$M_{2/x}B_{12}H_{12}$

Δ, $-H_2$

$M[B_3H_8]$

$H_3B\cdot L$

Δ, $-H_2$

oxidation

Δ, $-H_2$

$B_{10}H_{14}$

$M(BH_4)$

$[Et_4N]BH_4$

Δ

- I.B. Sivaev, V. I. Bregadze, S. Sjöberg, *Collect. Czech. Chem. Commun.* **2005**, *67*, 3719.
- M.G. Davidson, A.K. Hughes, T.B. Marder, K. Wade. *'Contemporary boron chemistry'*, RSC, **2000**.

Synthesis of alkali and alkaline-earth $[closo\text{-}B_{12}H_{12}]^{2-}$ compounds

Aqueous solution route

$$Cs_2[B_{12}H_{12}] \xrightarrow[-Cs^+]{\text{Amberlite IR-120}} [H_3O]_2[B_{12}H_{12}]$$

$$[H_3O]_2[B_{12}H_{12}] \xrightarrow[-CO_2,\ -H_2O]{M_xCO_3} M_x[B_{12}H_{12}]\bullet xH_2O \quad \text{(M= metal ion)}$$

$$M_x[B_{12}H_{12}]\cdot xH_2O \xrightarrow[-xH_2O]{\Delta} M_x[B_{12}H_{12}] \qquad \textit{Yield} \geq 85\%$$

M = Li, Na, K, Rb, Cs, Ca, Sr, Ba; L = NR_3, SR_2; x = 1 or

Non-aqueous solution routes

$$M[BH_4]_x \xrightarrow[-H_2]{B_{10}H_{14},\ \Delta} M_{2/x}[B_{12}H_{12}] \qquad \textit{Yield} \geq 64\%$$

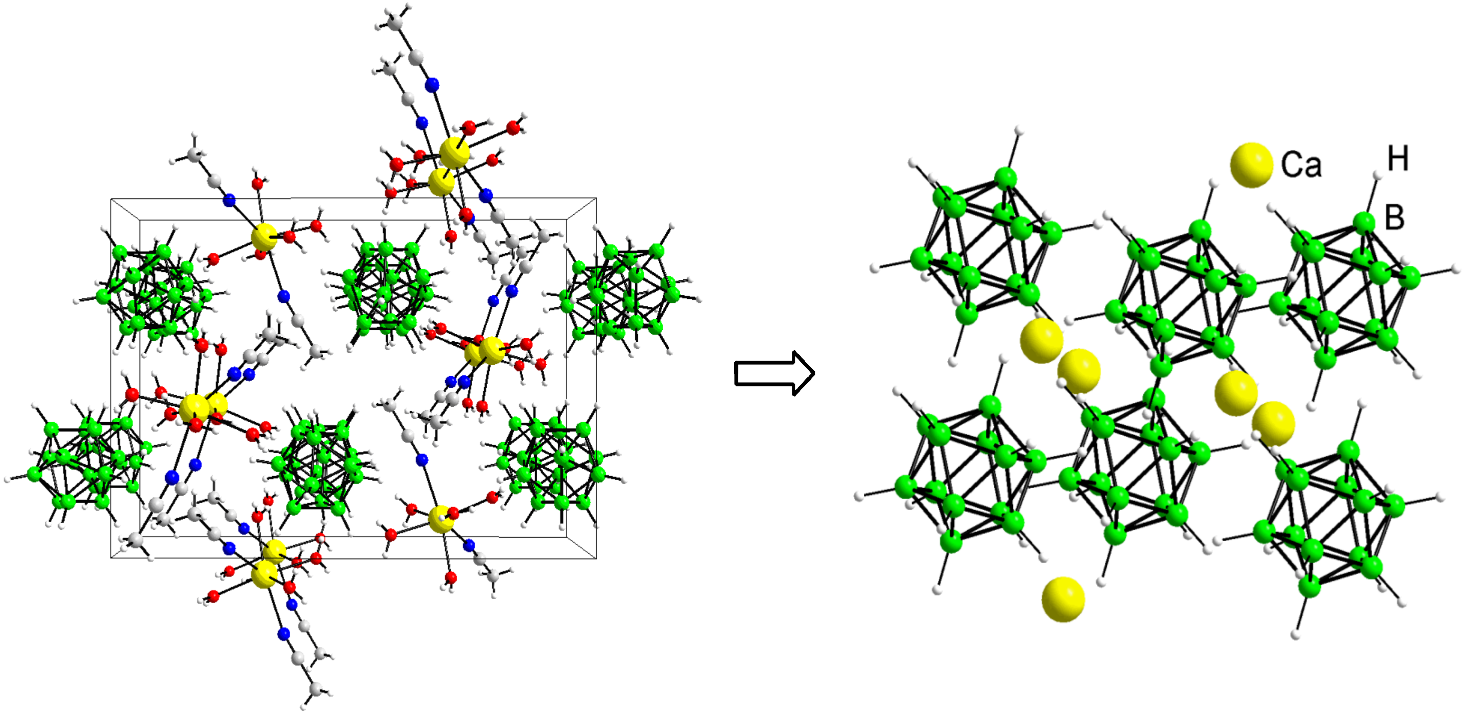
$$M[BH_4]_x \xrightarrow[-H_2]{H_3B\bullet L,\ \Delta} M_{2/x}[B_{12}\overset{x}{H}_{12}]\bullet xL \quad \text{(M= metal ion)}$$

$$M[B_{12}H_{12}]\bullet xL \xrightarrow[-xL]{\Delta} M[B_{12}H_{12}] \qquad \textit{Yield} \geq 70\%$$

M = Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba; L = NR_3, SR_2; x = 1 or 2

Anhydrous metal–$[B_{12}H_{12}]$ compounds

- Desolvation / dehydration of solvated / hydrated dodecahydro-*closo*-dodecaborate salts represents a convenient route towards anhydrous $[B_{12}H_{12}]^{2-}$ salts



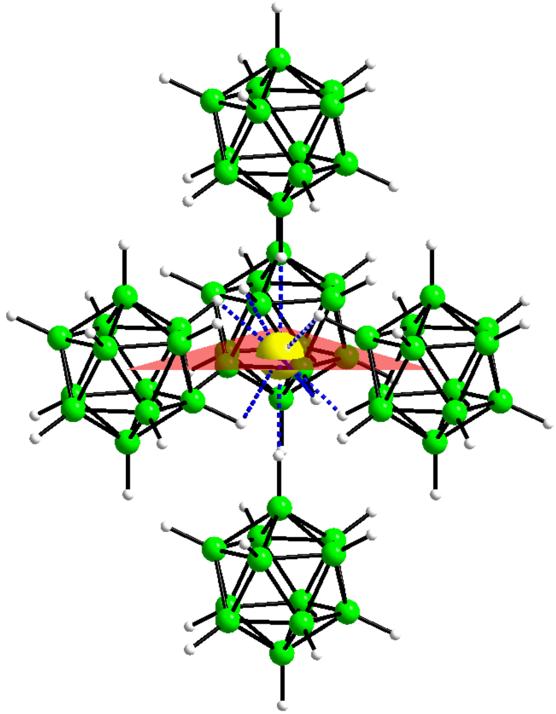
Solvated form

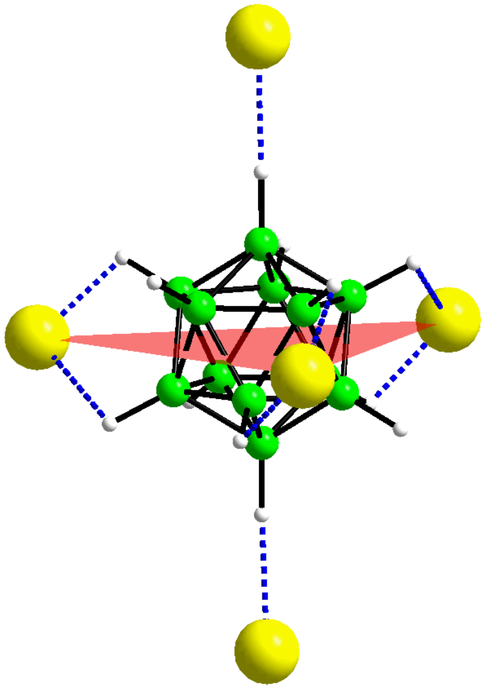
Anhydrous form

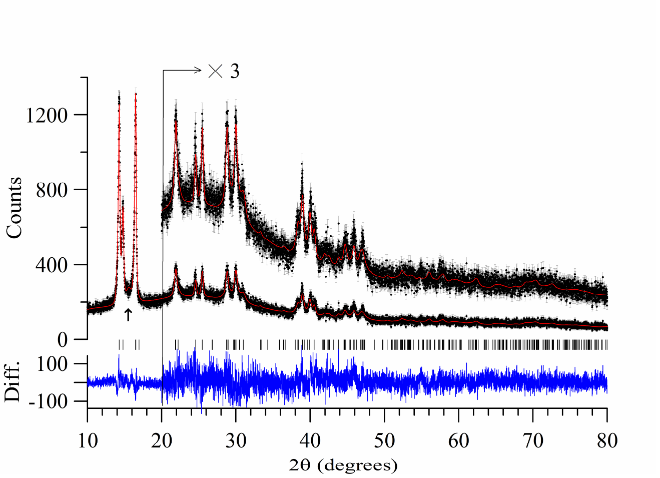
$$[Ca(H_2O)_5(MeCN)_2][B_{12}H_{12}] \xrightarrow[-MeCN,\ -H_2O]{\Delta} CaB_{12}H_{12}$$

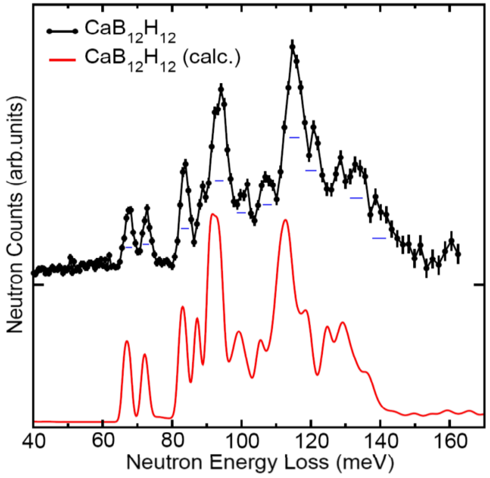
Crystal structure of $CaB_{12}H_{12}$

NIST data: *C*2/*c*, a = 7.242(1) Å, b = 11.971(3) Å, c = 10.744(2) Å, β = 89.82(3)°, V = 931.5(3) Å3, Z = 4







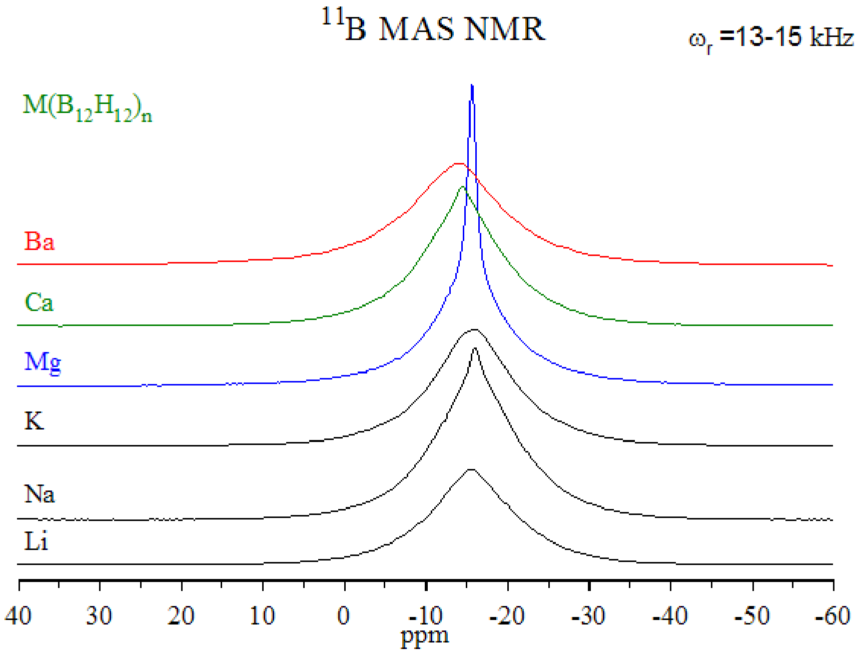


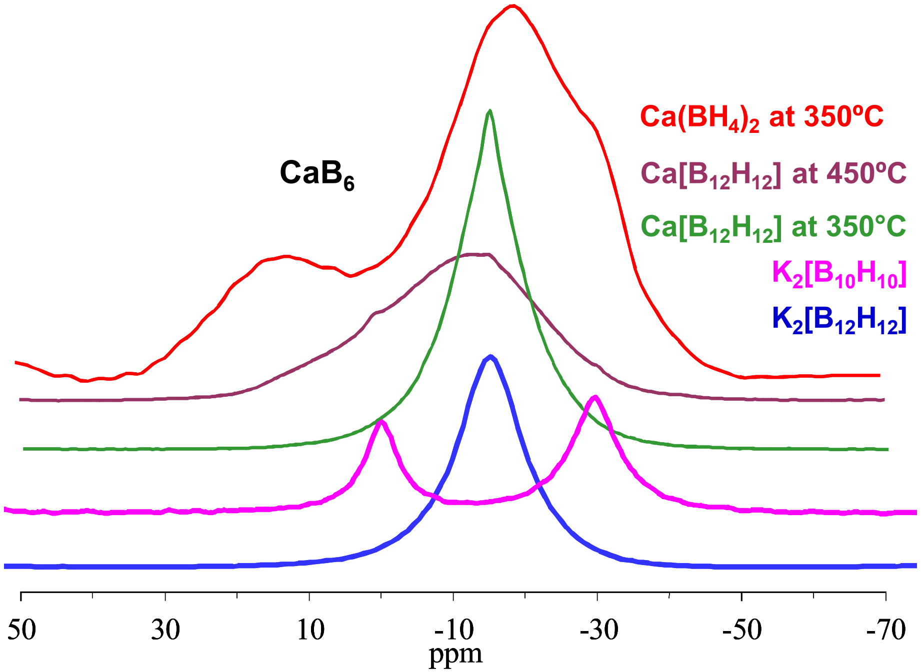
- ➢ Neutron Vibrational Spectroscopy confirmed the theoretically predicted monoclinic structure

📖 V. Stavila, J.-H. Her, W. Zhou, S. Hwang, Ch. Kim, L.A.M. Ottley, T.J. Udovic, *submitted.*

^{11}B MAS NMR of the $[B_{12}H_{12}]^{2-}$ compounds

The ^{11}B MAS NMR peak in the spectra of the alkali metal $[B_{12}H_{12}]^{2-}$ salts is centered around -15.5 ppm, while for the alkaline-metal compounds the peak is shifted slightly down field to about -14.5 ppm.





- ➢ A comparison of the ^{11}B MAS NMR spectra of the $[B_{12}H_{12}]^{2-}$ compounds with dehydrogenated metal borohydrides show important similarities in the spectral range where the intermediates of the dehydrogenation reactions are observed (-10 ÷ 25 ppm).

First-principle prediction of reactions involving $[B_{12}H_{12}]^{2-}$ species

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)
$5Mg(BH_4)_2 + 2LiBH_4 \longrightarrow Li_2B_{12}H_{12} + 5MgH_2 + 13H_2$	8.4	24.4	-29	6.0
$5Mg(BH_4)_2 + Ca(BH_4)_2 \longrightarrow CaB_{12}H_{12} + 5MgH_2 + 13H_2$	7.7	25.7	-18	4.4
$5Ca(BH_4)_2 + 2LiBH_4 \longrightarrow Li_2B_{12}H_{12} + 5CaH_2 + 13H_2$	6.7	37.9	83	6.2

$[B_{12}H_{12}]^{2-}$ reactions:

Predicted Reactions	Theoretical wt% H_2	ΔH^{300K} kJ/mol H_2	T_c (°C)	ΔS^{300K} kJ/mol H_2
$MgB_{12}H_{12} + 5MgH_2 \longrightarrow 6MgB_2 + 11H_2$	7.5	50.0	128	123.9
$CaB_{12}H_{12} + CaH_2 \longrightarrow 2CaB_6 + 7H_2$	6.3	47.0	86	130.7
$Li_2B_{12}H_{12} + 6MgH_2 \longrightarrow 6MgB_2 + 2LiH + 11H_2$	7.1	60.1	215	123.3

Sample preparation

$M_x[B_{12}H_{12}] + M_{2/x}H$

M = Li, Na, Mg, Ca
x = 1 or

1) Ball milling
2) Pelletizing
3) Hot sintering

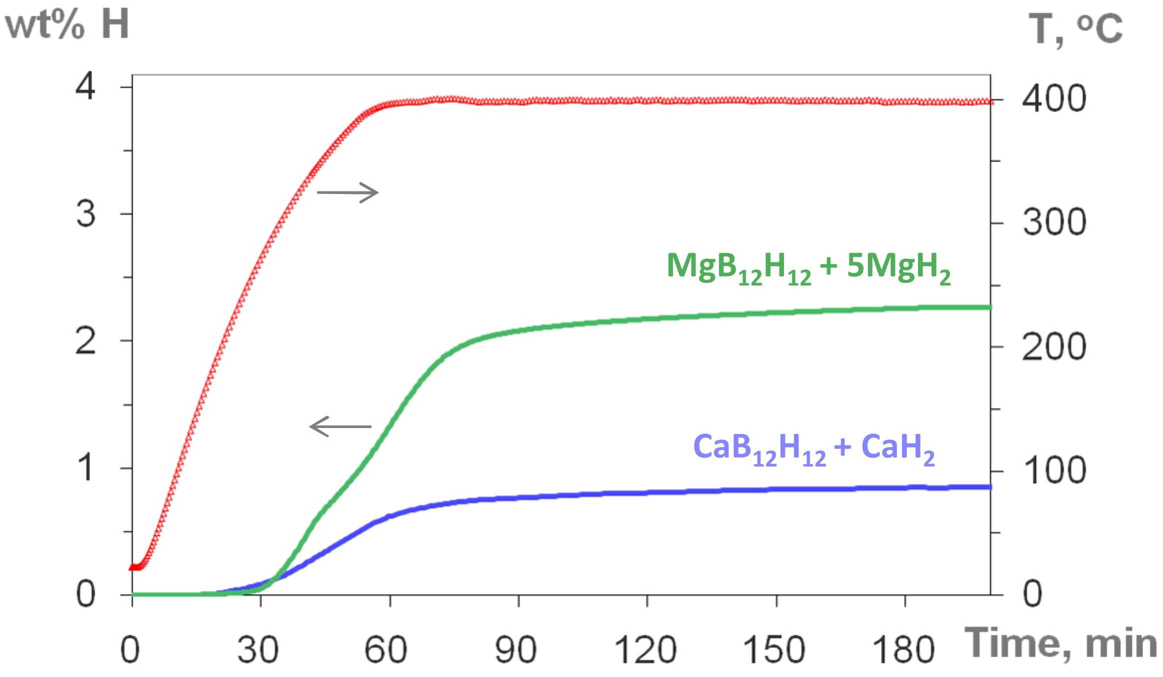
XRD
^{1}H, ^{11}B NMR
FTIR
Raman
TGA/DSC
TPD

Milling conditions : high-energy, 30-120 min; *Pelletization* : 30 MPa, 5 min
2
Hot sintering : 70 - 100 MPa H_2 pressure, 400-600 °C, up to 72 hours

High stability of $[B_{12}H_{12}]^{2-}$ compounds

$CaB_{12}H_{12} + CaH_2 \longrightarrow CaB_6 + H_2$ $\Delta H^{300K} = 50$ kJ/mol H_2

$MgB_{12}H_{12} + 5MgH_2 \longrightarrow MgB_2 + H_2$ $\Delta H^{300K} = 47$ kJ/mol H_2

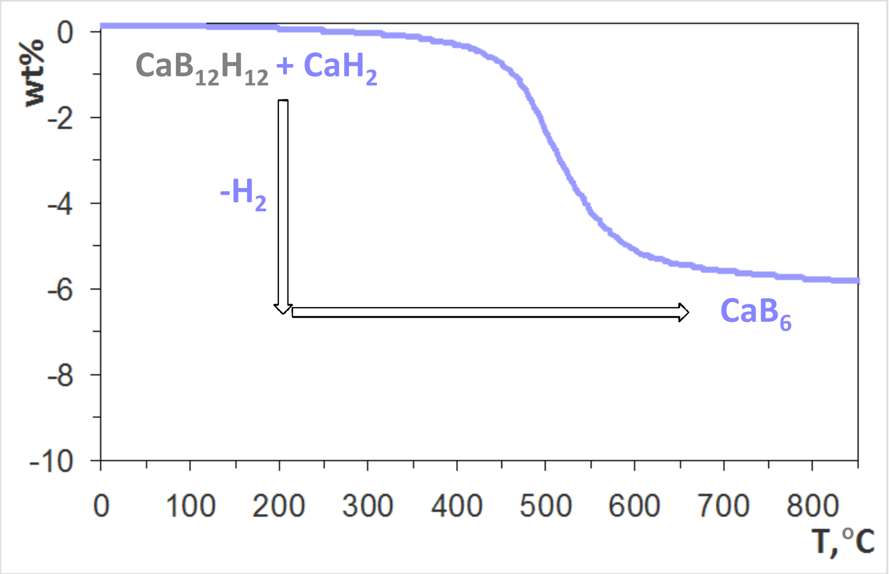


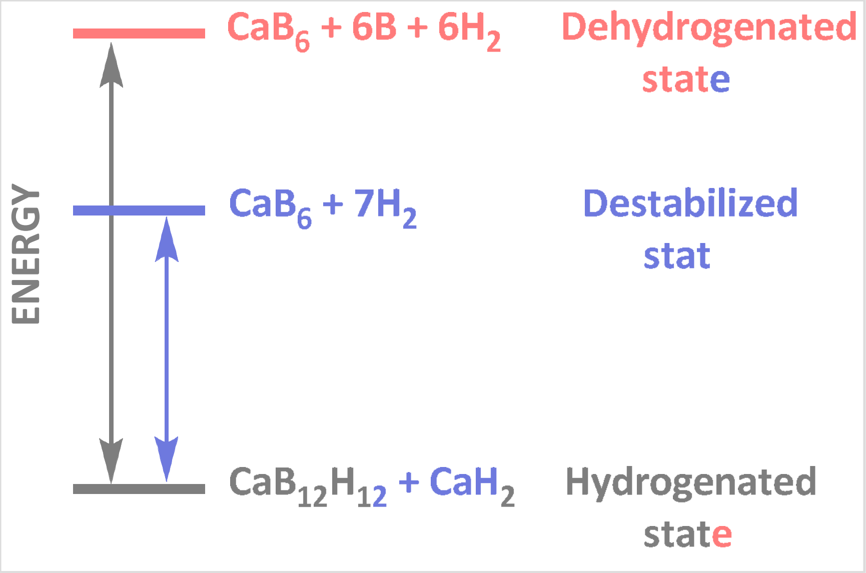
- No crystalline MgB_2 or CaB_6 are formed upon heating up to 400 °C.
- The reactions involving $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$ require high temperatures.

Metal hydrides can exhibit destabilizing effects on $[B_{12}H_{12}]^{2-}$ compounds

$CaB_{12}H_{12} \xrightarrow{\Delta}$ no CaB_6 up to 850 °C

$CaB_{12}H_{12} + CaH_2 \xrightarrow{\Delta} CaB_6 + H_2$





$CaB_6 + 6B + 6H_2$ Dehydrogenated state

$CaB_6 + 7H_2$ Destabilized stat

$CaB_{12}H_{12} + CaH_2$ Hydrogenated state

- The presence of CaH_2 decreases the temperature required to form CaB_6 by more than 200 °C; the magnitude of the destabilizing effect is similar to the one observed for metal borohydrides.

“Hot–sintering” under H_2 pressure

The predicted enthalpies of the $Mg(BH_4)_2$ and $Ca(BH_4)_2$ dehydrogenation reactions to form $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$ suggest that the reverse processes may be feasible under mild conditions.

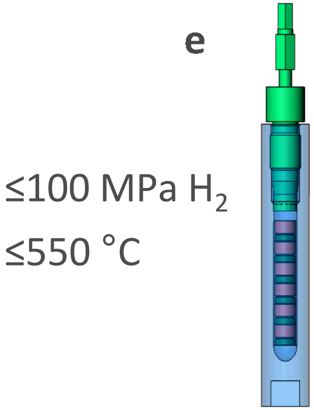
$$MgB_{12}H_{12} + 5\ MgH_2 \xrightarrow{+13H} 6Mg(BH_4)_2 \qquad \Delta H^{300K}=29.3\ \text{kJ/mol*}$$

$$CaB_{12}H_{12} + 5\ CaH_2 \xrightarrow{+13H_2} 6Ca(BH_4)_2 \qquad \Delta H^{300K}=39.2\ \text{kJ/mol*}$$

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

‘Hot-sintering’ under high H_2-pressure

- $MB_{12}H_{12}$ + Metal hydride + H_2
- Hydrogen pressure ≤100 MPa in a high-temperature reactor
- Temperature ≤550 °C
- Reaction time: several hours to several days



Results:

- No borohydride formation up to 450 °C and 100 MPa
- Only traces of $Ca(BH_4)_2$ formed above 500 °C

- ➢ $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$ are kinetically stable and not susceptible to rehydrogenation reactions, which may explain poor cycling characteristics of individual metal borohydrides.
- ➢ $[B_{12}H_{12}]^{2-}$ species are undesirable products of metal borohydrides decomposition.

Path to improved reversibility of borohydrides

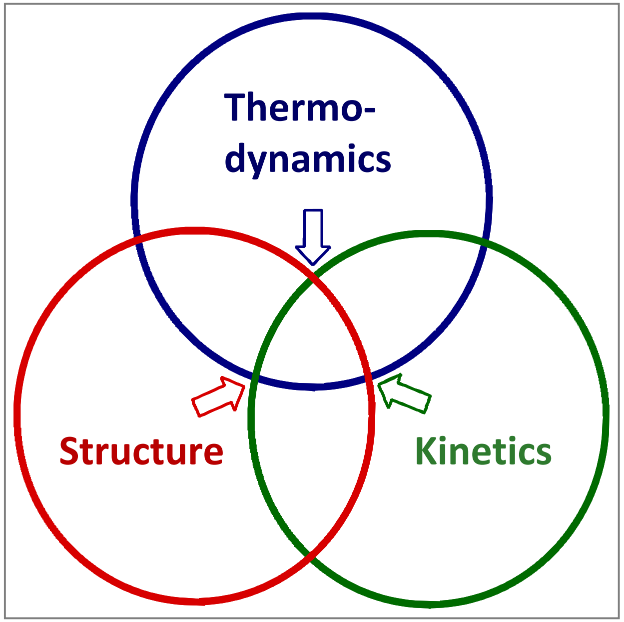
Alkali and alkaline-earth metal borohydrides form stable *closo*-borate compounds upon thermal decomposition which tend to limit their *reversibility*.
Possible solutions to this problem:

- *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.*

Pathway to new, reversible borohydride materials:

- ➢ 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



Summary and Conclusions

- Anhydrous alkali and alkaline-earth metal dodecahydro-*closo*-dodecaborates were isolated and their thermal stability was investigated.
- $[B_{12}H_{12}]^{2-}$ salts can be easily synthesized from metal borohydrides in the presence of other boron hydrides. Similar processes may occur during the thermal decomposition of metal borohydrides.
- No significant amounts of metal borohydrides can be isolated from the $[B_{12}H_{12}]^{2-}$ salts and metal hydrides under high hydrogen pressures using hot-sintering techniques.
- Metal dodecahydro-*closo*-dodecaborates are extremely stable and their formation during the cycling of metal borohydrides is undesirable.
- Stability of dodecahydro-*closo*-dodecaborate salts can be significantly altered by metal hydrides; a similar destabilizing effect was reported in the case of metal borohydrides.

Acknowledgements

Sandia National Laboratories:

Lennie Klebanoff, Jay Keller, Marcina Moreno, Eric Majzoub, Weifang Luo, Joe Cordaro, Rebecca Newhouse, Ewa Ronnebro (*currently at PNNL*), Dennis Morrison, George Sartor, Ken Stewart

Metal Hydride Center of Excellence:

John Vajo (*HRL*), Zak Fang (*U. Utah*), Joseph Reiter (*JPL*), Jason Zan (*JPL*), J.-C. Zhao (*OSU*) John Vajo (*HRL*), Craig Jensen (*UH*), Dan Mosher (*UTRC*)

Financial Support:

U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under the Hydrogen Storage Grand Challenge, Metal Hydride Center of Excellence (MHCoE) within DOE's National Hydrogen Storage Project