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Factors Affecting Hydrogen Release from Metal Borohydrides

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Metal 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, ^oC
$LiBH_4$	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*

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

$$3Ca(BH_4)_2 \xrightarrow{\Delta} 2CaH_2 + CaB_6 + 10H_2 \qquad wt\%H = 9.6$$

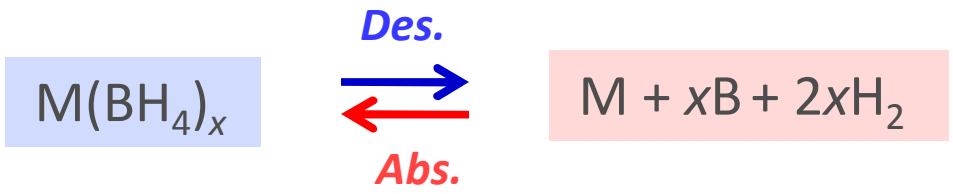
$$Mg(BH_4)_2 \longrightarrow MgB_2 + 4H_2 \qquad wt\%H = 14.9$$

📖 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.



Selected examples:

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

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

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

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

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

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.*

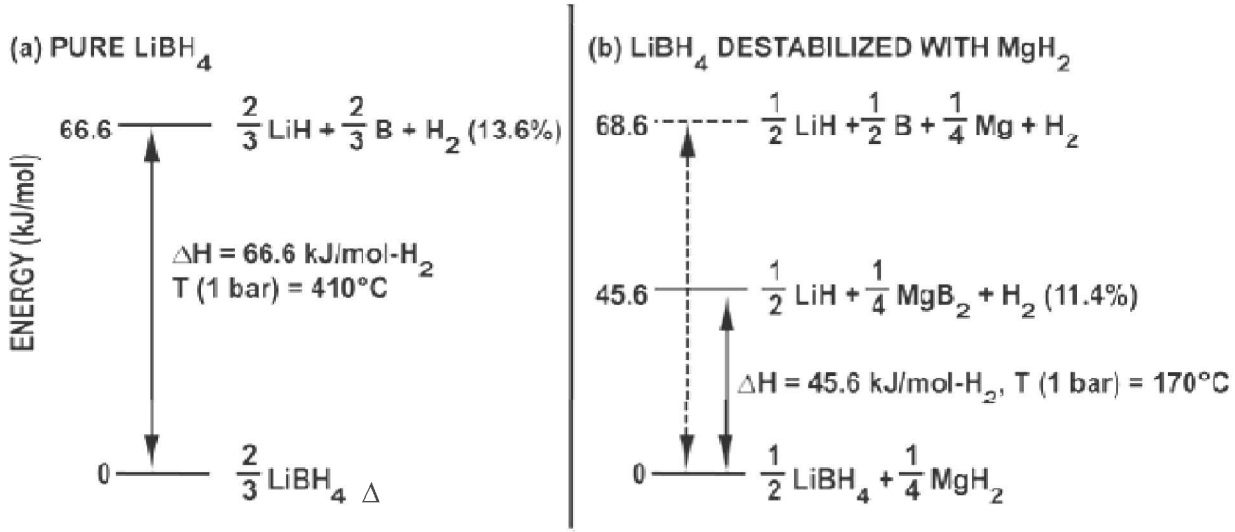
Destabilized borohydride systems

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

$$\ln P_{eq} = \Delta H/RT - \Delta S/R \qquad \textit{van't Hoff equation}$$

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

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

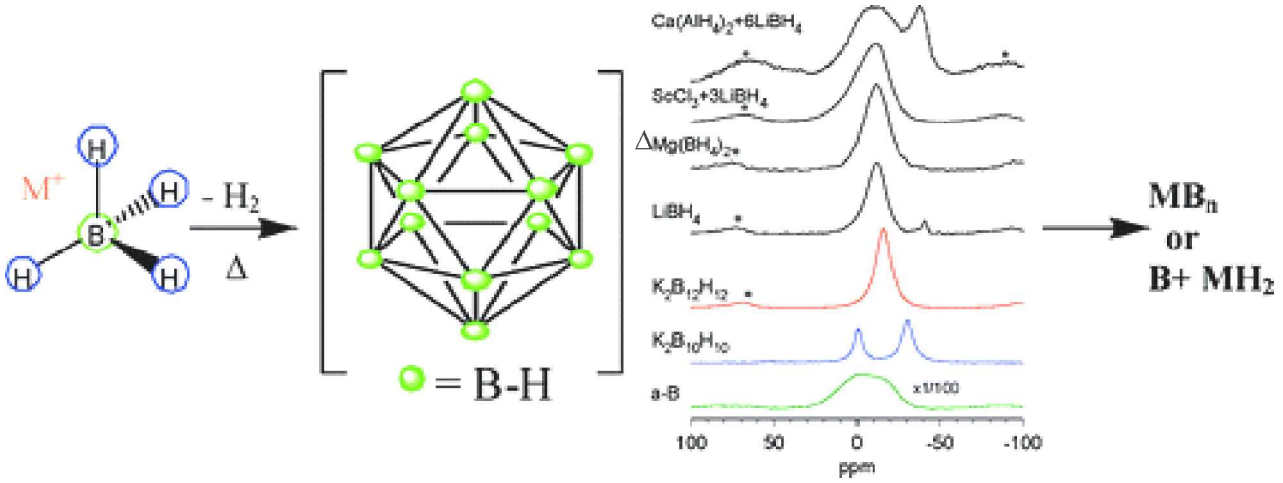


➢ MgB_2 formation decreases dehydrogenation enthalpy and lowers T_{1barH2} by 240 °C

📖 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 have been detected among the decomposition products of Li, Sc, and 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

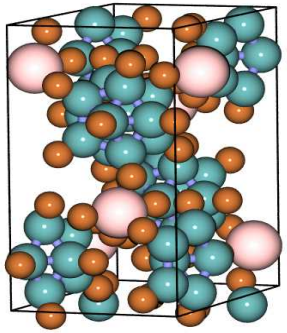
- Evidence of diborane and *closo*-polyborate cluster formation during borohydride desorption reactions prompted further analysis of $[B_{12}H_{12}]^{2-}$ salts

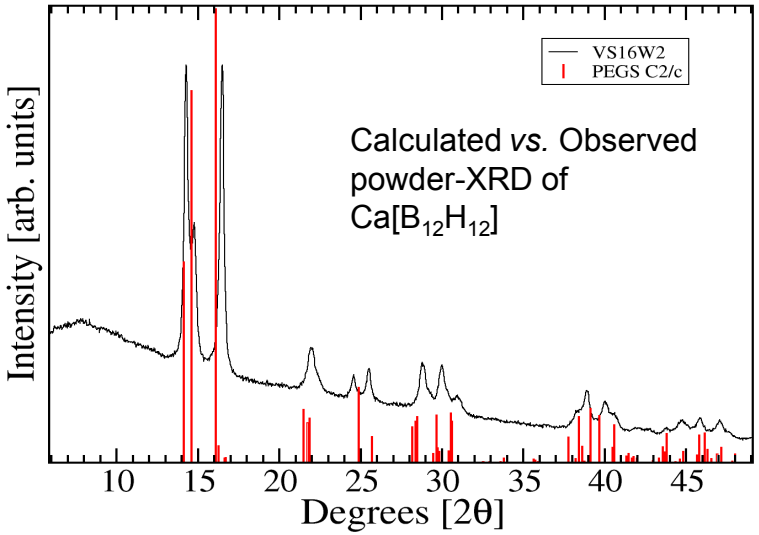
The Prototype Electrostatic Ground State (PEGS) technique was used for structure determination and ΔH estimates

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

Predicted Structure

*C*2/*c*
$Ca[B_{12}H_{12}]$

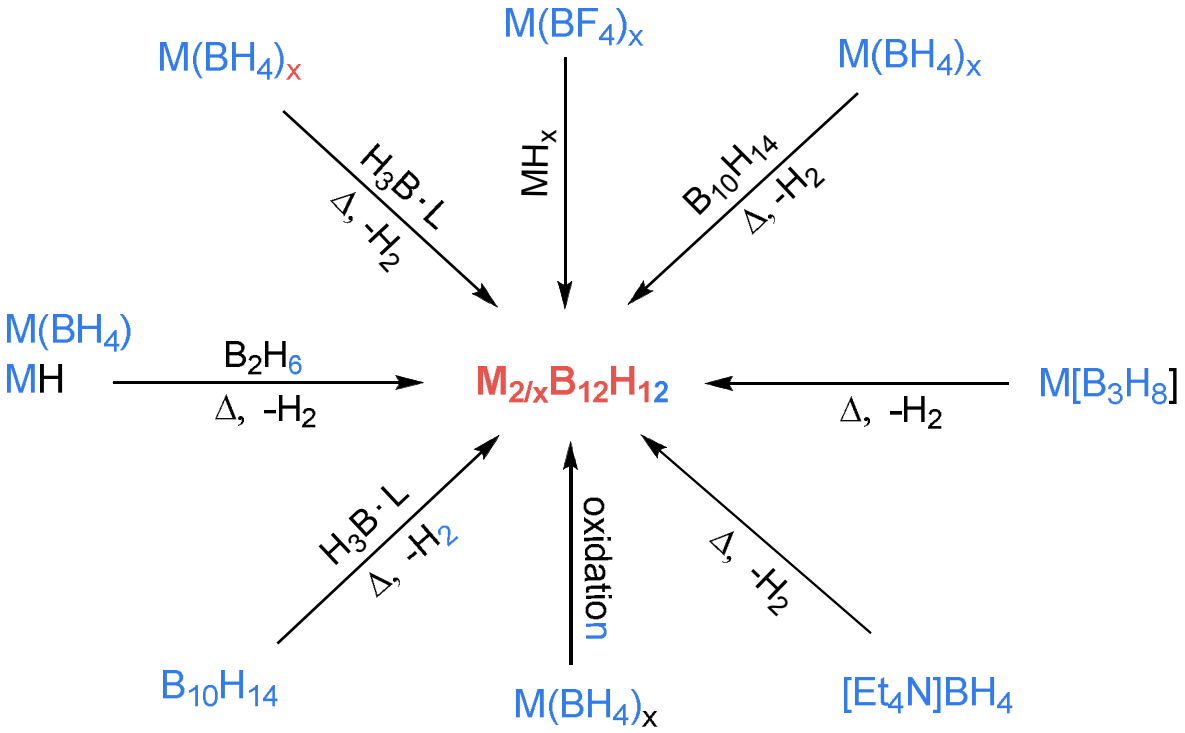




Compound	PEGS Structures	SNL/NIST Data
$Li_2B_{12}H_{12}$	*C*2/*m* (#12)	*Pa*-3
$Na_2B_{12}H_{12}$	$P2_1/n$ (#14)	$P2_1/n$*
$CaB_{12}H_{12}$	*C*2/*c* (#15)	*C*2/*c*
$MgB_{12}H_{12}$	*C*2/*m* (#12)	Amorphous
$Sc_2(B_{12}H_{12})_3$	*Cm* (#8)	Amorphous

J.-H. Her, W. Zhou, V. Stavila, C.M. Brown, T.J. Udovic, *J. Phys. Chem. C,* **2009**, *113*, 11187.

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



- 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*-$B_{12}H_{12}]^{2-}$ compounds

Aqueous solution route

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

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

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

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

Non-aqueous solution routes

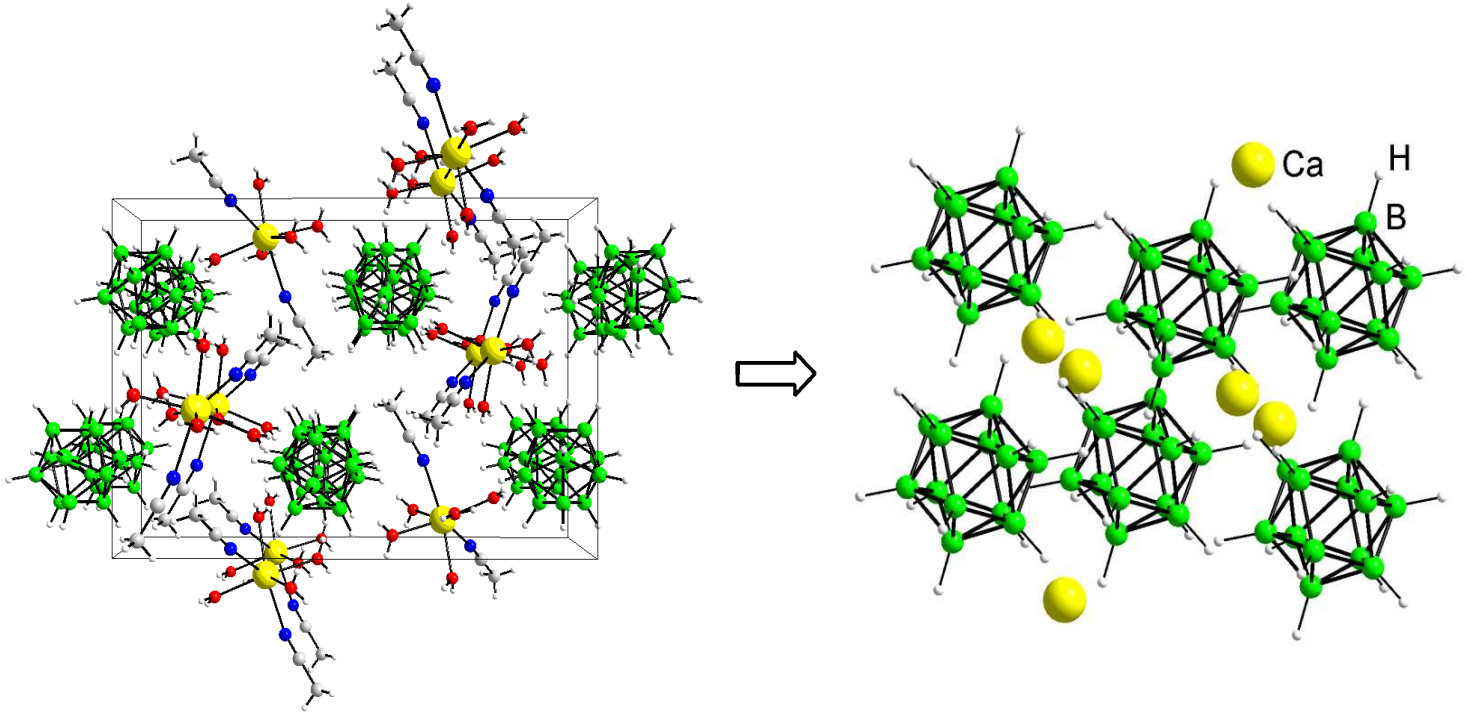
$$M[BH_4]_x \xrightarrow[-H_2]{B_{10}H_{14},\ \Delta} M_{2/x}[B_{12}H_{12}] \qquad \textit{Yield} \geq 64\%$$

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

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

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



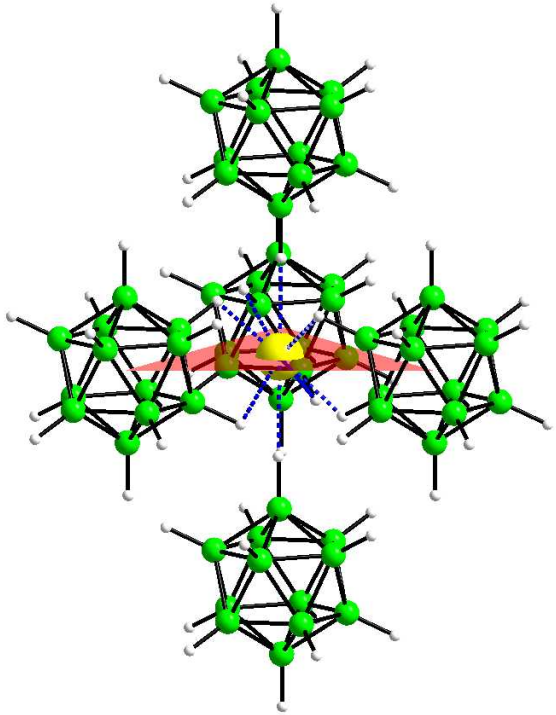
Solvated form *Anhydrous form*

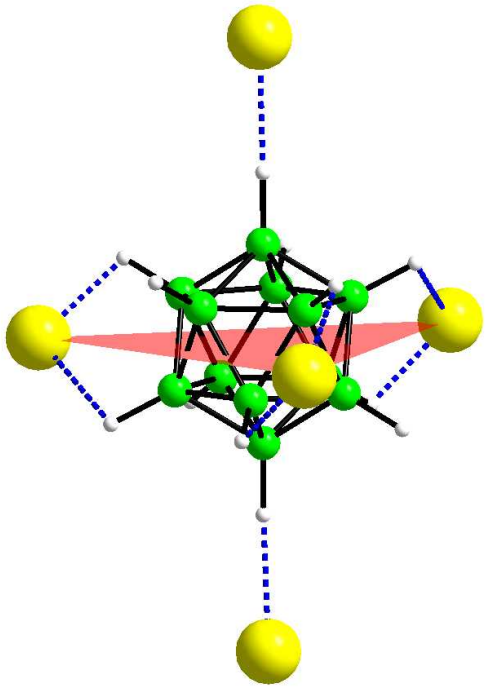
$$[Ca(H_2O)_5(MeCN)_2][B_{12}H_{12}] \xrightarrow[-MeCN,\ -H_2O]{\Delta} CaB_{12}H_{12}$$

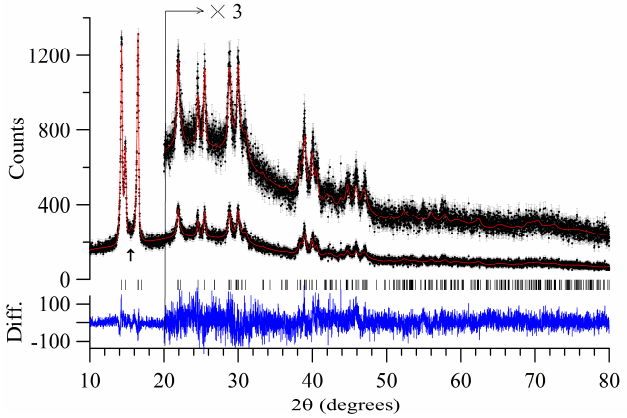
📖 V. Stavila, J.-H. Her, W. Zhou, S. Hwang, Ch. Kim, L.A.M. Ottley, T.J. Udovic, *submitted.*

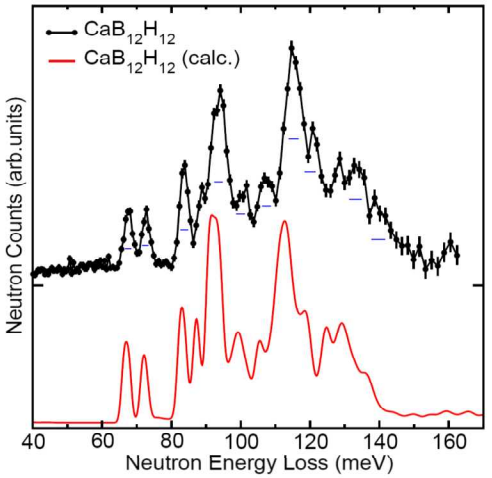
Crystal structure of $CaB_{12}H_{12}$

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







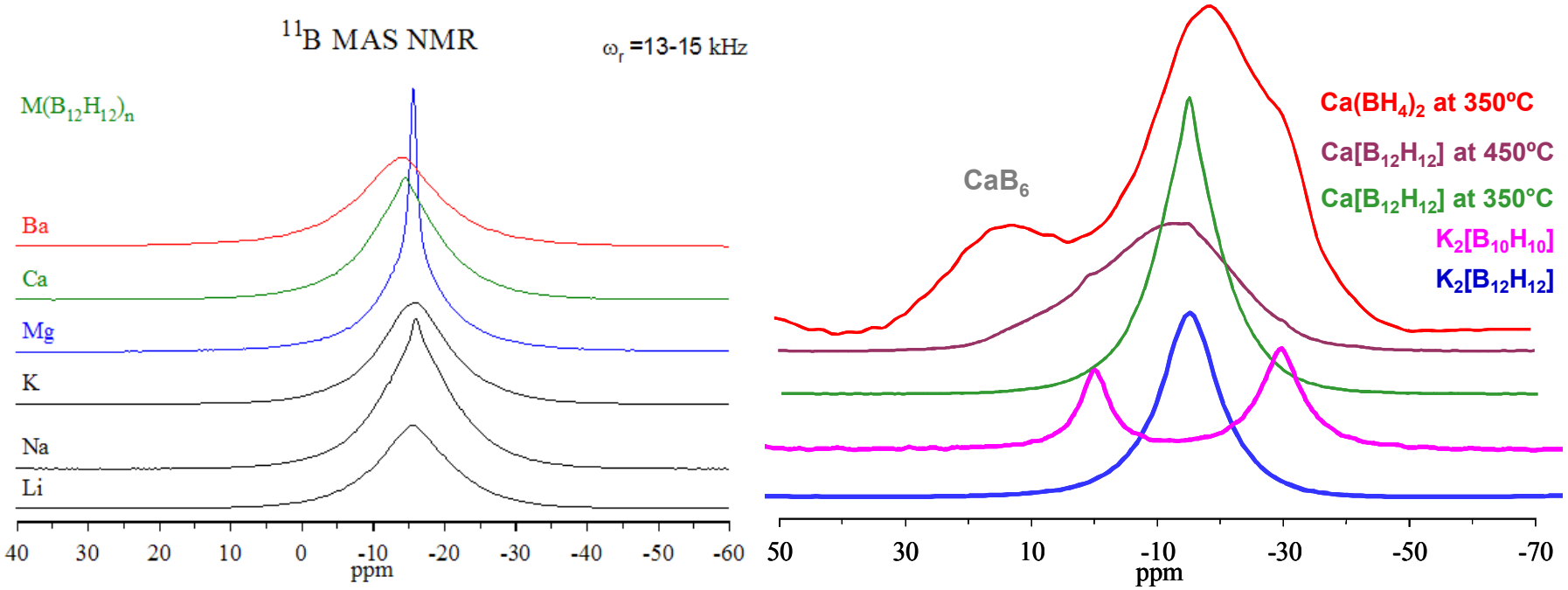


➢ Neutron Vibrational Spectroscopy confirmed the theoretically predicted monoclinic structure

📖 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-earth 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

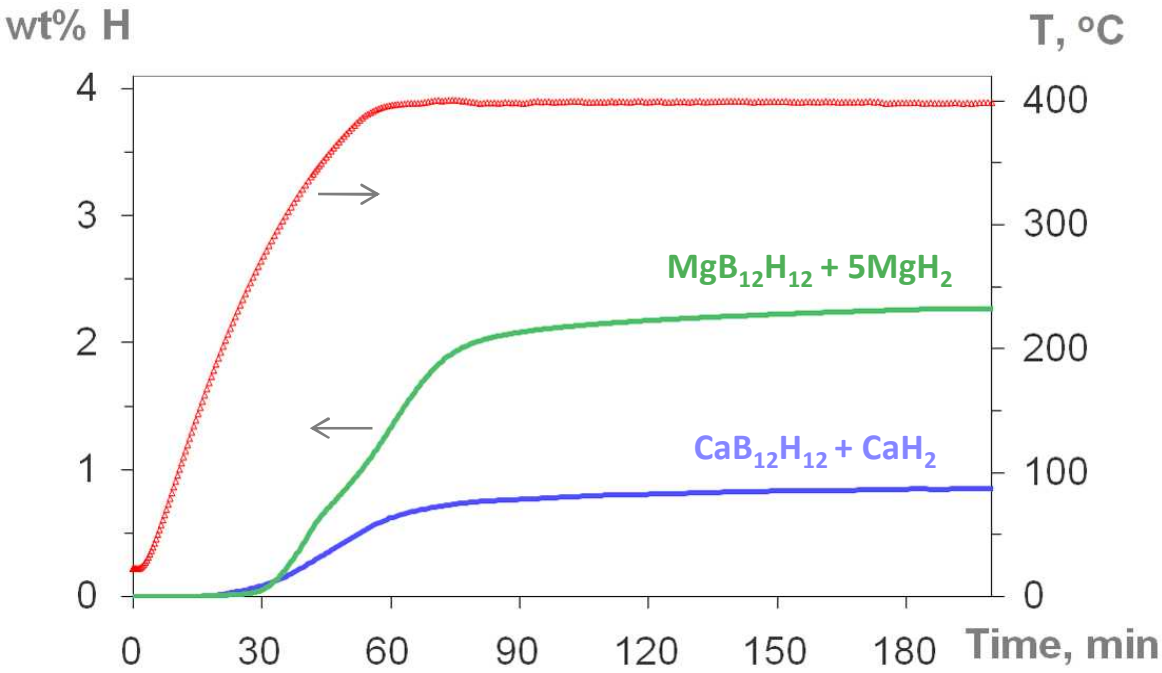
Milling conditions : high-energy, 30-120 min; *Pelletization* : 30 MPa, 5 min
Hot sintering : 70 - 100 MPa H_2 pressure, 400-600 °C, up to 72 hours




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

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

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

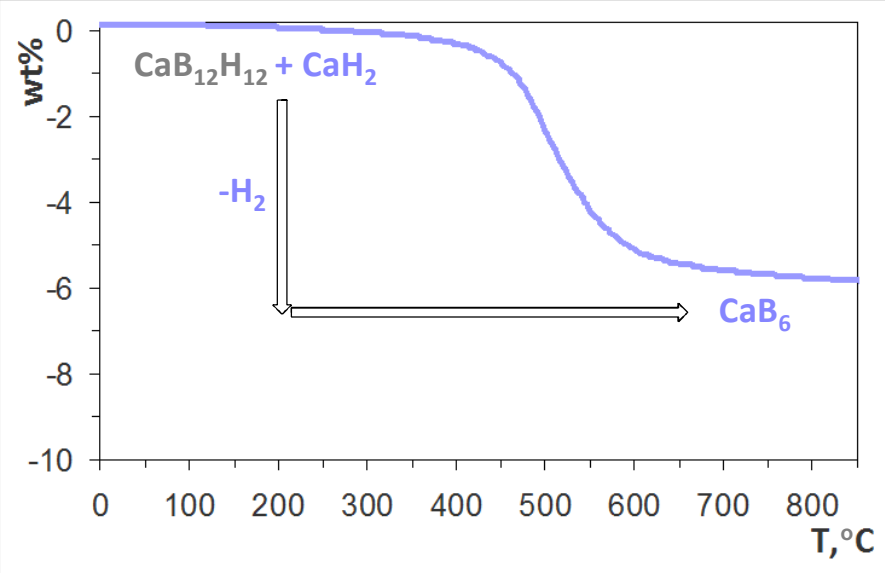


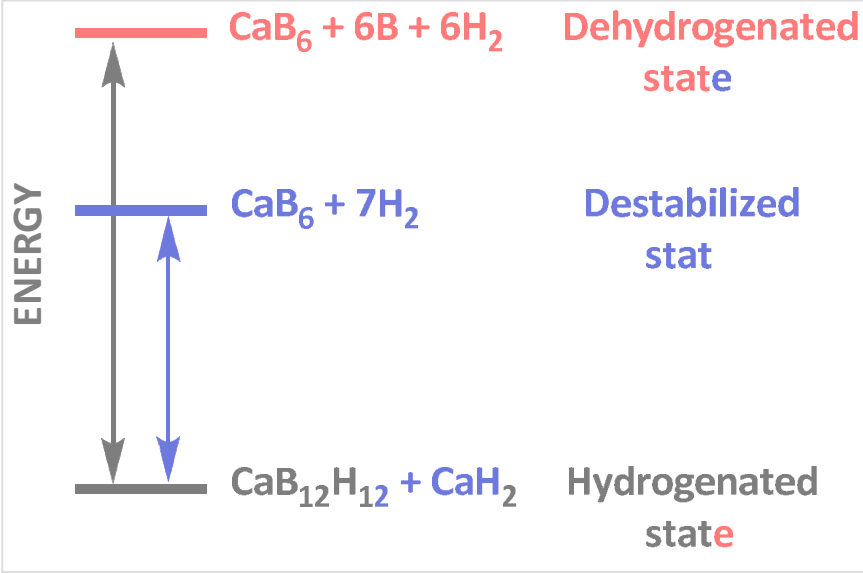
- No crystalline MgB_2 or CaB_6 are formed upon heating up to 400 °C.
- The reactions involving $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$ require high temperatures.

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

$$CaB_{12}H_{12} \xrightarrow{\Delta} \text{no } CaB_6 \text{ up to } 800\ ^oC$$

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





- 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 $LiBH_4$, $Mg(BH_4)_2$ and $Ca(BH_4)_2$ dehydrogenation reactions to form $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$ suggest that the reverse processes may be feasible under mild conditions.

$$Li_2B_{12}H_{12} + 10\ LiH \xrightarrow{+13H} 12LiBH_4 \qquad \Delta H^{300K} = 44.4\ kJ/mol^*$$

$$Na_2B_{12}H_{12} + 10\ NaH \xrightarrow{+13H_2} 12NaBH_4 \qquad \Delta H^{300K} - ?$$

$$MgB_{12}H_{12} + 5\ MgH_2 \xrightarrow{+13H_2} 6Mg(BH_4)_2 \qquad \Delta H^{300K} = 29.3\ kJ/mol^*$$

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

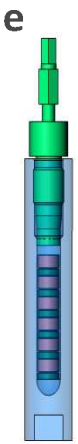
📖 Ozolins, Majzoub, Wolverton, *J. Am. Chem. Soc.*, **2009**, *131*, 230.

'Hot-sintering' under high H_2-pressure

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

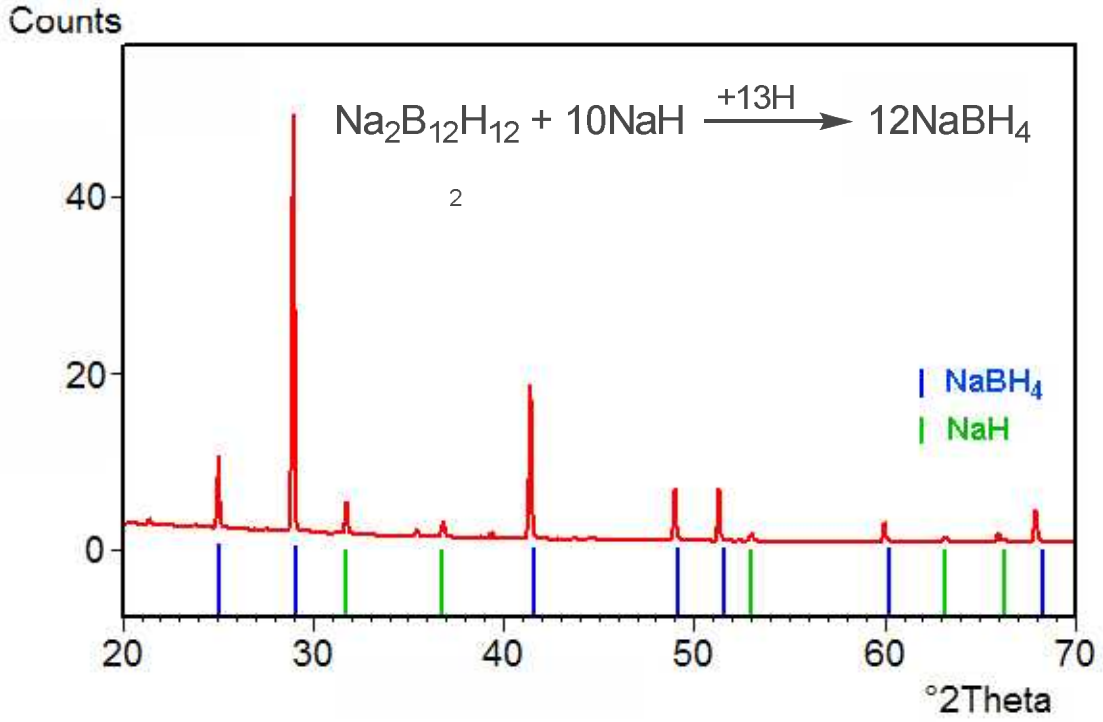
≤ 100 MPa H_2

≤ 550 °C



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

Rehydrogenation of $[B_{12}H_{12}]^{2-}$ salts



Results:

- $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$ – no borohydride formation up to 500 °C and 90 MPa H_2
- $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ – partial hydrogenation to $LiBH_4$ and $NaBH_4$ at 500 °C and 90 MPa H_2

- $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$ are not susceptible to rehydrogenation reactions; the rehydrogenation of $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ occurs only at high temperatures and pressures.
- $[B_{12}H_{12}]^{2-}$ 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*.

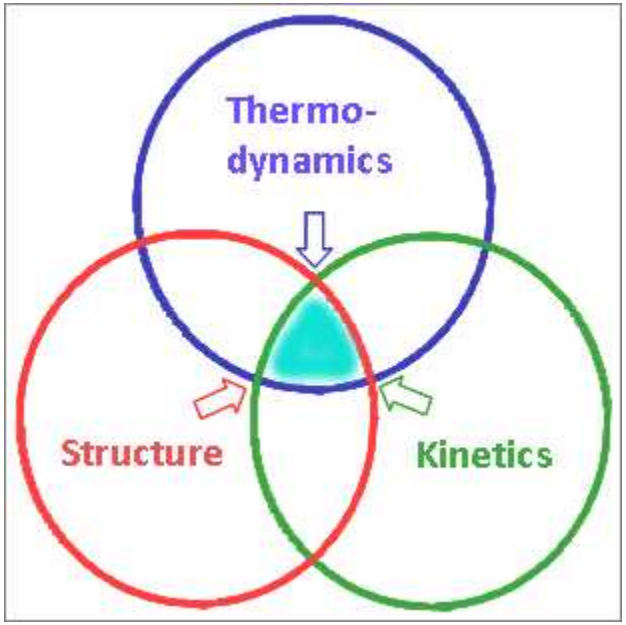
Possible solutions to this problem:

- *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 can occur during the thermal decomposition of metal borohydrides.
- Almost full conversion of $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ salts into corresponding borohydrides was achieved at 500 ^oC and 90 MPa H_2 pressure; under these conditions no notable amounts of $Mg(BH_4)_2$ and $Ca(BH_4)_2$ from $MB_{12}H_{12}$ (M = Mg, Ca) was observed.
- 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.

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