

# Discovery and Development of Metal Borohydrides

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*To be presented by Bjorn Hauback, IFE, Norway, Task22 Coordinator*

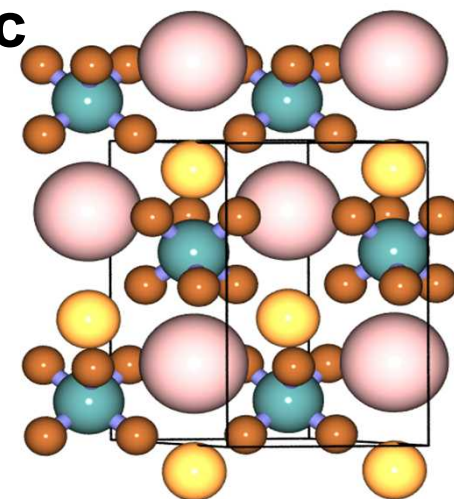
# Content

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- **Hydrogen storage in calcium borohydride:**  
decomposition pathway, reversibility
- **New alkali borohydrides:**  
 $AB(BH_4)_2$ : A and B = Li, Na, K, Ca
- **New transition metal borohydrides**
- **Summary and Future Plans**

# Screening for New H-storage Materials

- High-pressure synthesis (<2000bar, 500°C) and mechanical alloying (E. Rönnebro)
- Theory guidance: Prototype Electrostatic Ground State Search (PEGS) provides minimum energy structures for subsequent enthalpy estimates (E.H. Majzoub and V. Ozolins, PRB, in press)
- Examples of potential structures:
  - Metal borohydrides;  $\text{Mg}(\text{BH}_4)_2$  and  $\text{Ca}(\text{BH}_4)_2$
  - $\text{AB}(\text{BH}_4)_x$  (bialkali borohydrides)
  - Alkali transition metal borohydrides



*PEGS-generated  
Structure*

# Predicting Hydride Thermodynamics

## Database

- Inorganic crystal structure database
- ICSD data base contains 80,000 inorganic structures
- Looking for  $AB_2X_8$  yields ~100 inequivalent test structures

## New Alternative Technique

### PEGS

- Global optimization
- Simulated annealing
- Electrostatic interactions
- $MH_x$  anion is a rigid unit

ICSD

PEGS



Energy of Structure at  $T=0K$

# PEGS Generally Outperforms ICSD Per Formula Unit For Bialkali Alanates

System	Ground state	ICSD 2 f.u.	PEGS 2 f.u.
LiMgAlH <sub>6</sub>	3 f.u.-LiMnGaF <sub>6</sub> (P321)	+5.8	+6.7
NaMgAlH <sub>6</sub>	1 f.u.-RbGeIO <sub>6</sub> (P312)	0	0
KMgAlH <sub>6</sub>	4 f.u.-CsAgAlF <sub>6</sub> (Pnma)	+3.9	+9.6
LiCaAlH <sub>6</sub>	4 f.u.-LiBaCoF <sub>6</sub> (P2 <sub>1</sub> /c)	+12.1	+8.5
NaCaAlH <sub>6</sub>	4 f.u.-KNaSiF <sub>6</sub> (Pnma)	+29.5	+13.1
KCaAlH <sub>6</sub>	4 f.u.-KNaSiF <sub>6</sub> (Pnma)	+39.7	+22.2

E.H. Majzoub, V. Ozolins,  
*Phys. Rev. B*, In press

# New ICSD and PEGS Predictions for Bialkali Alanate Structures And Decomposition Reactions

Reaction	$\Delta H_0$ (kJ/mol H <sub>2</sub> )	Capacity (wt.% H <sub>2</sub> )
$\text{LiMgAlH}_6 \rightarrow \text{MgH}_2 + \frac{2}{3}\text{Al} + \frac{1}{3}\text{Li}_3\text{AlH}_6 + \text{H}_2$	+23.3	3.1
$\text{NaMgAlH}_6 \rightarrow \text{NaMgH}_3 + \text{Al} + \frac{3}{2}\text{H}_2$	+28.0	3.7
$\text{KMgAlH}_6 \rightarrow \text{KMgH}_3 + \text{Al} + \frac{3}{2}\text{H}_2$	+36.0	3.1
$\text{LiCaAlH}_6 \rightarrow \text{CaH}_2 + \text{LiH} + \text{Al} + \frac{3}{2}\text{H}_2$	+33.5	3.7
$\text{NaCaAlH}_6 \rightarrow \text{CaH}_2 + \frac{2}{3}\text{Al} + \frac{1}{3}\text{Na}_3\text{AlH}_6 + \text{H}_2$	+39.8	2.1
$\text{KCaAlH}_6 \rightarrow \text{CaH}_2 + \frac{2}{3}\text{Al} + \frac{1}{3}\text{K}_3\text{AlH}_6 + \text{H}_2$	+63.0	1.8

E.H. Majzoub, V. Ozolins,  
*Phys. Rev. B*, In press

T=0K, no phonon calculations

# Calcium Borohydride

# New Solid-state Synthesis of $\text{Ca}(\text{BH}_4)_2$

**Motivation: Theory predicts  $\text{Ca}(\text{BH}_4)_2$  has promising thermodynamics ( $\Delta H \sim 53 \text{ kJ/mol}$ ), 9.6 wt. %**



- Specific solid state reaction route:
  - ✓ Additive is crucial
  - ✓ High-energy ball milling (SPEX)
  - ✓ Heat-treatment under high  $\text{H}_2$ -pressures
  - ✓ Yield of product:  $\sim 75\%$

*Ewa Rönnbro and Eric Majzoub, J. Phys. Chem. B, 111 (2007) 12045.*

Notes: Other recently reported solid-state routes:

- $2\text{LiBH}_4 + \text{CaCl}_2 \rightarrow \text{Ca}(\text{BH}_4)_2 + 2\text{LiCl}$  (Nakamori, Orimo et al, J. Alloys Compd)
- $\text{MgB}_2 + \text{CaH}_2 + 4\text{H}_2 \rightarrow \text{Ca}(\text{BH}_4)_2 + \text{MgH}_2 \gg 8.3 \text{ wt\% calc}$  (Dornheim, Klassen et al, J. Alloys Compd)

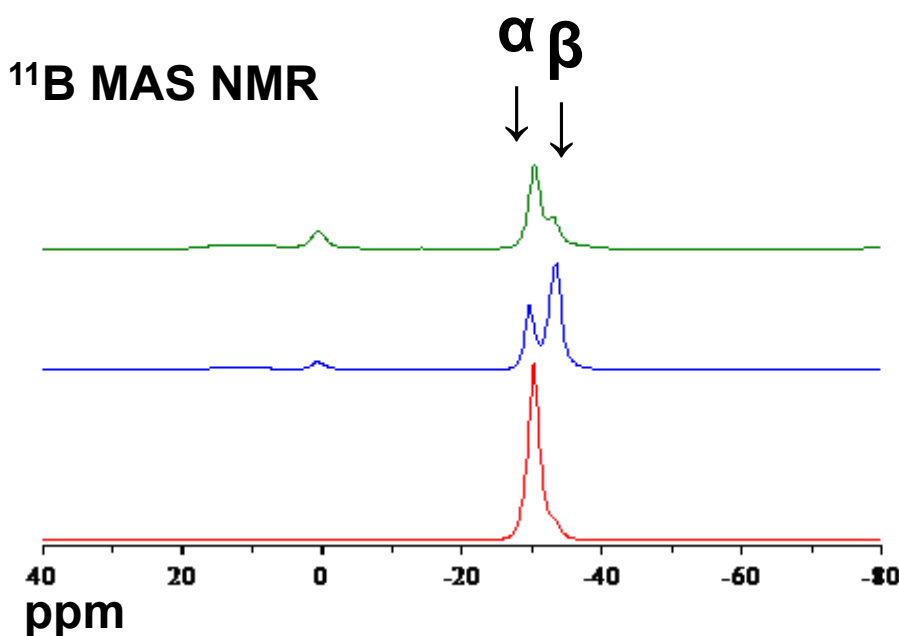


## Alternative $\text{Ca}(\text{BH}_4)_2$ Preparation Route

- Aldrich  $\text{Ca}(\text{BH}_4)_2(\text{THF})_2$  desolvated by heating up to  $\sim 150^\circ\text{C}$  in vacuum
- Yield is 100%
- Formation of polymorphs  $\alpha$  or  $\beta$  is depending on reaction conditions and size of sample
- Larger sample and longer reaction time results in more  $\beta$

# Ca(BH<sub>4</sub>)<sub>2</sub> Polymorphs at Room Temperature

## Nuclear Magnetic Resonance



Mixture α and β  
XRD: α:β 60:40

Mixture α and β  
XRD: α:β 50:50

'Pure' α  
XRD: α:β 95:5

Samples  
prepared by  
heating Aldrich  
Ca(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub>  
under vacuum

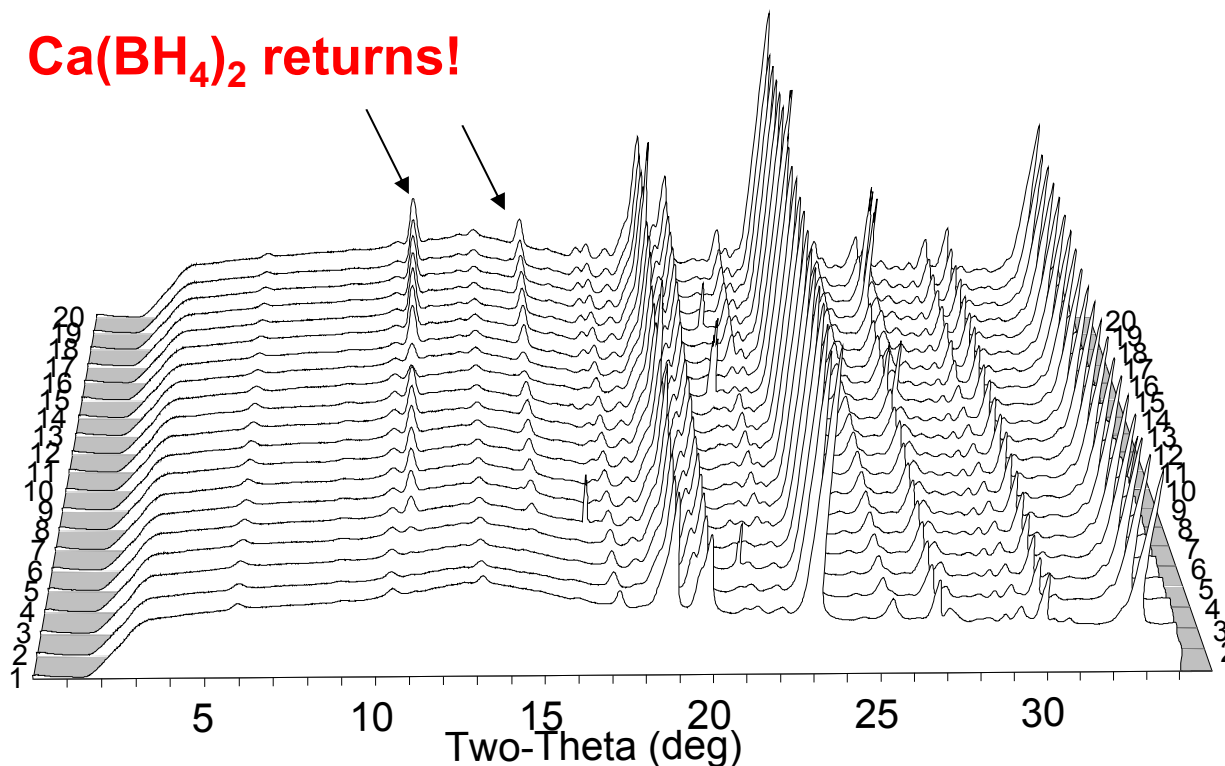
Ratio of α and β forming after 'desolvation process'  
depends on sample size, temperature and reaction time.

# Re-hydriding $\text{Ca}(\text{BH}_4)_2$ After Desorption

$\text{Ca}(\text{BH}_4)_2$  made at 700bar and 400°C

*In-situ synchrotron at Brookhaven, NSLS, beamline X7B*

**$\text{Ca}(\text{BH}_4)_2$  returns!**

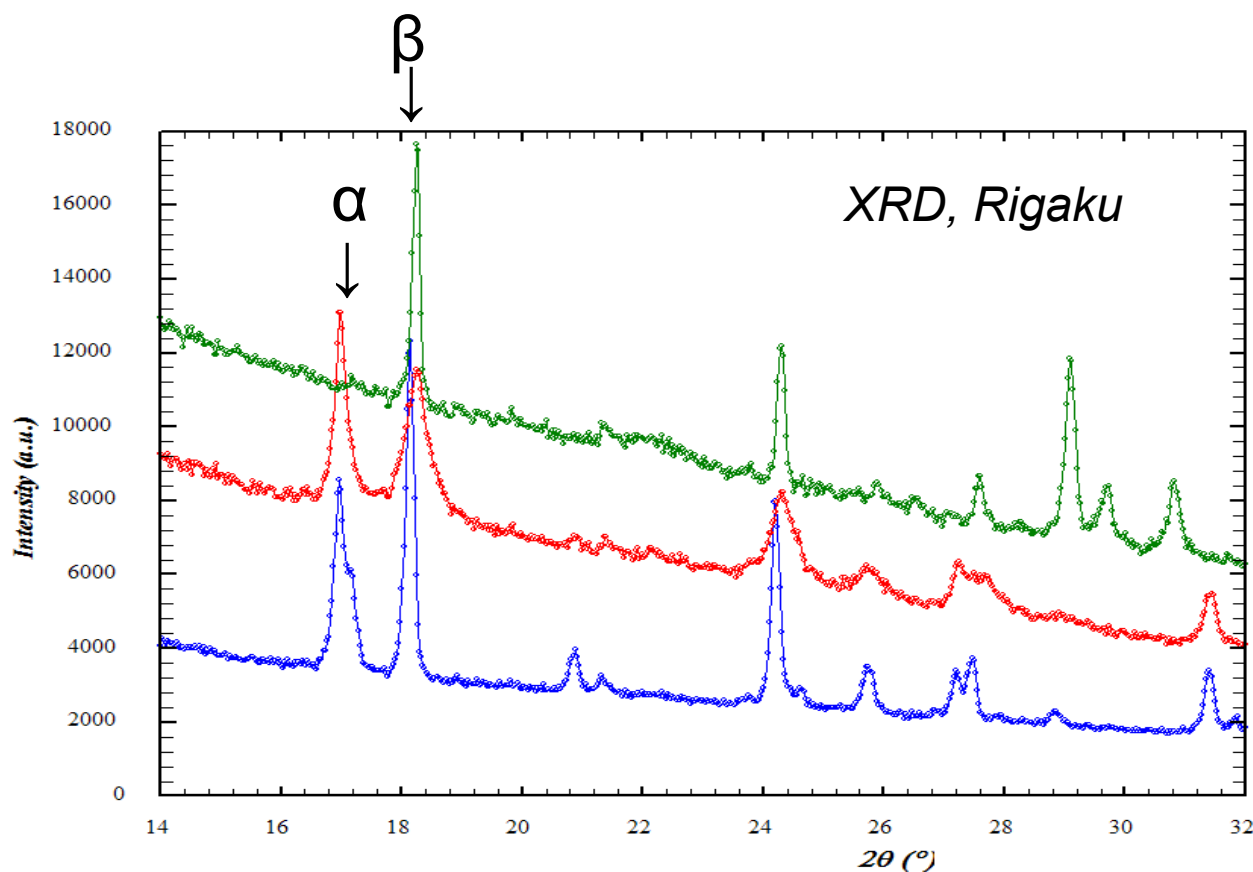


Job Rijssenbeek et al

**It was possible to re-hydride the sample @ 350°C & 1600 psi  $\text{H}_2$  after first quenching the desorbed sample**

# Studies of Reversibility of $\text{Ca}(\text{BH}_4)_2$

$\text{Ca}(\text{BH}_4)_2$  made by desolvating an Aldrich sample



$\alpha'$  and  $\beta$   
decompose  
into  $\text{CaB}_6$ , B  
and/or  
 $\text{CaB}_{12}\text{H}_{12}$   
(NMR in  
evaluation)

Re-hydrated

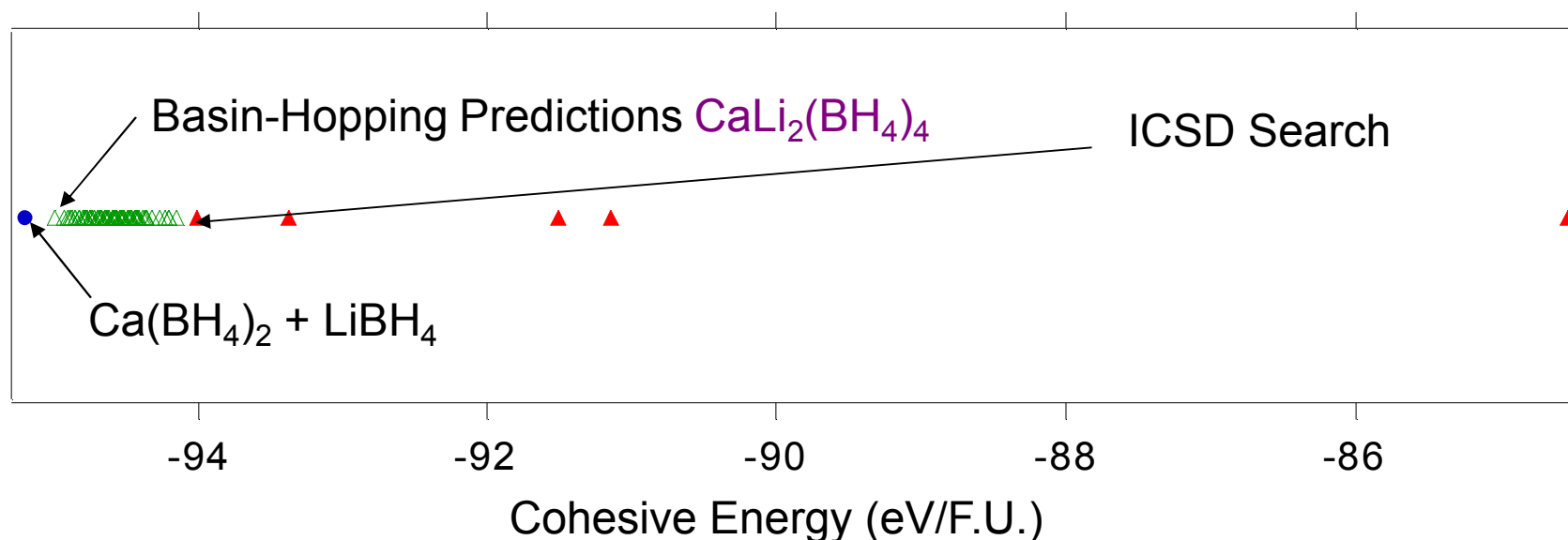
SPEX milled

Desolvated

Kinetics studies show ~7wt%  
desorbed and ~5wt% re-hydrated

# Alkali Borohydrides

# $\text{CaLi}_2(\text{BH}_4)_4$ is Unstable w.r.t. Separate Borohydrides

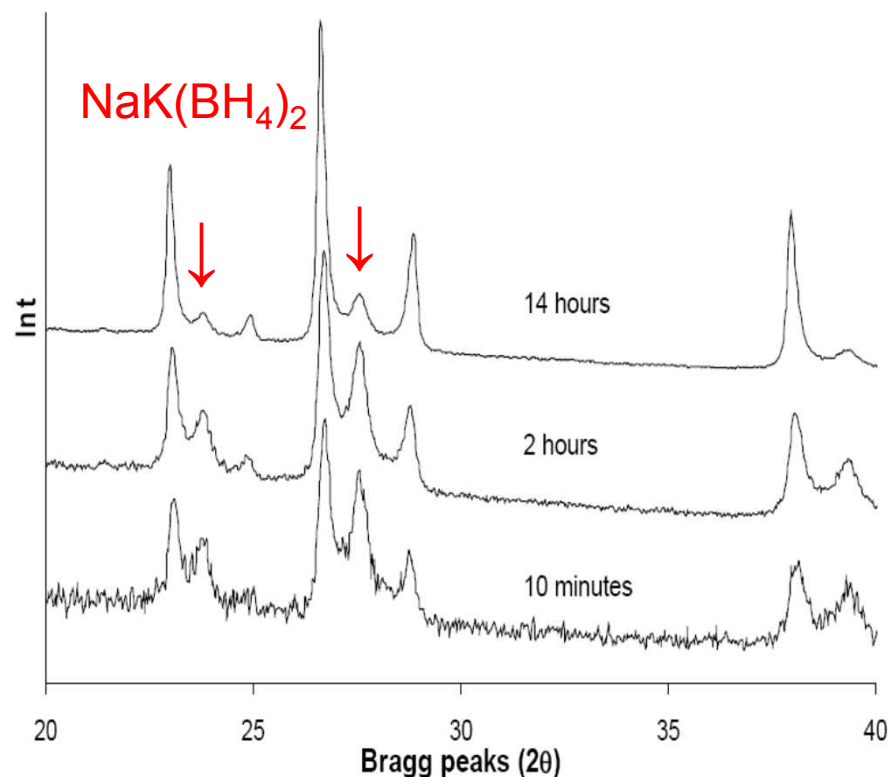


- Monte Carlo basin hopping easily beats the ICSD search
- Unfortunately, the lowest energy structure is unstable w.r.t. to phase separation to  $\text{Ca}(\text{BH}_4)_2$  and  $\text{LiBH}_4$

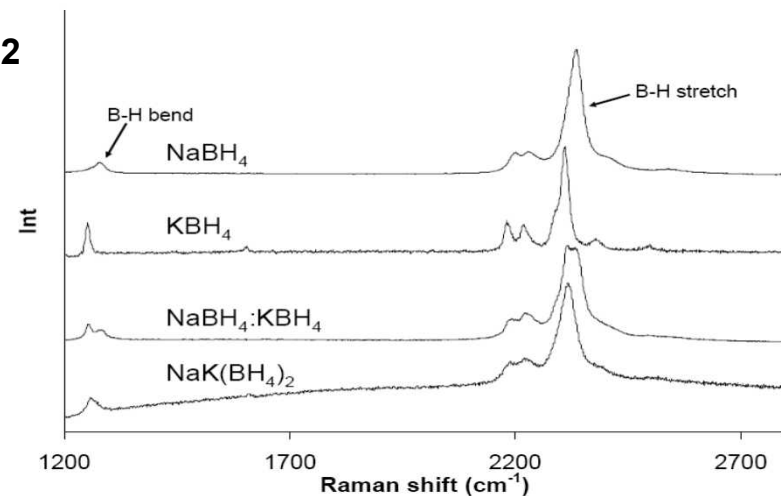
***$\text{CaLi}_2(\text{BH}_4)_4$  is not a first choice for synthesis attempts***

# Synthesis of $\text{NaK}(\text{BH}_4)_2$

Ball milling:  $\text{NaBH}_4 + \text{KBH}_4 \rightarrow \text{NaK}(\text{BH}_4)_2$

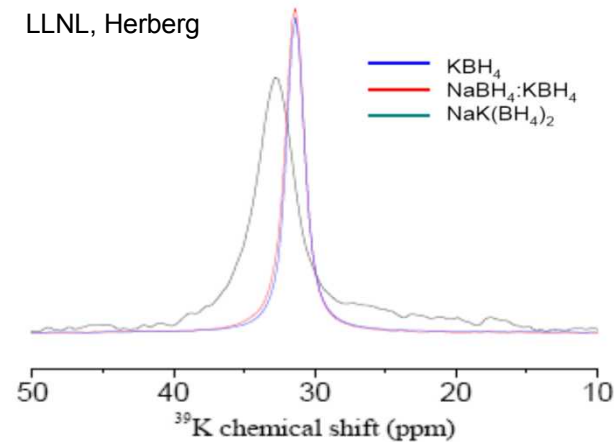


XRD pattern shows decomposition  
to:  $\text{NaK}(\text{BH}_4)_2 \rightarrow \text{NaBH}_4 + \text{KBH}_4$



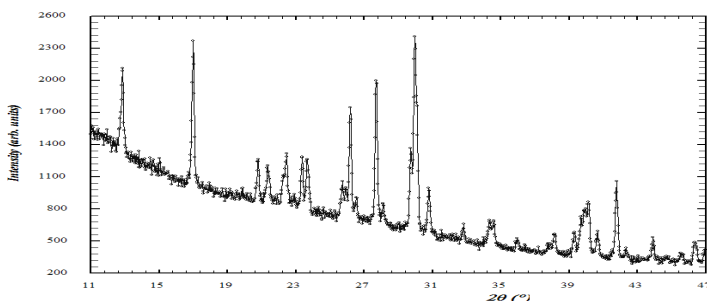
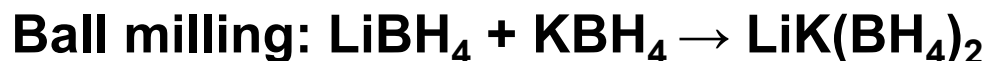
## Raman Spectroscopy

LLNL, Herberg



$^{39}\text{K}$  MAS-NMR

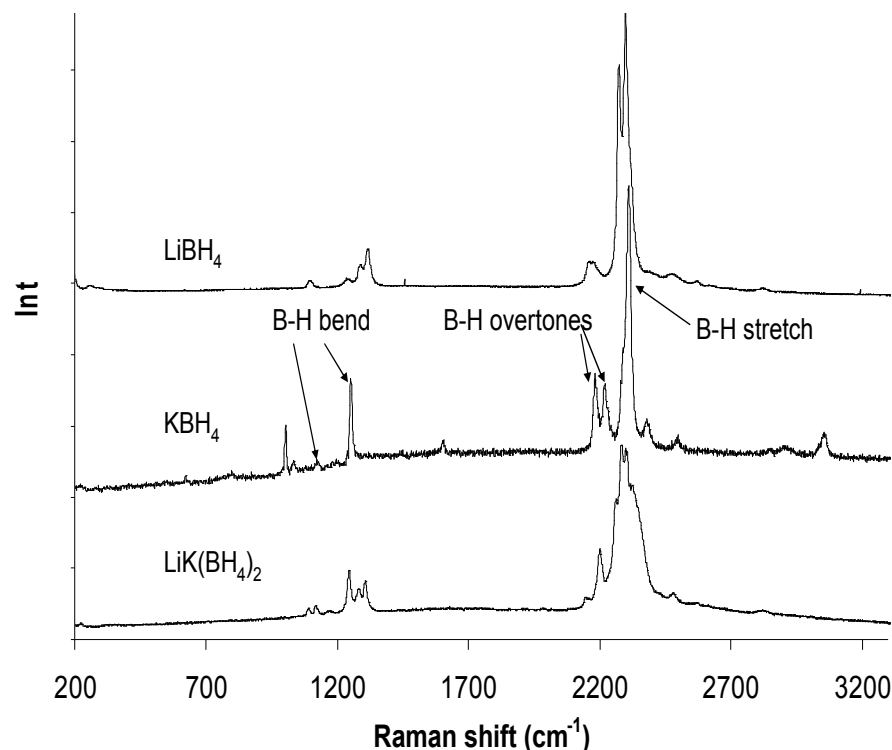
# Synthesis of $\text{LiK}(\text{BH}_4)_2$



❖ XRD (in-house) shows new phase plus ~10%  $\text{KBH}_4$

❖ Structure: unit cell with double c-axis as compared to  $\text{LiBH}_4$

❖ TGA did not show weight loss before 500°C



Raman Spectroscopy



# Alkali Transition Metal Borohydrides

U. Hawaii (Jensen et al) and Sandia (Rönnebro et al)

## ➤ Synthesis

- React metal borides with alkali/alkali earth binary hydrides (similar to  $\text{Ca}(\text{BH}_4)_2$  synthesis)

## ➤ Experimental

- High-energy ball milling (SPEX)
- High-pressure/temperature treatment (<2000bar, <500°C)

## ➤ Characterization

- XRD: amorphous materials
- DSC and TGA show new phase transitions and H-weight loss
- FTIR and NMR identifies new species

# Future Borohydride Plans

## Calcium Borohydride

- Thermodynamics, kinetics and cycle life to be explored
- Optimize re-hydriding conditions at *lower* pressures
- Explore impact of additives on required T, P for use
- Assess  $B_2H_6$  release upon  $H_2$  desorption

## Bialkali And Other Borohydrides

- Explore bialkali borohydrides guided by MC theory
- Explore reversibility of other metal borohydrides at our high-hydrogen pressure facility in collaboration with U. Hawaii (Jensen *et al*) and GE (Zhao *et al*)

# Future Work

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## ***Borohydrides***

- Synthesize bialkali borohydrides and explore reversibility of (Ca, Mg, Sc, Ti, Al etc) borohydrides based on theoretical predictions

## ***Synthesis of New Complex Anionic Materials***

- Discover new complex anionic materials from theoretical modeling

## ***Nanoengineering***

- Design nanostructured high-capacity materials to improve reversible performance
- Extend PEGS model to address nanoparticle thermodynamics for complex anionic hydrides

# Acknowledgements

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## **Sandians:**

*Eric Majzoub (now UMLS), Dennis Morrison, Ken Stewart, Ray Baldonado, Mutlu Kartin, Vitalie Stavila, Jay Keller, Lennie Klebanoff, Marcina Moreno, Blake Simmons*

## **MHCoE:**

*Bob Bowman (JPL), Son-Jong Hwang (Caltech), Chul Kim (Caltech), Channing Ahn (Caltech), Dhanesh Chandra (U. Nevada, Reno), Terry Udovic (NIST), Zak Fang (U. Utah), John Vajo (HRL), Don Anton (SRNL), J.-C. Zhao (GE), Craig Jensen (UH), Dan Mohser (UTRC)*

*Funding provided by 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*