

Discovery and Development of Metal Borohydrides

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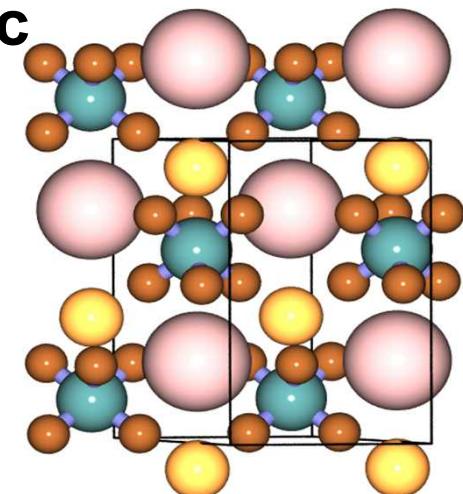
To be presented by Bjorn Hauback, IFE, Norway, Task22 Coordinator

Content

- **Hydrogen storage in calcium borohydride:** decomposition pathway, reversibility
- **New bialkali 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; $Mg(BH_4)_2$ and $Ca(BH_4)_2$
 - $AB(BH_4)_x$ (bialkali borohydrides)
 - Alkali transition metal borohydrides



PEGS-generated
Structure

Predicting Hydride Thermodynamics

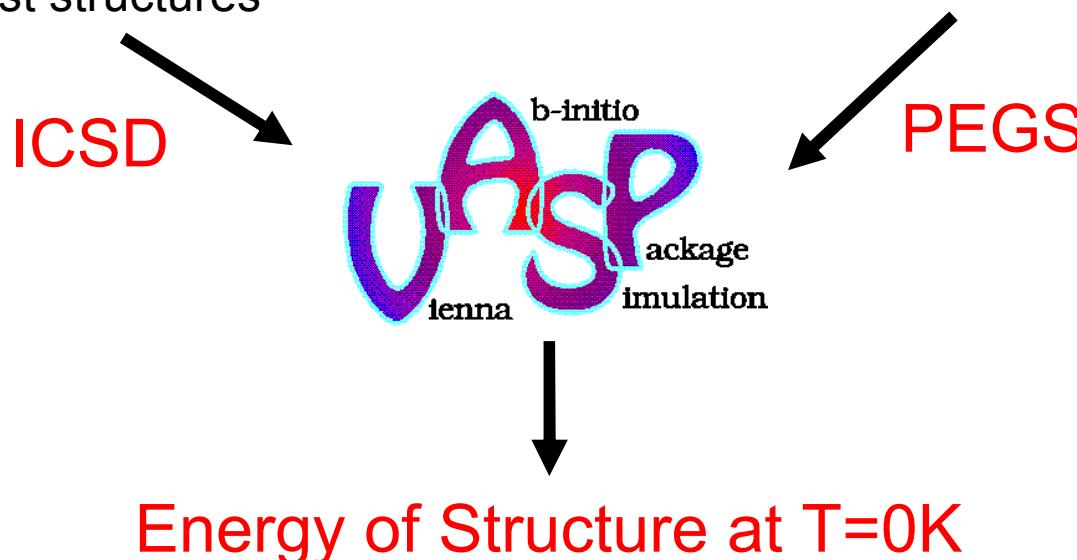
Database

- 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

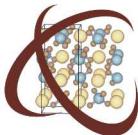
- Global optimization
- Simulated annealing
- Electrostatic interactions
- MH_x anion is a rigid unit



PEGS Generally Outperforms ICSD Per Formula Unit For Bialkali Alanates

| System | Ground state | ICSD 2 f.u. | PEGS 2 f.u. |
|----------------------|--|-------------|-------------|
| LiMgAlH ₆ | 3 f.u.-LiMnGaF ₆ (P321) | +5.8 | +6.7 |
| NaMgAlH ₆ | 1 f.u.-RbGeIO ₆ (P312) | 0 | 0 |
| KMgAlH ₆ | 4 f.u.-CsAgAlF ₆ (Pnma) | +3.9 | +9.6 |
| LiCaAlH ₆ | 4 f.u.-LiBaCoF ₆ (P2 ₁ /c) | +12.1 | +8.5 |
| NaCaAlH ₆ | 4 f.u.-KNaSiF ₆ (Pnma) | +29.5 | +13.1 |
| KCaAlH ₆ | 4 f.u.-KNaSiF ₆ (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 | ΔH_0 (kJ/mol H ₂) | Capacity (wt.% H ₂) |
|--|--|------------------------------------|
| $\text{LiMgAlH}_6 \rightarrow \text{MgH}_2 + \frac{2}{3}\text{Al} + \frac{1}{3}\text{Li}_3\text{AlH}_6 + \text{H}_2$ | +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 H_2 -pressures
 - ✓ Yield of product: ~75%

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

Notes: Other recently reported solid-state routes:

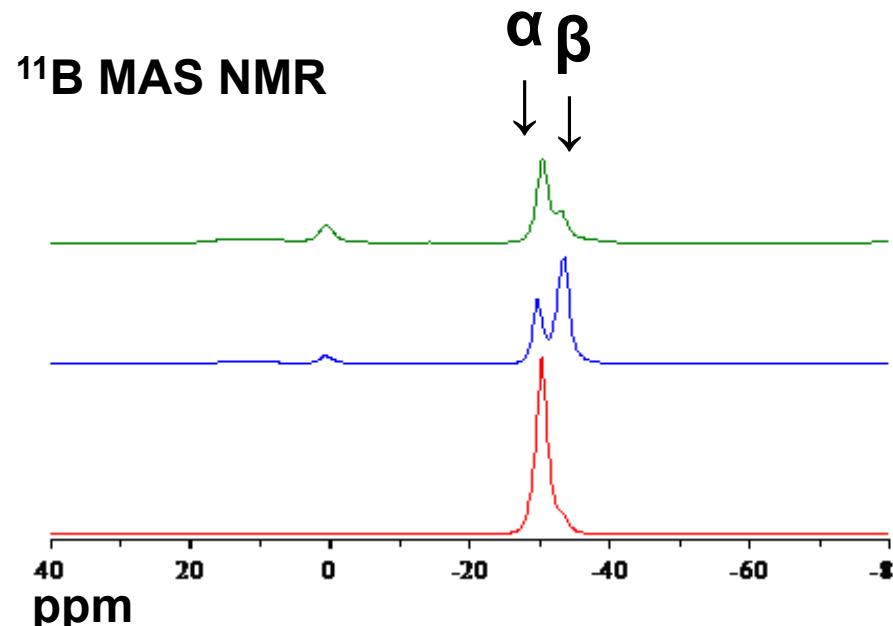
- $2\text{LiBH}_4 + \text{CaCl}_2 \rightarrow \text{Ca}(\text{BH}_4)_2 + 2\text{LiCl}$ (Nakamori, Orimo et al, J. Alloys Compd) 8
- $\text{MgB}_2 + \text{CaH}_2 + 4\text{H}_2 \rightarrow \text{Ca}(\text{BH}_4)_2 + \text{MgH}_2 \rightarrow 8.3 \text{ wt\% calc}$ (Dornheim, Klassen et al, J. Alloys Compd)

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 α or β is depending on reaction conditions and size of sample
- Larger sample and longer reaction time results in more β

Ca(BH₄)₂ 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(BH₄)₂(THF)₂ under vacuum

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

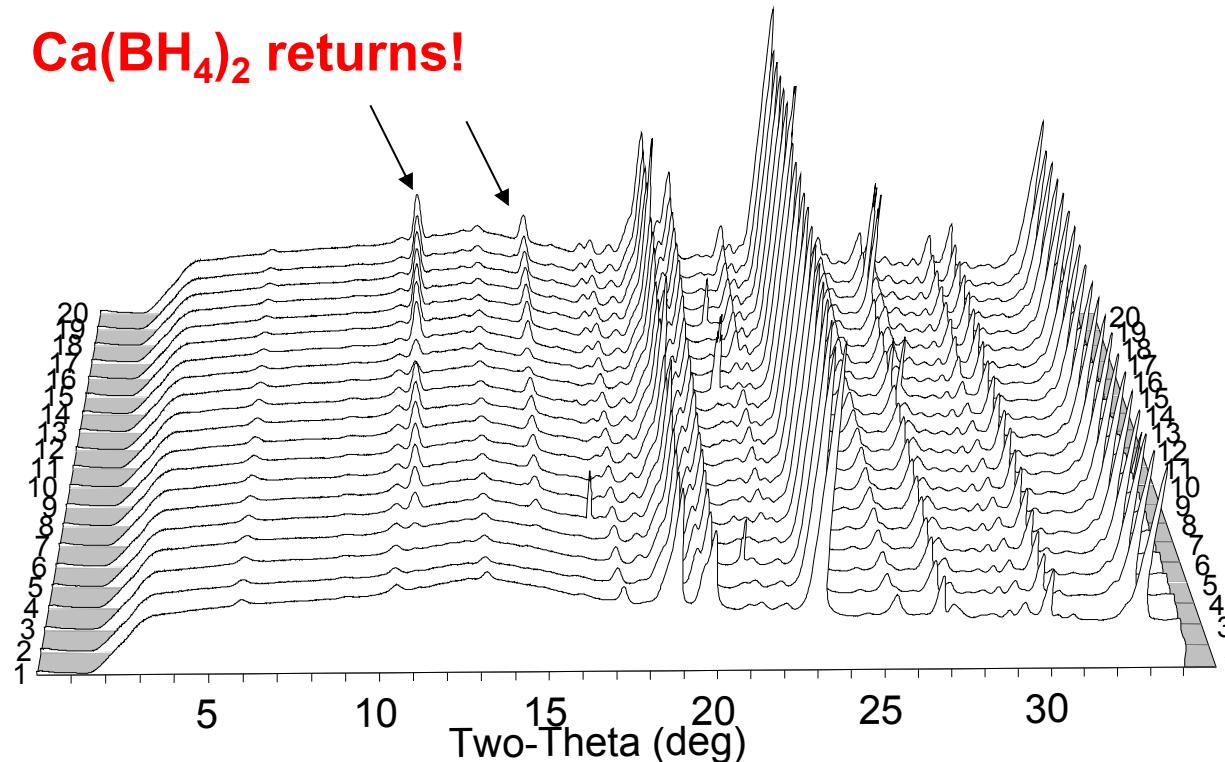


Re-hydriding $\text{Ca}(\text{BH}_4)_2$ After Desorption

$\text{Ca}(\text{BH}_4)_2$ 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

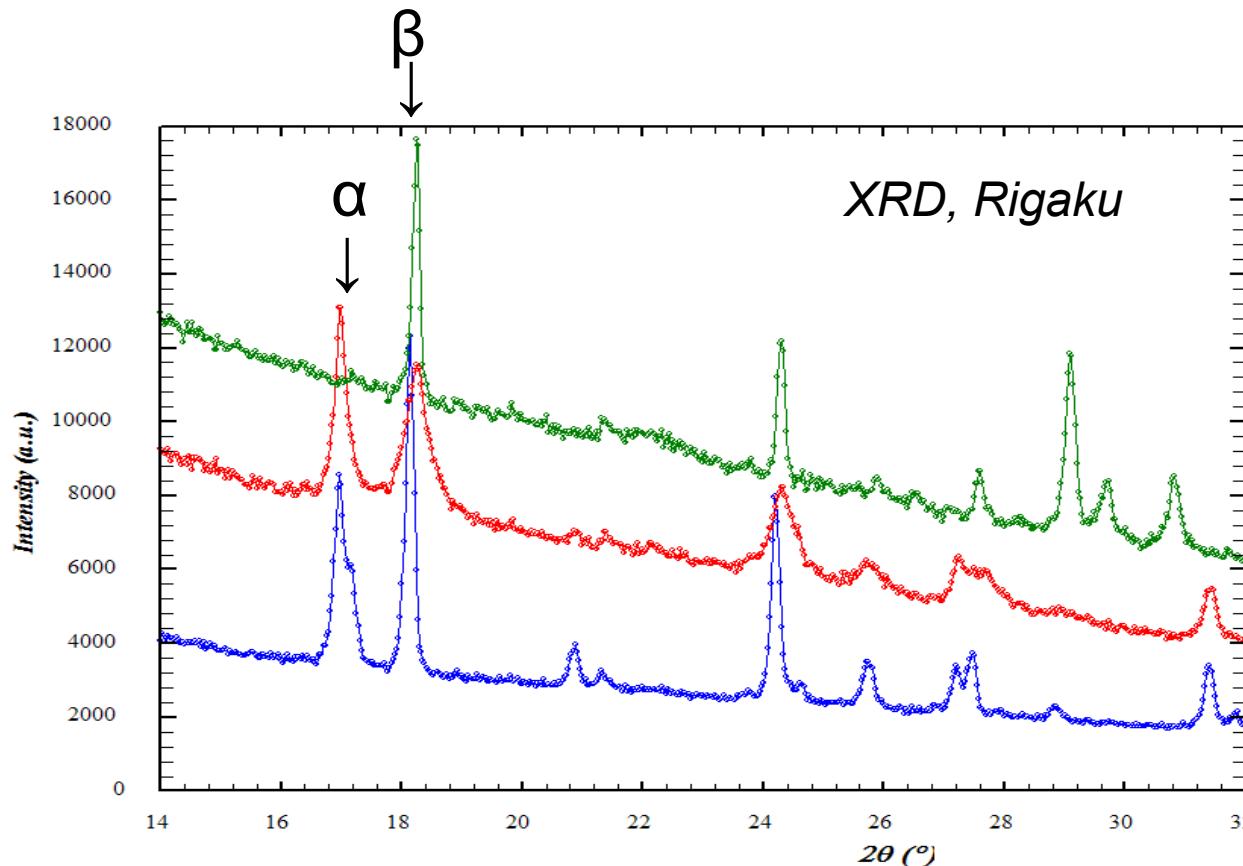


imagination at work

It was possible to re-hydride the sample @ 350°C & 1600 psi H_2 after first quenching the desorbed sample

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

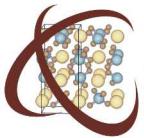
$\text{Ca}(\text{BH}_4)_2$ made by desolvating an Aldrich sample



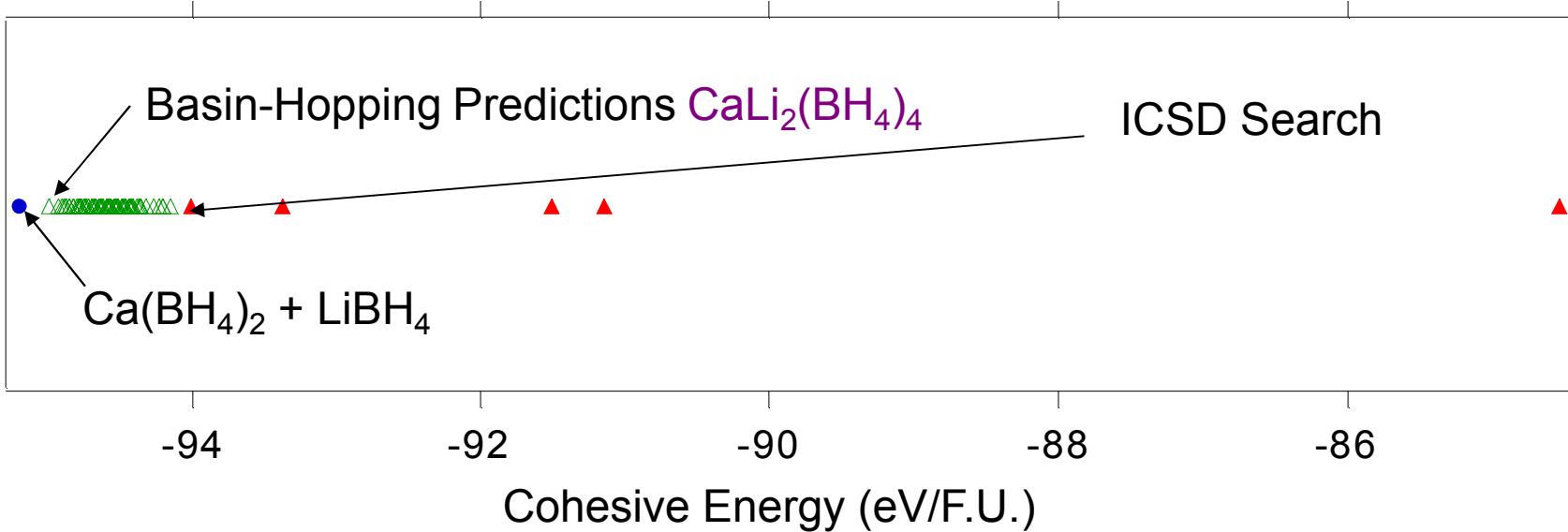
α' and β decompose into CaB_6 , B and/or $\text{CaB}_{12}\text{H}_{12}$ (NMR in evaluation)

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

Bialkali Borohydrides



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

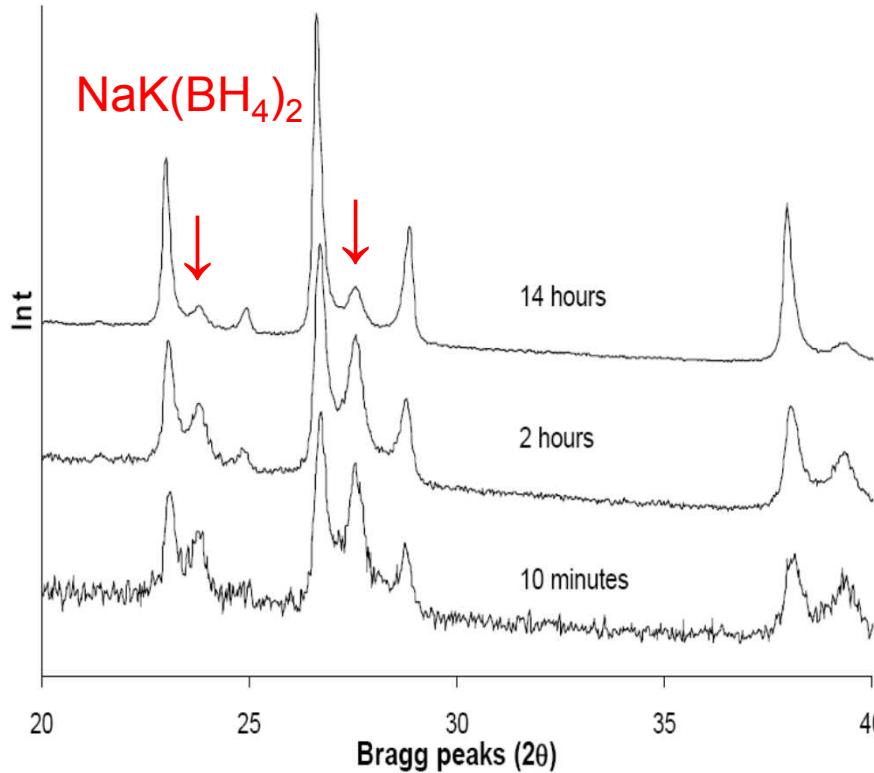


- Monte Carlo basin hopping easily beats the ICSD search
- Unfortunately, the lowest energy structure is unstable w.r.t. to phase separation to $\text{Ca}(\text{BH}_4)_2$ and LiBH_4

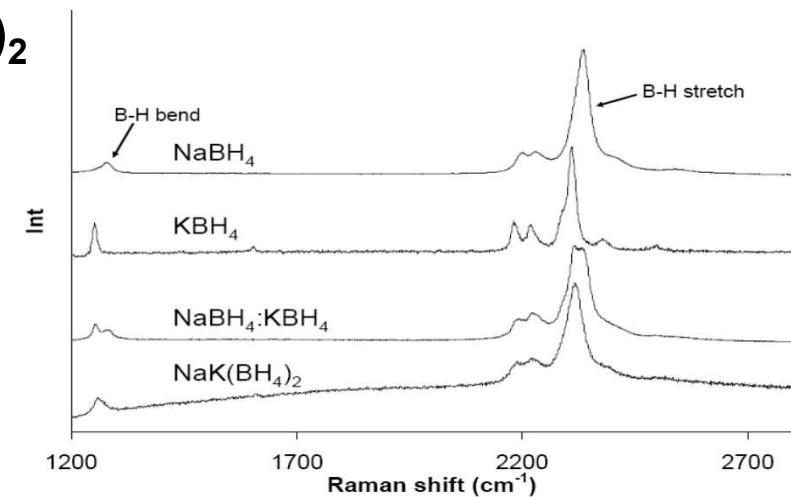
$\text{CaLi}_2(\text{BH}_4)_4$ is not a first choice for synthesis attempts

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

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

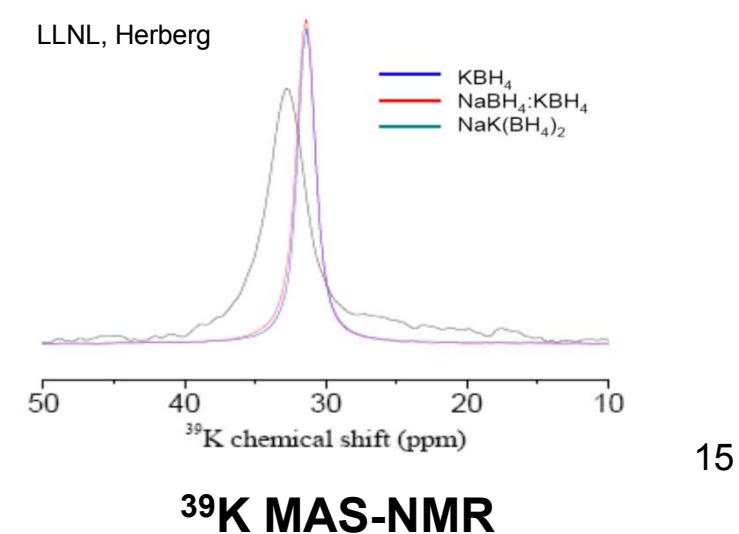


XRD pattern shows decomposition to: $\text{NaK}(\text{BH}_4)_2 \rightarrow \text{NaBH}_4 + \text{KBH}_4$



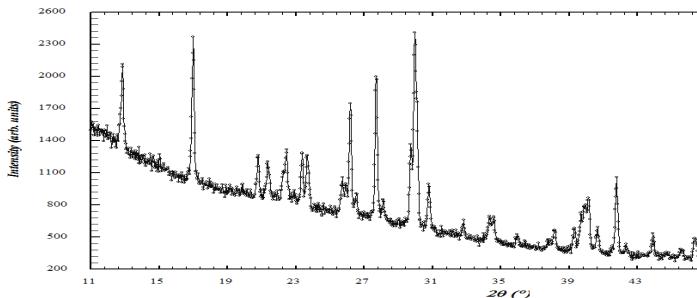
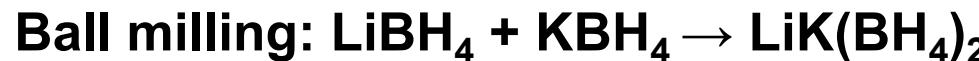
Raman Spectroscopy

LLNL, Herberg

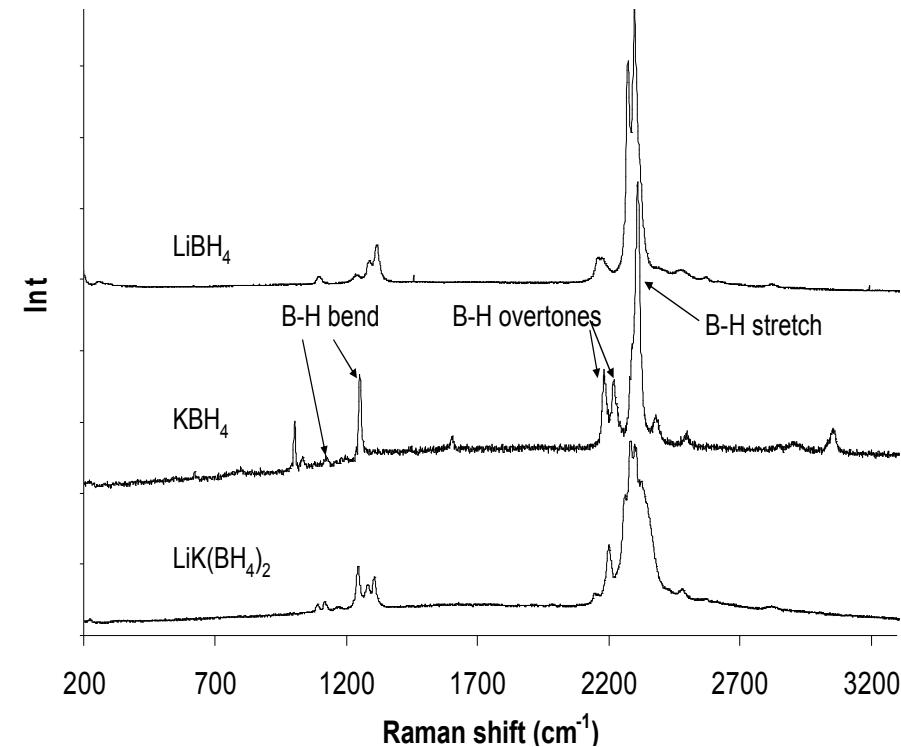


³⁹K MAS-NMR

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



- ❖ XRD (in-house) shows new phase plus ~10% KBH_4
- ❖ Structure: unit cell with double c-axis as compared to 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

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

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