



# Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Metal Hydrides

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University of Nevada, Reno (*UNR*)

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ST 37

## *Timeline*

**Project start date – FY05**

**Project end date – FY10**

**Percent complete – ~60%**

## *Budget*

**Total project funding (5yrs.) : \$ 1.5 M  
(Requested)**

**DOE share (5yrs.) : \$ 1.2 M**

**Contractor share (5yrs.) : \$ 301 K**

**Funding received in FY07 : \$ 520 K  
(Includes funding for major equipment)**

**Funding received in FY08 : \$ 250 K**

## *Barriers Addressed*

- **The effect of trace impurities on materials**
- **Poor mechanistic understanding of some materials**
- **Lack of characterization of material volatilization**

## *Partners*

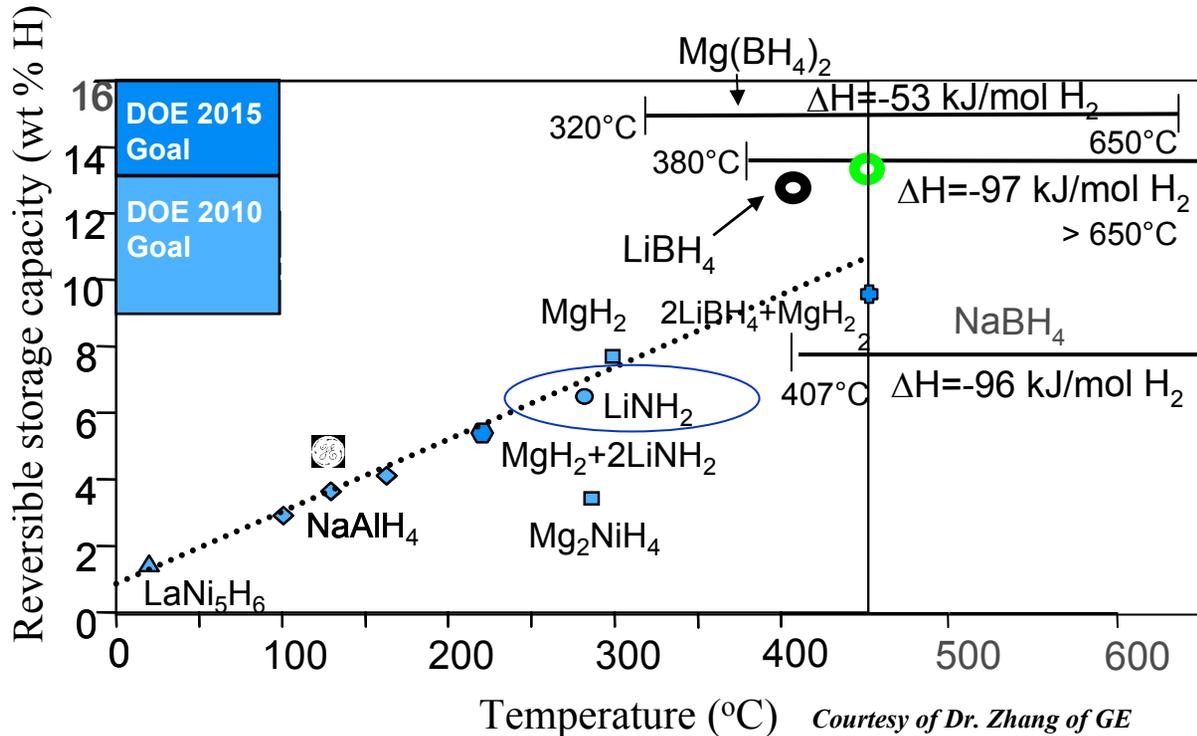
- **SNL – Ewa Rönnebro**
- **GE – Dr. J.C. Zhao (Now at Ohio State)**
- **ESRF, Grenoble , France – Yaroslav Filinchuk**
- **Univ. of Utah, - Dr. Z. Fang**

<p><b>Overall Objective</b></p>	<p><b><u>UNR's Focus Areas:</u></b></p> <ul style="list-style-type: none"> <li>➤ I. The primary objective of the UNR Project is to <u>determine the effects of gaseous trace impurities</u> such as O<sub>2</sub>, CO, H<sub>2</sub>O, CH<sub>4</sub> etc. in H<sub>2</sub> on long-term behavior of the complex hydrides/precursors by pressure cycling and/or thermal aging with impure H<sub>2</sub>.</li> <li>➤ II. Secondary related objectives: (a) Vaporization behavior of hydrides (b) Crystal Structure studies</li> </ul>
<p><b>2006</b></p>	<ul style="list-style-type: none"> <li>➤ Constructed high pressure (up to 100 bar) cycling equipment.</li> <li>➤ Performed hydrogen cycling studies on amide-imide and mixed alanates.</li> <li>➤ Vapor pressure behavior of Li<sub>3</sub>N and Mg(BH<sub>4</sub>)<sub>2</sub> initiated.</li> <li>➤ HP DSC experiments, in-situ neutron, and x-ray diffraction studies</li> </ul>
<p><b>2007 (May, 15 2007- April 1, 2008)</b></p>	<ul style="list-style-type: none"> <li>➤ <b><i>Thermodynamic Studies:</i></b> <ul style="list-style-type: none"> <li>A. <b><u>Extrinsic Hydrogen Charging/Discharging effects:</u></b> Determined the effects of gaseous impurities in hydrogen on Li<sub>2</sub>NH-LiNH<sub>2</sub> and other systems.</li> <li>B. <b><u>Vaporization Thermodynamics:</u></b> Worked on Mg Borohydride, and identified vapor species at moderate temperatures.</li> </ul> </li> <li>➤ <b><i>Crystal Structure Studies:</i></b> In-situ phase transformation studies on Ca(BH<sub>4</sub>)<sub>2</sub></li> </ul>

## Significance of Amide-Imide Studies

1.  $\text{Li}_2\text{NH-LiNH}_2 \rightarrow$  total capacity of  $\sim 10.5$  wt.% hydrogen, but currently  $\sim 5.6$  wt.% is reversible. Further studies may lead to increased capacities
2.  $\text{LiNH}_2\text{-Li}_3\text{AlH}_6 \rightarrow$  Mixed Amide-Alanates

are important because of their theoretical  $\sim 7$  wt.% hydrogen storage capacity



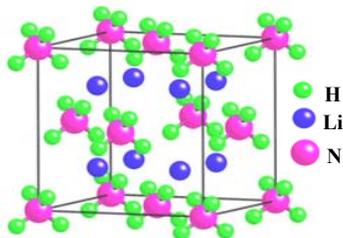
## Significance of $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ Studies

1.  $\text{Mg}(\text{BH}_4)_2 \rightarrow$   $\sim 15$  wt.%  $\text{H}_2$  capacity with  $\Delta H \sim -53 \text{ kJ/mol}$
2.  $\text{Ca}(\text{BH}_4)_2 \rightarrow$  Potential candidate for hydrogen storage candidate
3.  $\text{Mg}(\text{BH}_4)_2$  and  $\text{Ca}(\text{BH}_4)_2 \rightarrow$  Vapor Pressures are important to understand vaporization during evacuation cycle of the hydriding/dehydriding.

# Pressure Cycling Li-N-H

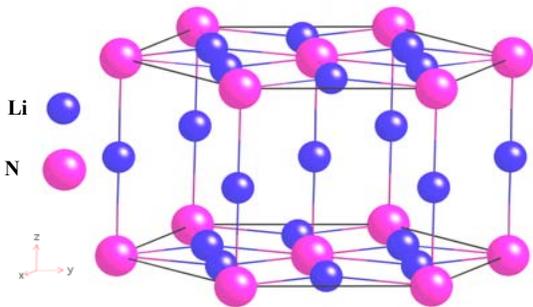
$\text{Li}_2\text{ND}$  - Cubic -  $\text{Fm-}3\text{m}$  -  $Z = 4$   
 $a = 5.0476 \text{ \AA}$ ,  $\text{Vol} = 128.602 \text{ \AA}^3$

$\text{Li}_2\text{NH}$

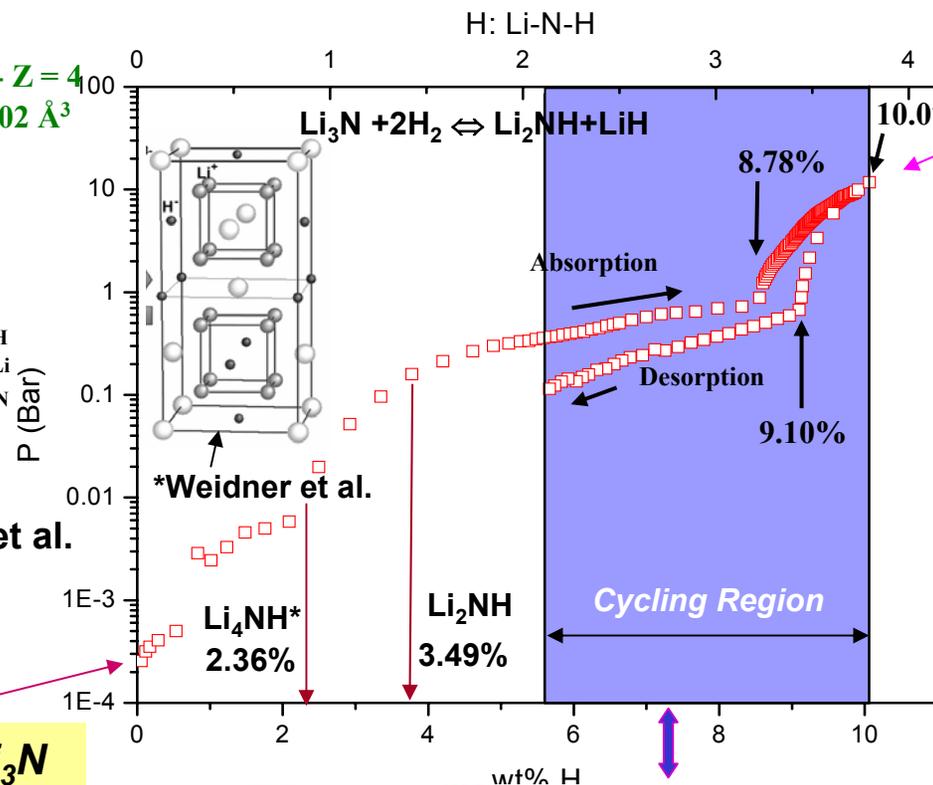


T. Noritake, Orimo, et al.  
*J. Alloys Compds.*  
 393 (2005),  
 264-268.

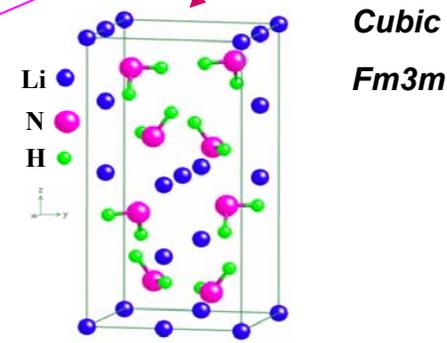
$\text{Li}_3\text{N}$



$\alpha\text{-Li}_3\text{N}$  - Hexagonal  
 $\text{P6}/\text{mmm}$  -  $Z = 1$   
 $a = 3.6587 \text{ \AA}$ ,  $c = 3.876 \text{ \AA}$   
 $\text{Vol} = 44.933 \text{ \AA}^3$



$\text{LiNH}_2 + \text{LiH}$



$\text{LiNH}_2$  -  $\text{BCTI-4}$  -  $Z = 8$   
 $a = 5.0695 \text{ \AA}$ ,  
 $c = 10.2599 \text{ \AA}$   
 $\text{Vol} = 263.68 \text{ \AA}^3$

K. Miwa, N. Ohba, S. Towata, Y. Nakamori, and S. Orimo  
*Physical Review*,  
 B71(2005), 195109.

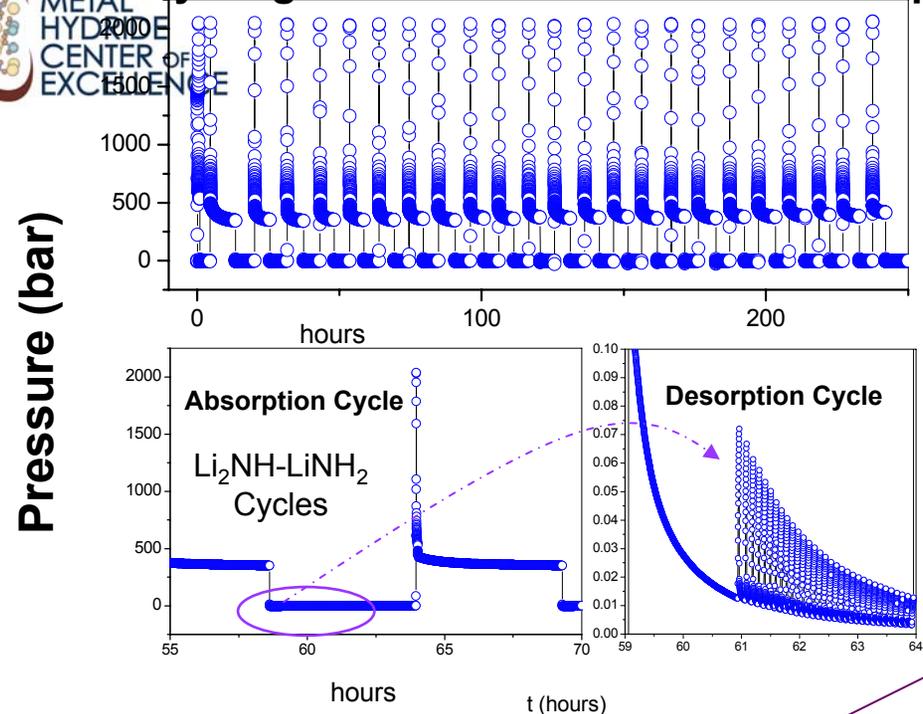
\*Weidner, E., D.K. Ross, et al. *Chemical Physics Letters*, 2007. 444(1-3): p. 76-79.

# Cycling Data of Imide-Amide with 100 ppm CH<sub>4</sub> in UHP Hydrogen



METAL HYDRIDE CENTER OF EXCELLENCE

This cycling data from CH<sub>4</sub> - H<sub>2</sub>

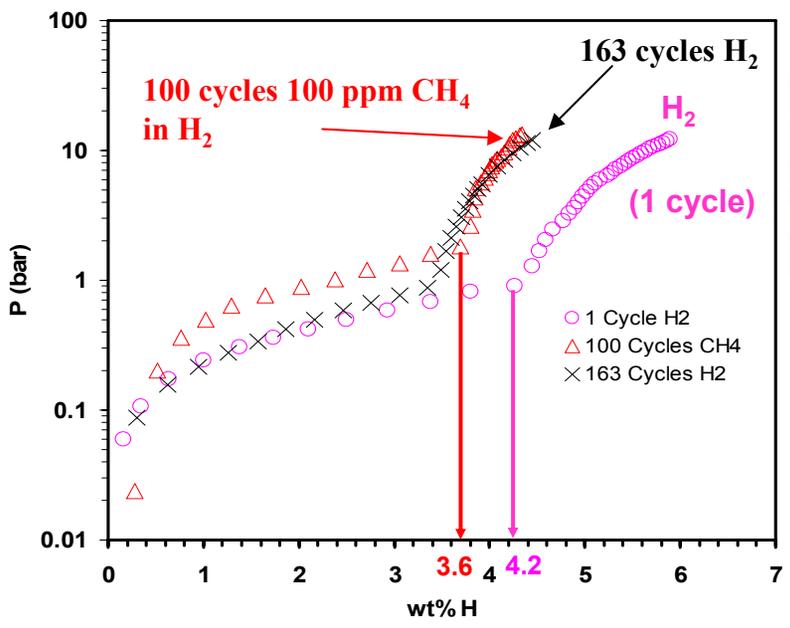


## Objective

To assess Loss in Hydrogen Capacity after Pr. cycling Nominally for ~100 cycles

## Experiments

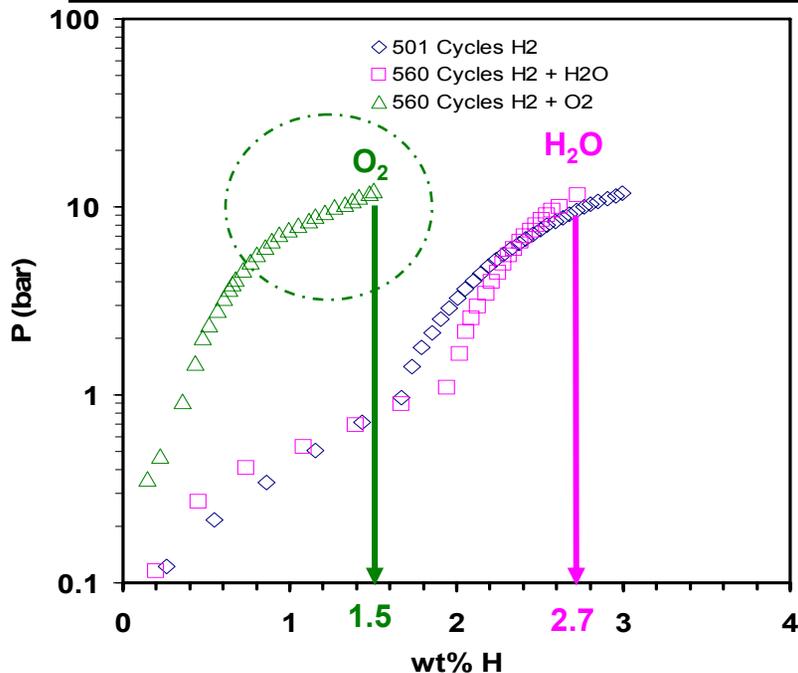
1. Li<sub>2</sub>NH ↔ LiNH<sub>2</sub> Pressure Cycled ~ 20 atm/vacuum at 225°C. Top-left
2. Absorption/desorption Isotherms (up to ~12 bar) using the Sieverts apparatus



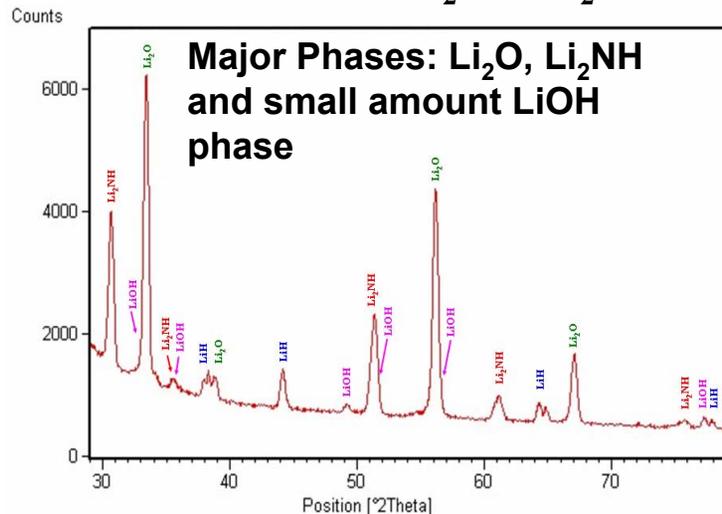
## Summary

➤ **Effect of 100 ppm CH<sub>4</sub> in H<sub>2</sub> :**  
**About 0.7 wt.% H<sub>2</sub> capacity was lost after 100 pressure cycles.**  
**There was virtually no change in kinetic behavior**

# Effect of O<sub>2</sub> and H<sub>2</sub>O in H<sub>2</sub> Cycling between Li<sub>2</sub>NH-LiNH<sub>2</sub>



## X-ray Diffraction Pattern - 560 Cycles with 100 ppm H<sub>2</sub>O in H<sub>2</sub>



Li<sub>2</sub>NH: Cubic (Fm-3m)

LiH: Cubic (Fm-3m)

Li<sub>2</sub>O (MAJOR): Cubic (Fm-3m)

LiOH (small Fraction): Tetragonal (P4/nmm)

### Results:

➤ **Thermodynamics:** After ~500 Pressure cycles at 225°C → remaining Hydrogen capacity is 1.5wt.% (with O<sub>2</sub> additions) and 2.7 wt.% out of ~5.6 wt.% with H<sub>2</sub>O (total reversible capacity).

➤ **Cycling of Li<sub>2</sub>NH ↔ LiNH<sub>2</sub> with Industrial hydrogen** Water ~32 ppm, O<sub>2</sub>~10ppm showed ~2.6% hydrogen loss (500 cycles under similar cycling conditions)

**Loss in Capacity** due to formation Li<sub>2</sub>O, and LiH and LiOH

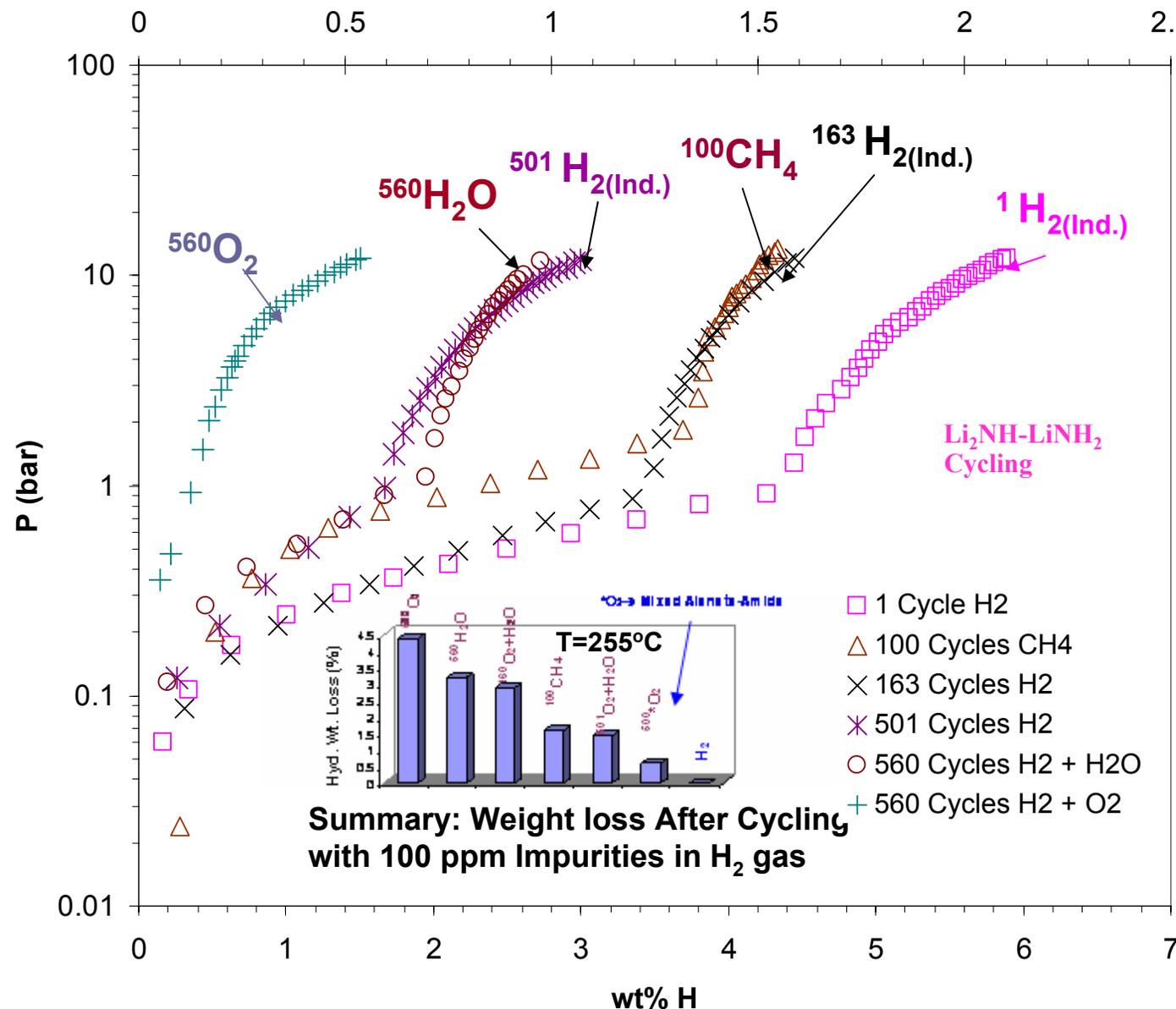
➤ **Importance:** Presence of water in H<sub>2</sub> is expected to have more impact on the loss of hydrogen capacity but it appears that there is greater loss observed when the experiments were conducted with O<sub>2</sub> impurity in H<sub>2</sub>

Dual Combined 100 bar  $\text{H}_2$  Cycling and Sievert's apparatus



Glove Box

H/Li-N-H



Summary: Weight loss After Cycling with 100 ppm Impurities in  $\text{H}_2$  gas

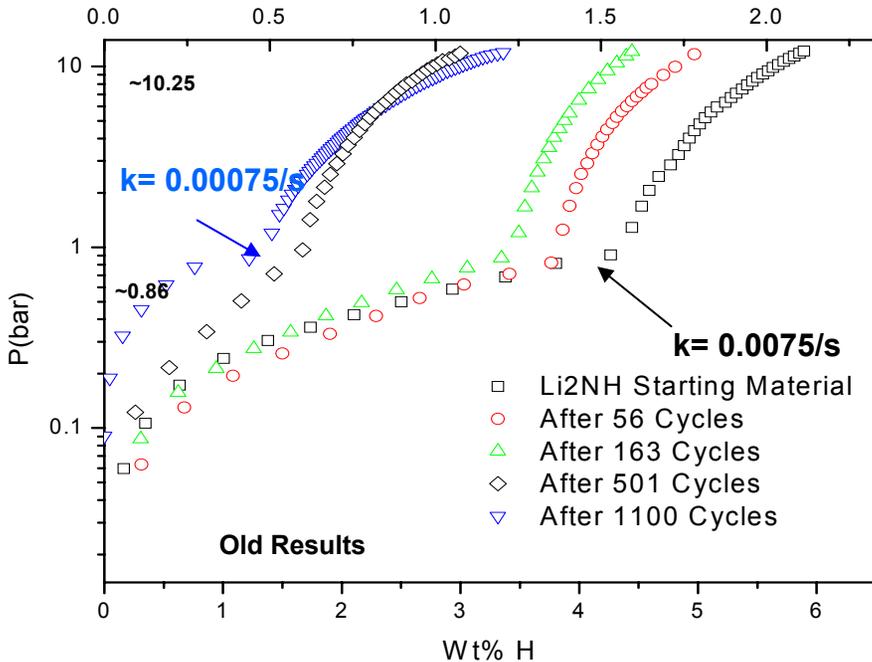
**Results:**  
**Pressure Cycling :** Significantly more losses with  $\text{O}_2$  and  $\text{H}_2\text{O}$  impurities. (Desorption cycles not shown for clarity)  
**Thermal aging: 100 ppm CO with  $\text{H}_2$ →very little loss in  $\text{H}_2$  capacity for the imide-amide system (results not shown)**

**XRD results show that there is residual  $\text{Li}_2\text{NH}$  along with  $\text{Li}_2\text{O}$  (major phases) and  $\text{LiH}$  phase.**

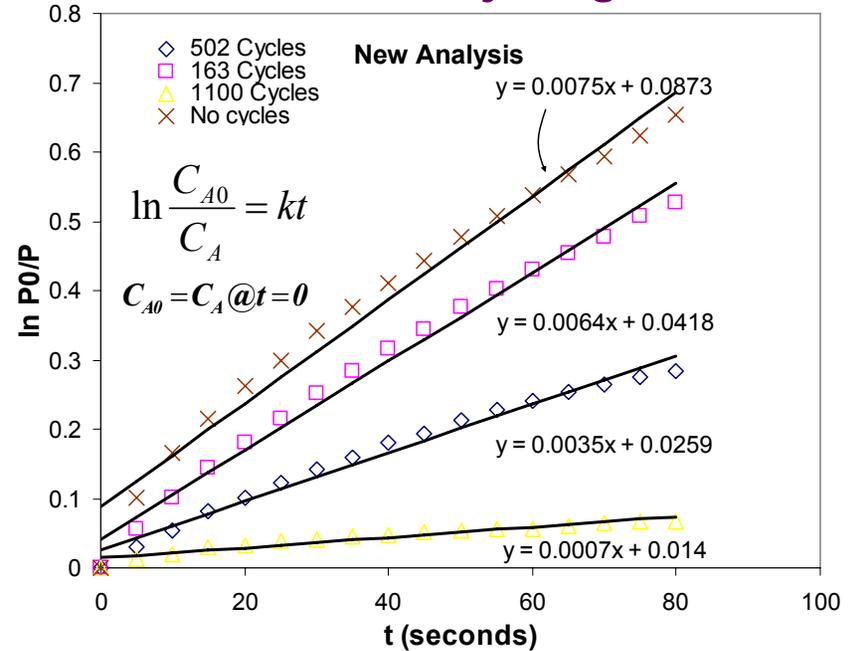
## Imide/amide Pr. Cycling with Industrial H<sub>2</sub> containing small levels\* of O<sub>2</sub> and H<sub>2</sub>O

Li<sub>2</sub>NH ↔ LiH ↔ LiNH<sub>2</sub> Cycle  
2 Bar - Industrial Hydrogen @T= 255°C

The PCI's were shown before ( as a reference ), and the kinetic data (right) is new H: Li-N-H



## Kinetic Plot for Cycling Data



$C_{A0}$  = Initial Conc. of Hyd. in gas – reaction  
 $C_A$  = Concentration at time (t) &  $C_{A_0} = C_A @ t = 0$

**Rate Constant for the Hydriding reaction:**

Cycles	k (1/s)
1	0.0075
163	0.0064
502	0.0035
1100	0.00075

**\*Please note:** Note that cycling Li<sub>2</sub>NH ↔ LiNH<sub>2</sub> in Industrial hydrogen Water ~32 ppm, O<sub>2</sub>~10ppm and others showed ~3.2% (out of ~4.4%) hydrogen loss after 1100 cycles under similar cycling conditions

## Pressure Measurements

- Torsion effusion system, available at UNR used to determine total equilibrium pressure we use the following Eq.: ('K'=Fiber Constant)

### **Pressure Equation**

$$P_T = \frac{K(2\theta)}{(a_1 f_1 d_1) + (a_2 f_2 d_2)}$$

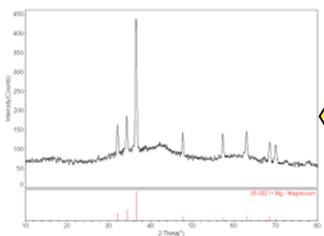
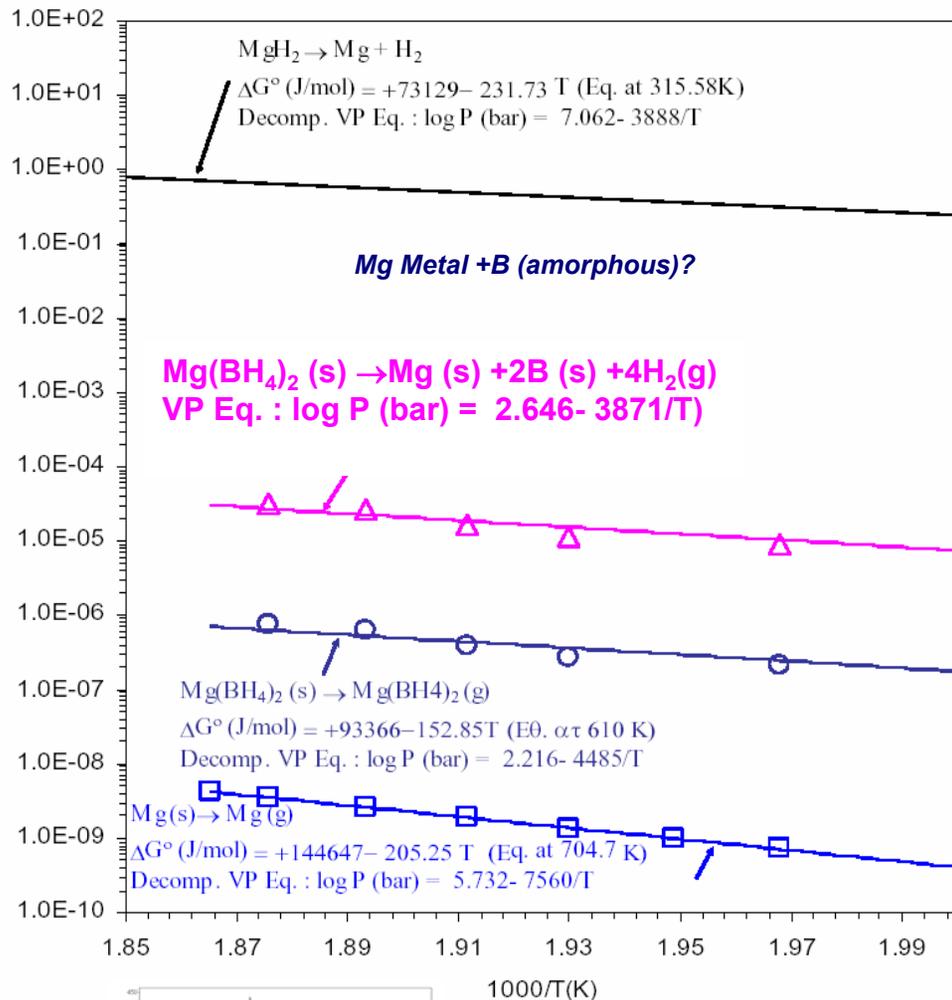
### Typical Pr. Temp. and Sample Size:

- Turbo Pump vacuum ( $<10^{-5}$  Torrs)
- ~ 1 gram
- Temperature capability:  $-20^\circ\text{C}$  to  $600-700^\circ\text{C}$
- Tungsten Knudsen Cells Used

## Molecular Weight Measurements of Vapors

- Determined by rate of weight loss (TGA)
- Disproportionation equations (below) in the vapor phase determined by equating the experimental  $M_{\text{AVG}}$  to the theoretical Mol. Wt. of the effusing gas species:

$$M_{\text{AVG}} = \frac{2\pi RT}{(2K)^2} \cdot \left( \frac{\left( \frac{dw}{dt} \right)}{\theta} \right)^2 \left[ \frac{(a_1 f_1 d_1) + (a_2 f_2 d_2)}{(a_1 c_1) + (a_2 c_2)} \right]^2 = \sum_{i=1}^n \left[ m_i M_i^{1/2} \right]^{-2}$$



XRD Pattern Showing Mg Metal (residual sample)

Portion of Glass tube with the baffles and Knudsen cell housing is shown

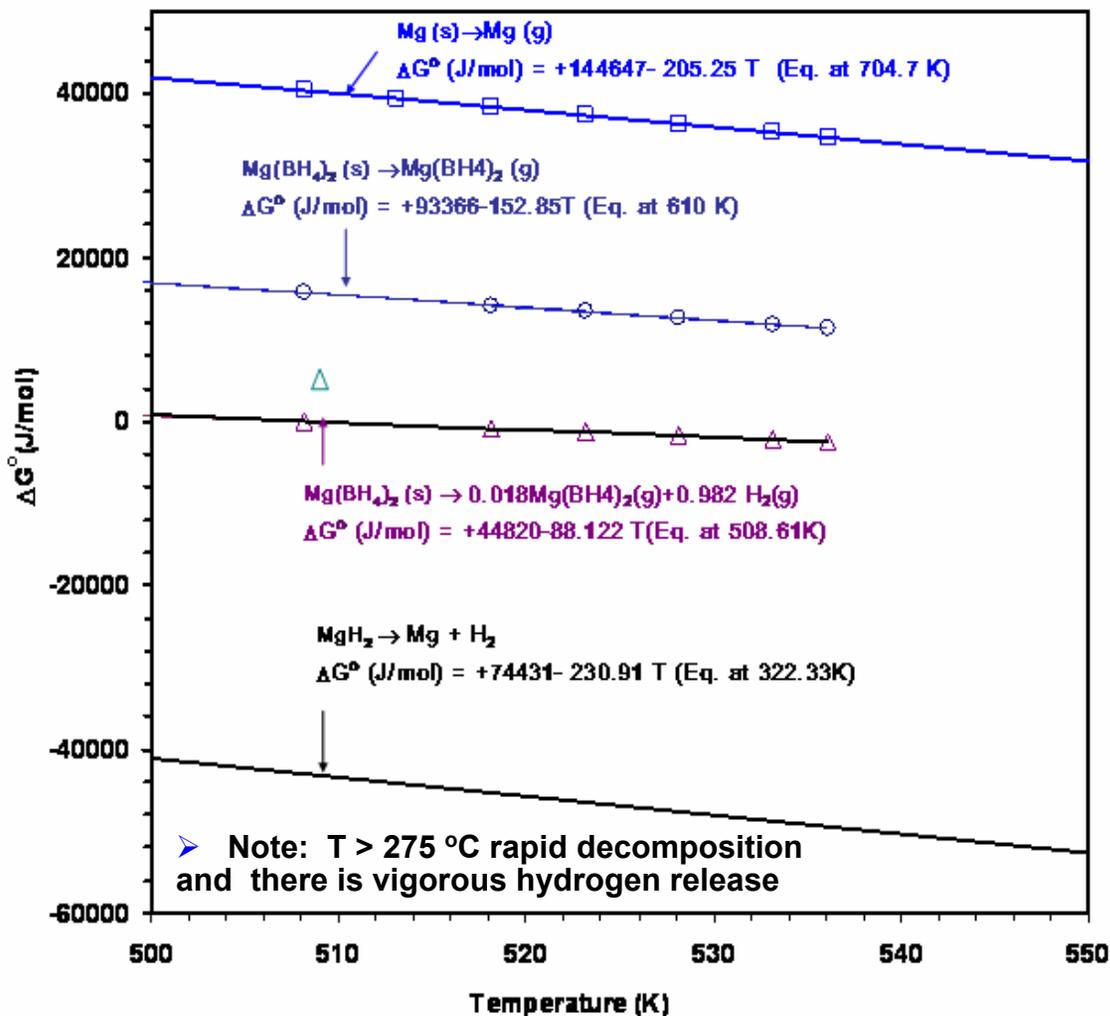


➤ **Knudsen Torsion Effusion apparatus used to measure thermodynamics**

➤ **V.P and Molecular weight of the effusing species.**



1. There are two principal reactions:  
 $Mg(BH_4)_2(s) \rightarrow Mg(BH_4)_2(g)$ .....(~ 2%)  
 Eq. :  $\log P$  (bar) = 2.216 - 4485/T
2.  $Mg(BH_4)_2(s) \rightarrow Mg(s) + B(s) + 4H_2(g)$   
 Eq. :  $\log P$  (bar) = 2.646 - 3871/T  
 thus Disproportionates.....(~98%)
3. The Average Mol. Wt. of effusing gas is 2.42 g/mol suggests that majority hydrogen is major component in vapor phase.



Issues related to formation solid or gaseous Boron (have significance in release of Borane gas)

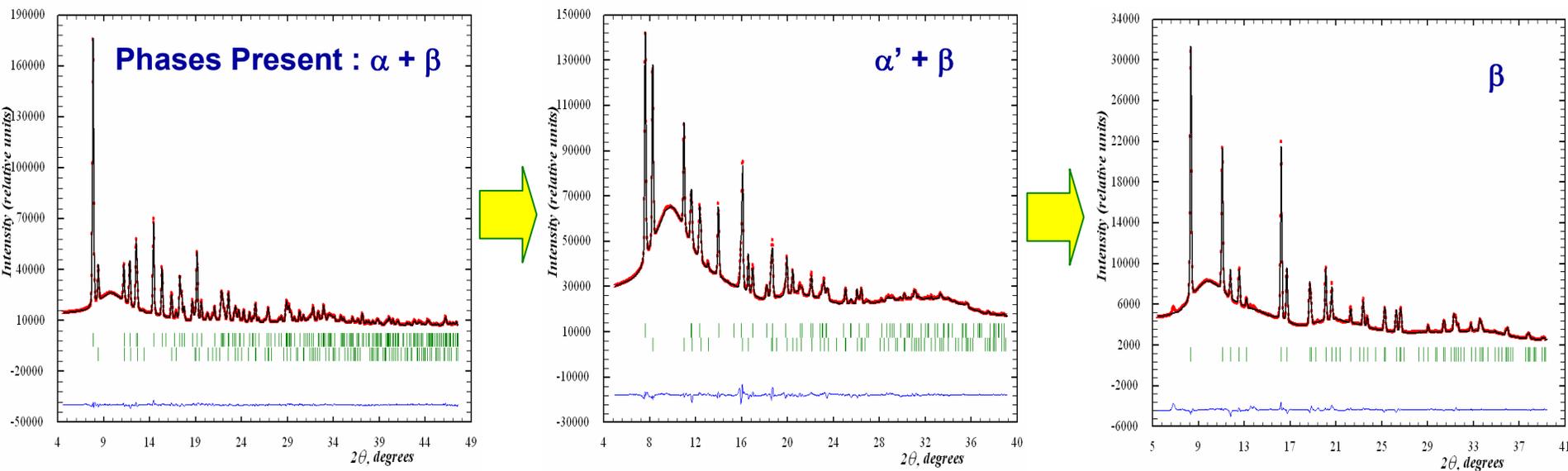


@ 298.15 K, 1 Bar  $\Delta G_{RXN} = -87.6$  kJ/mol (Possible)

@ 298.15 K, 1 Bar  $\Delta G_{RXN} = +1042.4$  kJ/mol (unlikely)

*These studies were performed using High resolution and high temperature synchrotron x-ray diffraction at ESRF, Grenoble to understand the phase stability of  $\text{Ca}(\text{BH}_4)_2$*

## Synchrotron Data from the $\text{Ca}(\text{BH}_4)_2$ Specimen

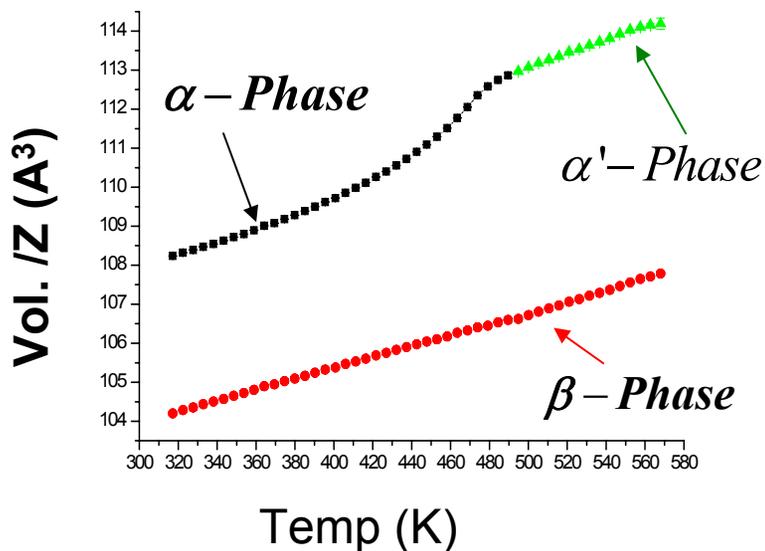
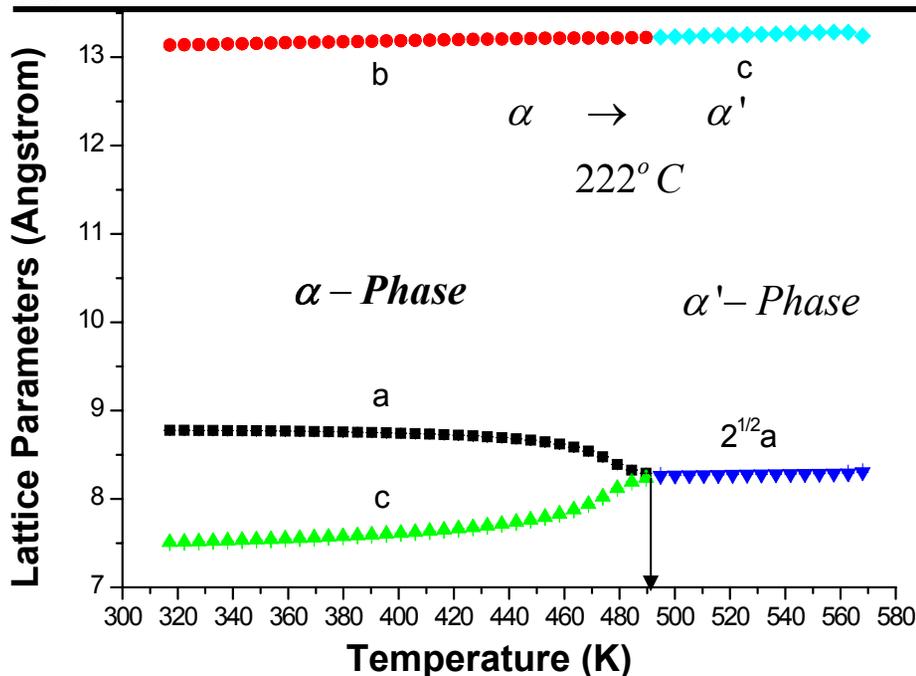


## Summary

- The sample contains 87%  $\alpha$ - $\text{Ca}(\text{BH}_4)_2$  and 13%  $\beta$ - $\text{Ca}(\text{BH}_4)_2$  phases at room temperature.
- Phase transition from  $\alpha \rightarrow \alpha'$  occurred at 222°C (second order transformation)
- Then  $\alpha' \rightarrow \beta$  occurred at 297°C
- Manuscript prepared: "Crystal Structures and Phase Transformations in  $\text{Ca}(\text{BH}_4)_2$ ", Y. Filinchuk, E. Ronnebro and D. Chandra, 2008.



# Variation of the Unit cell Parameters of $\alpha$ and $\alpha'$ - $\text{Ca}(\text{BH}_4)_2$ as a Function of Temperature



- ### Summary
- No change to lattice parameters of  $\alpha$  phase until  $\sim 165^\circ\text{C}$ ,
  - Unit cell volume per formula unit of the  $\alpha$  and  $\alpha'$  phases shows increases as temperature ramps up.
  - The volume of the unit cell of  $\beta$  phase shows linear increase during heating
  - Small amount of  $\beta$  phase are always present at the start of the experiment mixed with the  $\alpha$ - phase

Volume of the  $\text{Ca}(\text{BH}_4)_2$  / formula unit in the  $\alpha$ ,  $\alpha'$  and  $\beta$ -polymorphs as a function of temperature



## Future Work on Complex Hydrides (FY '08 and Beyond)

- **1. Continue Work on Effect of Impurities on Specific Contaminants**
  - Pressure Cycling on mixed Mg-Li based complex hydrides
  - New 8 station combined cycling/Sievert's hydriding apparatus
  - Testing of hydrides developed by MHCoe partners
- **2. In-Situ Neutron and X-ray Diffraction Studies on Hydriding/Dehydriding**
  - Studies on Borohydride using X-ray and neutron diffraction
- **3. Vapor Pressure Studies on  $\text{LiBH}_4$  and other Borohydrides**
  - Thermodynamics of vaporization of  $\text{LiBH}_4$  and others
- **4. Phase Diagram Determination of Mixed Complex Hydrides**
  - Develop experimental non-equilibrium/equilibrium phase diagrams
  - CALPHAD modeling at UNR
- **5. High Pressure Differential Scanning Calorimetric Research**
  - Dynamic heating behavior at up to ~ 50 bar hydrogen
- **6. Hydrogen Lattice Dynamics Studies on Complex Hydrides- Prof. Cantelli, Univ. of Rome - IPHE Proposal**
  - "Hydrogen Dynamics, Lattice interactions, and Atomic-scale Structure of Complex/Chemical Hydrides"
  - Collaboration between Cantelli-Rome, Italy and Chandra-Jensen, USA
- **7. IEA/IPHE Collaborative Studies at Uni. of Geneva and CRNS (France)**
  - Proposal to study defect structures in the complex hydrides such as Li-Al hydrides , Mg-Li amides, and others

## ➤ Imide-Amide ( $\text{Li}_2\text{NH-LiNH}_2$ ) Impurity Effects (UNR Sample)

- Studies on trace amounts of impurity gases (100 ppm) such as  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_4$ , in  $\text{H}_2$  and industrial hydrogen, up to ~1100 cycles.
- $\text{O}_2$  was most detrimental to the performance of amide-imide hydrides
- The kinetic analyses showed one order of magnitude change of the rate constants; from cycle 1 at  $7.5 \times 10^{-3}/\text{sec}$  to  $7.5 \times 10^{-4}/\text{sec}$ . after 1100 cycles.

## ➤ Vapor Pressure Measurement of $\text{Mg}(\text{BH}_4)_2$ (Sample from GE)

- No significant vaporization of  $\text{Mg}(\text{BH}_4)_2$ . Below  $233^\circ\text{C}$  not possible to record any data.
- Above  $233^\circ\text{C}$  the  $\Delta G^\circ$  becomes negative and vaporization starts.  $\Delta G^\circ$  of  $\text{Mg}(\text{BH}_4)_2$  was determined.
- Partial Pressures:  $P_{\text{H}_2} = 8.8 \times 10^{-6} \text{ atm}$ ,  $P_{\text{Mg}(\text{BH}_4)_2} = 2.03 \times 10^{-7} \text{ atm}$ , at  $225^\circ\text{C}$
- $\text{Mg}(\text{BH}_4)_2 (\text{s}) \rightarrow \text{Mg}(\text{BH}_4)_2 (\text{g})$  ( $\Delta H = 93.4 \text{ kJ/mol}$ ) (only ~2% of the vaporization).
- The majority of the vaporization was due to disproportionation of  $\text{Mg}(\text{BH}_4)_2 \rightarrow \text{Mg}(\text{s}) + \text{B}(\text{s}) + 4\text{H}_2(\text{g})$ ,  $\Delta H = 44.82 \text{ kJ/mol}$  (~98%)

## ➤ Structure and Phase Transformations in $\text{Ca}(\text{BH}_4)_2$ (UNR-SNL Sample)

- in-situ synchrotron data showed two polymorphs of  $\alpha\text{-Ca}(\text{BH}_4)_2$  and a small amount of  $\beta$ -phase formed upon removal of solvent from  $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ .
- A second order  $\alpha \rightarrow \alpha'$  phase transition occurred at  $222^\circ\text{C}$  (confirmed by DSC).
- Another phase transition,  $\alpha' \rightarrow \beta$  phase upon heating above  $297^\circ\text{C}$  and decomposes at  $382^\circ\text{C}$  into unknown products which according to TGA is associated with a weight loss, likely due to release of hydrogen.